Universidade de Aveiro
Ano 2014

Departamento de Ambiente e Ordenamento

REGINA CÉLIA ESPINOSA MODOLO

VALORIZAÇÃO DE RESÍDUOS SÓLIDOS DA INDÚSTRIA DE CELULOSE E PAPEL

VALORIZATION OF SOLID WASTES FROM CELLULOSE AND PAPER INDUSTRY

Universidade de Aveiro
Ano 2014

Departamento de Ambiente e Ordenamento

REGINA CÉLIA ESPINOSA MODOLO

VALORIZAÇÃO DE RESÍDUOS SÓLIDOS DA INDÚSTRIA DE CELULOSE E PAPEL

VALORIZATION OF SOLID WASTES FROM CELLULOSE AND PAPER INDUSTRY

Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Ciências e Engenharia do Ambiente, realizada sob a orientação científica do Doutor Victor Miguel Carneiro de Sousa Ferreira, Professor Associado do Departamento de Engenharia Civil da Universidade de Aveiro, co-orientação do Doutor João António Labrincha Baptista, professor Associado com agregação do departamento de Engenharia de Materiais e Cerâmica, da Universidade de Aveiro, e do Doutor Luís António da Cruz Tarelho, professor Auxiliar do departamento de Ambiente e Ordenamento da Universidade de Aveiro.

Este trabalho teve apoio financeiro da Fundação para a Ciência e Tecnologia (FCT), Portugal, através da bolsa de doutoramento SFRH/BD/75182/2010 e dos projectos de investigação PTDC/AAC-AMB/098112/2008 - FCOMP-01-0124-FEDER-008487 (Bias-to-soil), e PTDC/AAC-AMB/116568/2010 - FCOMP-01-0124-FEDER-019346 (BiomAshTech) financiados por Fundos FEDER através do Programa Operacional Fatores de Competitividade – COMPETE e por Fundos Nacionais através da FCT – Fundação para a Ciência e a Tecnologia.
.

This work was founded by *Fundação para a Ciência e a Tecnologia (FCT)*, Portugal, through PhD Grant SFRH/BD/75182/2010 and research projects PTDC/AAC-AMB/098112/2008 - FCOMP-01-0124-FEDER-008487 (Bias-to-soil), and PTDC/AAC-AMB/116568/2010 - FCOMP-01-0124-FEDER-019346 (BiomAshTech) financed by FEDER through *Programa Operacional Fatores de Competitividade – COMPETE* and national budget through *Fundação para a Ciência e a Tecnologia (FCT)*.

Dedico este trabalho ao eterno amigo Antônio Sérgio Fabres, à minha avó Mercedes Espinosa de Oliveira (97 anos), à minha família brasileira e à minha família portuguesa.

. . . Viva como se fosse morrer amanhã. . .
. . . Aprenda como se fosse viver para sempre.
M.M. Gandhi

“A gravidade dos desafios ambientais com que o planeta Terra se confronta, os quais não há como escamotear são da inteira e exclusiva responsabilidade da espécie humana, já não permitem abordagens paliativas de natureza incremental do género a que estávamos habituados até aqui. O tempo é pois para rupturas com as ineficazes e insustentáveis práticas do presente antecipando um futuro no qual o respeito pelo Planeta e pelas restantes espécies que nele connosco habitam será a regra e não a excepção.”

“The severity of the environmental challenges that the Earth Planet is facing, which there is no concealing are the sole and exclusive responsibility of the human species, no longer allow palliative approaches to incremental nature of the kind we are used to until now. The time is therefore to break with the ineffective and unsustainable practices of this anticipating a future in which, respect for the planet and the other species that inhabit it with us will be the rule rather than the exception.”

Fernando Pacheco Torgal e Said Jalali, 2010

o júri

Presidente

Prof. Doutor Fernando Manuel dos Santos Ramos
Professor catedrático da Universidade de Aveiro

Vogais

Prof. Doutor Fernando António Portela de Sousa Castro
Professor catedrático da Universidade do Minho

Prof. Doutor Mário Augusto Tavares Russo
Professor catedrático da Universidade do Minho

Prof. Doutor Fernando António Portela de Sousa Castro
Professor coordenador, Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Viana do Castelo

Prof. Doutor Victor Miguel Carneiro de Sousa Ferreira
Professor associado da Universidade de Aveiro (orientador)

Profª. Doutora Maria da Graça Madeira Martinho
Professora auxiliar, Faculdade de Ciência e Tecnologia, Universidade Nova de Lisboa

Prof. Doutor Nuno Lapa
Professor auxiliar da Faculdade de Ciência e Tecnologia, Universidade Nova de Lisboa

Profª. Doutora Ana Paula Duarte Gomes
Professora auxiliar da Universidade de Aveiro

Prof. Doutor Luís António da Cruz Tarelho
Professor auxiliar da Universidade de Aveiro (coorientador)

agradecimentos

Aos meus estimados orientadores, professor Victor Ferreira, professor Luis Tarelho e professor João Labrincha pelo apoio, paciência e total disponibilidade.

Um agradecimento muito especial à Eng. Maria Carlos e ao Vítor Rodrigues pela preciosa e incondicional ajuda.

Ao Instituto de Investigação da Floresta e do Papel e grupo Portucel Soporcel (fábricas de Cacia e Soporcel) e Weber-cimenfix (grupo Saint Gobain) aos técnicos e demais funcionários todo o meu carinho e agradecimento eterno.

A todos os meus colegas da sala de doutoramentos do departamento de engenharia civil da Universidade de Aveiro, aos funcionários e professores.

Aos técnicos da Universidade de Aveiro, em especial à Célia Miranda, Cristina Sequeira, Ana Ribeiro e Maria João Bastos, cuja ajuda preciosa de muito me valeu.

Um agradecimento muito especial e caloroso à minha família e estimados amigos.

Very special and warm thanks to my family and precious friends.

Veľmi zvláštne a príjemný na moju rodinu a blízkych priateľov, vďaka.

Un particolare e caloroso grazie alla mia famiglia e cari amici.

Un agradecimiento muy especial y cálido a mi familia y amigos queridos.

Un mulțumesc foarte speciale și cald la familia mea și de prieteni dragi.

palavras-chave

Resíduos sólidos industriais, caracterização, tratamento, valorização, materiais de construção, biomass, leito fluidisado

resumo

O presente trabalho reporta detalhadamente estudos de valorização de resíduos sólidos industriais como matérias-primas alternativas. Todos os resíduos testados são classificados como não perigosos e são gerados no processo de produção de celulose (pasta) e papel, nomeadamente lamas primárias, dregs, grits, lamas de carbonato e cinzas de fundo, estas geradas num processo que ocorre em paralelo à produção de celulose, cujo objectivo é a produção de energia para abastecimento da fábrica através da combustão de biomassa florestal em leito fluidisado. Uma caracterização geral minuciosa foi realizada a cada resíduo e de acordo com as suas características, seleccionaram-se três aplicações em materiais com potencial de utilização: Fibrocimento, Mistura betuminosa para camada de regularização e argamassas industriais (reboco de projecção e cimento-cola). Após o devido enquadramento do resíduo e aplicação, cada resíduo foi caracterizado especificamente para que se procedesse a definição de formulações contendo diferentes percentuais de resíduos em substituição da matéria-prima convencional. Como um caso isolado, as cinzas de fundo foram testadas, não somente como matéria-prima alternativa em materiais de construção, como também testou-se a sua reutilização em leito fluidisado no qual o resíduo é gerado. Tanto os dregs como as cinzas de fundo passaram por um tratamento específico para que fosse possível obter uma melhor qualidade do resíduo com o objectivo de não comprometer as características do produto final e processo. Os dregs foram testados em base tal e qual e lavados em escala laboratorial (para remoção de sais solúveis) e as cinzas de fundo foram lavadas em escala industrial (para remoção de sais solúveis, nomeadamente cloretos) e crivadas em escala laboratorial e industrial para eliminação da fracção grosseira do resíduo (partículas de dimensão superior a 1 mm). Os demais resíduos formam usados em base tal e qual, evitando assim custos adicionais. Os resultados obtidos em cada aplicação indicam potencialidades e limitações relativamente ao uso desses resíduos como matéria-prima alternativa, porém em alguns casos, as vantagens relativamente a valorização se sobrepõem às suas limitações, tanto nos aspectos ambientais, como económicos.

keywords

Paper-pulp solid wastes, biomass ash, fluidised bed combustion, valorization, construction materials

abstract

This thesis reports in detail studies of industrial solid wastes valorization as alternative raw materials. All tested wastes are classified as non-hazardous and are generated in the pulp and paper process, including primary sludge, dregs, grits, lime mud and bottom ash (this generated in a process that occurs in parallel to the production of cellulose, whose aim is the production of energy to supply the plant through the combustion of forest biomass in fluidized bed). A detailed general characterization was performed at each waste and according to their characteristics, they were selected some applications in materials with potential use, specifically in Fibercement, Bituminous Mixture for regularization layer and industrial mortars (rendering mortars and cementitious-adhesive). After decided to application each waste was specifically tested to proceed the setting up of formulations containing different content of waste in replacement of the raw conventional material. As an isolated case, the bottom ash was tested not only as an alternative raw material for construction materials, but also it was tested for its use in fluidized bed in which the waste is generated as raw material. Both dregs and bottom ash had undergone special treatment to make possible to obtain a better quality of waste in order do not compromise the final product characteristics and process. The dregs were tested in bituminous mixtures as received and also washed (on the laboratory scale to remove soluble salts) and bottom ash were washed and screened in industrial scale (for removal of soluble salts, especially chlorides and coarse fraction particles elimination - particles larger than 1 mm size). The remaining residues form used in such as received avoiding additional costs. The results indicated potential and some limitations for each application to the use of these wastes as alternative raw material, but in some cases, the benefits in relation to valorization overlap with its limitations in both aspects, environmental and economic.

List of Figures

List of Tables

Publications

This thesis is based on the following papers, referred by Roman numerals in the text:

i) Modolo R, Benta A, Ferreira VM, Machado LM. Pulp and paper plant wastes valorization in bituminous mixes. Waste Management 30 [4] (2010) 685-696. http://dx.doi.org/10.1016/j.wasman.2009.11.005

ii) Modolo R, Ferreira VM, Machado LM, Rodrigues M, Coelho I. Construction materials as a waste management solution for cellulose sludge. Waste Management 31 [2] (2011) 370-377. http://dx.doi.org/10.1016/j.wasman.2010.09.017

iii) Modolo RCE, Ferreira VM, Tarelho LA, Labrincha JA, Senff L, Silva L. Mortar formulations with bottom ash from biomass combustion. Construction and Building Materials 45 (2013) 275-281. http://dx.doi.org/10.1016/j.conbuildmat.2013.03.093

iv) Modolo RCE, Tarelho LAC, Teixeira ER, Ferreira VM, Labrincha JA. Treatment and use of bottom bed waste in biomass fluidized bed combustors. Fuel Processing Technology 125 (2014) 170–181. http://dx.doi.org/10.1016/j.fuproc.2014.03.040

v) Modolo RCE, Senff L, Labrincha JA, Ferreira VM, Tarelho LAC. Lime mud from cellulose industry as raw material in cement mortars. Materiales de Construcción 64 [316] October–December (2014). ISSN-L: 0465-2746. http://dx.doi.org/10.3989/mc.2014.00214

vi) Modolo RCE, Senff L, Labrincha JA, Ferreira VM, Tarelho LAC, Silva L, Silva T. Characterization of bottom ash from biomass combustion for its use as aggregate in cementitious-adhesive mortars. Fuel Processing Technology 129 (2015) 192-202. http://dx.doi.org/10.1016/j.fuproc.2014.09.015.

Other papers published during the course which partially overlapping with the work. Papers I, II, III, IV, V, VI and VII are presented in this document as appendixes.

I. Modolo R, Ferreira VM, Tarelho LA, Silva D, Labrincha JA. (2012) Bottom ash from biomass combustion as aggregate for mortars. Ash Utilisation 2012 - Ashes in a Sustainable Society, Stockholm, Sweden, p. 33 (oral presentation). Complete paper Available in: [http://www.varmeforsk.se/files/program/askor/regina_modolo.pdf]

II. Modolo R, Senff L, Ferreira, VM, Labrincha, JA, Tarelho LA. (2011) Use of lime-mud from pulp mill plant in cement-mortars. Wastes: Solutions, treatments and opportunities, International Conference, Portugal, p. 99 (oral presentation).

III. Modolo R, Senff L, Ferreira VM, Labrincha J. (2011) Ornamental stone sludge valorisation in mortars, VI International Materials Symposium, Materiais 2011, p. 201 (oral presentation).

IV. Senff L, Modolo RCE, Hotza D, Ferreira VM, Labrincha JA. (2014) The rheological behaviour and hardened properties of mortars with red mud addition. Congresso Luso-Brasileiro de Materiais de Construção Sustentáveis, Edição Universidade do Minho, ISSN 2183-1866 (oral presentation)

V. Modolo RCE, Ferreira VM, Labrincha JA, Tarelho LAC, Senff L, Costa N. (2013) Lime mud as raw material in lightweight aggregate production. 2nd International Conference, WASTES: Solutions, Treatments and Opportunities, In proceedings p. 437 (oral presentation) September 11th – 13th, Braga, Portugal.

VI. Tarelho LA, Teixeira ER, Silva D, Modolo R (2012) Treatment by leaching of Bottom ash from biomass combustion in fluidized bed. Ash Utilization 2012 - Ashes in a Sustainable Society, Stockholm, Sweden, p. 38 (oral presentation).

VII. Teixeira ER, Tarelho LAC, Silva TCSR, Silva DFR, Modolo RCE. (2013) Physical-chemical characteristics of ash flows in a biomass thermal power plant. Proceedings of the 21th European Biomass Conference and Exhibition, ISBN: 978-88-89407-53-0, Edited by ETA-Florence Renewable Energies, 03 to 07 June 2013, Copenhagen, Denmark. Pages 1192 - 1202. doi: 10.5071/21stEUBCE2013-2DV.3.56.

Other papers/congress participations papers published during the course of the work but out of the scope of this thesis are:

1. Senff L , Modolo RCE , Santos Silva A , Ferreira VM , Hotza D , Labrincha JA . Influence of red mud addition on rheological behaviour and hardened properties of mortars. Construction and Building Materials 65 [29] (2014) 84–91. http://dx.doi.org/10.1016/j.conbuildmat.2014.04.104

2. Modolo R, Senff L, Ferreira VM, Labrincha J, Tarelho LA. (2011) Lime-mud from pulp and paper mills effects in cement based materials, In 13th International Congress on the Chemistry of Cement, Madrid, Spain, ISBN: 978-84-7292-400-0 (oral presentation).

3. Modolo R, Dias VD, Ferreira VM, Tarelho LA, Labrincha JA. (2012) Waste Management solutions in construction materials for bottom ash from biomass combustion, CINCOS’ 12 - Congress of Innovation on Sustainable Construction, Aveiro, Portugal, de 20-22 de Setembro, 2012 (oral presentation).

4. Tarelho LAC, Teixeira ER, Silva DFR, Modolo RCE, Silva JJF. (2012) “Characteristics, management, and applications of ashes from thermochemical conversion of biomass to energy”. Proceedings of the World Bioenergy 2012, Conference and Exhibition on Biomass for Energy, 29 to 31 May 2012, Jonkoping, Sweden.

5. Calvo AI, Tarelho LAC, Teixeira ER, Modolo R, Alves C, Nunes T, Duarte M, Custodio E Coz D, Castro A, Artiñano B, Fraile R. (2013) Forest biomass waste combustion in a bubbling fluidised bed: characterisation of particulate matter emissions. European Aerosol Conference (Poster presentation) 1st-6th September, Prague, Czech Republic.

6. Modolo R, Cação A, Senff L, Labrincha JA. (2012) Uso de lama vermelha do processo Bayer na coloração de argamassas. 4º Congresso Português de Argamassas e ETICS, Coimbra, Portugal (Poster) www.apfac.pt/congresso2012/comunicacoes/posters/

7. Silva DFR, Modolo R, Teixeira ER, Silva JJF, Tarelho LAC. (2011) Valorização da cinza proveniente da conversão termoquímica de biomassa florestal, Simpósio – Floresta 2050 – Pensar o Futuro, Oeiras - Portugal, 6 e 7 de Outubro.

8. Tarelho LAC, Lopes MHSD, Silva DFR, Freire MSM. Teixeira E.R., Modolo R.C.E. (2014) Characteristics of biomass used as fuel and ashes produced in two thermal power plants with BFBC. Proceedings of World Bioenergy – Conference and Exhibition on Biomass for Energy, Jönköping, Sweden, 3-5 June.

9. Tarelho LAC, Teixeira ER, Silva DFR, Modolo RCE, Silva JJF, Gomes APD, Pereira C, Amorim MJ, Lopes MHD, Freire M. (2013) Forest biomass residues combustion in a thermal power plant with FBC and ash characteristics and management options. Proceedings of the 21th European Biomass Conference and Exhibition, ISBN: 978-88-89407-53-0, Edited by ETA-Florence Renewable Energies, Copenhagen, Denmark. Pages 100 - 112. doi: 10.5071/21stEUBCE2013-1BO.12.2.

10. Modolo RCE, Senff L, Ferreira VM, Labrincha J, Tarelho LAC. (2014) Influence of fly ash from biomass combustion on the durability of cement-based mortars. , Congresso Luso-Brasileiro de Materiais de Construção Sustentáveis, Edição Universidade do Minho, ISSN 2183-1866 (oral presentation).

List of Abreviations

AF-T (Failure in tile adhesive interface)

BA (Bottom ash)

BBW (Bottom bed waste)

BFBC (Bubbling Fluidized bed combustor)

BLO (Black liquor oxidation)

BM (Bituminous mixes)

BOD (Biological oxygen demand)

CBE (Portuguese Center for Biomass Energy)

CF-A (Failure within tile adhesive layer)

CFB (Circulating fluidized bed)

CF-S (Cohesive failure in substrate)

CHP (Combined heat and power)

CIB (Council International Building)

COD (Chemical oxygen demand)

CW (Control water)

DC (Conventional dregs)

DWLS (Dregs without lime sludge)

EDP (Energy of Portugal, S.A)

ELW (European List of Waste)

ESP (Electrostatic precipitator)

FA (Fly ash)

FBC (Fluidized bed combustor)

FBS (Fresh bed sand)

G (grits)

GWA (Ground bottom ash)

HHV (Higher heating value)

LHV (Lower heating value)

LOI (Loss on ignition)

MB (Methylene-blue)

MEEs (multiple-effect evaporators)

MSW (Municipal solid waste)

NDCE (Non-direct contact evaporator)

OBC (Optimum binder content)
OPC (Ordinary Portland cement)
PCC (Precipitated calcium carbonate)
PS (Primary sludge)
PVA (fiber of polyvinyl alcohol)
RBBW (Recycled bottom bed waste)
RBW (recycled bed waste)
S1 (Fine sand used in mortars formulations)
S2 (Conventional coarse sand used in mortars formulations)
SBA (Sugarcane bagasse ash)
SDT (Smelt dissolving tank)
S_e (Sand equivalent)
SEM (Scanning electron microscopy)
SR (Shopper Riegler)
TAS (Tensile adhesion strength)
TBA (Treated bottom ash)
TDA (Thermo-differential analysis)
TGA (Thermogravimetric analysis)
TPP (Thermal power plant)
TRS (Total reduced sulfur)
VLFP (Virgin long fiber pulp)
VMA (Voids in mineral aggregate)
WWA (Wood waste ash)
XRD (X-ray difractogram)
XRF (X-ray Fluorescence)

1 INTRODUCTION

1.1 Motivation and Framework

Industrial development and the pursuit of higher productivity rates lead to the increasing consumption of natural resources and, consequently, to an increase in the production of waste and by-products, most of them not directly recyclable. Cellulose and paper mills and construction are activities that generate high environmental impacts, due to the high consumption of water and energy, use of large amounts of non-renewable raw materials and generation of wastes.

The pulp and paper making industries are water intensive activities. Although the recycling of water is increasing through the adoption of closed systems, which promote the recirculation of process waters, the production of pulp and the manufacture of paper generate a considerable amount of wastewater and wastes that are purged from the process [Cabral et al., 1998; Thompson et al., 2001; Nurmesniemi et al., 2007]. Waste is gradually becoming an increasing environmental issue of concern. Achieving the European recycling targets defined for 2020, with the obligations about waste disposal in 2016, are the major environmental challenges for Southern Europe countries.

In this work industrial wastes originated from paper pulp or cellulose production and associated biomass combustion processes, produced in large amounts annually, are characterised and then recycled in distinct construction and building materials. It is known that construction industry is responsible for 30% of greenhouse gases emission while is the biggest consumer of raw materials (approximately 3000Mt/year) [Torgal and Said, 2010]. Sustainability issues are obviously associated to this activity, also because the amount of wastes produced is very significant. Considering the large amount of quarried aggregates being consumed, this thesis details the recycling of several wastes, through bench, pilot and industrial scales, as substitutes of primary aggregates. This way the landfilling is avoided, while costs are minimized and demand of natural resources and extraction activities are also reduced.

1.2 Objective and Structure

The general aim of this work is to contribute to the development of wastes management solutions through their valorization recycling them as substitutes of natural aggregates widely used in building and construction activities.

Specific objectives were defined upon the work progressing:

i) Identification and characterization of wastes generated in considerable amounts on paper pulp mill whose final destination is still the disposal on landfills, as well as the potential raw materials to be replaced by some of those;

ii) Testing of selected recycling solutions, defining and assessing the formulations in bench scale; during this process the need for waste treatment to improve its performance in the final application was also considered.

iii) After identification of an interesting waste content to be used in the final product tested as replacement of a primary raw material, it was verified the possibility of changing the test scale (from bench to industrial). It is important to refer that this process was limited to applications where available partners were identified, revealing mutual interest in implementing the potential solution verified in lab scale.

iv) The exhaust sand from the fluidized bed was also tested in the own generating process/unit. This work was developed in pilot-scale instead of industrial due to the access to available facility which permitted to control the whole process and final product.

v) Finally, the wastes valorization solutions in terms of advantages and limitations were identified and reported.

The first chapter of this thesis describes the targeted industrial sectors, pulp and paper mill, biomass combustion technology and construction materials. This literature review also refers the applicable legislation about the simplified licensing of waste management operations, aiming to clarify the main steps to be followed considering the legal procedures and showing how time consuming and bureaucratic this procedure is also given, to exemplify how time consuming and bureaucratic this process is..

The experimental research that was carried out is reported in chapters 2 to 8 of this document.

Chapter 2 describes experimental facilities used to characterize the raw materials and the wastes tested. It also describes the general procedures used to achieve the basic information related with the materials and wastes aiming their adequate application.

Chapter 3 focuses in evaluating the use of primary sludge from kraft hardwood pulping process in fiber-cement sheets production at an industrial scale. In this study, parameters such as the sludge characteristics and its quality as a raw material, incorporation level, the water quality in the process and the final product characteristics were assessed.

Chapter 4 describes the procedures developed to test the possibility of using pulp and paper inorganic wastes, namely dregs and grits, in asphalt concrete mixes as aggregate replacement in road regularization layers, through mix designs and specific characterization tests, contributing to reduce environmental effects of these wastes landfill disposal, which nowadays still has been their unique management solution.

Chapter 5 describes a detailed characterization of a rich calcium carbonate waste, named lime mud, generated in caustizing circuit of pulp mill process and its use as filler in cement-based mortars. Not only was the rheological behaviour of mortars evaluated, but also their properties on hardened state.

In chapters 6 and 7 the conventional aggregate (sand, herein named S2) used in industrial rendering-mortars and cementitious-adhesives was substituted by bottom ash produced from the forest residues biomass combustion in Bubbling Fluidised Bed Combustors (BFBC). The work emphasizes the biomass quality contribution in the ash characteristics and the need of pre-treatment procedures before substitution, namely screening/sieving and/or washing of waste. The environmental control of the waste was also evaluated aiming the characterization of the bottom ash to categorize the landfill class according to Decree-Law 152/2002.

Chapter 8 improves the knowledge on the characteristics of bottom bed waste from fluidized bed combustion of residual forest biomass in Portuguese thermal plants and cogeneration plants. Based on them, physical pre-treatment processes were applied aiming to regenerate the material to be reused in the bed of the bubbling fluidised bed combustor in pilot-scale equipment.

Chapter 9 discusses the viability and limitations of practical implementation of some studied solutions, in terms of materials fluxes, consumption/substitution of conventional/primary resources, and industrial processing adaptations.

Finally, the main conclusions of developed solutions are presented in chapter 10 including suggestions for future works which could be complement the actual achievements, particularly in defining suitable waste management operations in order to achieve sustainable solutions.

1.3 Literature review

1.3.1 Waste management

According to the definitions by the European Council Directive 2006/12/CE on Waste (EC, 1991), waste generally speaking shall mean any substance or object which the holder discards or intends to or is required to discard, and waste management shall mean the collection, transport, recovery and disposal of waste, including the supervision of such operations and after-care of disposal sites. In general, one fundamental aspect of the legislation on this question is the setting of goals for waste management [Nurmesniemi et al., 2007]. The Decree-Law n.º 73/2011 from June 17th and transposes the European Council Directive 2008/98/CE related to solid wastes, expresses on its legislative framing, the prevention of wastes, promoting its reuse and recycling to aim at extending its use in the economy before returning to the environment in safe conditions. Besides considering important to promote the entire exploitation in the new organized market of wastes as a mean of consolidation the wastes valorization, with advantages for economic agents, as well as to stimulate the use of specific wastes with high potential of valorization. The legislation also defines requirements for substances or objects resulting from a productive process that can be considered as a product and not a waste. So, in a positive perspective, the legislation defines criteria for certain solid wastes deprive the waste status, and thus can become a resource.

According to the Decree-law n.º 178/2006, industrial wastes are those ones generated in industrial productive processes, as well as those resultant from activities related with production and distribution of electricity, gas and water.

The wastes recycling can represent a significant opportunity along with major challenges. Industrial solid wastes, such as ashes from biomass combustion, construction and demolition materials, lime mud, organic and inorganic sludges from wastewater treatment can be valuable materials for some industrial processes. Much industrial waste is neither hazardous nor toxic, such as waste wood fiber produced in several industrial sectors related to agriculture or forestry products. These by-products have many of the properties as the conventional materials they could replace. Putting these commodities into productive use could save natural resources and contribute to a sustainable future. The main principles of the waste management strategy in the European Union have been summarized as follows:

- *Waste management hierarchy*. Waste management strategies must aim to prevent or reduce the generation of waste and decrease its noxious nature by developing clean technologies. In addition, efforts must be made in order to contribute, first to the development and marketing of products designed to have the smallest possible impact in terms of pollution, if any, and secondly to the development of appropriate techniques for the final disposal of dangerous substances contained in waste destined for recovery. Where the aforementioned strategies are not possible, or fail to be environmentally and economically viable at the same time, waste materials should be reused, recycled or recovered, or used as a source of energy, provided that these practices improve or, at least, do not significantly decrease the quality of the final product. As a final option, waste should be safely disposed of, e.g., in landfill sites;
- *Self-sufficiency at the community and, if possible, at Member State level.* Member States need to establish, in co-operation with other Member States, an integrated and adequate network of waste disposal facilities, taking into account geographical circumstances or the need for specialized installations for certain types of waste;
- *Best available techniques not entailing excessive cost.* Emissions from installations to the environment should be reduced as much as possible and in the most economically efficient way;
- *Proximity*. Wastes should be disposed of as close to the source as possible, by means of the most appropriate methods and technologies in order to ensure a high level of environmental and public health protection;
- *Producer responsibility*. Particularly, manufacturers have to be involved in closing the life cycle of their products, from production and throughout their useful life, until they finally become waste.
- The principle of the *protection of primary resources:* it is formulated in the wider context of sustainable development, and it underlines the need to minimize and enhancing efficiency in the use of primary resources, particularly non-renewable resources, with an emphasis on the use of secondary raw materials.
- The *substitution* principle: emphasizes the need to replace dangerous raw materials by non-dangerous raw materials, thus avoiding hazardous waste arising.

1.3.2 Pulp and paper mill

Europe hosts over nine hundred pulp and paper mills, playing an important role in a global perspective. The pulp and paper industry comprises companies that use wood as raw material and produce pulp, paper, card board and other cellulose-based products. This industry is dominated by north American (United States and Canada), northern European (Finland, Sweden, and North-West Russia) and east Asian countries (such as East Siberian Russia, China, Japan, and South Korea). Australasia and Brazil also have relevant positions. The United States had been the world's leading producer of paper until 2009, when it was overtaken by China [RISI, 2011]. The pulp and paper industry is an important producer of solid wastes. However, there is a growing trend towards the utilization of their solid wastes and industrial by-products in different sectors aiming their environmental compatible and sustainable valorization. The difficulties found, not only in terms of viable applications but also related with bureaucracies, make industrial solid wastes valorization a challenge for producers and end users. Considerable research is being conducted worldwide on the use of waste materials in order to avoid an increasing toxic threat to the environment or to simplify present waste disposal techniques, by making them more reasonable [Ahmaruzzaman, 2010]. Through the increasing use of recycled paper, the increased degree of water treatment, more restrictive legislation and increasing costs of solid wastes landfill, the pulp and paper industry has been forced to place more and more emphasis on waste management. Often, the solid wastes from one stage of the productive process can be used as resource in other processes. Nurmesniemi et al (2007) exemplified that for the bark and wood wastes produced during the sawmilling process, which can be used as a raw material for particle board and chemical pulp production. Furthermore, thermal energy can be produced by burning wood waste from the debarking plant, black liquor from the pulp making process, and biosludge from wastewater treatment plants (i.e., activated sludge plants). In addition, the fiber sludge from pulp and paper mills, and therefore also called paper mill sludge [Niutanen and Korhonen, 2002], is increasingly being utilized in the hydraulic barrier layer of landfills. The fly ash from the biomass thermal power plants (nowadays, usually fluidized bed boilers) can be used as an additive in earthwork construction to improve soil strength and to reduce deformation, or as a forest fertilizer, ceramic composite, or yet as a binder replacing material in cement mortars [Harila and Kivilinna, 1999; Jordan et al., 2002; Mroueh and Wahström, 2002; Hytönen, 2003; Rajamma et al., 2009].

Nevertheless, these and other types of solid wastes and by-products from the pulp and paper mills are often regarded as waste, without economic value and with inherent management costs, although there is an increasing interest in using them as resources. Makkonen et al. (2002) reported that materials which are used or that potentially could be utilized in several applications should not actually be classified as a waste.

Pulping is the process of separating individual fibres from wood chips or recycled paper by either chemical, semichemical, or mechanical methods. The chemical process is the most common for wood chips. Wood handling is the first step in the pulping process. In this step, wood logs are debarked and cut into pieces showing manageable sizes. Wood, the major raw material used in the pulp and paper industry, is basically composed of cellulose fibres, carbohydrates such as starch and sugar, and lignin, which acts as adhesive substance for the cellulose fibres [Nurmesniemi et al., 2007]. Paper is essentially a sheet of fibres with a number of added chemicals that affect the properties and quality of the sheet. Besides fibres and chemicals, manufacturing of pulp and paper requires a large amount of process water and energy in the form of steam and electric power. Consequently, the main environmental issues associated with pulp and paper production are emissions to water, emissions to air and energy consumption [IPPC, 2001].

Chemical pulping is dominated by two processes – the sulphate and the sulphite process. In the sulphate process, which involves alkaline digestion, the active cooking (digesting) chemicals are sodium hydroxide (NaOH) and sodium sulphide (Na_2S). This process is commonly named as Kraft method (Figure 5.1), and promotes the wood chips delignification into pulp for papermaking, while preserving the long fibers in the resulting strong pulp (composed by around 50 to 60% fibers). The sulphate or kraft process is the dominating pulping process worldwide, due to the superior strength properties of the produced pulp and its versatility to digest distinct (all) wood species. This process has operating interdependent units (wood storage park, cooking, laundering, thermoelectricity etc.) in which intermediate products are manufactured (shavings, raw pulp, bleached pulp, energy, etc.).

The pulp and paper industry is a source of a wide range of solid wastes. Nearly eleven million tonnes of waste are produced yearly by the European pulp and paper industry [Monte et al., 2009]. The amount and the composition of the solid wastes depend on the pulp/paper grade produced, the raw materials used, the applied processing techniques, and the final quality/properties of the pulp/paper. Sludges (primary and biological/secondary) from the wastewater treatment, lime mud, lime slaker grits, dregs from the green liquor washing, ashes and sand from the combustion of organic components in co-generation units, and wood processing residues, are the main wastes produced. Figure 1.1 shows a scheme of the production process of bleached Kraft pulp, emphasizing the steps where the mentioned wastes are generated. They are better described in the following sections of this chapter. Under normal running conditions, wastes characteristics are roughly constant, excepting the sludges that might show widely variable properties, depending on the type of operations carried out at the mill.

The wastes can be reused and valorised in a safe and environmental way, minimizing the use of landfills as the final destination. In fact, in countries such as Germany, Spain and Netherlands, certain waste streams cannot be disposed of at landfill sites. And as it was previously stated, current legislation and increased landfilling taxes stimulates the search for novel management methods of such wastes, favouring reusing alternatives [Monte et al., 2009]. More efficient techniques to separate, collect and properly store some waste fractions at source can be also beneficial to meet this aim [IPPC, 2010]. For economic and environmental reasons, chemical and semi-chemical pulp mills employ chemical recovery processes to reclaim spent cooking chemicals from the pulping process. At kraft pulp mills, spent cooking liquor, referred as “weak black liquor,” from the brown stock washers is routed to the chemical recovery area at kraft pulp mills. The chemical recovery process involves: (i) concentration of weak black liquor; (ii) combustion of organic compounds; (iii) reduction/elimination of inorganic compounds (dregs); and (iv) reconstitution of the cooking liquor. The chemical recovery process involves several steps that are described in the following subitems.

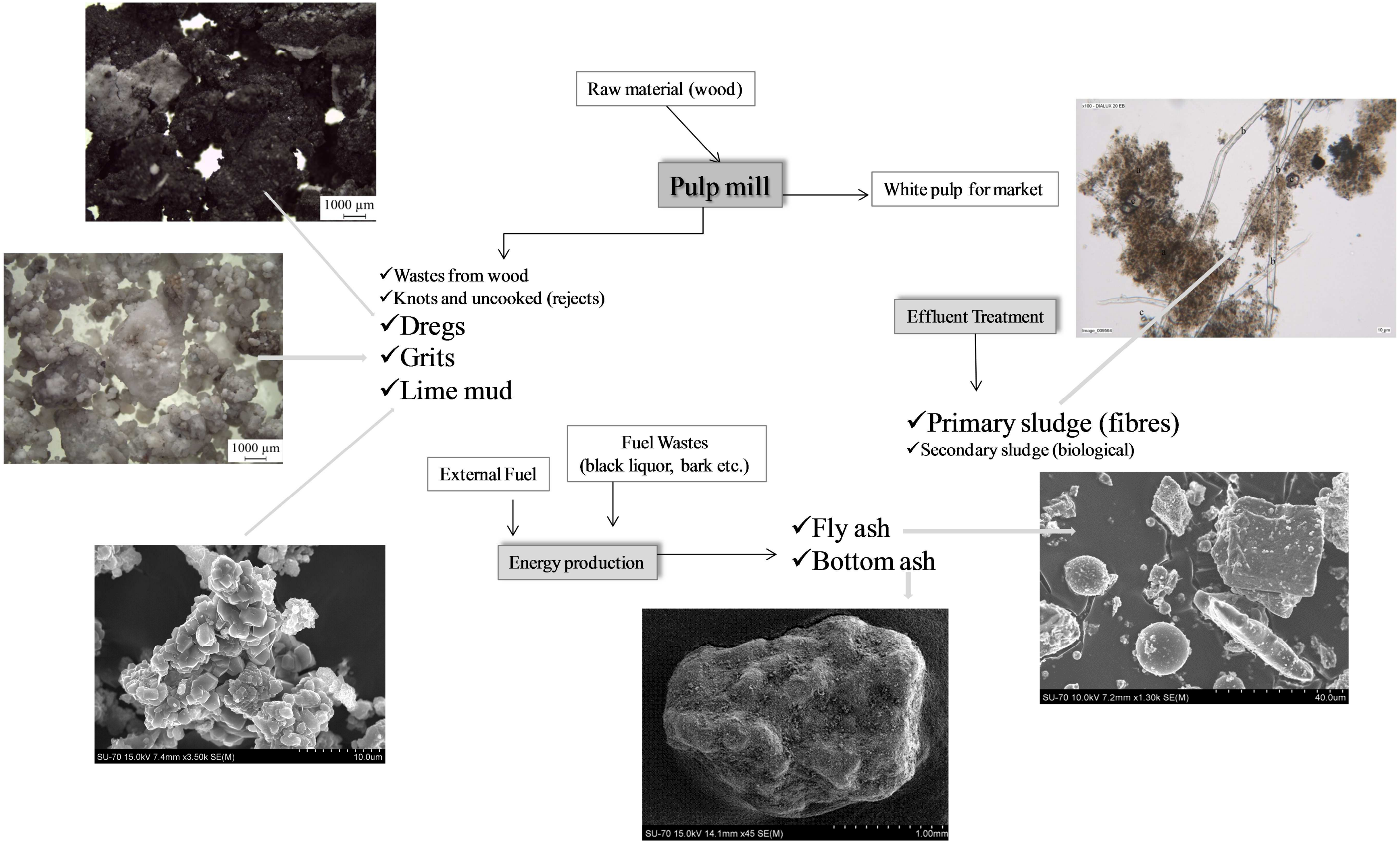


Figure 1. 1. Simplified scheme of integrated pulp mill and respective solid wastes.

1.3.2.1 Chemical recovering and causticizing wastes

The residual weak black liquor from the digesting process is a diluted solution (approximately 12 to 15 percent solids of total weight) of wood lignin, organic materials, oxidized inorganic compounds (sodium sulphate [Na_2SO_4], Na_2CO_3), and non-reactive initial white liquor (Na_2S and NaOH). The recovery of the black liquor starts with a concentration step, conducted through a series of multiple-effect evaporators (MEEs) that increase the solids content up to about 50 percent. At this stage the so called "strong black liquor" is formed. This liquor is either oxidized in the black liquor oxidation (BLO) system if it is further concentrated in a direct contact evaporator (DCE) or routed directly to a non-direct contact evaporator (NDCE), also called a concentrator. Oxidation of the black liquor prior to evaporation in a DCE reduces emissions of odorous total reduced sulphur (TRS) compounds, which are stripped from the black liquor in the DCE when it contacts the hot flue gases from the recovery furnace. The solids content of the black liquor after the evaporator/concentrator typically reaches 65 to 68 percent total weight. The concentrated black liquor is then sprayed into the recovery furnace, where the organic components are combusted, and the Na_2SO_4 is reduced to Na_2S. This process is strongly exothermic and the available energy is recovered as steam for process requirements, such as wood chips cooking, black liquor heating and evaporation, preheating of combustion air, and drying of pulp or paper products. Energy requirements are often supplemented by fossil fuel burning and/or wood firing on accessory boilers. Particulate matter (PM) (primarily Na_2SO_4) exiting the furnace with the hot flue gases is collected in an electrostatic precipitator (ESP) and added to the black liquor to be fired in the recovery furnace.

Additional makeup Na_2SO_4, or "saltcake," should also be added to the black liquor prior to firing. Molten inorganic salts, referred to as "smelt," are collected in a char bed at the bottom of the furnace. The smelt is drawn off and dissolved in water in the smelt dissolving tank (SDT) to form a solution of carbonate-rich salts called "green liquor," which is primarily constituted by Na_2S and Na_2CO_3. The green liquor also contains insoluble unburned carbon and inorganic impurities, named dregs (ELW: 030302), which are removed in a series of clarification tanks [Martins et al., 2007; Modolo et al., 2010; Mahmonoudkhani M., 2005].

Decanted green liquor is transferred to the causticizing area, where the Na_2CO_3 is converted to NaOH by the addition of lime (calcium oxide [CaO]). The green liquor is first transferred to a slaker tank, where CaO from the lime kiln reacts with water to form calcium hydroxide [$Ca(OH)_2$].

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{Heat [R1]}$$

From the slaker, liquor flows through a series of agitation tanks, referred to as causticizers, that allow the causticizing reaction to go to completion (i.e., $Ca(OH)_2$ reacts with Na_2CO_3 to form NaOH and calcium carbonate [$CaCO_3$]).

$$Ca(OH)_2 + Na_2CO_3 \leftrightarrow 2NaOH + CaCO_3\downarrow \text{ [R2]}$$

Insoluble removed from the slakers are denominated grits (ELW: 030302).

The causticizing products are then routed to the white liquor clarifier, which $CaCO_3$ precipitates are removed, being named “lime mud (ELW: 030309)”. The lime mud is washed in the mud washer to remove the last traces of sodium. The washed mud is then dried and calcined in the lime kiln to produce “reburned” lime, which is reintroduced in to the slaker. The mud washer filtrate, known as weak liquor, is used in the SDT to dissolve the smelt. The white liquor (NaOH and Na_2S) from the clarifier is recycled to the digesters in the pulping area of the mill.

In the kraft pulping and chemical recovery processes, carbon dioxide from biomass combustion is emitted to the atmosphere but the major part is dissolved/captured in the recovery furnace, forming Na_2CO_3 that exits in the smelt. Later on, the conversion of Na_2CO_3 into new pulping chemicals involves the transference of carbonate ions to $CaCO_3$ in the causticizing process. Only in the lime kiln, where $CaCO_3$ is converted to CaO, CO_2 is released to the atmosphere [EPA, 2009c].

In summary, grits, dregs and lime mud are the inorganic wastes generated in chemicals recovery process, being normally landfilled after dewatering (see Figure 5.1).

1.3.2.2 Biosludges

The pulp and paper production is a water-intensive activity. Although the recycling of water is increasing through the adoption of closed systems, which promote the recirculation of processing water, running units generate a considerable amount of organic rich wastewater that is purged from the process [Nurmesniemi et al., 2007; Cabral et al., 1998; Thompson et al., 2001]. Before discharge, the wastewater usually undergoes primary and secondary treatments. The primary stage is basically a sedimentation operation that is runned in a clarifier tank, aiming to remove suspended solids from the effluents. It is in this stage where **primary sludge (**ELW: **030310)** (Figure 1.2) is generated. This primary sludge is basically composed of wood fibres and inorganic impurities like sand, and calcium carbonate. Primary treatment can also lead to a reduction of the biological oxygen demand (BOD) [Nurmesniemi et al., 2007; Pöykiö et al., 2004].

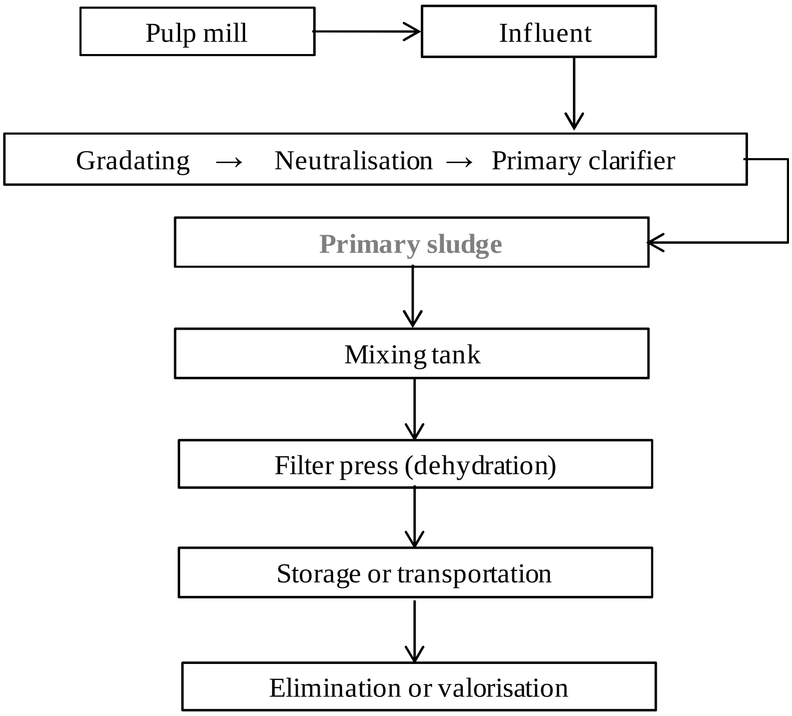


Figure 1. 2. Illustration of the primary effluent treatment flowsheet.

The secondary process is a biological treatment in which micro-organisms are used to reduce the amount of organic pollutants and BOD in the liquid effluent [Pöykiö et al., 2004]. The secondary sludge consists of the microbial biomass, as well as a small fraction of inorganic constituents, including macro-nutrients (nitrogen, phosphorus, and potassium) and micro-nutrients (iron, zinc, and other metals).

1.3.3 Biomass heat and power plants

Recently, pressures on global environment and energy security have led to an increasing demand on renewable energy sources, and diversification of Europe’s energy supply. In 2010, an overall ≈2200GWh of electricity was produced in Portugal from biomass combustion (excluding MSW and biogas) [DGEG, 2013], which corresponds to about 4% of the gross electricity generation in the country. Of this, about 1580GWh corresponds to electricity produced in combined heat and power (CHP) plants running by units of this industrial sector, mainly using black liquors (>80% of fuel feed [Patrao, 2011]) and eucalyptus bark and the remaining 610GWh were generated in dedicated thermal power plants, using essentially forest residues from eucalyptus and pine plantations (tops, barks, branches) and agricultural by-products. Those devoted power plants represent ≈105MWe total installed capacity [Patrão, 2011; Monteiro et al., 2012; AIFF, 2009; Santos, 2011; APREN, 2010], and more than 50% is owned by EDP Bioelectrica [Patrão, 2011]. The Portuguese Government objective for 2020 is an overall 250MWe of installed electric power generation from forest biomass residues, in which the new dedicated plants will have capacities typically below 20MWe [AIFF, 2010; APREN, 2010].

Biofuels, or biomass-derived fuels, are widely employed nowadays. They can exert an important role, since are considered renewable and CO_2 neutral energy resources, once the consumption rate is lower than the growth rate of the plants, and can potentially provide energy for heat, power and transports from the same installation [Pingoud & Lehtila, 1997; Tarnawski, 2004].

Portugal encloses an important potential of renewable energy resources in terms of biomass – forest residues and wood waste. The use of biomass to energy has other advantages beyond the reduction on greenhouse gases from using fossil fuel combustion and the decrease of the external dependence on energy. Fire risks are also reduced by forest cleaning and removal of combustible wastes. To utilize this potential, the Portuguese Government, already in 1990, inquired EDP [Energy of Portugal, S.A], to implement and manage a thermal power plant, in which the input would be the forestry biomass residues. CBE (Portuguese Centre of Biomass to Energy) performed the studies and chose locations to implement the thermal power plant, considering regions having thick forested areas. Another important reason for the location choice was the number of wood industries nearby, namely sawmills, which produce wood residues such as bark.

1.3.3.1 Fluidised bed combustion technology

At industrial scale, the available biomass combustion technologies often evolved from technologies designed for coal combustion with temperatures ranging from about 750ºC to well above 1000ºC. The widely used technologies for large-scale biomass combustion are stationary grates (up to 5MWth), moving/vibrating grates (many in range of 20-50MWth) and fluidized beds (typically within 10-100MWth) [Larsson et al., 2010; Edvardsson et al., 2006]. All of them are relatively simple to operate and can use a wide range of fuels of varying moisture and particle sizes. These combustion systems are commonly used as boilers to produce steam for different purposes. The solid biomass combustion in fluidised bed and grate furnace is a proven technology for heat and power production [Ferraris et al., 2009; Yin et al., 2008].

Fluidised bed combustion (FBC) has been used and widely researched due to its economic potential and lower environmental impact. It is adaptable for burning low-grade coals, biomass and organic wastes, and thereby mixtures of them [Tarelho LAC, 2001; Van Loo & Koppejan, 2008]. The fluidised bed combustion systems have been applied since 1960 for burning municipal solid wastes and distinct industrial wastes. Since then, commercial installations have been built worldwide [Van Loo & Koppejan, 2008]. In Portugal, the first steps in implementing this technology were done just over the last 20 years, to produce energy from wastes of the pulp and paper sectors (in Caima pulp and paper industry), and to combust tires [Tarelho LAC (2001]. Nowadays, Portugal has eleven plants operating with fluidised bed technology.

The fluidized bed combustion boiler is suitable for bark and wood residues (e.g., wood chips, sawdust) from wood-handling processes, as well as to burn biosludge generated in activated sludge plants [Harila & Kivilinna, 1999]. Energy generation from this type of biomass has been referred as sustainable and environmentally friendly alternative to other energy production process based on fossil fuels. The utilization of some of these biomass wastes as an energy source can be beneficial considering effects on carbon balances in ecosystems [Pingout & Lehtila, 1997; Tarnawski, 2004]. During fluidised bed combustion (FBC) the temperature has to be kept low (usually 650–900°C) in order to prevent ash sintering in the bed. Even so, this kind of technology presents high fuel conversion efficiency [McKendry, 2002; Khan et al., 2009]. This fact is also relevant when the environmental aspects in terms of solid wastes are considered.

Some problems associated with biomass combustion in FBC are related with the ash amount and properties, both in the thermal conversion process itself (for example, slagging, fouling, corrosion, bed agglomeration), and also the environmental management of the ashes [Rajamma et al., 2009; Werkelin et al., 2010]. There are two types of fluidised bed combustion technologies, bubbling (BFB) and circulating (CFB). Figure 1. 3 presents a scheme of these types of FBC in terms of material fluxes.

In the fluidised bed technology the primary combustion air enters the furnace from below through the air distributor and fluidizes the bed so that it becomes a seething mass of particles and bubbles [Mitsui Babcock Ltd., 1997; Van Loo & Koppejan, 2003]. In the BFB system, the fluidization velocity of air varies between 1.0 and 2.0 m/s, while in the circulating fluidised bed (CFB) this velocity changes between 5.0 to 10 m/s. Sand particles for CFB systems are smaller in size (0.2 to 0.4mm diameter) than those used in BFB boilers (0.5 to 1.0mm). This means that CFB boilers work under stronger turbulent regimes, what stimulates the heat transfer and assures a homogeneous temperature distribution [Van Loo & Koppejan, 2003].

Anyway, both types show the following attributes: high flexibility concerning moisture content and kind of biomass fuels; burning under a low excess of oxygen raises the efficiency and decreases the flue gas flow; there are no moving parts in the hot combustion chamber; and NO_x emissions are reduced by air staging. In terms of disadvantages we might refer high investment and operating costs; low tolerance in changes of size distribution of bed particles; tendency for bed agglomeration, especially when burning strongly alkaline fuels; need to manage the exhaust bed particles.

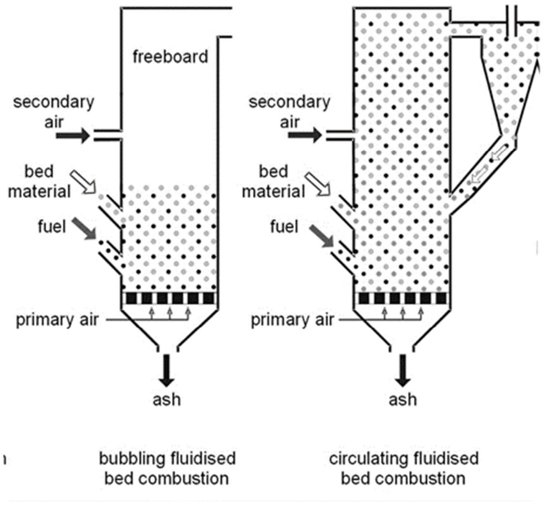


Figure 1. 3. Bubbling and Circulating fluidised bed combustion technologies for biomass and particles distribution system. [*Source:* van Loo & Koppejan (2003)].

1.3.3.2 Ashes from forest biomass combustion

During biomass combustion in FBT, two main types of ashes are generated: Fly ash and bottom ash. Two different fly ash fractions are normally distinguished: multi-cyclone fly ash and filter fly ash. According to van Loo & Koppejan (2003), multi-cyclone fly ash is fine when compared with bottom ash. They are mainly composed of inorganic ash particles carried with the flue gas and precipitated in the secondary combustion zone, in the boiler and especially in multi-cyclones placed downstream the boiler. The ash fraction from multi-cyclone consists of coarse fly ash particles. Filter fly ash is finer than multi-cyclone fly ash. The filter fly ash is collected in electrostatic filters, fibrous filters or is condensed as sludge in flue gas condensation units, normally placed downstream the multi-cyclone. The fly ash collected during fluidised bed combustion of biomass is classified as industrial waste, with code 100101 according to the European List of Wastes code.

The bottom ash is a waste generated upon periodic bed discharges in a FBC, required to assure bed renovation and to avoid agglomeration and consequent defluidization, as well as to maintain the bed height and the suitable particle size distribution. Those parameters are crucial to guarantee proper hydrodynamic conditions of the bubbling bed. Bottom ash consists of solid coarse particles predominantly irregular in shape and mostly siliceous in nature (quartz) with organic impurities. They are composed by the sand particles fed purged from the original bed, inorganic (soil and small stones) components of the fed and the biomass unburnt fraction. The bottom ash generated during biomass combustion in fluidised bed combustion is classified as industrial waste, with code 100124 according to the European List of Wastes.

According to some authors [Rajamma et al, 2009; Van Loo & Koppejan., 2003; Werther et al., 2000; Demirbas, 2005] the biomass combustion technology influences the amount and characteristics of the ash produced in a power plant. In grate furnaces the biomass ashes are subjected to higher temperatures (the maximum fuel bed temperature can be as high as 1000–1200 ºC) in comparison to a fluidised bed (less than 900ºC). In consequence, this influences the amount of organic species, several salts and heavy metals that volatilize in the furnace, and consequently the composition of the ashes. As already referred the ashes characteristics are also influenced by the biomass type and containing impurities, the residence time and, mainly, the bed temperature (low temperatures might cause incomplete burning and the amount of organic particles tend to increase in the ash).

The siliceous nature (prevalence of quartz) of the bottom ash makes it a candidate to replace natural aggregates in the construction sector, replacing calibrated sand for instance in industrial mortars. Natural aggregate consists of manufactured crushed stone and sand created by crushing bedrock, or naturally occurring unconsolidated sand and gravel. It is a major component of the most used construction materials, such as asphalt and concrete [Bleischwitz and Bahn-Walkowiak, 2006]. This subitem specifies some environmental considerations about the construction sector, including potential impacts of extraction and processing of aggregates. During combustion, most of the inorganic nutrients and trace elements in the wood are retained in the ash [Steenari & Linqvist, 1997]. Once the biomass is burned in the furnace, the heavy metals from the fuel becoming concentrated in the ash; the various ash fractions such as bottom ash, cyclone fly-ash, filter fly-ash and exit flue gas particles may contain relatively high concentrations of heavy metals [Narodoslawsky & Obernberger, 1996; Obernberger et al., 1997; Fujimori et al., 2004]. Generally, biomass ashes are composed of the biomass nutrients, as for example Ca, K, Na, Si and P. In case of wood biomass, the alkali metals content is high compared to silicon content (i.e., rice husks) [Thy et al., 2006; Masia et al., 2007].

1.3.4 Construction materials as a waste management solution

Worldwide, the construction industry consumes more raw materials (around 3000 Mt/year, almost 50% in mass) than any other economic activity, which shows its potential to become an unsustainable activity [Torgal e Jalali, 2010]. The Council International Building (CIB) defined in 1994 the 7 principles for sustainable construction, whose first two are described as the "Decreasing consumption of resources" and “Reuse of the resources” [Kibert, 2008].

Every year more than 1m^3 of concrete is produced per person worldwide [Scrivener and Kirkpatrick, 2008] with Portland cement being the key ingredient, but producing the greatest environmental burden. Presently around 3 billion tons of Portland cement are consumed worldwide [Zampini, 2009] and for the production of every 1 ton of cement, approximately 800 kg of carbon dioxide is released [Ban and Ramli, 2011], around 5–8% of all manmade CO_2 [Flatt et al., 2012]. While cement production is still based on the Ordinary Portland type (OPC), in the last few decades several other types started to be produced using supplementary cementitious materials to partially replace the clinker [Ali et al., 2008]. Anyway, in concrete and alphalt formulations the aggregates correspond to the highest volume fraction. Ready-mixed concrete is made of up to 80% aggregates, while pre-cast products and asphalt might contain 95% aggregates [Bleischwitz and Bahn-Walkowiak, 2006]. The environmental impacts caused by aggregates extraction and processing include changes in the landscape, noise due to vehicle movements from the pit or quarry, dust, vibrations from blasting, and degradation of groundwater and surface water. In that sense, the use of alternative supplementary materials might assure the following benefits: (1) reduction of the consumption of non-renewable natural resources; (2) reduction of energy consumption and emissions of greenhouse gases; (3) landfilling reduction [Frederico and Chidiac, 2009].

To design effective recycling solutions it is desirable to combine multidisciplinary skills. The properties of the raw materials and how they affect the behaviour of the final products, such as mortars, fibercement, bricks, etc, should be known. Chemical and physical characteristics need to be defined, while determination of effects on the mechanical performance and durability of the products is a crucial requirement to estimate the viability of the suggested recycling route. But at the same time, environmental issues need to be accomplished.

Next paragraphs will describe some examples of the use of wastes as replacement material in several types of construction materials. The use of pozzolanic wastes or by-products in mortar formulations goes back a few thousand years ago. The Thera volcano eruption in 1500 BC, which destroyed part of the island Santorini, was responsible for the appearance of vast amounts of ash which were used by Greek civilization in mortar formulations. The pozzolanic reactivity is the ability of the material to chemically combine with the calcium hydroxide. It is a complex property that depends on the chemical composition of the material, namely their silica and alumina contents, on the (low) degree of crystallinity, and on the particle size distribution [Gjorv, 1992; Liu, 1998].

In the cement industry both the material and energy contents contained in certain pulp and paper residues can be recovered. Sludges from primary clarifiers (or mixed with sludge from biological treatment) might be used as clinker components [Ahmadi and Al-Khaja, 2001; Cernec et al., 2005]. However, its suitability depends on the amount and type of inorganic compounds present in the material. The primary sludge is collected in a wet condition (about 50% moisture content) and need to be dried before addition to the clinker meal. Existing pre-dryers on the cement kilns might be used to reduce the moisture content down to 10–15%. Thus, when burning the dried sludge in the cement rotary kilns, the calorific value of the organic substances will reduce energy requirements in the calcination stage. The resulting ash will then compose the clinker [IPPC, 2001].

Ravina (1997) researched the utilization of large quantities of Class F fly ash of marginal quality in structural concrete as partial fine sand replacement. He studied the effect of such replacement on the properties of fresh [Ravina, 1997] and hardened [Ravina, 1998] concrete. Results showed beneficial effects on the workability and on the compressive strength of structural concrete and, while elasticity modulus was improved. The fineness of the ash explained that behaviour, since compactness was improved.

Andiç et al (2005) investigated the effect of low-lime fly ash (conforming to relevant Turkish standard) on the mechanical properties of tile adhesives. Formulations were prepared by partially substituting cement or sand by the waste. Cement replacement by fly ash in all levels (from 5 to 25%wt) induces reduction on the flexural and compressive strength in all studied ages. By contrast, ash for sand substitution, at percentages up to 10 wt%, did not affect much the tensile adhesion strength of the material. A good correlation between changes on the tensile adhesion, flexural and compressive strength values and fly ash for cement replacement content was observed.

Andrade et al (2009) discussed through experimental results, the influence of the use of coal bottom ash as a replacement for natural fine aggregates on some properties of concrete. They studied the influence of the bottom ash porosity on the potential water absorption and water loss of the material, as well as on the water consumption of concretes produced with bottom ash. The results showed that in the fresh state the concretes produced with the bottom ash are susceptible to water loss by bleeding and the higher the percentage of bottom ash used as a natural sand replacement the lower the deformation through plastic shrinkage. The results also showed that the setting time is affected by the presence of bottom ash in the concrete. This study concluded that different forms of bottom ash mix result in concretes with different properties in the fresh state, but the behavioural tendencies are maintained when bottom ash is employed as a replacement for natural aggregates.

Typically, ashes from biomass combustion have more alkali (i.e. Na and K) and less alumina than coal ashes [Llorente and Garcia, (2006); Thy et al., 2006]. According to

Etiegni (1990) wood ash in Europe had been used as a feedstock in the manufacture of Portland cement. Almost ten years later, Naik (1999) reported that wood ash had a substantial potential for use as a pozzolanic mineral admixture and activator in cement-based materials. He further indicated that wood ash has significant potential for use in numerous other materials including controlled low strength materials (CLSMs), low- and medium-strength concrete, masonry products, role compacted concrete pavements, materials for road base, and blended cements. Due to high carbon content in wood ash, its use is limited to low- and medium-strength concrete materials [Siddique, 2012].

Rajamma et al. (2009) studied the incorporation of fly ashes from forest biomass combustion in cement based formulations. They figured out that this type of biomass is similar to class C fly ash to EN 450 on the basis of chemical composition and concluded that up to 20% fly ash could be incorporated as cement replacement in cement-based mortars in order to maintain an acceptable mechanical strength. As well, Ramos et al. (2013) evaluated a wood waste ash (WWA) in mortar as a partial cement replacement material to ascertain applicability in cement-mortars. They developed an extensive experimental program carried out on mortar containing this ash to assess strength and durability parameters (carbonation and alkali-silica-reaction) and concluded that WWA seems to be a promising pozzolanic material for partial substitution of cement (20%wt), with no strength loss while enhancing the durability and thus contributing to sustainable construction.

According to Sale and Lima (2010) many types of ash do not have hydraulic or pozzolanic reactivity, but can be used in civil construction as inert materials. Based on the physicochemical characterization of sugarcane bagasse ash (SBA - bottom and fly ash), mortars and concretes were produced by using such waste as sand replacement (between 10 and 100%wt sand replacement). They observed that SBA can be recommended as replacement of fine aggregate for the manufacture of artefacts and ordinary structures. SBA can be used as a partial substitute of sand in concretes made with cement slag-modified Portland cement for structures requiring strength values up to 30 MPa.

Garcia and Sousa-Coutinho (2013) tried to assess the effects of using ground bottom ash (GWA) as cement replacement in mortars. The non-pozzolanic character of the waste did not contribute to improve the mortar durability, so the material may be used as filler in cement-based formulations providing marginal durability loss and improving strength at later ages.

In bricks production, the addition of 5–15% of paper sludge as raw material will improve the porosity of the fired matrix, then reducing the weight and improving the thermal insulation. Heat released due to burning of organic components will save energy upon firing. The product tends to be more resistant to cracking during drying and firing stages, but mechanical resistance diminished [Cernec and Zule, 2005; Cernec et al., 2005].

Demir (2005) investigated the potential utilization of wastes from kraft pulp production, namely sludge basically composed by short cellulose fibers (primary sludge), in clay bricks. Results were somewhat similar to the ones previously reported: up to 5 wt% addition, an effective pore forming effect was observed in the clay bodies, while the mechanical properties are acceptable. The control of extrusion conditions of green bodies is also easily achieved, by increasing the water content in the mixture to adjust the plasticity level.

1.4 Legal Procedures

There is a clear need for guidelines to a sustainable management of solid wastes in order to enhance and to establish practices of correct management of these by-products. For that, it seems important to characterize for knowing and controlling these wastes properties and qualities focusing on their application/recycling as alternative to landfilling, thus saving natural resources as well. Some aspects related with bureaucratic process (licenses, dispatch notes, charters etc) many times subject the all process that occurs from industrial preliminary tests until the solution implementation. In Portugal, at least three entities are involved in the request of simplified licensing process for waste management: the applicant, the Commission of Coordination and Regional Development (CCDRs) and ANR (Wastes National Authority). The standard procedure for simplified licensing of waste management operations in Portugal includes procedures defined in the following legislation.

Decree-Law n.º 178/2006, September 5th (Defines the general polices for waste management and applies to waste management operations, including any transaction collection, transportation, storage, category, treatment, recovery and disposal of waste and the decontamination of soils and monitoring of disposal sites following the closure of their premises).

Ordinance n.º 1023/2006, September 20th - Indicates the elements that constitute the simplified licensing request.

Ordinance n.º 50/2007, January 09th - Presents the template of license for carry out waste management operations.

Ordinance n.º 209/2004, March 03rd - The European Wastes List (Decree-Law n.º 237/97, contained in this ordinance ensures harmonization of regulatory prevailing in the identification and classification of residues while facilitating a perfect knowledge by economic agents of the legal system to which they are subject.

1.4.1 Main Steps of simplified licensing process

Portugal has a specific standard which goal is to clarify and systematize the organization of simplified procedures for licensing waste management operations coordinated by CCDR, under the writing and flow chart form – steps, content and responsible conduct of these processes simplified licensing, according to the legislation above referred. This standard shall govern the relations between CCDR, the applicants and ANR in these processes and it should be systematically applied to all cases of this type in which the Commission of Coordination and Regional Development – Lisbon - Tejo Valley (CCDR-LVT) will be involved. Figure 1.4 illustrates a simplified scheme numbering the three main steps present in the whole process of simplified licensing of wastes management operations related with storage, separation, treatment, valorization and elimination. This scheme is detailed in figure 1.5 where the systematization of the main steps related with the process phases necessary to obtain the license are indicated.

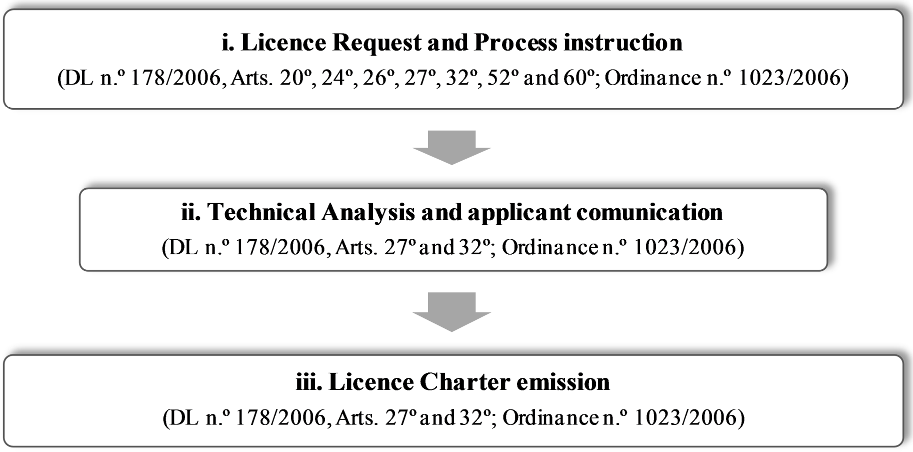


Figure 1. 4. Main steps of simplified licensing process.

1.4.2 Specification according to Ordinance n.º 1023/2006

Before following the steps listed in figure 1.5 it is necessary to elaborate the description memory (specification) of the project according to Ordinance n.º 1023/2006 (September 20th). The elements requested to elaborate this document are as following:

I. Project of Installation/facility (specification)
   a. Facility location where the waste management operations are based. The information should indicate the address, telephone, fax , email address and Company Activity Economic Code (CAE);
   b. Identification of waste handled, foreseeable origin, quantitative and qualitative characterization and their classification according to Decree-Law n. º 209/2004, March 3rd;
   c. Identification and quantification of other substances used in the process;
   d. An indication of quantities and characteristics of the final product;
   e. Indication of the number of workers, the regime of operation and social character facilities, medical and health at work;
   f. Full display of identification and qualifications of technician employees responsible by the management operation;
   g. Detailed description of the operations to be carried out subject to licensing, with the presentation of process diagram and their classification according to the provisions of Annex I and II of Decree -Law n. º 178/2006 of September 5th in writing by Decree -Law n.º 73/2011, June 17th;

h. Indication of rated capacity installed or to be installed for operation (R or D); Operations related with wastes described in Decree-Law n.º209/2004 of March 3rd: R – Wastes Valorization; D - Wastes Elimination;
i. Description of facilities including storage;
j. Identification of equipment, machinery and other equipment, stating the main emission sources of noise and vibration , and security systems;
k. Identification of pollutants sources;
l. The quantitative and qualitative characterization of liquid and gaseous effluents as well as waste resulting from the activity;
m. Description of internal measures to minimize, reuse and recovery of wastes produced, indicating their qualitative and quantitative characterization, when possible;
n. Identification of the destination for the waste generated internally, indicating their qualitative and quantitative characterization and description of the onsite storage of own production if any;
o. Description of environmental measures proposed to minimize and treat wastewater and respective monitoring indicating the proposed final destination;
p. Description of environmental measures proposed to minimize and treat the waste gases and respective monitoring, characterization and chimneys design when applicable law requirements;
q. Sources of internal and external risk, security organization and means of prevention and protection, particularly with regard to the risks of fire and explosion.

II. Drafts

a. Plan, scale 1: 25000, indicating the location of the facility and, in the case of hazardous waste management and incineration or co-incineration of non-hazardous waste operations, covering a radius of 10 km from the installation, and main building, such as hospitals and schools;
b. Location plan, scale 1:2000;
c. Layout of the facility, which shall include the operation, scale 1:200, indicating in particular the location of areas of waste management, storage of raw materials, products and wastes, wastewater treatment systems and location of their final

discharge point, workshops, warehouses, offices and outdoor circuits. The cover shall be identified and not covered permeable and impermeable.

With the delivery of the final decision, it is issued and sent to the operator the respective license, which shall, in particular refer:

a. The licensee identification, including the full email address of the facility licensed and its georeferencing;
b. The type of waste management operation for which the operator is licensed, including those applicable technical standards and the method of treatment usable;
c. Accurate indication of the type of waste covered according to the European List of Waste (Decree-Law n.º209/2004 of March 3rd), the total amounts and the object of waste recovery or disposal operations classified in accordance with Annexes I and II of Decree-Law n.º209/2004 of March 3rd;
d. The conditions to which the transaction is subject to waste management including precautions for safety;
e. Identification of the technician responsible for the operation of waste management;
f. Identification of facilities and equipment or licenses , including an indication of their number and the relevant technical requirements;
g. The license validity period;
h. Monitoring and control operations required;
i. The provisions as necessary regarding the closure and after-care closure;
j. Indication of the energy efficiency of the process, if an incineration as an incineration operation is concerned or co-incineration with energy recovery;
k. The consequences of non-compliance with license conditions.

However, even with a standard that facilitates the fulfilment of the criteria for completion of an application for simplified licensing of waste management operations, also helping to understand the legal procedures as well as to give an estimated forecast period from submission of the request until of the process this is very time consuming and bureaucratic. Consequently, this quite complex procedure often can lead the applicant to withdraw the request, even when it is recognised that the economic benefits of the waste management operation surplus the cost involved in all the licensing request process.

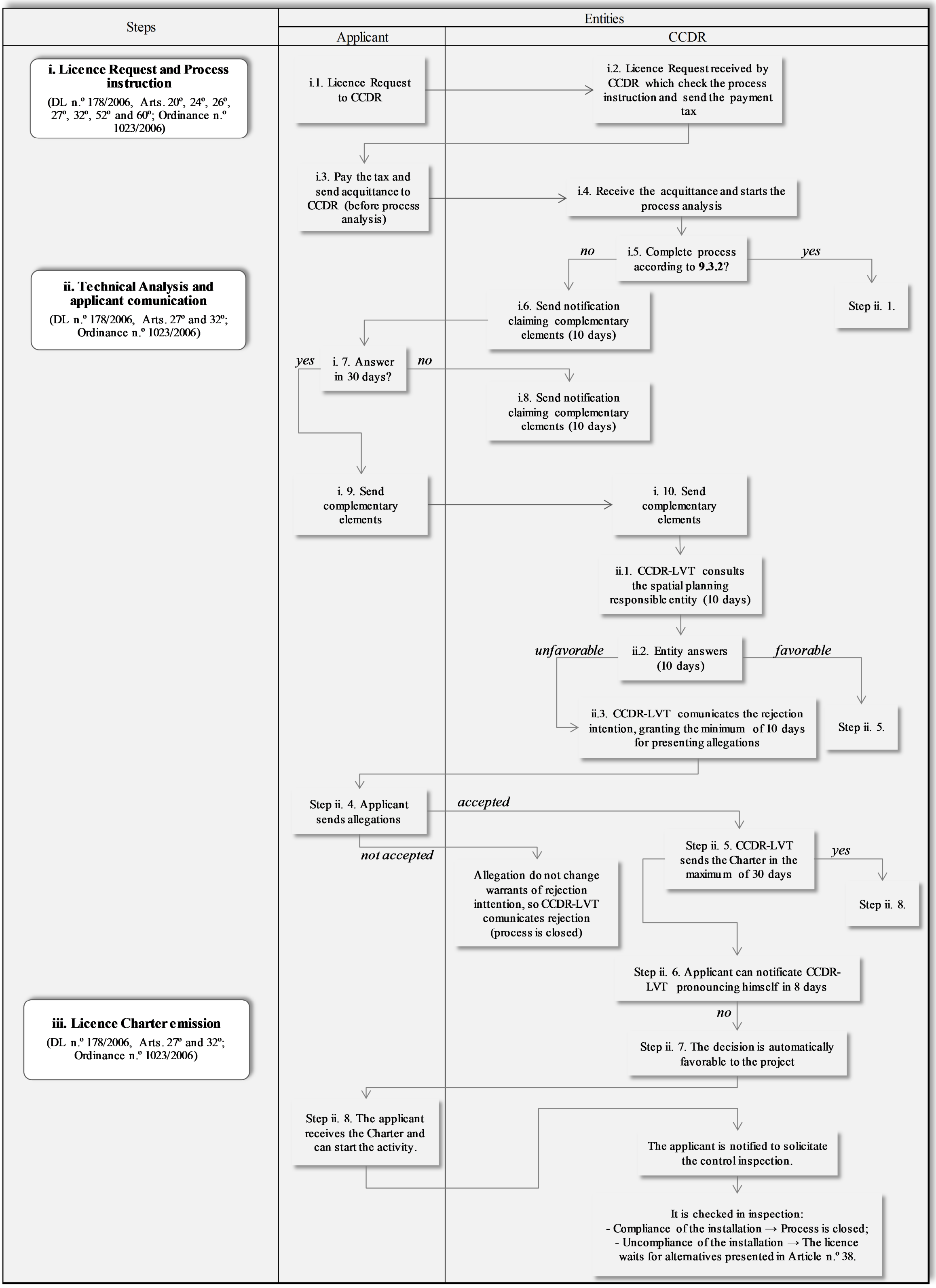


Figure 1. 5. Fluxogram of the simplified licensing process steps [Standard of Procedure, 2012].

2 EXPERIMENTAL WORK

This work was planned considering three stages of development: bench scale tests, pilot-experiments and industrial applications. The bench scale was considered for all wastes and applications. Tests were developed first with a general characterization wastes and raw materials, in terms of physical, chemical and mineralogical properties. Then samples were produced and characterised, aiming to optimize the relevant properties. Considering applications for which large-scale experimental facilities were available, in a tentative of testing process adaptations for real solutions.

2.1 Experimental Methods

2.1.1 Physical characterization

To determine the water content of the solid samples they were dried to constant mass during at least 24h in an oven at 105ºC ± 5. The water content was generally expressed in total weight percent (EN 12880:2000; Characterization of sludges – Determination of dry residue and water content). The particle density and water absorption was determined for some solid wastes and raw-materials using the standard NP EN 1097-6: 2003; the method was used to determine the density of the foundation soil, solid waste and their mixtures, but also to understand changes occurring during modification of the components of a material. For density determination, the mass of sample was taken after being dried, and the volume is determined by the weight of the volume of water displaced by the dry particles in a known volume of the picnometer; the volumic mass was determined by the expression below:

$$\rho = \frac{(M_3 - M1)}{[(M_3 - M_1) - (M_4 - M_2)]}$$

Where:

M1 – picnometer mass (g)
M2 - picnometer and water masses (g);
M3 – picnometer and dry sample masses (g);
M4 – picnometer, saturated sample and water masses (g).

The particle size distribution of materials was determined by using two techniques:

i) Sieving

The manual sieving was performed according to NP EN 933-1:2000. The used sieves were comprehended between 25 mm and 0.63 mm. Before sieving, materials were dried at 105ºC to remove the moisture and then to prevent the agglomeration of fine particles and clogging of the sieves. The mass used was adjusted according to the particle size characteristics of the material. The amount retained in different sieves was weighed.

ii) Laser diffraction particle size analyzer

The particle size distribution of fly ashes (below 1mm) was determined on a Coulter LS 230 (Coulter Electronics, Krefeld, Germany) apparatus, equipped with PIDS (Polarization Intensity Differential Scattering). The Coulter consists of a vessel where the particles are dispersed in a fluid. This suspension is forced through a small opening where existing electrodes will impose an electric current. When a particle passes through the opening, there is a disturbance in the electrical current, corresponding to a sudden increase of resistance. This change is directly related with the volume of the particles, which allows the determination of the size distribution and the mean value [Ferraris et al., 2004]. The Coulter LS 230 uses a laser of 750 nm and double Fourier lens for focusing the scattered light on the ring-shaped detector setup. The detection range (angles) for diffraction is claimed to be 40 nm – 2000 µm, thus theoretically covering the desirable size range.

The specific surface area was determined by nitrogen adsorption using a specific method developed by Brunnauer, Emmett and Teller, which is called by the BET method [Brunauer et al. 1938]. The equipment used was a Micromeritics Instrument Corporation model, Gemini 2380, working at a pressure of 763 mmHg

2.1.2 Chemical and mineralogical characterization

Thermal gravimetric and differential thermal analyses (TG/DTA) were performed up to 1000ºC/1200ºC with a heating rate of 10 ºC/min, in a simultaneous TG/DTA (STA 409 EP) apparatus. The data were analyzed with software programs supplied by the instrument. The thermo gravimetric curve was corrected for buoyancy effect, while the differential thermal analysis curve was corrected for baseline effect. Adjustments for buoyancy and baseline effects were acquired in a blank run using empty crucibles.

Thermal gravimetric and differential thermal analysis (TG/DTA) were performed up to 1000ºC/1200ºC with a heating rate of 10 ºC/min, in a simultaneous TG/DTA (STA 409 EP). The data were analyzed with software programs supplied by the instrument. The thermo gravimetric (TG) curve was corrected for buoyancy effect and the differential thermal analysis (DTA) curve was corrected for baseline effect. Adjustments for buoyancy and baseline effects were acquired in a blank run using empty crucibles which were later used to run the sample in a second run, but the two experimental runs were made under identical conditions.

The chlorides content of certain solid wastes was determined by the Argentometric method (CHLORIDE, 4500-Cl-; Standard Methods Committee, 1997). In order to prepare the samples for the analysis, 100 g of dried material is dissolved in 1 liter of distilled water, while suspension is then stirred for 24 hours. Then, 100 mL of filtered solution are titrated. Chlorides are titrated with a silver nitrate solution in the presence of chromate anions. The end point is denoted by the appearance of a red colour corresponding to the formation of silver nitrate. By decreasing the pH value, silver chromate solubility grows up due to the protonation of chromate anions, while at high pH values silver reacts with hydroxide anions and precipitates as AgOH and Ag_2O. Both reactions interfere with the determination accuracy. So the pH of the solution is reduced to 7 by adding sulphuric acid. Potassium chromate solution is used as indicator, to create a slightly yellow colouration. It was titrated against 0.0141M silver nitrate. At the end of the chloride precipitation as white silver chloride, the first excess of titrate precipitates as silver chromate, which signals the end point. Corresponding reaction are given below.

$$Ag + Cl \rightarrow AgCl\ (s)\ [R5]$$

$$2Ag + CrO_4 \rightarrow Ag_2CrO_4\ (s)\ [R6]$$

By knowing the stoichiometry and moles consumed at the end point, the amount of chlorides in an unknown sample can be determined.

The chloride content on mortars (see chapters 6 and 7) was determined according to EN 1015-17:2000 (Determination of water-soluble chloride content of mortars). Ten grams of material was milled (< 150 µm) and dissolved in 100 mL HNO_3 solution (10% w/w), by boiling for 15 minutes. After this, the sample was filtered and washed with hot distilled water until complete 500 mL of solution. The chloride content was determined by potenciometry using a selective ionic electrode (Consort, model C860) in 50 mL of the final solution.

The sulphate content was determined by gravimetry (SULFATE, 4500-SO4-2; ignition of residue, Standard Methods Committee, 1997). Samples were dried, weighed and dissolved in diluted HCl. Barium chloride solution was added in excess to precipitate barium sulphate, and the precipitate was digested in the hot solution (between 80 – 90ºC). The precipitate was filtered through a filter paper which was then ignited (at 800 ºC for 4 hours) and completely combusted. Weight ratio between precipitate and initial sample amounts corresponds to the sulphate %. The precipitation reaction is described by equation R7.

$$Ba^{2+}\ (ag) + SO_4^{2-}\ (ag) \rightarrow BaSO_4\ (s)\ [R7]$$

Crystalline phases or mineralogy of the materials were detected by X-ray diffraction on a RIGAKU-Geigerflex X-ray diffractometer. Analysis was performed under 40 kV/30 mA, and scan mode continuous/speed-2◦ (min^{-1}). A C Series; CuKά radiation is used and the angle range 2Ө was 10º - 80º.

The chemical characterization of the samples was performed for major and minor chemical elements by X-Ray Fluorescence (XRF), using a Panalytical Axios spectrometer. Prior to analysis, the samples were subjected to a grinding process in an Agatha mill, followed by drying at 101 ºC ± 1 ºC for at least 12 hours. The chemical analysis was performed considering: i) Loss on ignition (LOI), and ii) XRF analysis on a pressed pellet previously prepared. For LOI determination, approximately 1.5 grams of the sample, milled and dried, were heated to 1100 ºC for 3 hours in a Carbolite furnace; the LOI was obtained based on the loss of weight after the heating at 1100 ºC.

The samples morphology was analyzed by Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS), using an ultra-high resolution analytical scanning electron microscope HR-FESEM Hitachi SU-70. Optical microscopy analysis was developed by microscope V (Leica EZ4 HD).

These techniques required powder as samples for analysis. To enable the application the samples were dried and milled (700 rpm/ 5 minutes) in a fast agate mill until a thin powder to be obtained before testing.

2.1.3 Sample characterization methods for specific applications

Application in fibercement production (Chapter 3)

The Schopper-Riegler test is designed to measure the rate of drainage of a diluted pulp suspension. The drainage rate is related to the surface conditions and swelling of the fibers. It is widely used to track the changes in the drainage rate of various chemical pulps during beating and refining. In principle, this method is applicable to all kinds of pulp in aqueous suspension. However, in practice, the Schopper-Riegler test provides acceptable results only if a sufficiently dense mat of fibres is formed on the wire screen. For this reason, the test is not recommended for some extremely short-fibred pulps, such as those obtained from well-beaten hardwoods, as most of the fibres will pass through the wire screen, resulting in anomalous reduction of the SR number. The most reliable results are obtained within the range of 10 to 90 SR number. The SR/Pneumatic used in this study is used for the determination of drainability of pulp suspension in water. The drainability is the measurable index of the refining degree of pulps. The refining of pulps is one of the most important stages in the paper production process and strongly determines the sheet forming process and then the physical properties of resulting material. In this specific case, fiber-cement sheets were considered (ISO 5267/1:1999 – Pulps: Determination of drainability - Part 1: Schopper-Riegler method). Some testing characteristics include: speed of sealing cone = 100 ±10 mm/s; calibrated bottom orifice = 149.0 ±1.0 s for 1litre of H_2O drainage chamber volume = 1000 mL; drainage area = 100 cm^2; pneumatic driving pressure = 2.0 kgf/cm^2; measuring scales = 0-100 SR; resolution = 1 SR; air supply = 2 kgf/cm^2; and air consumption = 0.1 m^3/h.

Application in bituminous mixes (Chapter 4)

Two techniques were applied to determine the concentration of fine particles, here considered as impurities since they are basically constituted by the unwanted clay fraction, in the aggregates used as raw-materials for bituminous mixes: Methylene-blue (MB) and Sand equivalent (S_e). The tests were developed according to NP EN 933-9: 2000 and NP EN 933-8: 2000, respectively. In summary, the MB technique involves the determination of adsorption of such dye by a defined amount of aggregate particles. Increments of a solution of methylene-blue are successively added to a water suspension containing the test specimen. The adsorption of the methylene-blue solution by the sample is verified by conducting test spots on filter-paper to detect the presence of free methylene-blue visually, recognized by the presence of a halo on the spot (Figure 2.1). The volume of MB solution used to titration is registered and the results are expressed in grams of adsorbed MB per kilogram of sieved fraction assayed.

In the sand equivalent test, a sample of aggregate passing through 4.75 mm sieve and a small amount of flocculating solution are poured into a graduated cylinder and are agitated to remove the clay-like fine particles that might be present in the batch. The sample is then irrigated with additional flocculation solution to assure the complete removal of such clay-like fraction. After a prescribed sedimentation period (the complete test procedure is described in NP EN 933-9:2000), the height of flocculated clay fraction and the sand mass are determined. This ratio gives the sand equivalent value, and higher values correspond to a “cleaner” aggregate material.

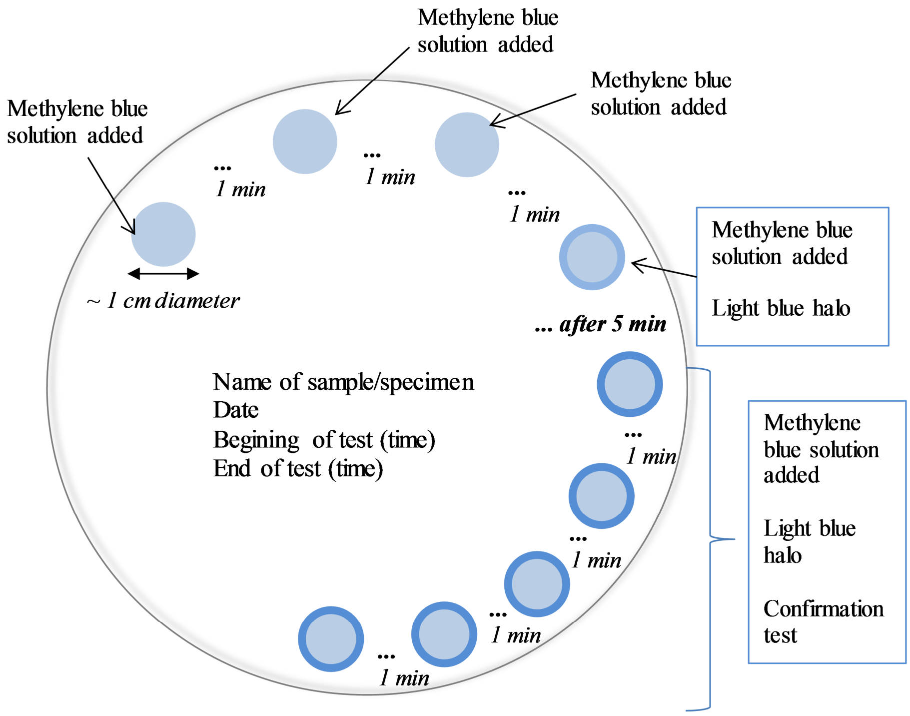


Figure 2. 1. Scheme of methylene blue test.

2.2 Pilot scale combustion facility

The biomass combustion experiments were performed in a pilot-scale facility including a 30kW$_{th}$ fluidized bed combustor (Figure 2.1). A detailed description of the experimental work developed in this facility is presented in Chapter 8 of this thesis, including the set of operating conditions as well as the specific experimental procedures used during the combustion experiments. More detailed information about the pilot-scale infrastructure can be found in several published works [Tarelho, 2001; Tarelho et al., 2004; Tarelho et al., 2005; Tarelho et al., 2011].

This pilot-scale combustion facility can be divided into three main systems: the fluidized bed combustor, the gas sampling and analysis, and the control and data acquisition. The combustion reactor is a thermally insulated bubbling fluidized bed (AISI 310 Stainless Steel) with overall dimensions of 0.25 m intern diameter and 3 m height. The reactor has a bed of silica sand (250 μm – 710 μm particles) with a static bed height of 0.23 m, supported on a nozzle-type distributor for the primary combustion air injection as fluidizing agent, nine ports for gas sampling probes and for monitoring pressure and temperature along the reactor height (three of which inside the bed), ports for charging/discharging of bed solids, as well as specific ports accommodating a variety of devices: an auxiliary gas burner, a zirconia cell for in-situ O_2 monitoring, a port for the fuel feeding, a port for the secondary combustion air supply, and water-cooled heat-exchangers. The biomass fuel is fed to the reactor by a screw-feeder located on top of the freeboard and falls down through a vertical stainless steel tube and is discharged at bed surface. This vertical tube also permits to inject the secondary air together with the fuel. The freeboard temperature is controlled by a water-cooled heat exchanger wound around the vertical fuel feeding tube. In turns, the bed temperature is controlled by eight radial water-cooled probes inserted into the bed. The fuel feeding system is calibrated manually by means of a scale for each type of biomass to be used as fuel. Also integrated in the bottom part of the reactor and located upstream of the primary air distributor plate (that is, in the wind-box) it is located an electrical element intended to be used for heating the primary combustion air during the start-up procedure of the reactor.

Figure 2. 2. Pilot scale bubbling fluidized bed combustor (Department of Environment and Planning of University of Aveiro, Portugal).

The pneumatic circuits for controlling the various gas streams entering the fluidized bed reactor (e.g. combustion air, N_2 purging gas, propane for the start-up gas burner) make use of solenoid valves to be able to operate the system either in an automatic or manual mode.

The gas sampling and analysis system comprises a series of water-cooled probes, suitable pneumatic lines integrating gas conditioning units and a PTFE diaphragm pump, a set of online gas analyzers (for example for O_2, CO_2, CO, NO), as well as pressure sensors and thermocouples (K-type). The water-cooled gas sampling probes are inserted into the abovementioned sampling ports located at several positions along the reactor height, each one equipped with a K-type thermocouple, a plug filter at the tip located inside the combustor chamber for removing particles, and a condenser located at the rear part of the probe for removing water and heavy hydrocarbons. There is also a heated probe and sampling line (180ºC) inserted into the freeboard through the reactor top flange for hot gas sampling for total hydrocarbons quantification. The pneumatic circuits are integrated into automatic gas control and distribution units which permit to selected a specific probe for sampling gases and turn the online gas analyzers into service in a controlled way. The experimental system is controlled by a computer based data acquisition and control system. The experimental data collected during each experiment run was recorded by the data acquisition system for subsequent analysis.

2.3 Industrial scale test

Twenty five tons of bottom ash from forest biomass combustion in an industrial bubbling fluidized bed combustor (BFBC) at a pulp and paper mill were treated by washing and sieving (< 1000μm) at an industrial facility (dealing with treatment of raw material for the construction sector, namely, prepares natural sand as aggregate for the construction industry). The goal was to make the treatment of the bottom ash in order to be used as recycled material in substitution to conventional raw material in industrial mortars (Chapters 6 and 7). With this industrial test, it was possible also to evaluate the efficiency the washing and sieving treatment process, considering the process conditions. In Figure 2.2 it is shown the macroscopic aspect of the raw bottom ash, the layout of the industrial installation where the treatment of the bottom ash was done and respective process steps.

The bottom ash from forest biomass combustion in an industrial bubbling fluidized bed combustor (BFBC) was transported from the pulp and paper mill to the treatment installation and stored for 24 hours before test. The bottom ash treatment was performed in a continuous way in the industrial plant, and included a continuous shower using an Liquid/Solid (L/S) ratio equal to 2, and has a processing capacity of 10 ton/h; the washing solution is treated by sedimentation in order to be reused in further washing cycles, in this way maximizing the use of water resources.

The physical, chemical and mineralogical characterization of the solid wastes previously to the specific valorization as replacement material led to select some interesting alternatives for these wastes valorization. However, many other specific characterization and its results are presented and evaluated in detail in the next seven chapters of this document.

Figure 2. 3. Industrial test for bottom ash treatment. (a) Raw bottom ash (BA) storage, (b) Washing and sieving installation, (c) Initial stage of the treatment and dust generated during introduction of bottom ash in the treatment process, (d) Bottom ash processing, (e) Bottom ash washing stage; (f) Conveyor belts and sieves that make the separation of bottom ash particles by size fractions; (g) Useful particle size (< 1000 µm) after bottom ash treatment, (h) Washing liquid effluent treatment by sedimentation.

3 CONSTRUCTION MATERIALS AS A WASTE MANAGEMENT SOLUTION FOR CELLULOSE SLUDGE

Regina Modolo*, Victor M. Ferreira, Luis M. Machado, Marco Rodrigues, Isabel Coelho

Published in **Waste Management** 31 (2011) 370–377
DOI: http://dx.doi.org/10.1016/j.wasman.2010.09.017
Impact Factor (5- year): 3.49; ISSN: 0956-053X
WebQualis: A1 (Environmental Science); B1 (Materials)

Abstract

Sustainable waste management system for effluents treatment sludge has been a pressing issue for pulp and paper sector. Recycling is always recommended in terms of environmental sustainability. Following an approach of waste valorisation, this work aims to demonstrate the technical viability of producing fiber-cement roof sheets incorporating cellulose primary sludge generated on paper and pulp mills.

From the results obtained with preliminary studies it was possible to verify the possibility of producing fiber-cement sheets by replacing 25% of the conventional used virgin long fiber by primary effluent treatment cellulose sludge. This amount of incorporation was tested on an industrial scale. Environmental parameters related to water and waste, as well as tests for checking the quality of the final product was performed. These control parameters involved total solids in suspension, dissolved salts, chlorides, sulphates, COD, metals content. In the product, parameters like moisture, density and strength were controlled. The results showed that it is possible to replace the virgin long fibers pulp by primary sludge without impacts in final product characteristics and on the environment. This work ensures the elimination of significant waste amounts, which are nowadays sent to landfill, as well as reduces costs associated with the standard raw materials use in the fiber-cement industrial sector.

3.1 Introduction

Sustainability concept is becoming increasingly important for several industrial sectors, including the paper and pulp sector as well as the building sector, because they present a strong impact as important economical activities [Lopes et al., 2003]. The waste management is becoming a priority and the building sector is one of the most useful sectors for diverse applications, in order to close with value the life cycle of certain products.

The use of industrial waste and by-product materials is widely recognized as one of the major preferred options towards the achievement of sustainable development. The prevailing environment policies require the waste to be treated before going to landfill. Treating waste and valuing them as raw materials for construction or other ends is more sustainable, particularly, when wastes are already on site [Snelson et al., 2009].

A pulp and paper mill generates, in all stages of process production, large amounts of solid wastes differing greatly in composition and moisture content. In its fiber production line, the screening equipment discharges uncooked material from the digester and smaller screening rejects. The chemical recovery cycle produces mainly inorganic material (called dregs and grits), energy production in the biomass boiler giving, as solid waste, fly ash and purged sand in the case of bubbling fluidized bed (BFB) boilers and, finally, also sludges coming from effluent treatment plant, classified as primary and biological sludges according to their treatment procedure.

Indeed, wastewater treatment plant is the biggest solid waste producer, generating two types of sludges, primary and biological. Primary sludge is mainly composed of fiber, lost in different equipments along the fiber line and settled in primary effluents treatment area. It also contains inorganic suspended solids, mainly calcium carbonate from the caustic area. These solids are also decanted and become a primary sludge constituent. On integrated pulp and paper mills this type of sludge has a much higher content of inorganic fractions, as a consequence of the precipitated calcium carbonate used as filler in paper production and in paper machine white water excess.

Biological sludge comes from the biological treatment unit and it contains microorganisms. This unit generally involves activated sludge reactors and sludges are obtained through secondary decanters, sludges thickeners and final belt press dewatering.

Wastes from pulp and paper industry are usually managed, in terms of waste disposal, using several approaches including landfills, incineration, recycling in cement or ceramics plants, lightweight aggregates, asphalt, agriculture, anaerobic treatment, and others [United Nations Economic and Social Council, 2001; Hassini et al., 2005; Demir et al., 2005; Huet, 1982; Shao et al., 2001; IZF, 1994; Podobnik and Zule, 2006; Krigstin and Sain, 2006; Monte et al., 2009; Lynde et al., 1997]. Wastewater sludges were already used in different sectors and the main applications are associated to agricultural purposes, biomass, incorporation in clay bricks, lightweight aggregates and in moulded gypsum cardboards production [Modolo et al., 2007; United Nations Economic and Social Council, 2001; Demir et al., 2005].

Considering the large amount generation of primary sludge production and its fibrous nature, this work attempts to develop a solution to add value to this material incorporating in a construction material where their fibrous nature could be advantageous. For that, preliminary studies were developed at a laboratory level in a base composition used in fiber-cement sheets. The results showed that primary sludge could be incorporated in fiber-cement sheets in low contents, without damaging the final product characteristics [United Nations Economic and Social Council, 2001].

Fiber-cement is usually used as a building material in covering roofs, although it can be used for other constructive purposes. Its composition incorporates up to 2.6% of cellulose fibers coming from kraft softwood pulp (virgin long fibers pulp - VLFP) in order to make advantageous use of its fiber content. These fibers are longer and coarser than most fibers and have been found to provide many benefits in fiber-cement applications due to their high modulus and high fiber strength [Morton et al., 2006].

The focus of this work is to evaluate the use of primary sludge from kraft hardwood pulping process in fiber-cement sheets production at an industrial scale. At this level, there is a need to control parameters such as the sludge incorporation level and its quality as a raw material, the water quality in the process and the final product characteristics.

3.2 Experimental

Virgin long fiber pulp (VLFP) represents 2.6% of total fiber-cement composition in proportion of dry raw materials. Conventionally the used fiber in fiber-cement process production is from softwood. In this experimental work, these softwood long fibers were replaced by hardwood fibers from primary sludge generated in pulp and paper mill effluent treatment at a fixed replacement level of 25%.

3.2.1 Materials

Standard Materials

The fiber-cement sheet samples were prepared with standard fiber-cement raw materials: *Portland cement* (to provide strength): Commercial available ASTM Type I - 42.5R, *PVA–fiber* (the long term durability PVA fibers is used as reinforcement in cement-base (Akers et al., 1989), and other commercial characteristics, such as, high modulus polyvinyl alcohol, elongation (~6.5%); *Amorphous-silica*: Dry silica fume (Elken Microsilica Grade 940), with high SiO_2 content (>90%), low moisture (<1,0%), loss on ignition less than 3,0%, particle retention at 45 micron sieve below 1,5%, Bulk density (undensified: 200-350 kg/m^3); *Virgin long fiber pulp:* kraft pulp softwood fibers, bleached, moisture (≈ 10%), Ash content (< 1,0%); *Additives:* (i) Flocculant (Magnafloc 1011): White granular powder, solid grade polymer, particle size (98% < 1400 µm), Bulk density (~0,65g/cm^3); (ii) Antifoam (STRUKTOL J650): Polyalcohol based on polyoxyethylene-polyoxypropylene blockcopolymers.

Primary sludge

The primary sludge is generated in the clarification of process water by kidney treatments, e.g. dissolved air flotation [Monte et al., 2009]. The sludge consists of hardwood fibers (~70%, where a small content of this total may be associated with insoluble lignin) and fillers (~5% of sand and 25% of precipitated calcium carbonate (PCC)). The PCC content in the sludge is generated in the integrated kraft pulp and paper process by the chemical reaction $CaO+CO_2\leftrightarrow CaCO_3$, being limited by the calcium content measured as 10.37% (Table 3. 1) and its atomic mass (40 g/mol). The primary sludge specific characterization is presented on Table 3. 1. Figure 3.1. shows fiber nature of this sludge and part of the inorganic content material present in them.

3.2.2 Methods

In order to replace VLFP with primary sludge in fiber-cement production at an industrial scale, the following aspects were verified:

- ✓ Process and environmental control: characterization tests in process water (suspended solids and dissolved salts, chlorides, sulphates, COD and metals) and cellulose VLFP beating degree - Shopper Riegler test - ºSR (ISO 5267-1:1999);
- ✓ Final product: chemical and mechanical characterization tests in final product (according to Standard procedure); and
- ✓ Solution sustainability: evaluation of the sustainability of this waste management solution.

Table 3. 1. Specific characterization results for primary sludge (Metals content was measured by ICP - Inductively coupled plasma).

Parameters	Value	Parameters	Value
Metals		*Potentially Toxic Metals*	
Ca (% dried waste)	10.37	Ni (mg/kg dried waste)	12.1
Mg (% dried waste)	0.19	Cu (mg/kg dried waste)	10.7
Na (% dried waste)	0.22	Pb (mg/kg dried waste)	16.3
Fe (% dried waste)	0.09	Zn (mg/kg dried waste)	36.5
Al (% dried waste)	0.05	Cd (mg/kg dried waste)	1.7
Mn (% dried waste)	0.03	Cr total (mg/kg dried waste)	13.4
Others		Au (mg/kg dried waste)	0.2
pH (Sorenson scale)	8	Co (mg/kg dried waste)	10.0
Condutivity (mS/m)	37	Ar (mg/kg dried waste)	5.8
Density (g/cm^3)	0.5		
Moisture (%)	67	Sulphates (% dried waste)	0.3
Volatile total solids 550+25ºC (%)	70	Chlorides (% dried waste)	0.6

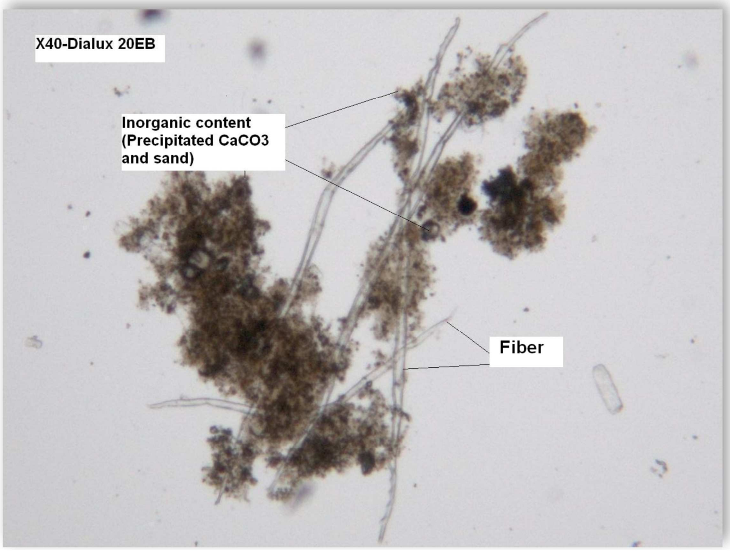


Figure 3. 1. Primary sludge microscope image (x40 – DIALUX 20 EB).

Regarding the transportation process and incorporation, the sludge was divided in “big bags” and previously weighed (Figure 3.2). The primary sludge was characterized and tested on the day that it was received at the factory.

The fiber-cement production process (Figure 3.3) begins with VLFP disintegration and a beating process. The beating process can be defined as a mechanical treatment of pulp carried out in the presence of water and, in this case, by passing the pulp fibers suspension through a disk refiner consisting of a rotating bladed element that moves in conjunction with a stationary bladed element. The term “beating” is usually applied to the batch treatment of pulp suspensions [Coutts, 2005].

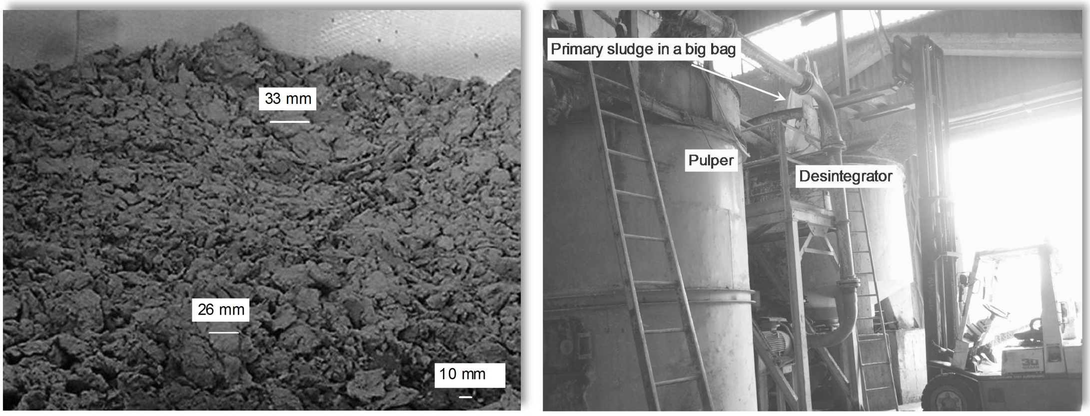


Figure 3. 2. Primary sludge ready to be processed and to be incorporated to the disintegrator in big bags.

Coutts and Kightly (1984) state that refining plays an important role in producing surface area for fiber-to-fiber or fiber-to-matrix (in case of composites) bonding and, more important, can assist in controlling the drainage rates of processing liquids during the fabrication of products. Refining affects the hydraulic properties of the fiber effectively reducing its average diameter. This process also promotes an internal fibrillation or delamination on fibers, external fibrillation of its surface and fines formation.

In the pulp beating, the VLFP and sludge were mixed with water. The disintegration process lasts around 30 minutes. In this point a suspension sample is collected to measure the Shopper Riegler degree (ºSR). If an acceptable ºSR value (between 55 and 70 ºSR) is obtained, the suspension is sent to the pulper. Meanwhile, the silica was already mixed with water before processing. The pulp is mixed with cement, amorphous-silica and PVA in the mixer. The final suspension is carried to the fiber-cement sheet forming machine which includes a felt belt and four vats that filter the fiber-cement sheets water excess. The fiber-cement sheets are taken to the drying oven at 85ºC to remove the moisture.

The global fiber-cement sheets production involves the following steps:

1. VLFP and/or Primary sludge disintegration
2. VLFP and sludge mixes beating
3. Pulper preparation
4. Silica suspension preparation
5. Sheets production
6. Sheets cutting
7. Sheets corrugations molds
8. Drying (naturally on air and in oven)
9. Removing moulds and pallet processing.

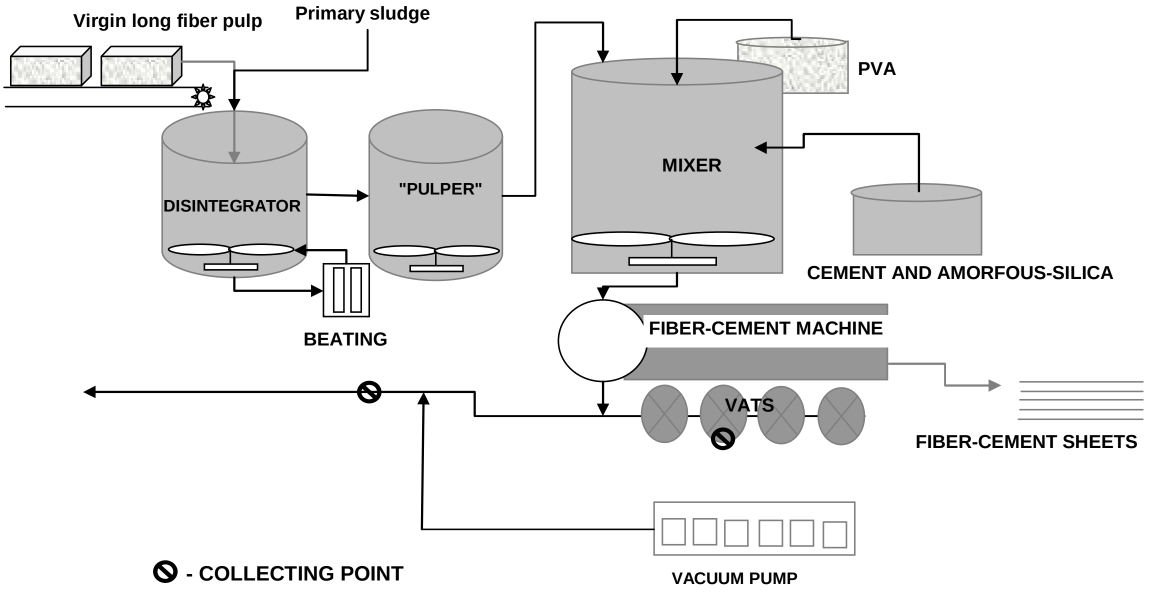


Figure 3. 3. Fiber-cement process and water collecting places.

25% of the virgin long fibers pulp (VLFP) used in fiber-cement production were substituted by primary sludge in the industrial test. The fiber-cement sheets are produced in batches. Each production batch involves, in this particular factory, a consumption of 195kg of virgin long fibers cellulose pulp. Hence, each batch received 48,75kg (dry base) of primary sludge and 146,25kg of virgin long fibers pulp during industrial test days. Twelve fiber-cement series with primary sludge were produced in two days. The samples with sludge incorporation were collected for tests in this period and the reference samples were collected a week before, on normal production days. The cellulose sludge chemical parameters were previously determined (Table 3.3) and involved moisture, pH, organic contents (550ºC), fiber content, conductivity, chlorides, sulphates, metals and density. Water samples from the process were also collected before and during the industrial test. The samples named as CW represent the “Control Water” and the PSW samples represent the “Primary Sludge Water”. The measured water parameters were total suspended solids, dissolved salts, chlorides, sulphates and COD (Chemical Oxygen Demand) and metals content. The water samples collection places in the process are also presented on Figure 3. 3. The parameters measurement and methods are presented on Table 3.2.

Table 3. 2. Samples control, parameters and respective Standard.

Samples	Parameters and Methodology
Sludge	pH (EN 12176:1998); Conductivity (NP EN 27888:1996); Moisture in 105ºC (EN 12880:2000); Silic and metals (ICP - JY Inductively Coupled Plasma - Instrumental analysis technique based on atomic emission spectrometry), Fixed and Volatile Total Solids in 525ºC (EN 12879:2000); Schopper Riegler Degree and Beating time
Water	Suspended total solids; Dissolved salts; Sulphates (4500D-SO4-2, STANDARD METHODS, Gravimetric with drying of residue, 4-177); Chlorides (4500D-Cl-, STANDARD METHODS, Potenciometric method, 4-69); COD; Metals
Final product	Load at rupture; Beding Moment ; density ; moisture (NP EN 494:2004 + A3:2008)

During the fiber-cement production process, the pulp and the sludge were beat and the Shopper Riegler (ºSR) parameter was measured. This parameter allows evaluating the pulp beating degree. This method is designed to provide a measure of the rate at which a dilute suspension of pulp may be dewatered. The determination of the drainability of a pulp suspension in water is described in terms of a Shopper Riegler (ºSR) number. The drainability is related to the surface conditions and swelling of the fibers, and constitutes a useful index of the amount of mechanical treatment to which the pulp has been subjected [Morton et al., 2006]. In this fiber-cement production study case, the acceptable results are obtained within the range of 55 to 70 ºSR, following the standard proceedings. The highest this value less drainable is the fibers cake.

The industrial test took 12 hours in constant production. In the first 6 hours of manufacturing, 1500 sheets were produced with primary sludge and 15 of them were randomly chosen as samples during the test time and submitted to quality control parameters checking. In the last 6 hours, 1500 standard sheets (without sludge) were produced and 15 standard fiber-cement sheets were selected for tests with the same procedure as above. The controlled parameters in the chosen sheets were moisture and wet density (in fresh conditions), dry density, bending moment and load at rupture (at the seventh day of curing). The methodology used to carry on the tests is described in NP-EN494:2004+A3:2008 and the standard geometric sheets characteristics are presented on Table 3.3 and Figure 3.4.

Table 3. 3. Fiber-cement sheet geometric characteristics.

Sheet geometric characteristics	Nominal Value (mm)	Tolerance
Lenght of sheet (*l*)	1250	± 10
Widht of sheet (*w*)	1095	± 10
Pitch of the corrugations (*a*)	177	± 2
Height of the corrugations (*h*)	51	± 3
Thickness of the sheet (*e*)	6.5	± 0,6
Height of edge of the descending corrugations (*h1*)	11	8 to 15
Height of edge of the ascending corrugations (*h2*)	45	42 to 49
Category (according to the *h*)	C (40 to 80)	
Class	1X	

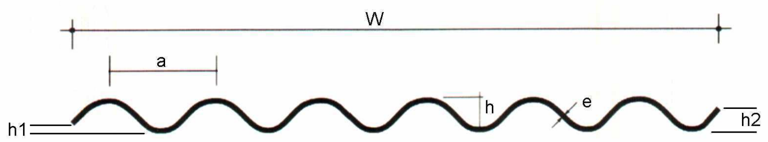


Figure 3. 4. Sheet profile and geometric symbols.

3.3 Results and discussion

3.3.1 Process and environmental control

In terms of chemical characteristics, the primary sludge does not present undesirable agents for fiber-cement production. It consists primarily of fibers, fines and inorganic material in mills that employ fillers in their products [Monte et al., 2009].

Figure 3.5 presents the fibers microscopic aspect. It is possible to verify the difference between the Eucalyptus and Pinus fibers thickness, around 10 to 20 µm and 40 to 60 µm, respectively. *Eucalyptus globulus* fiber achieves ~1 mm as maximum length. The Pinus fibers are longer than *Eucalyptus globulus* fiber. This characteristic could condition the sludge incorporation content and final product characteristics.

The Schopper-Riegler and refinement time results are presented on Figure 3.6 and Figure 3.7, respectively. It was possible to decrease the refinement time in the process with the primary sludge incorporation. The *Eucalyptus* fibers achieve the same ºSR degree using lower energy time comparing to *Pinus* fibers. Lower refinement time represents low energy consumption compared to the standard process containing only virgin long fibers pulp. A 30% saving time was estimated during the industrial test procedure.

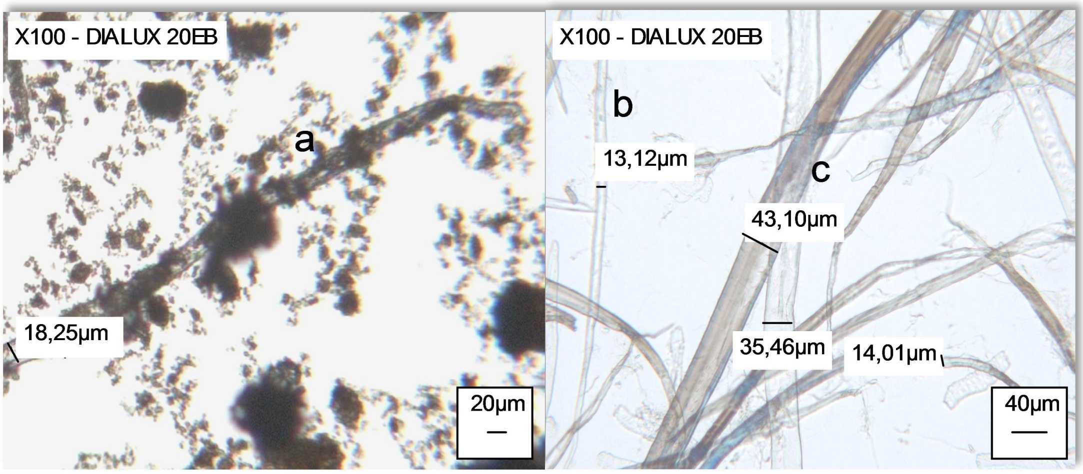


Figure 3. 5. Microscope images: [a] Primary sludge *Eucalyptus globulus* fiber (Sample collected from primary sludge generated in kraft hardwood mill), [b] *Eucalyptus globulus* fiber and [c] *Pinus pinaster* fiber (Sample was collected from virgin pulp produced in kraft hardwood and softwood mill). (X 100 – DIALUX 20 EB).

Table 3. 4. Well and Vat 2 water samples results.

Parameters	Results Averages			
	WellCW$^{(1)}$	WellPSW$^{(2)}$	Vat2CW$^{(1)}$	Vat2PSW$^{(2)}$
Total Suspended Solids (g/l)	26.9	36.1	26.5	31.5
Chlorides (g/l)	2.5	2.4	2.5	2.3
Sulphates (g/l)	8.4	8.2	7.8	7.2
Dissolved salts (g/l)	20.8	26.3	23.8	26.0
Chemical Oxygen Demand (g O_2/l)	1.3	1.7	1.0	1.1
Na (g/l)	0.6	0.7	0.7	0.7
K (mg/l)	8.2	7.4	8.1	7.6
Ca (g/l)	0.8	0.8	0.8	0.8
Al (mg/l)	*0.2*	*0.2*	*0.2*	*0.2*
Fe (mg/l)	0.2	0.3	0.2	0.3
Pb (mg/l)	*27.0*	*27.0*	*31.7*	*28.6*
Cr (mg/l)	2.2	2.1	2.4	2.3
Cu (mg/l)	*18.7*	*24.4*	*24.4*	*26.8*
Zn (mg/l)	*35.6*	*36.4*	*46.5*	*35.2*

* *Italic values indicate result under quantification limit.*

(1) CW - Control Water; (2) PSW - Primary Sludge Water

No alterations were observed in terms of the suspension dispersion or flocculation with the sludge incorporation. No corrections during the tests were needed in terms of flocculants.

Table 3.4 presents the measured water quality parameters (control and sludge samples). The values do not indicate significant alterations comparing them in terms of COD, chlorides, sulphates, dissolved salts and metals during the test period. Due to the solids presence and shorter fibers, there is a possibility for fines passing to the process water. Total suspended solids in PSW are only slightly higher than the control value sample (Table 3.4).

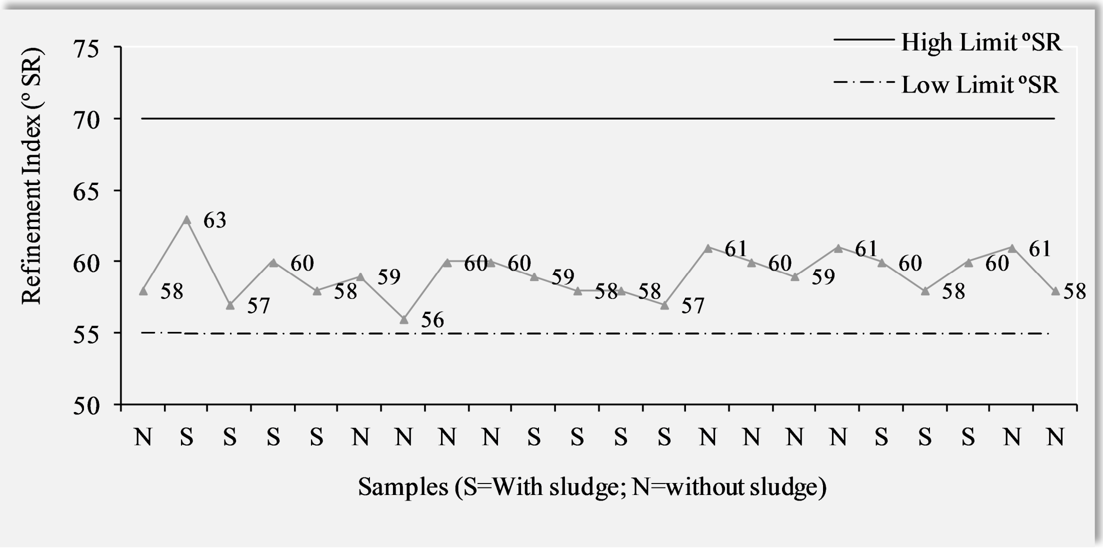


Figure 3. 6. Schopper-Riegler and refinement time results (S- with sludge; N- No sludge).

The VLFP represents 2.6% of dry material in fiber-cement production. 25% of this amount was substituted by primary sludge. Knowing that 40% of primary sludge composition is composed by inorganic material, the sludge suspended solids contribution in fiber-cement production is estimated in 26 kg per ton of dried fiber-cement produced. This maximum solids content increasing might be retained on fiber-cement sheets or drained to the process water together conventional solids. The increasing of sulphates and chlorides present in sludge composition parameters didn’t have significant alterations in terms of process.

3.3.2 Final product control

In terms of moisture content, every value for sheets produced with primary sludge achieved the specification limits. Fiber-cement sheets produced with primary sludge tend to present higher wet density values than the standard sheets. This happens because of shorter fibers presence in their composition. These fibers could more easily retain water and solids between the sheet mesh spaces (Table 3.5). Primary sludge includes in its composition almost 40% of inorganic solids, namely, sand. These inorganic charges increase the fiber-cement sheet density in wet and dry state.

Table 3. 5. Fiber-cement sheets control parameters results.

Parameters	Continue production time/Average sheets value				Quality control	
	Standard Fiber-cement (0-6h)	s (Deviation)	Primary Sludge Fiber-cement (6-12h)	s (Deviation)	min	max
Moisture (%)	36	1.28	36	0.88	32	42
Wet density (kg/dm^3)	1.801	0.02	1.813	0.01	NA*	1.850
Dry density (kg/dm^3)	1.476	0.03	1.485	0.03	1.400	NA*
Load at Rupture (N)	4693	2.12	5267	3.08	4655	NA*
Bending Moment (Nm/m)	56	15.12	63	16.8	55	NA*

*NA= Non applied

The bending moment values of quality product control are between 55 and 71 Nm/m and load at rupture minimum acceptable value is 4655 N. According to the obtained results every fiber-cement sheet produced with primary sludge incorporation presented acceptable values for both parameters on the final product quality control (limits presented in Table 3.5).

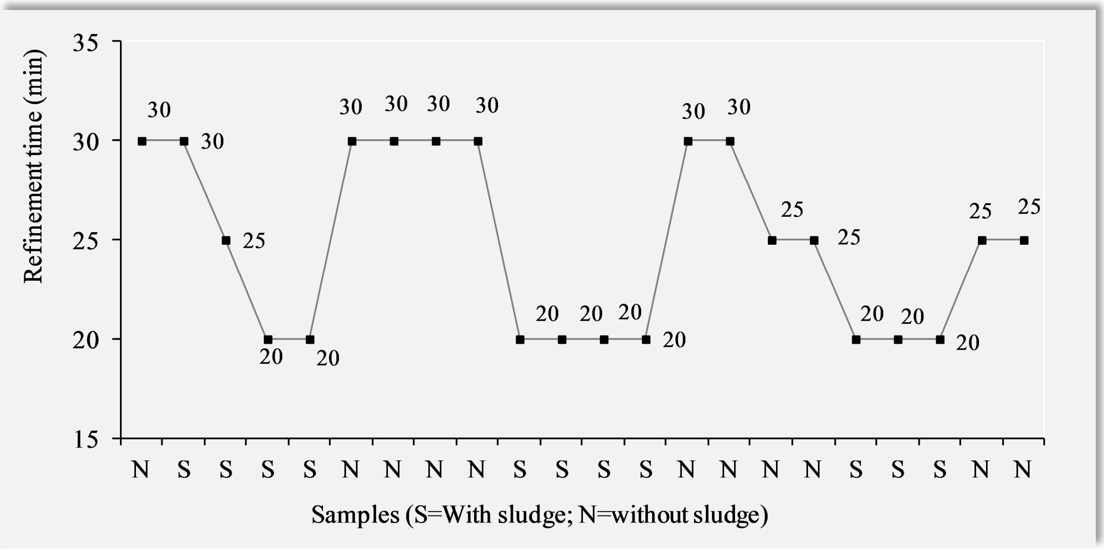


Figure 3. 7. Refinement time results (S- with sludge; N- No sludge).

Figure 3.8 and Figure 3.9 shows the surface of both types of samples. They present similarities in aspect and the viewed surfaces present large amounts of fibers as expected. Small particles of hydrated cement matrix were clearly distinguished from the fibers. The analysis shows fiber-cement surfaces containing fibers arrangement. It was not possible to distinguish Eucalyptus from *Pinus* fibers by SEM in the fiber-cement matrix. To get additional information regarding the fibrous aspect of these materials, surface samples of the produced fiber-cement, with and without sludge, were scratched, prepared and observed by SEM (scanning electron microscope analysis).

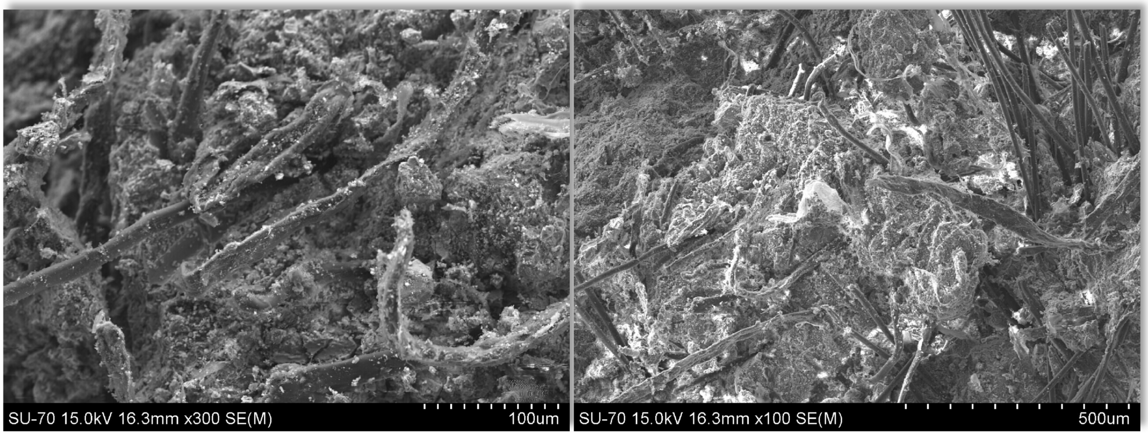


Figure 3. 8. Scanning electron microscopy of fiber-cement sheet containing primary sludge.

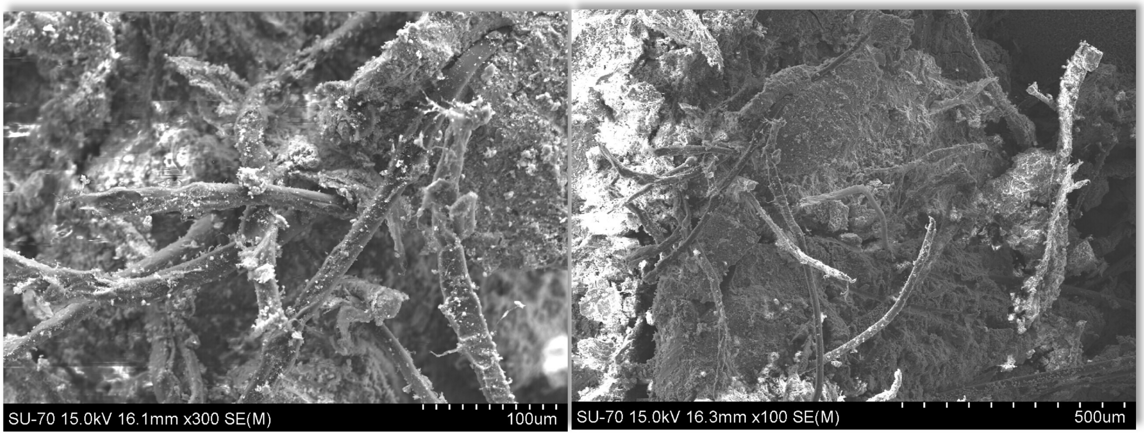


Figure 3. 9. Scanning electron microscopy of control fiber-cement sheet.

3.3.3 Evaluation of solution sustainability

In 2008, the average fiber-cement production in this case-study factory was estimated at 20000 ton/year, consuming around 600 ton/year of VLFP. The costs associated to this cellulose-based product amount were estimated in 350000 €/year (VLFP = 585 €/ton). By adopting this recycling solution, this fiber-cement company saves around 87500 €/year on costs related to the virgin long fibers pulp purchase. The impact of the partial substitution of virgin pulp by primary sludge in the matrix of fiber-cement production was estimated based on the pulp costs, sludge transportation and energy costs related to refinement process. Table 3.6 presents the values used in this assessment and the estimated results. At the same time, this application allows to put in practice a sustainable waste valorisation solution, avoiding disposal of 500 ton/year (150 ton/year in dry base) to waste landfill, with an estimated cost around 11200 €/year (based on a landfill cost of 22.40 €/ton). The costs for the paper and pulp mill, related to this particular waste disposal, must be replaced by waste transport to the fiber-cement factory, which were estimated at

11200 €/year. This value was calculated using a base price of 0.08 €/ton/km for waste transportation and admitting a total distance of 280 km in a two way travel between the particular factories involved in this case study.

This waste valorisation represents an environmental solution avoiding the waste landfill. Even if the transportation costs were supported by the fiber-cement factory this waste valorisation would present an economic benefit solution.

Table 3. 6. Primary sludge valorisation in fiber-cement (Costs/benefits analysis).

Fiber-cement production	STANDARD	with PRIMARY SLUDGE
Pulp (€/t)	585	NA
Pulp dry base (t/year)	600	450
Primary sludge dry base (t/year)	0	150
Moisture (%)	NA	30
Pulp cost (€/year)	351,000.00 €	263,250.00 €
Energy (€/kWh)		0.085 €
Refinement time (t/h)	2.6	1.7
Energy (€)	1,538.46 €	1,153.85 €
	NA	256.41 €
Distance (km)		280
Transport (€/year)	NA	11,200.00 €
Total costs (€/year)	352,538.46 €	275,860.26 €
Benefits (€/year)	**76,678.21 €**	

NA - no applied

3.4 Conclusions

It was possible to verify the incorporation of cellulose sludge in this construction material, without affecting its general product characteristics or its processing.

Replacing 25% of the long cellulose fiber traditionally used by primary sludge from effluent treatment allowed the production of fiber-cement sheets, with properties within the recommended specifications for the final product.

The obtained values in water control does not indicate significant alterations comparing them in terms of COD, chlorides, sulphates, dissolved salts and metals during the test period.

The 40% of inorganic charges present in primary cellulose sludge promotes an increase on the fiber-cement sheets wet density but, the results are within the acceptable limit value. The bending moment and load at rupture for sheets with primary sludge were also acceptable according to the final product quality control.

In summary, the substitution of conventional cellulose fiber for primary sludge from pulp and paper is a sustainable recycling and valorisation solution without significant impact on the fiber-cement production, the final product and in the environment. Furthermore, this waste valorisation not only presents an economic benefit around 87500 €/year to the fiber-cement factory but also avoids the waste landfill disposal for the paper and pulp company. If the transportation cost is supported by the fiber-cement company then its saving with this recycling solution will be around 76.300 €/year.

Acknowledgements

The authors would like to thank Cimianto - Sociedade Técnica de Hidráulica, SA, Forest and Research Institute – RAIZ, Portucel/Soporcel group for their help and contribution to this study.

4 PULP AND PAPER PLANT WASTES VALORISATION IN BITUMINOUS MIXES

Regina Modolo*, Agostinho Benta, Victor M. Ferreira, Luis M. Machado

Published in **Waste Management** 30 (2010) 685–696
DOI: http://dx.doi.org/10.1016/j.wasman.2009.11.005
Impact Factor (5-years): 3.49; ISSN: 0956-053X
WebQualis: A1 (Environmental Sciences); B1 (Materials)

Abstract

Nowadays, the increasing amount of wastes is a concerning reality and the environmental aspects has become a major priority. Following this worry, the purpose of this experimental study was to investigate the possibility of using pulp and paper inorganic wastes, named dregs and grits, in bituminous mixtures as aggregate replacement to reduce environmental effects of these wastes disposal. First, the wastes were chemically and physically characterized and also tested primarily taking into account the requirements for aggregates in bituminous mixtures. Then, formulations were prepared replacing aggregates with wastes in different amounts. The mechanical properties of these mixtures containing wastes were compared with reference samples based on standard methods. According to the results it was possible to verify that grits had a good performance and it might be directly tested industrially as an aggregate in road construction. On the other hand, dregs need to be treated before incorporation to guarantee stable mixes in terms of water sensitivity.

4.1 Introduction

The re-use of wastes is important from different points of view: It helps to save and sustain the natural resources which are not replenished; it decreases the pollution of the environment and it also helps to save and recycle energy in production process [Hassani et al., 2005; Rocha, 2003]. The productive use of wastes material represents a way of solving some problems of solid waste management [Davis and Cornwell, 1998]. Moreover, suitable landfill sites are becoming more difficult to find as urban areas expand [Ngoc & Schnitzer, 2009].

Wastes and industrial by-products could be valuable materials as alternative resources for building and construction and other applications [D. van Beers et al., 2009]. The European Directive Nº 2006/12/CE leads to several legal dispositions for the management of wastes in which environmental objectives are set, namely, the need of restricting and in a short time the volume of wastes deposit in landfill.

Several studies were published on the use of waste material in pavements. These include the use of fly ash [Jackson et al., 2009], waste pumice [Saltan, 2008], glass, steel slag, tires and plastics [Huang et al., 2007], marble quarry waste [Akbulut & Gürer, 2007], cement and mortars [Coutinho & Garcia, 2008], polypropylene fibers [Serkan, 2008]. Following this perspective, this research describes a study developed with wastes from pulp and paper industry in asphalt pavements application.

The pulp and paper industry generates large volume of wastes which is technology-dependent but the estimate is around 100 tons of waste for 550 tons of pulp production [Celpa, 2008]. In terms of Europe, eleven million tonnes of waste are produced yearly by this sector [Monte et al, 2009]. It generates, in all stages of its production process, solid wastes with different composition and moisture content [Modolo et al., 2008].

The produced wastes are of organic and inorganic origin, some of them with reuse potential. Two of these wastes, named as dregs and grits, are still sent for landfill disposal. Dregs are essentially sodium and calcium carbonates (Na_2CO_3 and $CaCO_3$), sodium sulphide (Na_2S) and a small organic fraction that was not totally burned in the recuperation biomass boiler. Different salts are present in their composition coming from the pulp and paper mill process. They result from the smelt dissolution with the white liquor. Smelt is a flux material that is drained from the burning process in the recuperation boiler. This waste (dregs) is generated by the separation of $CaCO_3$ and CaO in the green liquor clarifier. Grits are formed basically by $CaCO_3$ and CaO which did not react in the slaker. Slaker is the place where the reaction between Na_2CO_3 (present in green liquor) plus CaO (lime coming from lime oven) and H_2O occurs, giving NaOH plus $CaCO_3$, which constitutes the lime sludge that will be filtered and re-sent to lime oven for calcination.

The purpose of this experimental study was to investigate the possibility of using these pulp and paper wastes in asphalt concrete mixes as aggregate replacement in road regularization layers, through mix designs and specific characterization tests, contributing to reduce environmental effects of wastes disposal.

4.2 Experimental

The two bituminous pavement top layers involve aggregates and bitumen (Figure 4.1). The experimental tests were done with mixes specimens developed according to Dense Bituminous Layer specifications [Portuguese Road Authority – EP, 2008]. This layer was chosen because it excludes external environmental agents' access and it has flexible specific conditions for specific aggregates.

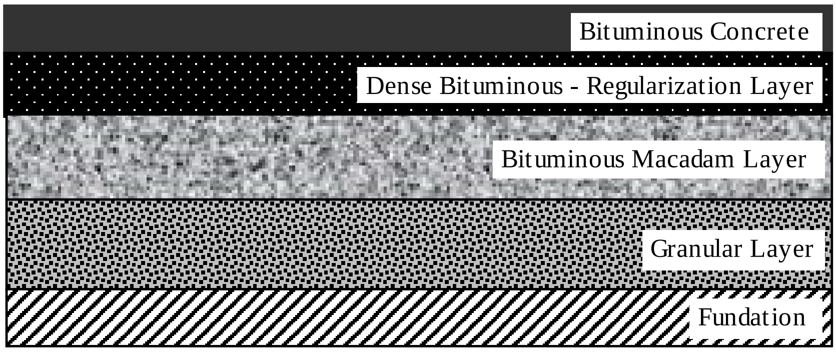


Figure 4. 1. Flexible pavement example.

Hence, the wastes were first chemically and physically characterized and also tested as specific aggregates for bituminous mixes.

In all the work stages, Marshall specimens were prepared in laboratory scale according to EN 12697. This method is applied to every dense bituminous layer types with maximum nominal aggregates dimension equal or lower than 25mm. The procedure implies that aggregates and bitumen are heated at temperatures around 160ºC. The specimens were compacted using a Marshall automatic hammer, with 75 compaction blows on each side. The specimens were compacted and kept at room temperature (20ºC) for a week. The specimens' bulk specific and apparent gravity were measured. The mineral aggregate voids (VMA) and air voids were determined. The specimens were kept in warm water (60ºC) for 20 minutes before submitting to Marshall Stability test (maximum weight which promotes the specimens fracture) and the Marshall flow test (maximum deformation in which the specimen rupture occurs). Marshall stability and flow tests were used to verify the pavements wastes potential applicability.

The standards used to obtain Marshall Test results for this study were:

(a) EN 12697-30: 2000. Bituminous mixes (BM) - Test methods for hot mix asphalt - Specimen preparation, impact compactor: Mixes preparation;
(b) EN 12 697-10: 2002. BM - Test methods for hot mix asphalt – Compatibility;
(c) EN 12697-6: 1996. BM - Test methods for hot mix asphalt - Determination of bulk density of bituminous specimen by hydro-static methods;
(d) EN 12697-8: 2003. BM - Test methods for hot mix asphalt - Determination of void characteristics of bituminous specimens;
(e) EN 12697-12: 2003. BM - Determination of the water sensitivity of bituminous specimens ("Conserved Strength").

Based on Marshall mix design results, the optimum binder content (OBC) for mixes was determinated. The OBC results were used to prepare the final mixes for the "Conserved Strength". The specimens' results were controlled and compared to the Portuguese code for dense bituminous mix asphalt values for typical heavy traffic type values. They are presented in Table 4.5. The final "Conserved Strength" results were considered to examine the positive effects of wastes in the mixes.

4.2.1 Materials

Wastes: Grits (G), Conventional Dregs (DC) and Dregs without lime sludge (DWLS) were collected in a pulp and paper mill. The DWLS was taken from a filter press, which allows having dregs without lime precoat that provided a more homogeneous waste. The DC was taken from the vacuum rotary drum, which receives lime precoat during the waste filtration process. These wastes aspect is shown in Figure 4.2. The wastes were dried at 105ºC and automatically and manually ground for the characterization tests and mix design phase. The characteristics of the wastes used in this study are summarized in Table 4.1.

Table 4. 1. Wastes characteristics.

Properties	G	DWLS	DC	Standard
pH (in the waste)	13,1	12,7	12,8	EN 12176:1998
Conductivity (mS/m - in the waste)	2076	--	2621	NP EN 27888:1996
Moisture in 105ºC (%)	15,7	50,6	50,8	EN 12880:2000
Fixed Total Solids in 525ºC(%)	97,6	83,2	91,7	EN 12879:2000
Volatile Total Solids in 525ºC(%)	2,4	16,8	8,3	EN 12879:2000
Soluble Clorides (% of dried waste)	0,1	1,6	0,8	4500D-Cl-, STANDARD METHODS, Potenciometric method, 4-69
Sulphates (% of dried waste)	0,4	--	0,3	4500D-SO4-2, STANDARD METHODS, Gravimetric with drying of residue, 4-177
Carbonates - CO_3^{-2} (% of dried waste)	60,1	38,7	43,3	Potenciometric method
Density (g/cm3)	2,73	2,67	2,87	ISO-TS 17892-3:2004
Sand Equivalent (%)	81	19	40	NP EN 933-8:2002
Methylene Blue (g/100g)	0,03	2,14	0,19	NP EN 933-9:2002
Liquid limit, wL	NA	56	41	ISO/TS 17892-12:2004
Platicity limit, wP	NA	38	28	ISO/TS 17892-12:2004
Plasticity Index, IP	NA	18	13	ISO/TS 17892-12:2004
Potencially toxic metals (mg/kg of dried waste)				
Ni (mg/kg of dried waste)	14,4	157,0	174,9	ICP - JY Inductively Coupled Plasma - Instrumental analysis technique based on atomic emission spectrometry. Model: J4/2000 -ISO 11885
Cu (mg/kg of dried waste)	6,4	175,0	129,0	
Pb (mg/kg of dried waste)	35,5	21,0	45,2	
Zn (mg/kg of dried waste)	14,0	246,0	241,5	
Cd (mg/kg of dried waste)	4,8	1,5	4,5	
Cr total (mg/kg of dried waste)	10,7	102,0	38,9	
Hg (mg/kg of dried waste)	0,1	0,3	0,2	
Co (mg/kg of dried waste)	20,5	7,0	22,3	
Metals (g/kg of dried waste)				
Ca (g/kg of dried waste)	380,1	119,0	179,8	ICP - JY Inductively Coupled Plasma - Instrumental analysis technique based on atomic emission spectrometry. Model: J4/2000 -ISO 11885
Mg (g/kg of dried waste)	2,0	25,0	51,4	
Na (g/kg of dried waste)	16,1	154,0	61,1	
K (g/kg of dried waste)	0,9	7,7	5,1	
Fe (g/kg of dried waste)	2,7	4,3	4,2	
Al (g/kg of dried waste)	0,4	4,1	3,0	
Mn (g/kg of dried waste)	0,1	5,1	8,6	
Silic (g/kg)	2,0	3,2	4,0	

Figure 4. 2. (a) Grits (G), (b) Dregs without lime sludge (DWLS), (c) Conventional Dregs (DC).

Aggregates and Bitumen/Asphalt:

Fine aggregate - Hydraulic lime and crushed limestone;

Coarse aggregate - Natural crushed limestone aggregate, with maximum particle size of 19mm while the smallest aggregate present a maximum size 12.5mm.

Binder – Bitumen, penetration grade 50/70.

The aggregates and bitumen properties are presented in table 4.2. The materials gradation for this specific study according to Highways Autonomous General Directorate of Portugal (JAE) is presented in table 4.3.

Table 4. 2. Properties of used materials.

Property	Material/Value				Standard
	Hydraulic lime	Crushed stone	Coarse aggregate 1	Coarse aggregate 2	
Bulk Specific Gravity (kg/m^3)	2801	2630	2690	2732	NP EN 1097-6/ASTM C 127-80
Apparent Specific Gravity (kg/m^3)	--	2700	2718	2756	NP EN 1097-6/ASTM C 127-80
Water Absorption (%)	--	1,6	1,6	1,6	NP EN 1097-6/ASTM C 127-80
Shape Index	NA	NA	17	18	NP EN 933-4:2002
Flakiness Index	NA	NA	19	15	NP EN 933-3:2003
Sand Equivalent (%)	<1	69	NA	NA	NP EN 933-8:2002
Methylene Blue (g/100g)	0,6	0,21	NA	NA	NP EN 933-9:2002
Moisture in 105ºC (%)	1,1	0,3	NA	NA	EN 12880:2000
	Binder (Bitumen)				
Penetration at 25ºC, 1/10mm	50				ASTM D 5 (pr EN 1427)
Softening Point (%)	54,8				ASTM D 36 (pr EN 1427)
Flash Point (ºC)	230				ASTM D 92 (pr EN 22592)
Solubility in Toluene or Xylene (%)	97,5				ASTM D 2042 (pr EN 12592)
Kinematic Viscosity (mm^2/s) [135ºC]	295				ASTM D 2170 (pr EN 12595)
Loss on ignition (%)	0,08				ASTM D 2872 (pr EN 1426)

Table 4. 3. Wearing gradation according to Highways Autonomous General Directorate of Portugal (JAE).

Sieve size (mm)	Accumulated passing (%)							
	Hydraulic lime	crushed stone	Coarse aggregate		G	DC	DWLS	Lime sudge
25	100	100	100	100	100	100	100	100
19	100	100	100	84	100	100	100	100
12,5	100	100	97	12	100	100	100	100
4,75	100	96	1	0	92	100	100	100
2	100	75	1	0	73	100	100	100
0,425	100	32	0	0	33	66	74	100
0,18	97	17	0	0	22	55	56	100
0,075	78	9	0	0	15	43	21	97

4.2.2 Methods

The work was divided in three phases. The formulations samples identification is shown in Table 4.4. In all phases the Marshall Test specimens were tested according to EN 12697.

Phase I (Wastes and conventional aggregates characterization and preliminary mixes characterization):

In this phase, the wastes were submitted to a specific characterization (Chemical and Physical) to identify and quantify possible undesirable compounds as sodium, heavy metals. To evaluate the fines content, specific characterization tests for wastes in pavements sector were included. These results lead to a preliminary study with the aggregates replacing in bituminous mixes. Preliminary experiments on Marshall specimens established the mixture proportions used in phase I. In this experiment, 20 specimens were produced (four for each formulation) and the bitumen content was determined to be 5.4% (5.4% by weight of bituminous mix). In this phase, the bituminous mixes with 0%, 5% and 10% of wastes content were investigated.

Table 4. 4. Work phases distribution and Mixes identification.

Identification code (IC)	Details	Developed work
MBBr (Control)	Conventional specific formulation	Preliminary study - Phase I
MB5%DC	5% of conventional dregs	
MB10%DC	10% of conventional dregs	
MB5%G	5% of grits	
MB10%G	10% of grits	
MBBr (Control)	Conventional specific formulation	Optimum Binder Content (OBC) - Phase II
MBDC1%	1 % of conventional dregs and 2% of "filler"	
MBDC2%	2 % of conventional dregs and 1% of "filler"	
MBDC3%	3 % of conventional dregs and 1% of "filler"	
MBDC4%	4 % of conventional dregs and 0% of "filler"	
MBG5%	5 % of grits replacing crushed lime stone parcial content	
MBG10%	10% of grits replacing crushed lime stone parcial content	
MBDC2%washed	2 % of conventional washed dregs and 1% of "filler"	Washing Efficiency Tests - Phase III
MBDC4%washed	4 % of conventional washed dregs and 0% of "filler"	
MBDWLS2%washed	2 % of washed DWLS and 1% of "filler"	
MBDWLS4%washed	4 % of washed DWLS and 0% of "filler"	

Phase II (Mixes design (OBC) and mixes water sensitivity):

After the preliminary study validation in phase I, the dregs content was varied as 1, 2, 3, 4 % and the grits content varied as 5 and 10%. The bitumen content was varied as 4.5, 5.0, 5.5 and 6.0% (% by weight of bituminous mix) in the formulations. The test results provide indication on the stability, flow, air voids content, voids in mineral aggregate (VMA) and voids filled with bitumen. These values are essential for the mixes' behaviour understanding. The optimum bitumen content (OBC) was determined according to the Marshall stability, voids content of compacted specimens, specific gravity and flow for each formulation. Using the OBC, more 42 specimens with the appropriated OBC were made and the "Conserved strength" was evaluated. Six specimens for each formulation were prepared. They were separated in 2 sets of three specimens. One set was packed in water at 40ºC and the other group in a controlled room at 20ºC during 72 hours. After this, Marshall stability and flow were checked.

Phase III: Mixes design with washed wastes (DC and DWLS).

In this phase, mixes with washed wastes were tested in order to try to reduce or eliminate water sensitive detected in phase II. The washing process involved the following procedure: The wastes samples were weight (approximately 1200g) and dried (105ºC). Then the waste was set into 3 litres of heated distilled-water (around 70ºC) and stirred during 10 minutes to guarantee the complete agglomerates dissolution. The water was heated to simulate the original dregs generation process. The solution was filtered after 10 min. The conductivity and soluble salts content in the filtrate were analysed to control the washing efficiency (250 ml for each sample). The process was repeated in every sample until it presents low constant values. In the solid waste sample, methylene-blue (MB) test was used before and after washing, in order to check the waste washing efficiency. MB is a basic colorant, represented by the formula $C_{16}H_{18}N_3ClS.2H_2$ and constituted by lamellate molecules with unit effective area of 107 Å [Gomes, 1986]. There is a relationship between the MB parameter and CEC (cation exchange capacity) and these values permit to evaluate the material and indicate if it has a plastic behaviour [Gomes, 1986].

4.3 Results and Discussion

4.3.1 Phase I

General characterization

DC and DWLS present high moisture content (~50%) which represents energy costs if the material needs drying. The sodium content for DC (6.1%) and DWLS (15.4%) is considered high because this element is soluble in water which might be a problem for the final material application. Grits is practically constituted by calcium carbonate [(38%Ca/40gCa)*100gCaCO3) = 95%], which is interesting for building materials application since calcium carbonate is used as raw materials in many of them.

The Volatile Total Solids at 525ºC content in G and DC wastes is acceptable in bituminous aggregate criteria. For pavements application, DWLS formulations must be carefully designed to try not to exceed the acceptable limits for organic inert contents (<1%).

The potentially toxic metals wastes obtained results are under the permitted limits by Environmental Legislation. They are classified as inert-wastes according to DL 152/2002.

Soluble salts are not convenient for bituminous aggregates. The chlorides content might represent a problem for DC and DWLS. The soluble salts make the mixes "Conserved strength" values to decrease. Gradation results are presented in Table 4.3 and Figure 4.3. Grits (G) present similar grain size distribution compared to crushed stone usually used on bituminous mixes as fine aggregate. The DC curve presents the finest composition, compared to the other wastes. DC presents lime sludge (where 97% of lime particles size is below 75 µm) in its composition and it represents around 40% of this waste (40% value reflects the way how the vacuum rotary drum is operated). Lime sludge presents fine particle size and it may influence DC grain size results.

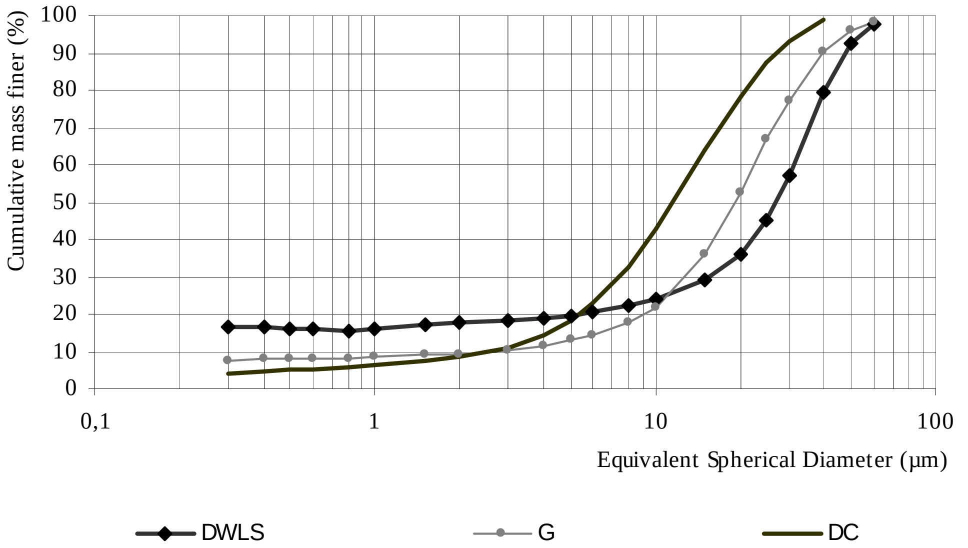


Figure 4. 3. Fine wastes particle size distribution (<0.063mm - SediGraph Method).

Grits (G) sand equivalent value is similar to crushed stone for bituminous mixture. This is not observed for Dregs (DC and DWLS) because of their high content in fine material. DC and DWLS based samples results presented some plasticity behaviour (Table 4.1). The plasticity behaviour might cause higher bitumen absorption and consequently might turn the mixes susceptible to volumetric changes. This test showed that Grits is non-plastic. Aggregates for bituminous applications must present Methylene-Blue (MB) value below 0.8% [Picado Santos, 2002]. MB test results for grits (G) were acceptable (Table 4.1). DC presented 0.19% and DWLS presented 2.14%. This higher value for DWLS is associated to the lime sludge absence that has a high cation exchange (CEC). The characterization results made possible to evaluate the wastes incorporation content and some mixes behaviour.

Mix design (Preliminary study)

Table 4.5. shows the preliminary study results. Grits mixes (5 and 10% of incorporation) achieved the established values for all parameters. Besides, the stability result for MB10%G is even better than the control mix. Marshall Stability was achieved for all mixes according to established values.

Table 4. 5. Preliminary study (phase I).

Mixes Identification	units	MBBr (Control)	MB5%G	MB5%DC	MB10%G	MB10%DC
Bitumem	%			5,4		
Bulk gravity	g/cm3	2,437	2,436	2,437	2,434	2,431
Apparent gravity	g/cm3	2,335	2,343	2,318	2,340	2,264
Voids (n)	%	4,2	3,8	4,9	3,8	6,9
Bitumen volumetric content (BVC)	%	12,2	12,3	12,2	12,3	11,9
VMA [void in mineral aggr.(n+BVC)]	%	16,4	16,1	17,0	16,1	18,7
Bitumem saturation (n+BVC)	%	74,5	76,3	71,4	76,1	63,3
Stability	kN	12,0	10,6	11,2	13,8	9,4
Flow	mm	3,9	2,9	2,5	2,8	2,5
Stability/Flow	kN/mm	3,1	3,7	4,6	4,9	3,8

Figure 4. 4. Bituminous mixes optical microscope images: (a) MBBr (50x), (b) MBG5% (10x) and (c) MBD5% (10x).

Mixes with dregs (MB10%DC) presented a not acceptable value in terms of voids (6.9%). When this parameter is higher than the specific value the mixes loose durability, workability and fragile (they have lower deformation strength). High dregs content promote more bitumen absorption, which increases bituminous mixes costs. This fact limited the dregs content in the next development phase. Figure 4.4 presents the mixes microstructure photos. It is clearly visible on Figure 4.4"c" that the dregs mix is dried and opaque compared to the other ones.

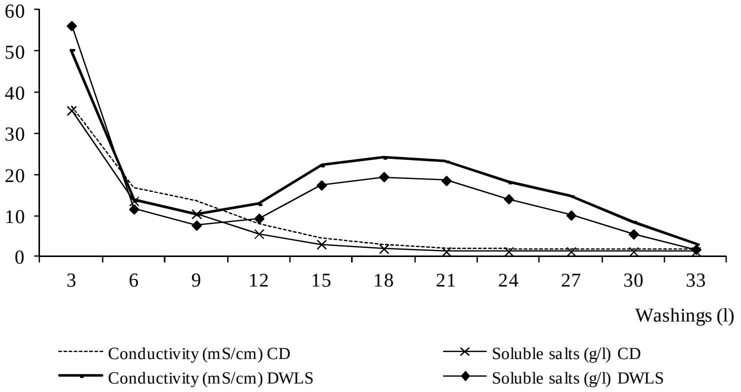


Figure 4. 5. Washing efficiency results for DC and DWLS mixes.

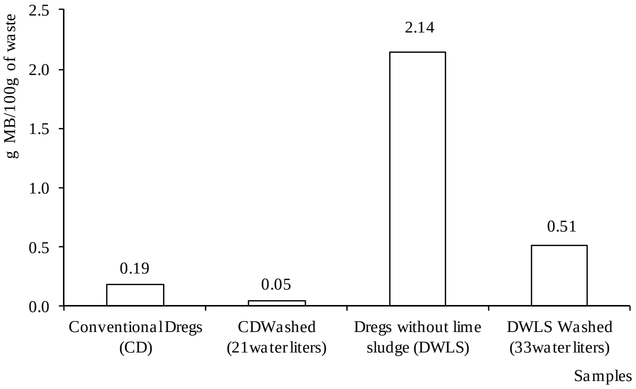


Figure 4. 6. Wastes MB test results for DC and DWLS mixes.

4.3.2 Phase II

Figure 4.7 presents the aggregates mix gradation. The values are included in the limits for this type of mixes. Marshall Mix design results are presented from Figure 4.8 (control specimen) to Figure 4.14 (MBG10%). MBDC4% (Figure 4.12) presented a high-maximum value (24.3 kN) for this parameter. The flow value indicates the flexibility and plasticity properties of the asphalt concretes under traffic load. All mixes indicated a consistent relationship between the flow and bitumen content. As much the binder content is increased the flow also increases. The highest and the lowest flow value registered were for MBDC1% (5.84mm) and MBDC3% (2.91mm), respectively. Mixes should present flow values up to 4 mm, which is the highest allowed value indicated. When 6% of bitumen was used, only MB5%G mix presented a lower value for this parameter. The bulk specific gravity is uniform and acceptable for all mixes. MBDC4% presented the lower value compared to the other mixes including the control reference one.

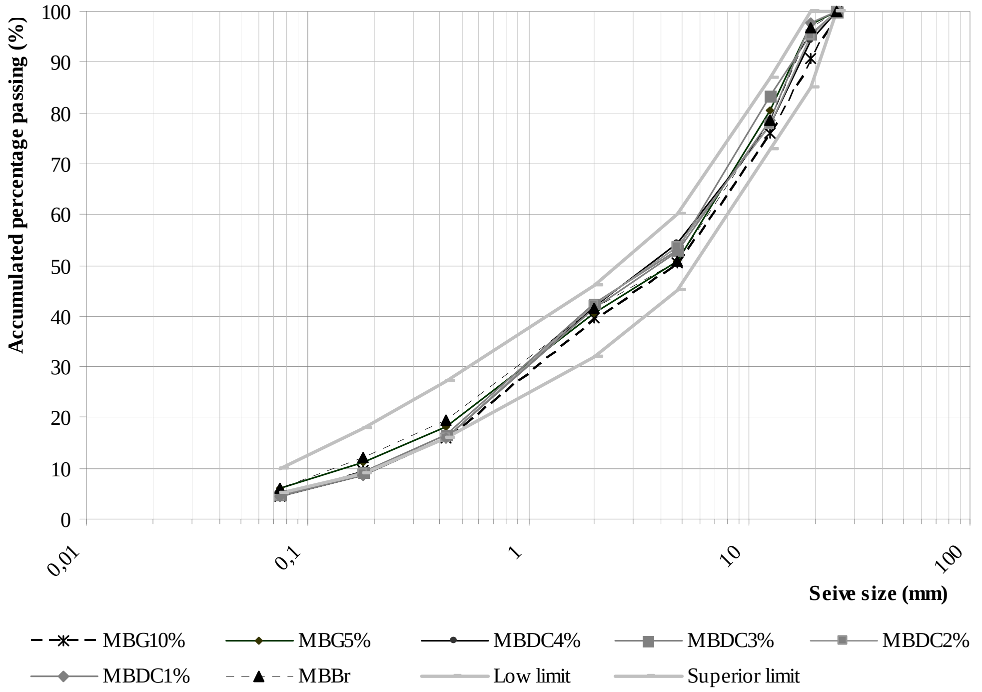


Figure 4. 7. Aggregate mix gradation.

The voids content for the mixes prepared with 5.5 and 6.0% of bitumen, except MBDC3% (Figure 4.11) and MBDC4% (Figure 4.13), presented values below the allowed minimum limit (3%). This low value has a direct influence in the mixes apparent gravity and bitumen saturation. The mixes become more susceptible to permanent deformation. These parameters are associated to the compaction mix level and permit to improve the pavement general performance. MBDC4% presented the highest VMA value (16.8%). This result might be associated with the dregs' content and the filler absence. All mixes presented VMA values between 14.8 to 16.8%.

Table 4. 6. National mix design specifications for hot mix asphalt*.

Marshall method	Traffic		Gradation Limits (%)
Mix criteria	Min	Max	100
Compactation, number of blows each end of specimen	75	75	85-100 73-87
Stability (N)	8000	15000	45-60
Flow (mm)	--	4	32-46
% Air-void	3	6	16-27
% VMA	13	--	9-18
Conservated Strengh (%)	75	--	5-10

*JAE, 1998

Table 4. 7. “Conserved Strength” mixes results (phase II).

Mixes (ID)	OBC	Voids (%)	EN 12697:12/2003		
			Parameters	specimens in the water to 40ºC	specimens condditioned 20ºC
MBBr	4,8	3,3	Apparent Gravity (g/cm3)	2,422	2,420
			Stability (kN)	15,96	17,59
			Conserved strength (%)	90,7	
MBDC1%	5,2	2,7	Apparent Gravity (g/cm3)	2,415	2,410
			Stability (kN)	17,36	17,30
			Conserved strength (%)	75,8	
MBDC2%	4,9	3,6	Apparent Gravity (g/cm3)	2,411	2,407
			Stability (kN)	13,65	16,54
			Conserved strength (%)	62,3	
MBDC3%	4,9	3,2	Apparent Gravity (g/cm3)	2,413	2,425
			Stability (kN)	12,03	16,89
			Conserved strength (%)	53,8	
MBDC4%	5,3	2,5	Apparent Gravity (g/cm3)	2,405	2,425
			Stability (kN)	0,00	14,15
			Conserved strength (%)	0,0	
MBG5%	4,7	3,6	Apparent Gravity (g/cm3)	2,418	2,425
			Stability (kN)	15,03	19,10
			Conserved strength (%)	78,7	
MBG10%	4,8	3,3	Apparent Gravity (g/cm3)	2,422	2,429
			Stability (kN)	15,37	17,65
			Conserved strength (%)	87,1	

Grits (MBG5% and MBG10%) and control mixes (MBBr) presented lower voids content than mixes with Dregs (MBDC1, 2, 3, 4%). This is because the mixes filler content is between 2 and 3% as in the control sample (3% of filler). When filler is completely substituted by dregs, it makes the mix more porous and less workable. Void filled with asphalt (bitumen) results suggest that dregs absorb more bitumen than the other mixes. The optimum binder content (OBC) was determined by Marshall mixes design results. This value was used to achieve the mixes “conserved strength” in Table 4.6. Mixes MBBr, MBDC1%, MBG5% and MBG10% presented a good behaviour. 75% of conserved strength was achieved for them. MBDC2%, MBDC3% and MBDC4% presented water sensitivity. This behaviour was already expected because Dregs present soluble salts in their composition.

MDC1% and MDC4% voids content results are below the permitted value (3-6%). MBDC4% specimen dissolved in water, which made impossible to perform the test. Regarding the “conserved strength” behaviour of Grits-containing mixes, their performance is acceptable compared to the control mix. Incorporation of 5% Grits gave slightly worse result than the mix with 10% of Grits, probably related with the particle size distribution in the mixture and higher voids content in the 5% Grits mix. This phase II results demonstrated a bad performance for dregs mixes. In a tentative to obtain acceptable values for dregs formulations for this application, it was decided to treat the wastes to eliminate the soluble salts. On the next phase, dregs without lime sludge (DWLS) were used in the mixes to evaluate the effect of removing this fine material usually associated to Dregs generation in the process. This waste will replace the conventional dregs technology in some pulp and paper mills in the future.

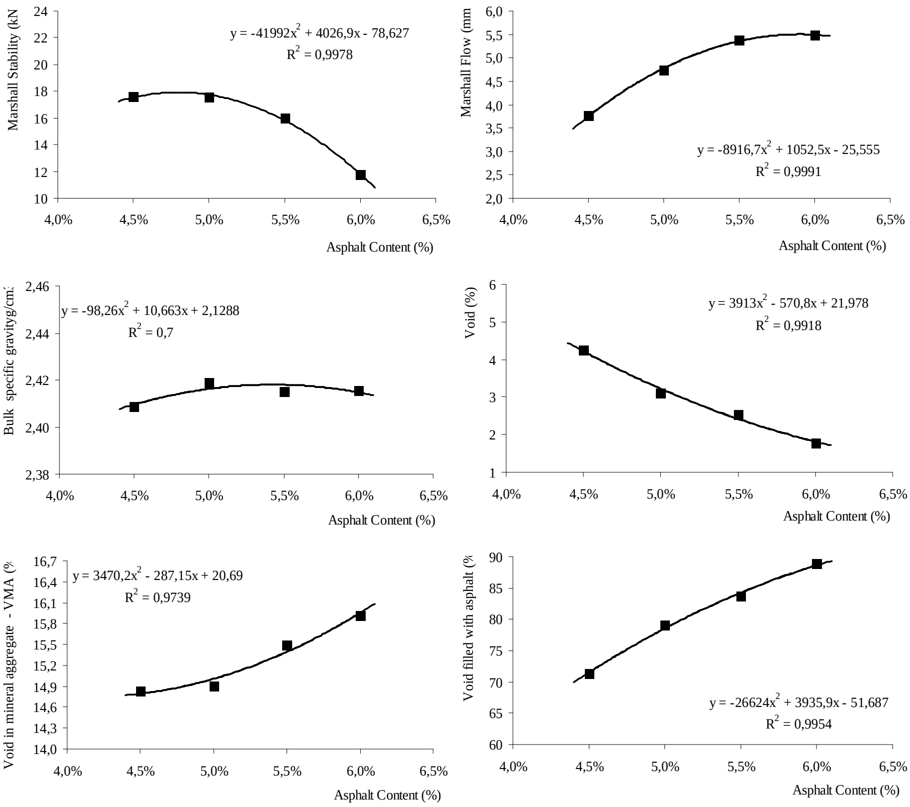


Figure 4. 8. MBBr Marshall mix design values.

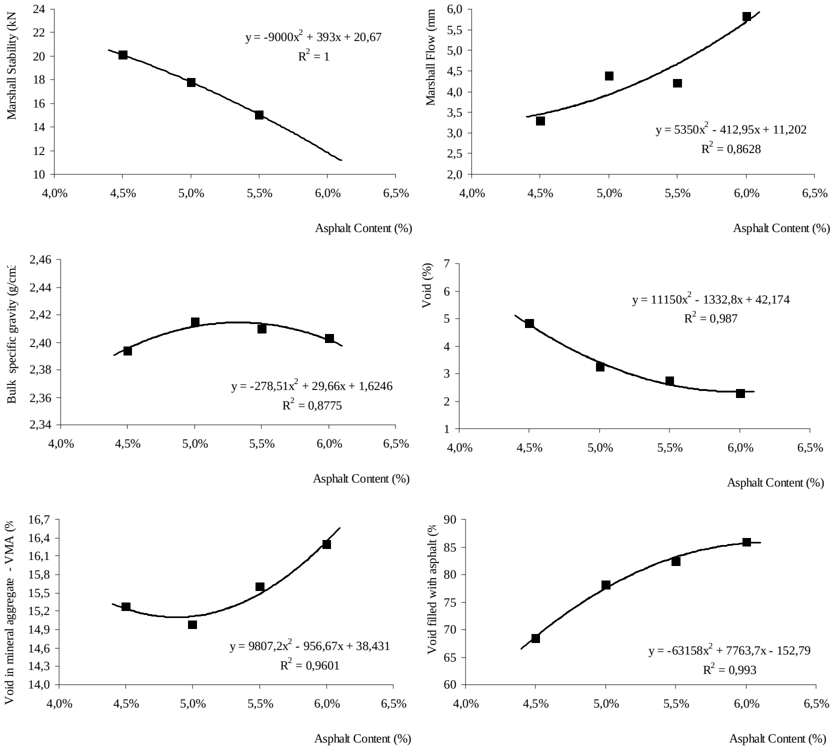


Figure 4. 9. MBDC1% Marshall mix design values.

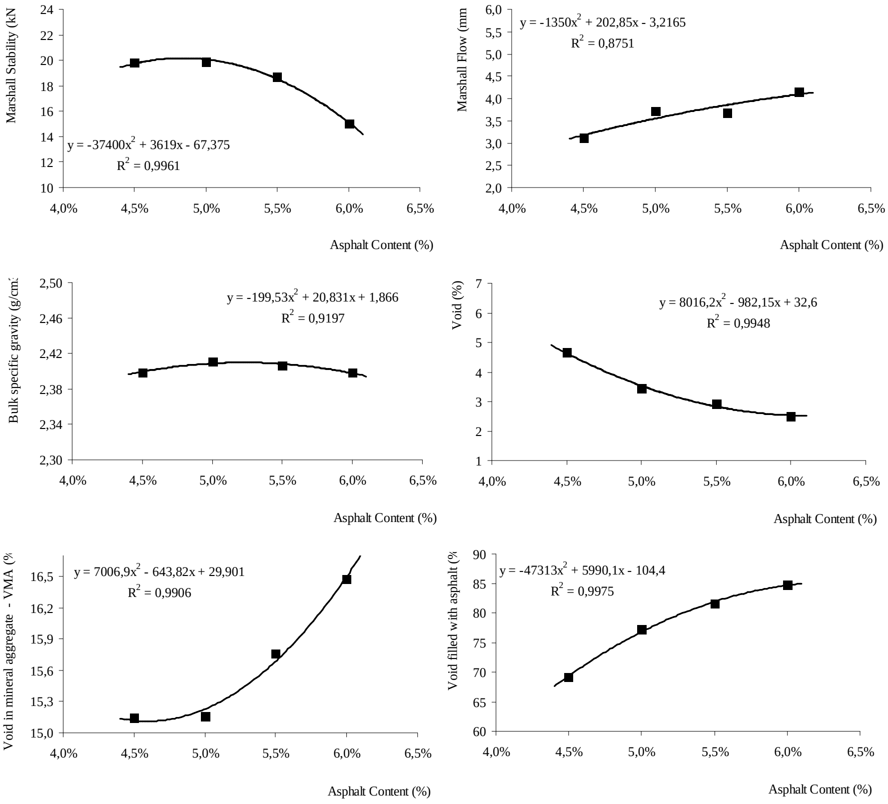


Figure 4. 10. MBDC2% Marshall mix design values.

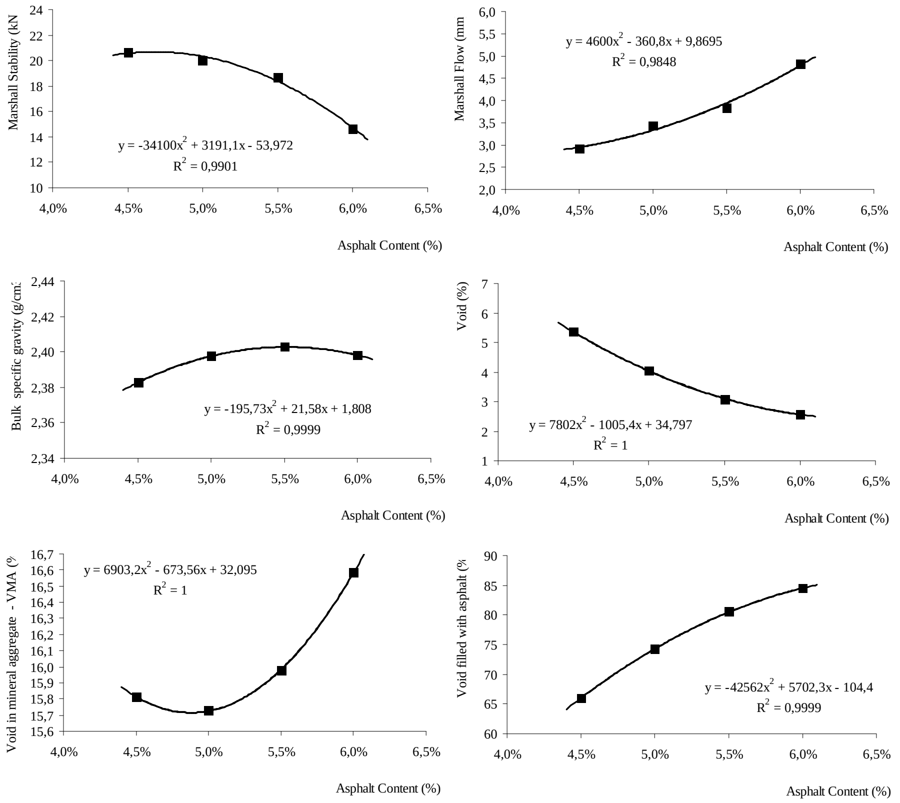


Figure 4. 11. MBDC3% Marshall mix design values.

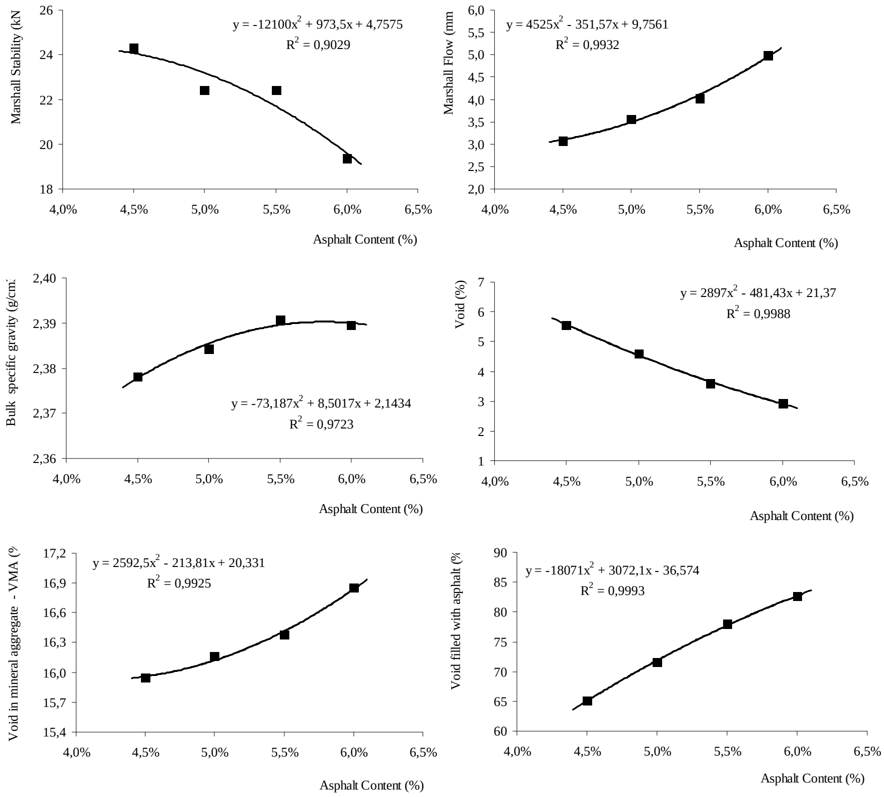


Figure 4. 12. MBDC4% Marshall mix design values.

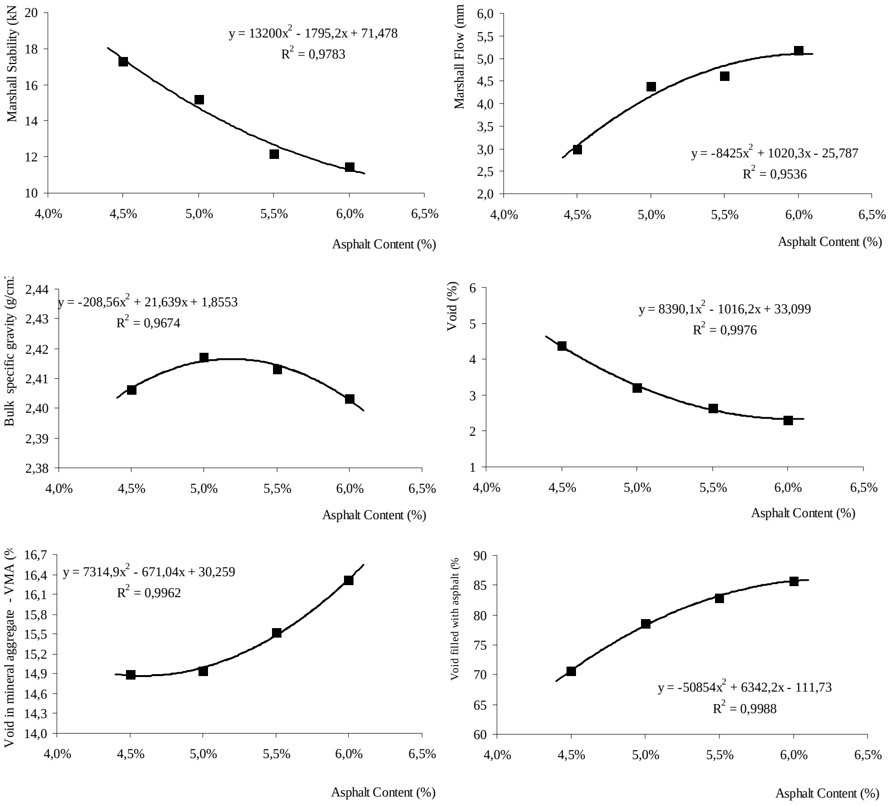


Figure 4. 13. MBG5% Marshall mix design values.

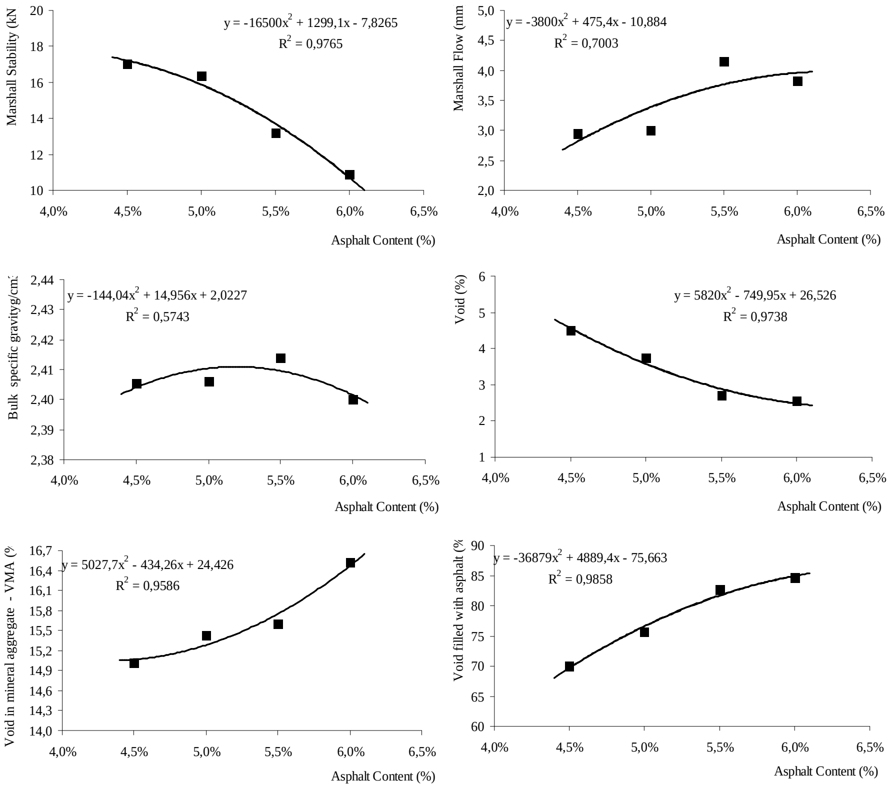


Figure 4. 14. MBG10% Marshall mix design values.

4.3.3 Phase III

Washing process

The Dregs washing process caused physical and chemical positive alterations on the wastes, making them more workable. This process demonstrated that is possible to obtain a better material after a simple treatment. The monitored parameters results during DC and DWLS washing can be seen in Figure 4.5. The measured parameters become lower and almost constant with the washing process for both wastes. The soluble salts decreasing content is an important factor for the possibility of re-using these materials in pavement sector. This kind of salts represents a problem in terms of “conserved strength” properties affecting the final product.

In terms of gradation, the final material presented fewer particles between 2 to 0.425mm sieves compared to the wastes gradation before washing. These particles were disaggregated and dissolved in smaller particles with dimensions between 0.18 and 0.075 mm (Table 4.7). Now, washed DC and washed DWLS gradation is “similar” to hydraulic lime (compare the results checking Table 4.2.

The MB parameter was also checked on the wastes. The washing results for MB parameter for DC and DWLS decreased the MB values considerably. The results are shown in Figure 4.6. The plasticity index after washing wasn’t checked but it would be interesting if it is lower.

To achieve the “conserved strength” value for dregs mixes, DC and DWLS were washed and tested in two incorporation contents (2 and 4%), using the same OBC found for these formulations in phase II. Good results were obtained for all parameters in every mixes (Table 4.8). MBCD4% presented a very good performance (97%) compared to the control mix, MBBr (90.7%), even with voids content lower than the allowed value. This problem might be easily solved by a particle size adjustment of the aggregate. The problem with water sensitivity was solved with the washing procedure.

Table 4. 8. Gradation of wastes before and after washing process.

Sieve size (mm)	Accumulated percentage passing			
	DC before washing	DC after washing	DWLS before washing	DWLS after washing
25	100	100	100	100
19	100	100	100	100
12,50	100	100	100	100
4,75	100	100	100	100
2,00	99,6	100	99,5	100
0,425	66,0	99,5	74,1	99,3
0,180	54,6	94,0	56,4	97,1
0,075	43,4	91,3	21,1	85,5

Table 4. 9. "Conserved Strength" Washed dregs mixes results (phase III).

Mixes (ID)	OBC	Voids (%)	EN 12697:12/2003		
			Parameters	specimens in the water to 40ºC	specimens condditioned 20ºC
MBBr	4,8	3,3	Apparent Gravity (g/cm3)	2,422	2,420
			Stability (kN)	15,96	17,59
			Conserved strength (%)	90,7	
MBDC2% washed	4,9	2,9	Apparent Gravity (g/cm3)	2,438	2,425
			Stability (kN)	17,59	19,68
			Conserved strength (%)	89,3	
MBDC4% washed	5,3	2,4	Apparent Gravity (g/cm3)	2,43	2,43
			Stability (kN)	12,23	12,58
			Conserved strength (%)	97,2	
MBDWLS2% washed	4,9	4,0	Apparent Gravity (g/cm3)	2,41	2,40
			Stability (kN)	19,22	21,31
			Conserved strength (%)	90,2	
MBDWLS4% washed	5,3	4,0	Apparent Gravity (g/cm3)	2,38	2,39
			Stability (kN)	17,78	20,03
			Conserved strength (%)	88,7	

4.4 Conclusions

In this work, the properties of pulp and paper mill wastes were compared with conventional aggregates used in asphalt pavements, in order to value them as raw materials for this application. Hence, standard aggregates and pavements tests were carried out and the main conclusions were:

1. According to the results, it was possible to verify that grits could be directly tested as an aggregate for this pavements construction sector. Indeed, Grits mixes are acceptable and ready to be tested in industrial scale. This waste is compatible with crushed stone already used as aggregate for road pavements.
2. Dregs presented soluble salts that didn't allow direct applications as-received from the production process. After washing process, Dregs mixes had compatible values compared to the reference mixes. They achieved Marshall Stability and flow values as expected.
3. Washing process efficiency was demonstrated based in the results of conductivity, soluble salts and methylene blue tests. These removed salts can be returned to the pulp and paper mill representing, for this industry, also a valuable economic and

recycling aspect resulting from this work. In terms of gradation, DC and DWLS had a significant reduction in particle size after washing, becoming finer. This fact made them more compatible with the conventional “fillers” used in pavement sector.

4. In terms of waste management, it is possible to conclude that these wastes, generated in huge amounts during pulp paper production, can easily be drained by this large tonnage activity (pavement construction sector), avoiding their landfill and contributing at the same time for natural resources preservation.

Pulp and paper mill permits to adapt a waste treatment stage quite easily. It even promotes wastes’ salts recovering to the pulp process. The water used in the treatment can also be re-processed into the mill and recovered. The costs relative to the wastes landfill are superior to the implementing solution, economically and environmentally. Furthermore, this treatment allows having wastes ready to be used in pavements application.

Acknowledgements

The authors would like to thank Forest and Research Institute – RAIZ, Portucel Soporcel group, Engª Fátima Matos, Engº Paulo Martins, Manuel Vieira & Bacalhau, Lda, for their help and contribution to this study.

5 LIME MUD FROM CELLULOSE INDUSTRY AS RAW MATERIAL IN CEMENT MORTARS

Regina C.E. Modolo*, Luciano Senff, João A. Labrincha, Victor M. Ferreira, Luis A. Tarelho

Published in **Materiales de Construcción** 64 [316] October–December (2014)
Impact Factor (5-year): 0.757; ISSN: 0465-2746
WebQualis: B1

Abstract

This study reports the use of lime mud (LM) in cement-based-mortars. Lime mud is a waste generated in the production of cellulose by the kraft mill process. It is mainly composed of $CaCO_3$, a small amount of magnesium carbonate and other trace minerals. Mortars were prepared by adding different amounts of LM (10, 20 and 30% by weight of cement) in dry weight. The mortar compositions were evaluated through rheology and flow table measurements, assuring that all the samples exhibited adequate conditions for testing in both equipments. The hardened state properties were also evaluated through mechanical strengths at 7, 28 and 90 days of curing. Following a waste management solution perspective, this work intend to provide a general evaluation of LM application in cement based mortars, looking at both fresh and hardened properties in order to guarantee that the final application requirements are not hindered.

.

5.1 Introduction

The negative influence of wastes on the construction materials properties require further research in order to optimize the characteristics of them. In recent years, the environmental damage and the wastes generated from industrial activity, increased significantly worldwide and one of the most common solid waste disposal means is in controlled landfills. Thus, the raw natural materials have become scarce and the adverse impacts on the environment are visible [Binici et al., 2008; UMTC, 1995; OECD, 1997]. Best available techniques for reducing waste is to minimize the generation of solid waste and/or use these by products as alternative raw-materials, wherever practicable. Pulp and papers mills generates thousands tons of solid waste (organic and inorganic) every year that go for landfill disposal (mainly inorganic types). The amount and the composition of these wastes depend necessarily on the process techniques applied and the raw materials used to obtain the pulp and/or the paper quality desired. In general, the solid waste composition from pulp and paper mills is known and constant, as a result of the current, highly controlled production process which permits the use and valorisation of the wastes in safe and environmental way [Monte et al., 2009]. Some applications of theses wastes have been frequently researched including aggregates for bituminous mixtures [Modolo et al., 2010], cement [Ahmadi and Al-Khaja, 2001; Coutinho and Garcia, 2008], brick [Cernec et al., 2005] and fiber-cement [Modolo et al., 2011]. From pulp mills, inorganic sludges are separated from the chemical recovery cycle and normally landfilled after dewatering. Lime mud is an industrial pulp and paper kraft mill solid waste of the chemical recovery unit [Figure 5.1]. It has the code 03 03 09 in the European List of wastes (2004). It is mainly composed by calcium carbonate, small amount of magnesium carbonate and other trace minerals [Gaskin, 2004; Li et al., 2012]. Normally, the major part of this sludge is used as raw-material in the limestone make up process. Although this waste is partially used as raw-material in the own pulp and paper process, in this specific case, due to limitations of the lime kiln, the limestone make-up does not drain all lime mud generated by the production process. Then, the lime mud surplus has been landfilled (approximately 500 tons/month in wet base). Essentially, the production of industrial pre-mixed mortars exceeds several million tons each year, consuming a huge amount of natural but pre-treated raw materials (e.g. siliceous sand) as aggregate as well as cement. This activity could be looked as a target for the use of lime mud, as currently happens with the ashes generated from the coal and biomass combustion in concrete [Ampadu et al., 2002; Cordeiro et al., 2008]. Several studies related with the use of wastes as filler, aggregates or cement replacement material in mortars or concrete have been researched. Some of them indicate that may be the wastes could be classified as a pozzolanic material (i.e. cane bagasse ash), but some points that their activity depends significantly on its particle size and fineness [Cordeiro et al., 2008; Rajamma et al., 2009; Taylor and Tait, 1999; Modolo et al., 2013; Pérez-Carrión et al., 2014; Argiz et al., 2013]. Specifically, some uses for lime mud, such as in bricks, cement and pavements could be good alternatives to drain huge amounts of this solid waste. Eroğlu (2006) tested lime mud also as soil stabilization of forest roads. The results obtained showed that roads deformation could be stabilized and maintained by using lime mud. In another work, lime mud was tested as additive in composite cement and the results confirmed it as a potential waste for this application [Eroğlu et al., 2007]. The use of limestone fillers in concrete and mortars has becoming more and more common in recent years, pushed by economic and ecological drivers. Even the cement production is now dominated by type II formulations, where the clinker is partially replaced by limestone fillers (up to 35 wt.%). In most cases limestone fillers simply acts as a component in the cement/mortar [Vuk et al., 2001; Benachour et al., 2008; Felekoglu, 2007]. However, European Standards relating to aggregates for mortars (EN 13139: 2003) allows up to 22% in mass as an aggregate component.

Following the waste management perspective of finding an efficient alternative of lime mud valorisation, this work intend to show, through bench scale developed work, a solution for this waste incorporation in cement-based materials providing not only a general approach of lime mud characteristics, but also present results about the final product properties (mortars) in the fresh and hardened state.

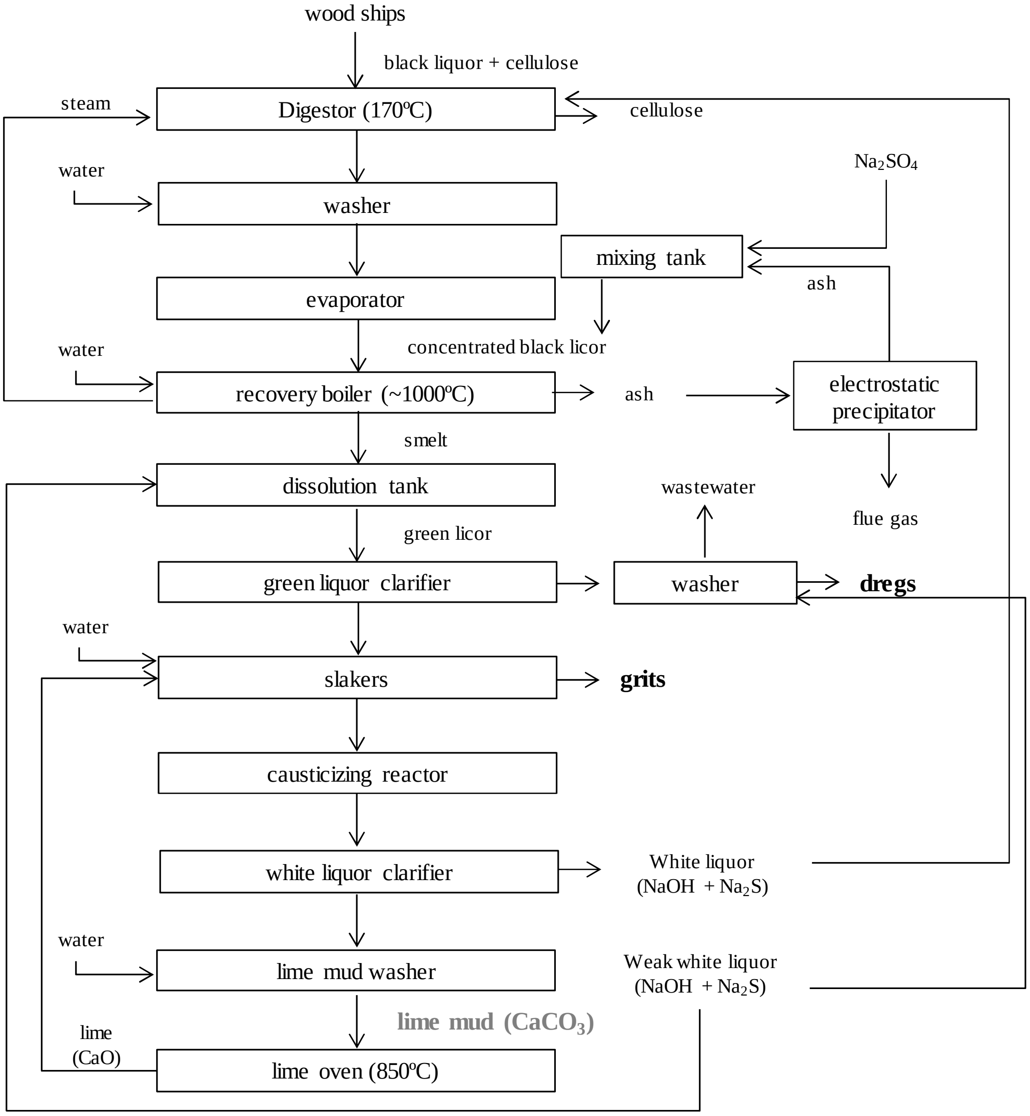


Figure 5. 1. Kraft process flowsheet example; waste under study generated in the caustification line is written in gray color.

5.2 Experimental procedure

Lime mud (LM) sample was used as collected, from a rotary filter chamber located in a pulp paper plant in Aveiro, Portugal. Ordinary Portland cement (OPC) type II -32.5 N, produced with 65-79% of clinker, 21-35% of lime and 0-5% other components including calcium sulphate as setting regulator, was used in the present study to prepare pastes and mortars. OPC has an average particle size of 14 µm.

Avoiding energy costs in the future; the lime mud was tested without dewatering. The moisture content (34%) was kept as collected and used in the mortars production. The water final ratio was calculated adding up the waste water content plus additional fresh water. Siliceous sand was sieved through a 1.18 mm before use in the mixture as aggregate. Its average size is 0.830 mm. The particle size distribution of LM was performed using a Coulter LS particle size analyzer (LS230FM). The real density of LM particles was determined with picnometer method (ISO/TS 17892-3/2004). The specific surface area was measured by nitrogen adsorption method according to Brunauer, Emmett and Teller (BET). Thermal gravimetric and differential thermal analyses (TG/DTA) of the LM were performed up to 1000ºC with a heating rate of 10 ºC/min, in a simultaneous TG/DTA (STA 409 EP). The chemical composition of the LM and CEM II 32.5N were evaluated using X-ray fluorescence spectroscopy using a Panalytical Axios spectrometer. The microstructure of the LM was studied using a scanning electron microscope (SEM - Hitachi SU-70). The chloride content was determined in the solid waste (LM) and in the mortars by the Argentometric method (CHLORIDE, 4500-Cl-; Standard Methods Committee, 1997). The sulfate content was determined in LM by Gravimetric method (SULFATE, 4500-SO_4^{-2}; ignition of residue, Standard Methods Committee, 1997). Cement pastes (w/b = 50 wt.%.) and cement mortars (water/binder ~ 62 wt.%.) were prepared using different amounts of LM (10, 20 and 30% by weight of cement) in dry weight. The amount of water used in the mixtures was defined regarding the dosage of LM, in order to obtain an adequate workability condition to test in the rheometer and flow table. The workability of mortars was determined through rheology and flow table measurements, assuring that all samples exhibited an adequate condition in both equipments. In this way, it was possible to obtain a more complete characterization in the fresh state. The complete cement-mortars formulations are shown in Table 5.1.

The procedures used to prepare the formulations included: (i) placing lime mud into the water; (ii) mixing for 1 min at a low rotation speed of 60 rpm; (iii) stopping for 1 min; (iv) mixing again for 1 min at a higher rotation speed (120 rpm). A rheometer (Viskomat PC model, Schleibinger) was used to measure the rheological behaviour of fresh mortars, using a maximum speed rotation (100 rpm) and 60 min of total test time. The rheological parameters (yield stress and plastic viscosity), was defined by using the Bingham model [Paiva et al., 2009; Ferraris et al., 2000; Banfil, 2003; Senff et al., 2012]. The workability of mortars was also measured through the spread diameter on flow table, according to EN 1015-3:1999. The setting time of samples was determined by the Vicat needle penetration method following EN 196-3:2005, while the kinetic of hydration was determinate in a quasi-adiabatic calorimeter. For the mechanical test (flexural and compressive tests, EN 1015-11:1999), mortars specimens with 40 × 40 × 160 mm were produced and tested after 7, 28 and 90 days cured in standard conditions (temperature = 22ºC and relative humidity = 65%) (EN 1015-2:1998). Apparent density and water absorption were also determined by the immersion technique according to EN 1015-10:1999. Capillary was measured in mortars specimens according to EN 1015-18:2002. The crystalline phases of LM and mortars were detected by X-ray diffraction – XRD (equipment RIGAKU-Geiger flex diffractometer).

Table 5. 1. Cement-mortars formulations.

Formulations	Cement	Sand	Lime-mud (dry base)	Super Plastisizer	Water
	% (total mass)			% (total solid mass)	
REF	25.0	75.0	0.0	0.0018	15.5
LM10%	24.4	73.2	2.4	0.0017	15.1
LM20%	23.8	71.4	4.8	0.0017	14.8
LM30%	23.3	69.8	7.0	0.0017	14.4

*LM was used as collected on formulations (with ~34% of moisture content)

5.3 Results and discussion

5.3.1 Characterization of lime mud

The particle size distribution of LM was typically below 26 µm being the size average around 10 µm (Figure 5.2).

Table 5. 2. Lime mud and CEM II 32.5 physical and chemical characteristics.

Parameter	[1]RD	[2]SA	MO	LOI	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	[3]SO_4^{-2}	[4]Cl-
	g/cm^3	m^2/g	%wt											
LM	2.83	5.17	34	43.7	0.29	0.2	0.03	0.48	51.8	1.9	0.1	0.9	0.05	0.08
[5]PC	2.98	5.18	<1	14.0	15.4	3.82	2.36	1.41	58.5	ND	NQ	NQ	<3.5	<0.1

[1]Real density; [2]Specific area; [3]Sulphates - According to NP EN 196-21; [4]Chlorides - According to NP EN 196-2; [5]Portland cement type II 32.5; ND – Not detected; NQ – Not quantified

The real density and the BET surface area of LM and OPC are presented in **Error! Reference source not found.**table 5.2. LM real density was slightly lighter than OPC. LM presented a surface area of 5.17m^2/g and its microstructure is shown in figure 5.3. The chemical analysis of LM is shown in table 5.2. LM contained a chloride content of 0.08 wt% and sulphate content 0.05 wt%. The presence of chlorides in cementitious materials can accelerate the setting time and together sulphates can also reduce durability by deterioration of microstructure [Rajamma et al., 2009]. LM is basically constituted by calcium carbonate ($CaCO_3$). In this case, the LM was collected in a rotary drum without passing through a washing step. This washing permits to remove more soluble chlorides content what would be good for cement materials production. The major variation in weight was seen in the TG/DTA in the range of 800-900ºC around 40% (Figure 5.4). This variation represents the thermal decomposition of calcite ($CaCO_3$) and evidences the X-ray diffraction result.

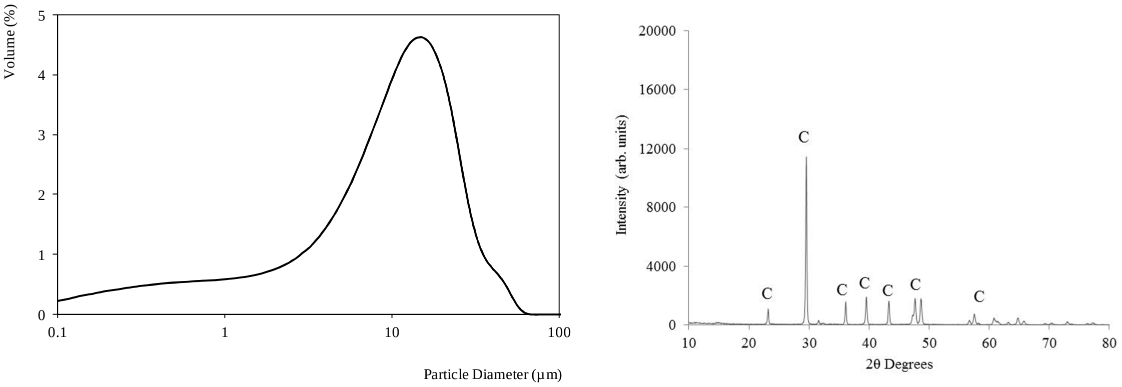


Figure 5. 2. Particle size distribution and DRX results of lime mud (C=calcite).

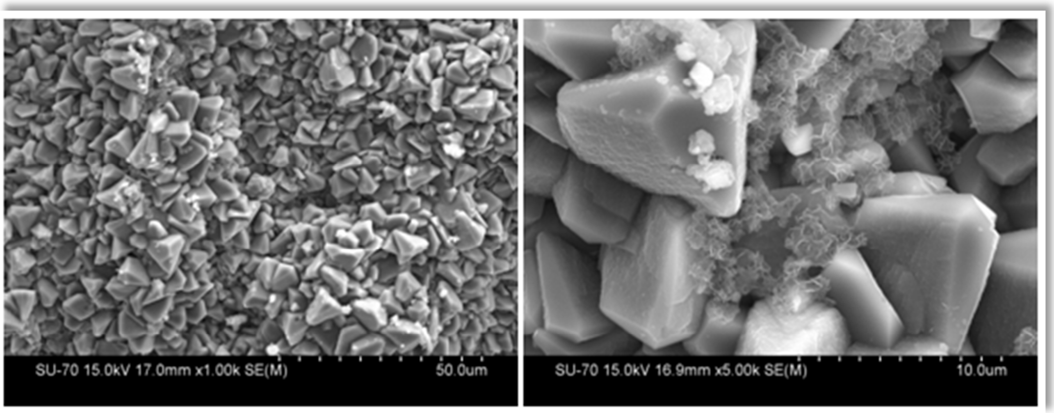


Figure 5. 3. Microstructure of Lime mud.

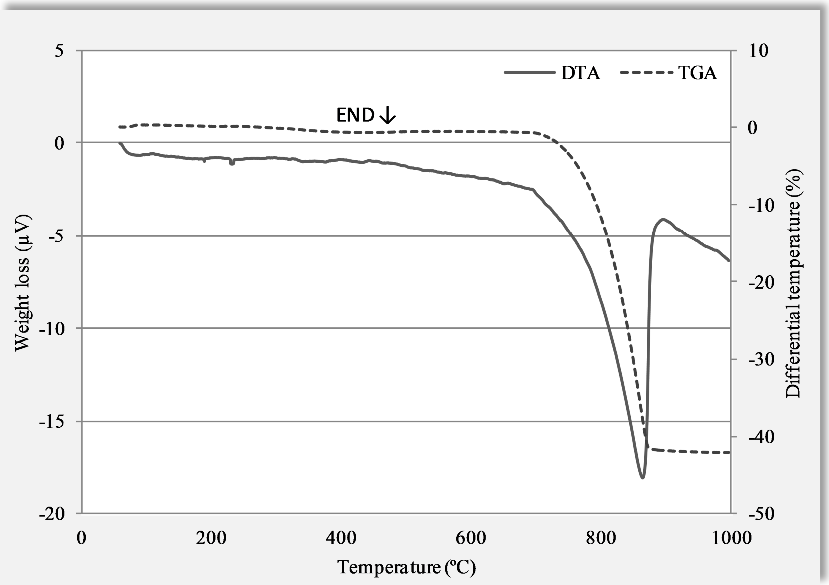


Figure 5. 4. TGA/DTA curves of Lime mud.

5.3.2 Cement lime mud formulations

5.3.2.1 Fresh state properties

In general, LM-containing samples modified the rheological behaviour in different levels as indicate in the Fig. 5.5. Mortars containing 30% LM showed highest torque and yield stress values along the time. The presence of fine particles in the mixtures requires an extra dosage of water or superplasticizer additive to keep the workability invariable. However, the mentioned factors influence significantly the rheological behaviour [Senff et al., 2012; Vaysburd and Emmons, 2004] and the eventual impact due to fine particle is hard to be quantified. Is important remind here that the purpose of this experimental research is evaluate the real influence of LM, keeping them invariable. The reduction of plasticity can be related to the cohesiveness and intense particle attrition. Moreover, the presence of agglomeration or tridimensional structures formation can also affect particularly the torque and yield stress evolution along the test. In fact, the yield stress was the main rheological parameter affected regarding then plastic viscosity that remained almost constant at the end of the test.

As much as lime mud has been added the mortars spread (flow table) has decreased (Figure 5.6). The workability of mortars with 30% LM decreased ~ 15% regarding the control sample. This fact can be due to the particle cohesion increasing and the remaining water content, as mentioned before.

The same behaviour was observed by Felekoglu et al (2007). The authors testing two types of materials (quarry waste limestone power – QLP, and powder produced by direct grinding of Limestone – PLP) showed that PLP compositions flowability do not differ significantly when compared with reference sample. On the other hand, an accentuate flowability decreasing was observed on QLP compositions. They concluded that this fact was associated to the powders particles fineness and shape. Finer powder (PLP) improved the spread flow values compared to coarser powder (QLP). The authors recalled that at first sight, due to the increased surface area, it seems not logical to expect higher flow values from a mixture incorporating finer powders when other variables are kept constant (in particular water content). However, just beside particle size, particle surface characteristics and surface porosity can play significant roles in designating the fresh state behaviour of cement pastes.

The setting time revealed distinct behavior when LM was added in the mixtures (Figure 6). The control sample exhibited the highest period, while 30LM-containing mortars reduced ~25%. This fact could be related to water remaining in the cement matrix because of the fineness effect of the added particles in the LM composition. In addition, the pH of hydration solution can also influence the hydration mechanism in cements [Rajamma et al., 2012]. Some other factors can also contribute to the setting anticipation, i.e. the presence of Cl^- ions on LM. Chlorides exert some influence on the kinetics of hydration, becoming higher in cement with extra dosage of LM. However, according to the EN 998-1:2003 standard, the global content of Cl- ions should not exceed 0.1wt.% of mortar/concrete constitution, since the efflorescence formation is often observed, compromising the durability of the material [Vaysburd and Emmons, 2004; Kaushik and Islam, 1995; Sanjuan, 1995]. Besides, the reaction between Cl- ions and C_3A (tricalcium aluminate) or C4AF (tetracalcium aluminoferrite) imply in the chloroaluminates formation [Sanjuan, 1995], in which the expansion occurrence increase the porosity that diminishes the mechanical strength.

The kinetics of hydration results measured by calorimetric are illustrated in the Figure 7. The maximum values of exothermic peak were registered after a period of 12h. In general, two main peaks can be observed, when the Portland cement is mixed with the water [Older, 1998], as follows: (i) the first peak occurs few minutes after contact with water, where several Ca^{2+}, SO_4^{2-}, Na^+, K^+, and OH^- ions are release to the aqueous solution from gypsum, C_3S, C_3A and C_4AF phases; (ii) the second peaks occur is caused by faster crystallization of CH and C-S-H. In both of cases, the presence of LM did not influence significant the results regarding the control sample. In fact, developed studies demonstrated that cements with small additions of limestone filler could be expected to have better performance if they have higher C_3S content and at the beginning of hydration, limestone do not significantly change the heat of hydration. Vuk et al (2001) also verified that the addition of limestone exhibited a strong effect on the initial setting measured by Vicat needle. The authors suggested that setting time is related to the type of used clinker and fineness cement (higher the limestone addition higher was the fineness of cement).

5.3.2.2 Hardened state properties

The mechanical and physical properties of the freshly prepared and hardened mortars containing LM are listed in Table 3. Some authors consider the effect of limestone on cement to be only physical, taking into account the increase in strength [Soroca and Stem, 1976].

In this case, the mechanical strength of mortars (7, 28 and 90 days) did not show any significant differences between the studied compositions and the control mortar (Table 5.3). The compressive strength of LM containing samples increased around 8% compared to the control sample at 28 days of curing. This difference between samples decreased at 90 days, but not significantly.

According to the results obtained for all mechanical strengths, LM does not influence in a negative way the mortars properties which suggest that this waste could be used as alternative material for conventional fine aggregates replacement. Specifically in terms of bulk, the filler effect is obvious, whereby mortar densifies up to an optimum value situated between 10 and 20% of LM amount. Nevertheless, it is observed that mixes with 30% of LM presented a slightly decreasing on this parameter at 28 days of curing. This fact was also observed by Bénérina et al. (2005). They proved that a density increase of dry mix up to an optical value of filler amount which represents 9 to 16% sand mass replacement (depending on the sand), and a regular decrease for higher proportions. They interpreted this as filler powder first filling voids around sand grains, up to the optimum and concluded that higher filler amounts, those voids being completely filled; filler powder occupies the place of sand grains, hence diminishing sand proportion, and consequently the mix density.

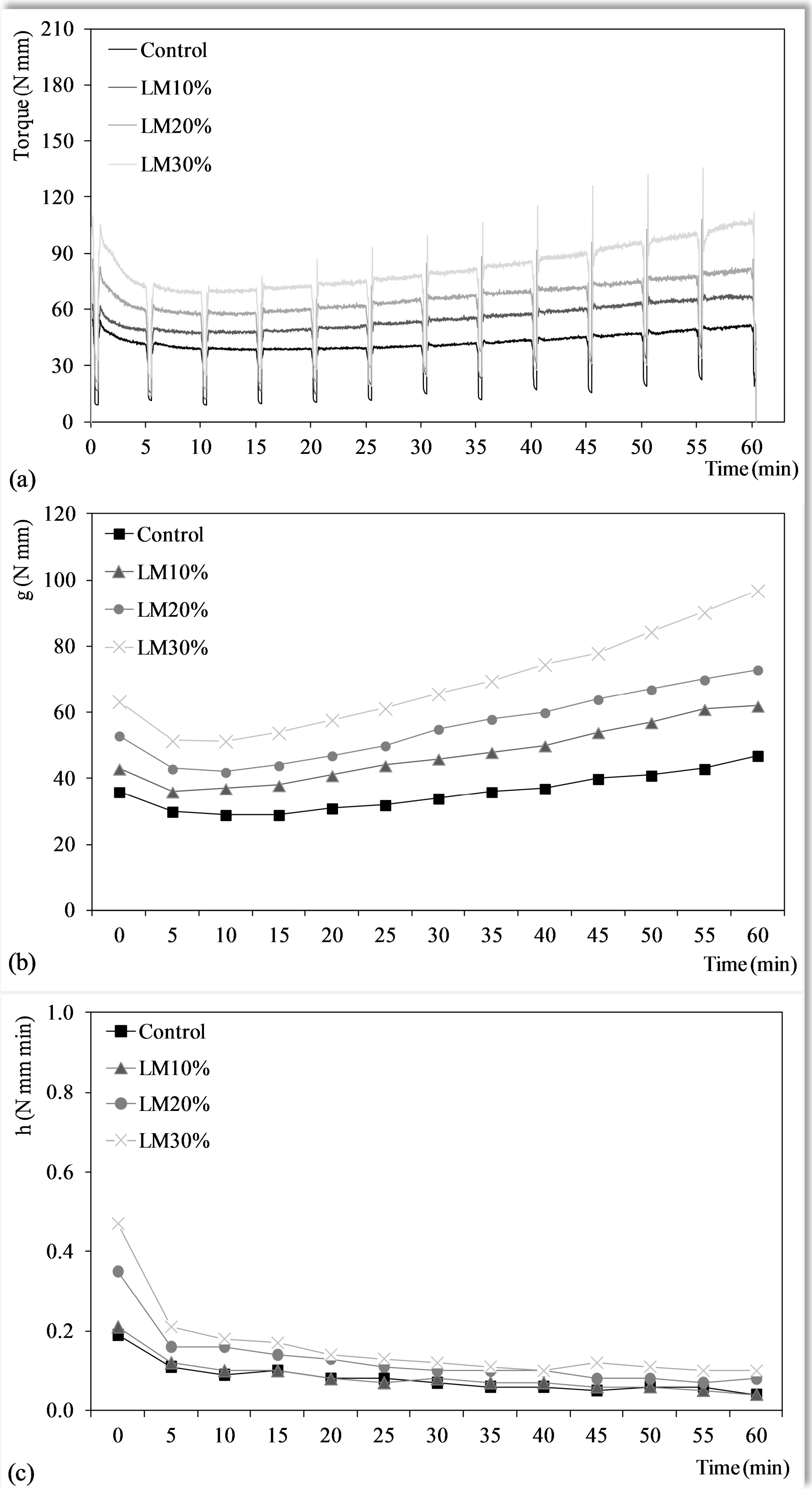


Figure 5. 5. Torque (a), Yield stress (b) Plastic Viscosity (c) evolution during rheological testing of distinct mortars.

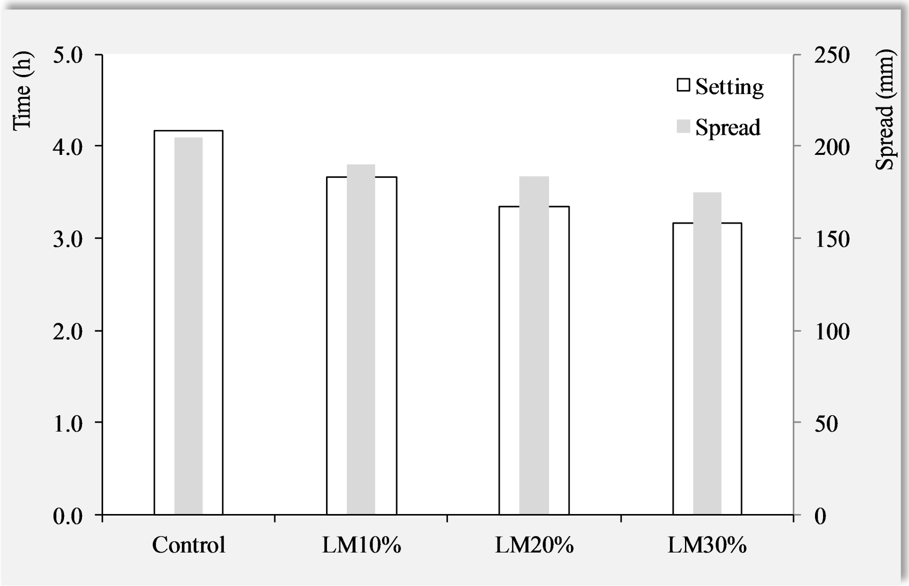


Figure 5. 6. Setting and spread diameter of cement lime mud mortars.

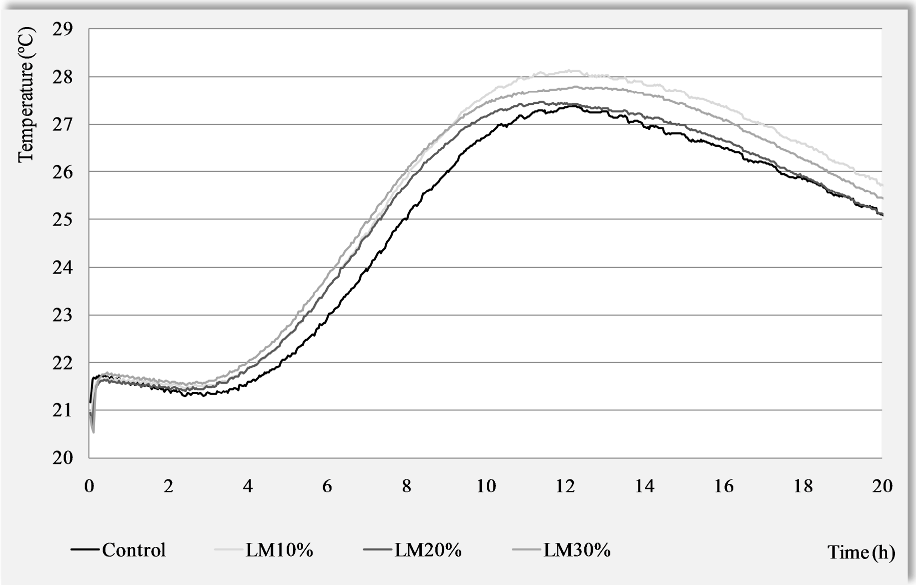


Figure 5. 7. Calorimetric evaluation of hydration process of cement lime mud pastes.

According to the results obtained for all mechanical strengths, LM does not influence in a negative way the mortars properties which suggest that this waste could be used as alternative material for conventional fine aggregates replacement. Specifically in terms of bulk, the filler effect is obvious, whereby mortar densifies up to an optimum value situated between 10 and 20% of LM amount. Nevertheless, it is observed that mixes with 30% of LM presented a slightly decreasing on this parameter at 28 days of curing. This fact was also observed by Bénérina et al (2005). They proved that a density increase of dry mix up to an optical value of filler amount which represents 9 to 16% sand mass replacement (depending on the sand), and a regular decrease for higher proportions. They interpreted this as filler powder first filling voids around sand grains, up to the optimum and concluded that higher filler amounts, those voids being completely filled; filler powder occupies the place of sand grains, hence diminishing sand proportion, and consequently the mix density.

Table 5. 3. Lime mud and control mortars properties (SD – Standard Deviation).

Samples	Control	LM10%	LM20%	LM30%
Apparent Density	2.14	2.13	2.12	2.12
Rf(MPa) [7/28/90 days]	5.5/5.3/5.3	5.2/5.1/5.6	4.9/4.9/5.4	5.1/4.2/5.6
Rc(MPa) [7/28/90 days]	17.1/17.9/22.3	16.6/19.4/23.1	16.0/19.4/22.2	18.3/19.4/22.6
B(g/cm^3) [7/28/90 days]	1.86/1.92/1.93	1.95/1.91/1.94	1.93/1.90/1.93	1.90/1.80/1.93
WA (%)	12.2/12.5/10.8	12.1/12.4/12.2	12.0/12.2/10.7	11.7/12.0/10.6
C (kg/m^2) [28 days]	3.40	2.63	2.23	2.24
Particle <0.075 mm (%)	22.3	25.9	27.1	29.9

Rf – Flexural strength; Rc - Compressive strength; B – Bulk density; WA – Water absorption; C – Coeficient of capillary.

The mortars capillarity was measured for a period of about 90 minutes (Table 5.3). The mortars absorption behaviour can be related to the pores content and/or pore sizes present in the mortars surface contact area. As much as the LM content increases in the cement mortars, lower becomes the capillarity coefficient. Many factors could influence this parameter and also it might be associated with the mortars structural arrangement. As the LM particles sizes are finer than the used sand, they could fill out same spaces inside the cement matrix causing this capillarity decreasing effect. The improvement is ascribed to reduced porosity [Benérina et al., 2005]. Regarding the filler effect phenomena, Moosberg-Bustnes et al (2004) observed that up to certain amount, the insertion of fine filler particles allows denser packing of cement paste and Benachour et al (2008) demonstrated that higher filler content increases the total porosity, but the macro-porous population diminishes in relation to the micro-porous.

5.4 Conclusions

This paper showed that samples prepared with higher dosages of $CaCO_3$ present in the LM makes this waste an interesting material to be used as a fine mineral aggregate in cement-based-mortars.

If flow table and rheometer are used to define mortars formulations the maximum amount to be added is restricted. In fact, the rheometer limited the LM content to 30% maximum. The yield stress increased with the content of LM and along the test time. The plastic viscosity did not showed noticeable change after the first 10 min of test, being the yield stress the rheological parameter that suffers the highest influence of LC incorporation. The spread on table of mortars containing 30% LM decreased about 15% regarding the REF. The mechanical strength was not significantly influenced by LM addition.

Regarding the economic aspects, there would be an opportunity to avoid the landfill of thousand tonnes of LM per year due to the expressive waste volume generated and, at the same time, savings in a natural raw material such as limestone could be achieved. Nevertheless, the moisture content of the LM has to be eliminated in case of using this waste as filler in dry-mixed industrial mortar preparation.

Acknowledgements

The authors would like to thank RAIZ and Portucel Soporcel group for their valuable help and contribution in this work. The authors also acknowledge FCT - Fundação para a Ciência e Tecnologia (grant SRFH/BD/75182/2010) for financial support for this work.

6 MORTAR FORMULATIONS WITH BOTTOM ASH FROM BIOMASS COMBUSTION

Regina C. E. Modolo*, Victor M. Ferreira, Luis.A.Tarelho, João A. Labrincha, Luciano Senff, Luis Silva

Published in **Construction and Building Materials** 45 (2013) 275–281
DOI: http://dx.doi.org/10.1016/j.conbuildmat.2013.03.093
Impact Factor (5-year): 2.76; ISSN: 0950-0618
WebQualis: A2 (Materiais)

Abstract

The management of bottom ashes generated from biomass combustion in bubbling fluidized bed combustors (BFBC) is a relevant environmental issue due to the increasing volume of production in recent years. In this work, bottom bed ashes from combustion of forest biomass residues in BFBC were used as aggregates in rendering mortar formulations. The ashes were characterized considering their particle size distribution and chemical/phases composition. When compared to conventional calibrated sands used as aggregates, the ashes are composed by particles covering a wider size distribution. SiO_2 is the major oxide but CaO content is over 10 wt%, suggesting some cementitious activity that was not confirmed. The amount of chlorides is significant and then water leaching and screening pre-treatment improved the quality of the ashes, despite requiring devoted installation and investment. Mortars produced by replacing commercial sand with equivalent mass of 50 and 100 wt% of ash show similar characteristics to the reference (ash-free) formulation, and satisfied all tested standard specifications. Main worries are caused by the variation of water level of the ashes along the time and the need to control the concentration of chlorides.

6.1 Introduction

Fluidized bed combustion (FBC) is recognized as the most appropriate technology for biomass combustion, due to the inherent advantages of low processing temperatures, isothermal operating conditions and fuel flexibility. The existing FBC technology at industrial scale includes bubbling fluidized bed combustors (BFBC) and circulating fluidized bed combustors (CFBC). Among other characteristics, these technologies differ in the pattern of gas-solid hydrodynamics in the reactor, the size of the bed particles, the heat and mass transfer rates in the reactor, and the temperature and flue gas composition profile along the reactor. This in turns influences the characteristics of the ashes produced during biomass combustion, and thus, flows of ashes with distinct properties will be produced in these installations [Van Loo S & Koppejan, 2008; Yin et al., 2008].

During biomass combustion in BFBC, two main types of ashes are produced: bottom bed ashes and fly ashes. The bottom bed ashes are composed by the sand particles (mainly quartz) purged from the original bed, inorganic (soil and small stones) components of the fed and the unburnt biomass fraction. In opposition to a grate furnace, where the bottom ashes represent the higher percentage of the total ashes produced, in the BFBC the bottom bed ashes often represent the lower fraction; the bottom bed ash fraction can represent 5%wt [Latva-Somppi et al., 1998], 10%wt [Dahl et al., 2009], 17%wt [Dahl et al., 2010], or be as high as 50%wt to 60%wt as often observed in some Portuguese thermal plants BFBC [Tarelho et al., 2012]. The bottom ashes are generated upon periodic bed discharges that are required to assure the renovation and to avoid agglomeration and defluidization, as well to maintain the bed height and the suitable particle size distribution. Those parameters are crucial to guarantee proper hydrodynamic conditions of the bubbling bed [Van Loo & Koppejan, 2008; Latva Somppi et al., 1998].

The bottom bed ashes from BFBC have the code 100124 [European List of wastes, 2004] and are normally non-hazardous wastes. They are mostly composed by silica sand (quartz) particles, ranging in size from few micrometers until some millimeters, often containing a relatively thin (with a few micrometers) coating layer that is mainly composed of inorganic glassy material [Vassilev et al., 2010].

Since the emissions from burning of biomass are considered CO_2 free, several new plants were installed in the past few years [Van Loo & Koppejan, 2008; Tarelho et al., 2011]. As a consequence, the amount of ashes generated increased considerably.

Controlled landfilling is their common destination but recycling alternatives should be pursued. According to Maschio et al (2011), the use of bottom ash in cement, mortars or concrete is feasible and can have a beneficial impact on environment. However, products must be durable and show suitable mechanical properties, while the release of potential hazardous elements should stay below the legal limits.

For example, the actual production of industrial pre-mixed mortars exceeds several million tons each year, consuming a huge amount of natural but pre-treated raw materials (e.g. quarried sand) as aggregates as well as cement or other binders. This activity can be looked as a target for the incorporation of bottom ashes, as currently happens with the fly ashes generated from the coal combustion in concrete [Ampadu & Torii, 2002]. Maschio et al (2011) tested fly and bottom ashes from biomass combustion as cement replacement in mortar formulations. Other authors tested coal ash and biomass fly and bottom ashes as substitute of natural aggregates in concrete and mortars [Pandey and Sharma, 2000; Ravina, 1997; Cheah & Ramli, 2012; Esteves et al., 2012; Kim & Lee, 2011; Kim et al., 2012]. Fresh and hardened properties were evaluated, including the rheological behaviour and water demand, mechanical strength, air permeability, and resistance to carbonation. Under limited and controlled conditions, the solutions are promising.

In the actual study, the conventional aggregate (sand, herein named S) used in industrial rendering-mortars was substituted by the bottom ash produced from the burning of biomass in BFBC. The need of pre-treatment operations before incorporation, namely washing and screening/sieving, was also evaluated. The leaching of chlorides is crucial to avoid deleterious effects on the durability and also to control the setting behaviour [Scherer, 2006; EN 998-2:2003]. At the same time, the adjustment of particle size distribution of the aggregates is also relevant to control the workability [Senff et al., 2009] of the mix and the compactness of the bodies, which determines their mechanical strength [Senff et al., 2011].

6.2 Methodology

6.2.1 Thermal power plant characteristics

The bottom bed ashes here studied were collected from a 50 MWth BFBC, located in the centre of Portugal. It burns forest biomass residues, namely eucalyptus bark and remains from logging activities. The temperature of the bubbling bed ranges from 800ºC to 900ºC, while the O_2 concentration in the flue gas varies between 4%v/v and 7%v/v (dry basis). The ash was directly collected in the ashtray of the combustor, schematically represented in Figure 6. 1.

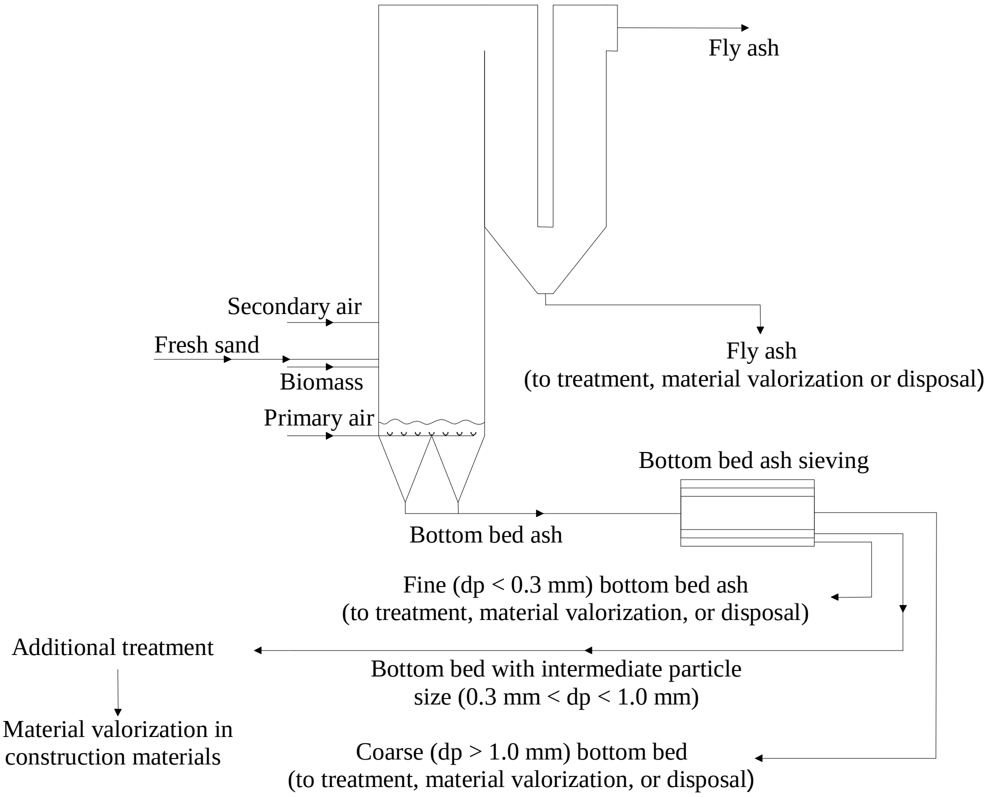


Figure 6. 1. Schematic view of the ash flows generated in the BFBC, including the basic operations implemented for potential further valorization.

6.2.2 Raw material characterization

The bottom bed ash was used in two different conditions, as shown in Figure 6. 2:

(i) just sieved (between 250 to 1000μm) in a lab-scale equipment to adjust the particle size distribution to the one of the commercial aggregate (sand) normally used in mortar formulations; the ash was here identified as BA (Bottom Ash);

(ii) pre-treated (washed and sieved), intending to diminish the content of soluble salts (namely chlorides) – identified as TBA (Treated Bottom Ash). The treatment was performed in a continuous way in an industrial plant that prepares natural sand as aggregate for the construction industry. The process includes a continuous shower that fixes the L/S (liquid to solid) ratio = 2, and has running capacity = 10 ton/h; the washing solution is then treated by sedimentation to be reused in further washing steps.

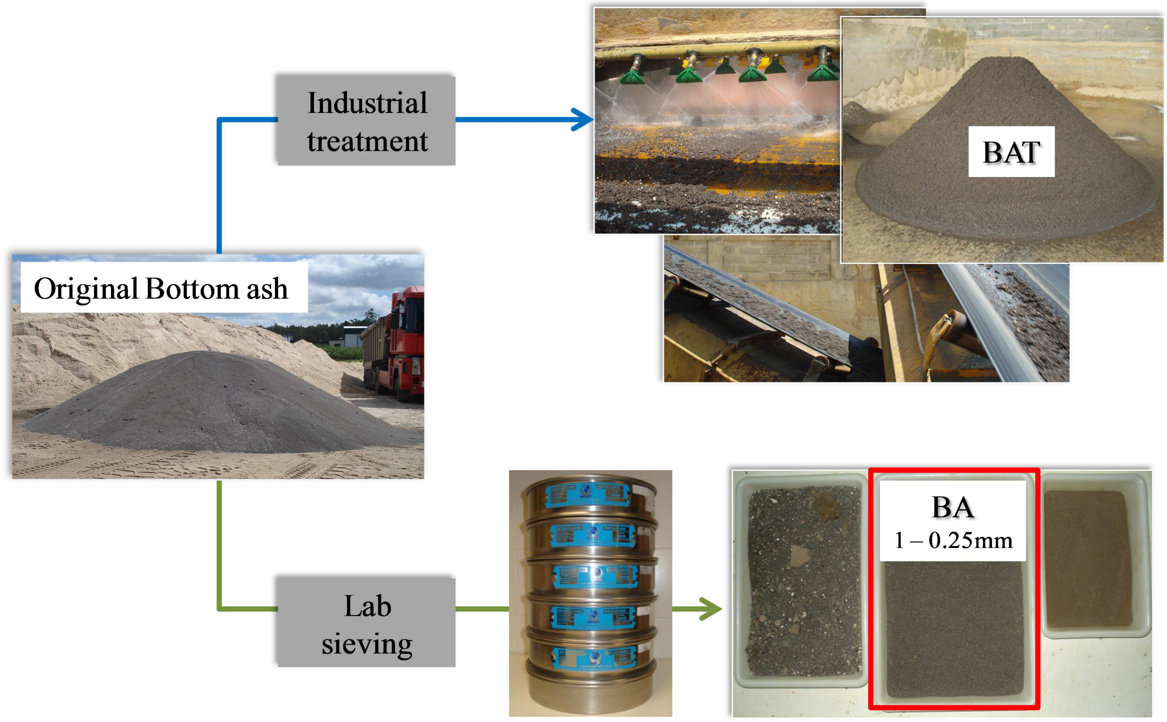


Figure 6. 2. Methodology of processing bottom ashes for rendering-mortars production

The chemical composition of ashes and other of the other constituents was determined by X-Ray Fluorescence Spectroscopy –XRF (Panalytical Axios spectrometer), while the crystalline phases were detected by X-ray diffraction – XRD (equipment RIGAKU-Geiger flex diffractometer). BA and TBA particles were also observed by Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS HR-FESEM Hitachi SU-70). The loss of ignition of the ashes was estimated upon firing at 1000°C. The particle size distribution of the coarse aggregate fraction (S2) and of the ashes was obtained by sieving [EN 933-1: 2000].

6.2.3 Mortar formulation and characterization

Prepared formulations are presented in Table 6. 1. Aggregate's fines are composed by limestone filler (LSF) and S1 sand. The preparation of mortars included: (i) water weighing and addition to the solids; (ii) mixing for 30 seconds at a low rotation speed (60 rpm); (iii) stopping for 1 min; (iv) mixing again for 1 min at the same low speed and, (v) keep the mixture in stand by for 10 minutes before testing the fresh state properties. Properties evaluated in the fresh condition are listed in Table 6. 2. Then samples were cured at 20ºC and 65%RH, in a climate room. Finally, the hardened mortars were characterised by following, when existing, standard procedures (see Table 6. 2).

Table 6. 1. Mix proportions tested.

Samples Identification	Portland Cement (Type I, 42.5R)	BA	TBA	S1	S2	LSF	Water
	(w.t%)						
REF*	14	0	0	45	20	20	16.5
BA50		10	0		10		
BA100		20	0		0		
TBA50		0	10		10		
TBA100		0	20		0		

Table 6. 2. Standards used in the characterisation of the mortars.

Product State	Test	Test period	Unit	Standard
Fresh	Apparent density	Immediately after mixing	g/cm^3	EN 1015-6:1998
	Setting time		h	EN 196-3: 2005
	Water retentivity		%	EN 1015-8:1998
	Flow Table		mm	EN 1015-3:2007
	Air content		%	EN 1015-7:2007
Hardened	Water-soluble chloride	After 90 days of curing	%	EN 1015-17:2000 (eluate) Potenciometry (determination)
	Unrestrained shrinkage	After 7 and 28 days	mm/m	Cachiers du CSTB (2669-4): A3.3
	Compressive Strength	After 7 and 28 days of curing	MPa	EN 1015-11:1999
	Elasticit Modulus	28 days	MPa	Cachiers du CSTB (2669-4): A3.2

To estimate the concentration of chlorides leached from cured specimens, samples were broken in small pieces and then milled and sieved (< 125µm). After drying at 105ºC, the powders (10g) were immersed in distilled water (100mL) and the leaching process was conducted according to EN 1015-17:2000. After 24h, the solution was filtered and the concentration of chlorides was measured by potenciometry, by using a chloride selective ion electrode.

Two prismatic specimens (25x25x285mm) from each formulation were used to measure the dynamic elastic modulus (E), by determining the longitudinal resonant frequency and accounting for the density and length of the sample. The measurement was conducted with an Oscilloscope – HAMEG HM303-4 (30Hz) coupled to a power amplifier (LDS PA25E) and a current source 4102C (DYTRAN Instruments). The product validation was done by comparing the characteristics of the samples with current product specifications, listed in Table 6. 3.

Table 6. 3. Current product specifications.

State	Characteristics		Industrial Portuguese Render	
			Minimum	Maximum
Fresh	Apparent Density	g/cm^3	1.65	1.80
	Flow table	mm	140	170
	Air content	% wt	18	21
	Water retentivity	% wt	93	97
	Setting time (min)	Beggining	275	410
		End	370	505
Hardened	Unrestrained shrinkage	%	0.5	0.8
	Elasticity modulus	MPa	7.500	10.000
	Compressive Strength	MPa	3.5	*NA

*Not Applied

6.3 Results and discussion

6.3.1 Materials and mixtures

Chemical and mineralogical compositions of used raw materials are presented in Table 6. 4. SiO_2 and CaO represent more than 90 wt% of the composition, being the first oxide clearly dominant as a result of sand purging from the bed. The ratio (CaO + MgO)/SiO_2 are equal to 0.26 and 0.16 for BA and TBA respectively.

Table 6. 4. Chemical and mineralogical composition of used components.

Parameters			Raw material					
			BA	TBA	S1	S2	LSF	CEM 42,5 I
SiO_2 (% wt)			72.18	80.09	99.43	97.53	0.60	20.16
CaO (% wt)			17.15	11.79	0.07	0.28	56.37	59.91
Na_2O (% wt)			0.88	1.11	0.03	0.07	0.05	0.17
Al_2O_3 (% wt)			2.29	2.02	0.00	1.21	0.00	4.82
MgO (% wt)			1.96	1.54	0.07	0.01	0.06	2.27
Loss on ingnition (% wt)			2.08	1.27	0.09	0.24	41.26	2.26
Cl^- (mg/kg)			472	160	20	10	1	190
Retained material content in the respective sieves**	(mm)			(%)				
	1.000		0	10	0	16	100% < 0.063 mm	NQ*
	0.500		86	83	2	50		
	0.250		14	7	75	29		
	0.125		0	0	18	3		
	0.063		0	0	4	1		
Density (Picnometer)			2.65	2.67	2.68	2.66	NQ*	NQ*
Mineralogy (by DRX)	Quartz	SiO_2	√	√	√	√	X	NQ*
	Calcite	$CaCO_3$	√	√	X	X	√	NQ*
	Larnite	Ca_2SiO_4	√	√	X	X	X	NQ*
	Microcline	$KAlSi_3O_8$	√	√	√	√	X	NQ*
	Andalusite	$Al_2(SiO_4)O$	X	√	X	X	X	NQ*

*Not Quantified; √ - Presence; X - not detected

** According to EN 933:1/2000

Comparing with values used in the characterisation of coal fly ash, we are far below the limit of 1.4 that defines hydraulic activity (Maschio et al., 2011; Matjie et al., 2008). Even so, some detected phases are commonly found on cement, e.g. larnite (Ca_2SiO_4). Quartz, calcite ($CaCO_3$), and microcline ($KAlSi_3O_8$) were also detected.

The loss on ignition (LOI) of BA and TBA were found to be 2.1% and 1.3%, respectively, revealing that burning conditions were efficient. The decrease observed on pre-treated ash is a result of the removal of soluble components (salts) and of some organic matter initially present in the material.

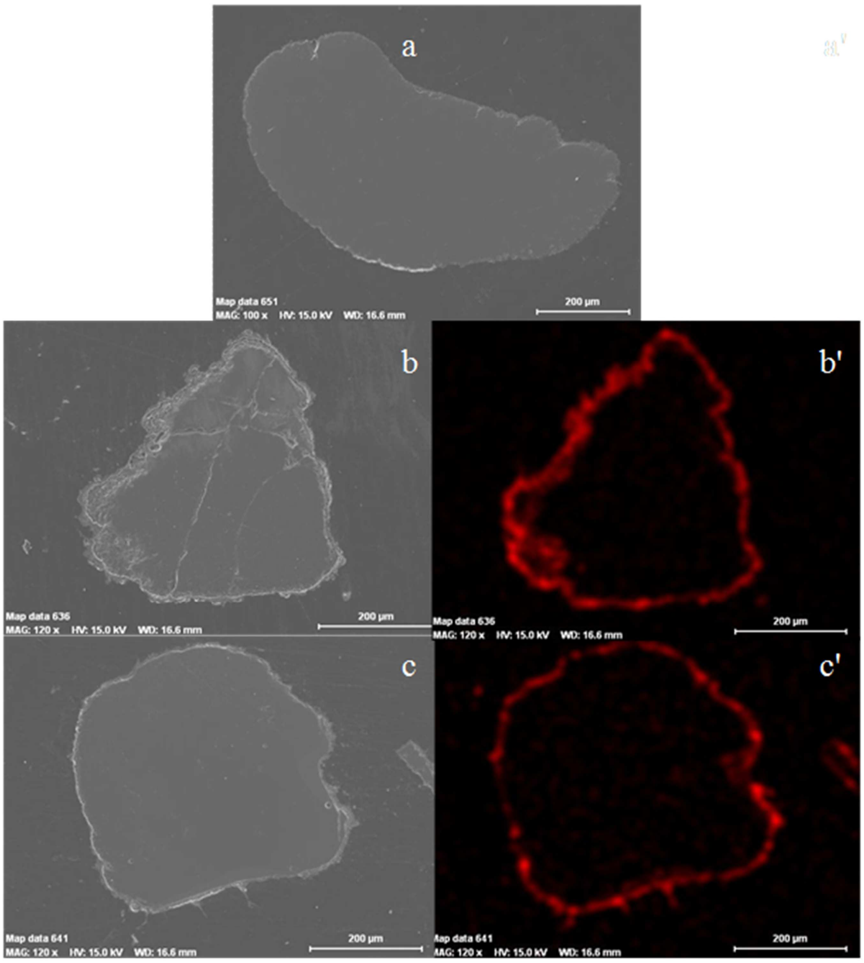


Figure 6. 3. Low magnification SEM views of particles (left) and corresponding EDS mapping for Ca (right side in red) on the surface layer: a - conventional sand; b - BA; c – TBA

According to the EN 998-1:2003 standard, the global content of Cl^- ions should not exceed 0.1wt.% of mortar/concrete constitution. The decrease of Cl^- concentration (about 60%) in TBA ashes (Table 4), when compared to BA, reflects the washing efficiency of the applied industrial treatment. The presence of chlorides tends to anticipate the setting process [Nilforoushan & Sharp, 1995; Kaushik & Islam, 1995; Makaratat et al., 2011], but cause then strong deleterious effects on hardened bodies. Formation of efflorescence is often observed, compromising the durability of the material [Vaysburd &Emmons, 2004; Kaushik & Islam, 1995]. Additionally, Cl^- ions tend to react with C_3A (tricalcium aluminate) and C_4AF (tetracalcium aluminoferrite) phases forming chloroaluminates (Sanjuan, 1997) with associated expansion and porosity enhancement that diminishes the mechanical strength. Anyway, TBA shows chloride concentration below that of cement (Table 6. 4), and then those problems are not predicted in the prepared mortars.

The particle size distribution of the components is one of the basic criteria considered by mortar producers, in order to adjust the mixing process and to improve the compactness of the samples. The fine sand (S1) is mostly constituted by particles having dimensions between 63 and 300 µm, while the average size of coarse aggregate particles (S2) is 0.5 mm. Its size distribution is somewhat broad; including particles smaller than 0.125 mm and a significant portion above 1 mm. BA particles are all comprised between 0.25 and 1mm, but TBA ones presents around 10 wt% of its particles above 1.0 mm. It is because the laboratorial sieving process is more controlled than the industrial process.

Figure 6. 3 shows of cross section SEM low magnification views of bottom ash particles. For comparison, conventional S2 sand particles were also analysed. Images confirm the dimensional and shape similitude between S2 conventional sand particles and the ashes. EDS analysis reveals the presence of a Ca-rich coating layer (in red) in BA and TBA particles, denoting the occurrence of surface reactions between inorganic biomass-bearing components and the sand. The detected calcium silicate and calcite phases are probably concentrated in the skin.

6.3.2 Characterization of mortars

Fresh state properties

Figure 6. 4 shows the setting time of the prepared mortars. BA and TBA containing formulations tend to show the beginning of setting slightly anticipated in comparison to the reference (REF) mix. The open time (period between the beginning and final setting) is also shorter, particularly on mortars where S2 was fully replaced by ashes (BA100 and TBA100). Apart some minor influence of the compactness of the mixes, the presence of chlorides might be the main responsible for the changes [Demirbas, 2004; Makaratat et al., 2011; Nilforoushan & Sharp, 1995].

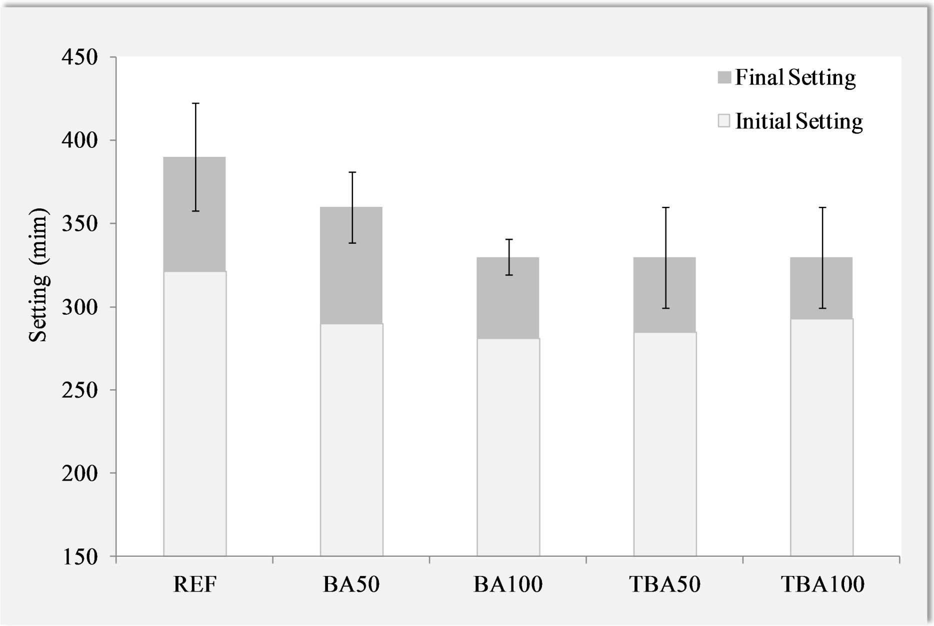


Figure 6. 4. Beginning and final setting time of the mortars.

Table 6. 5. Entrained air content and water retentivity shown by the mortars.

Samples	Air Content (%)			Water Retentivity (%)		
	lower value	higher value	SD*	lower value	higher value	SD*
REF	19.0	19.5	0.25	97.54	97.67	0.09
BA50	18.0	18.0	0.00	96.24	96.35	0.08
BA100	18.0	18.5	0.25	97.18	97.24	0.04
TBA50	18.0	18.0	0.00	94.98	95.02	0.03
TBA100	17.5	18.0	0.25	97.15	97.36	0.15

SD* (Standard Deviation)

Bulk density and values of spread in the flow table of mortars are presented in Figure 6. 5. Differences on the average bulk density are minor, but ash-containing formulations tend to be slightly more compact. Ash particles are relatively smaller than S2 ones and the mixes are thicker. As a consequence, the flowability of ash-containing mixes tends to decrease. Anyway differences are minor and easily adjustable if required. Specifications recommend the preparation of mixes that show spread values between 140 and 170 mm (Table 6. 3).

The replacement of S2 by BA and TBA did not influence meaningfully the air content and the water retentivity of the renderings (Table 6. 5). The low samples standard deviation indicates that the data tends to be very close to the expected. They were comprehended between 17.5 to 19.5% in case of air content and 95 to 97.6% in case of water retentivity. It is observed that the air content of samples tends to decrease with the replacement material when compared to REF. In case of water retentivity, it decreases when BA and TBA is added in relation to REF, but increases between than when the content of replaced material increases.

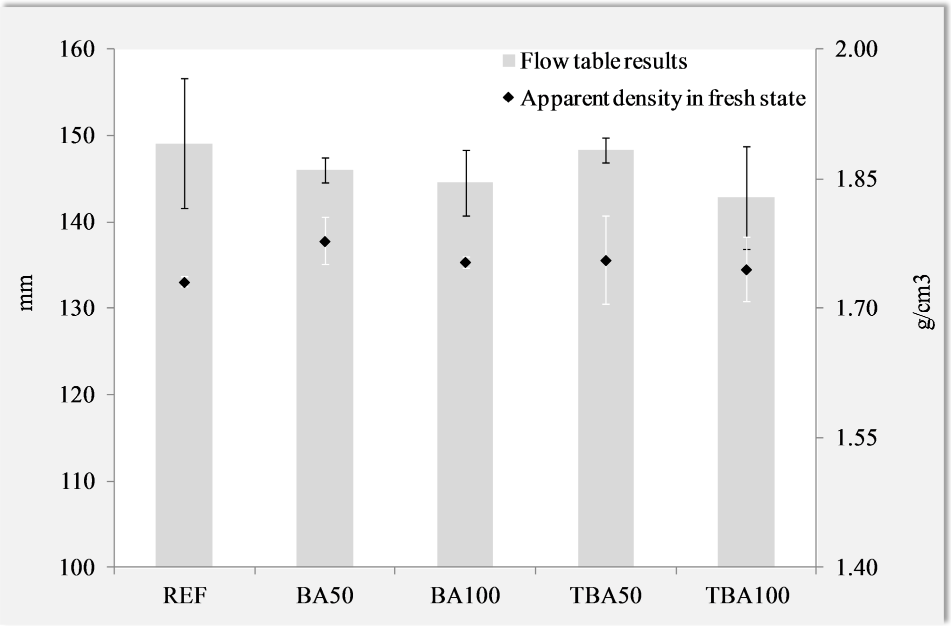


Figure 6. 5. Apparent density and values of spread in the flow table of the mortars.

Hardened state properties

Figure 6. 6 shows the amount of chlorides extracted from the mortars cured for 90 days. Hypothetically, the increase of BA and TBA levels should enhance the concentration of chlorides, especially when non-treated BA ashes are used.

However, the extraction of soluble components from a solid matrix is strongly influenced by physical and microstructural parameters, which certainly determine the access and percolation of the leaching media through the material. As expected, REF shows the lowest level of chlorides, and an increase is noticed for samples containing 50% ash. The pre-treatment of the ash seems efficient in minimising the contents of chlorides extracted from the mortars, particularly in those containing 100% replacement. Figure 6. 7 shows values of compressive strength of specimens cured for 7 and 28 days. In general values tend to increase with the use ashes but differences are minor (0.1-0.3 MPa) in comparison to REF. This slight increase could result from the better compactness of the samples.

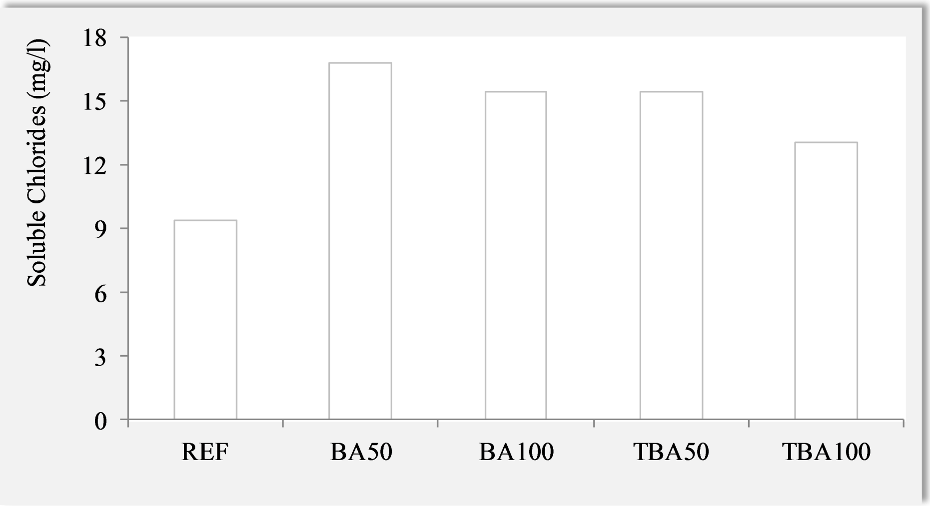


Figure 6. 6. Amount of chlorides leached from mortars cured for 90 days.

Anyway, all samples comply with the standard required limit of 3.5 MPa, also represented (dotted line) in Figure 6. 7. We also determined the dynamic elasticity modulus (E) and values are shown in Figure 6. 8. This property expresses the stiffness of the material and like other mechanical properties depends on the microstructural development of the mortar that is controlled by the hydration extent, and by the arrangement of particles (compactness). Morphological details like size, shape and rugosity of grains are then important.

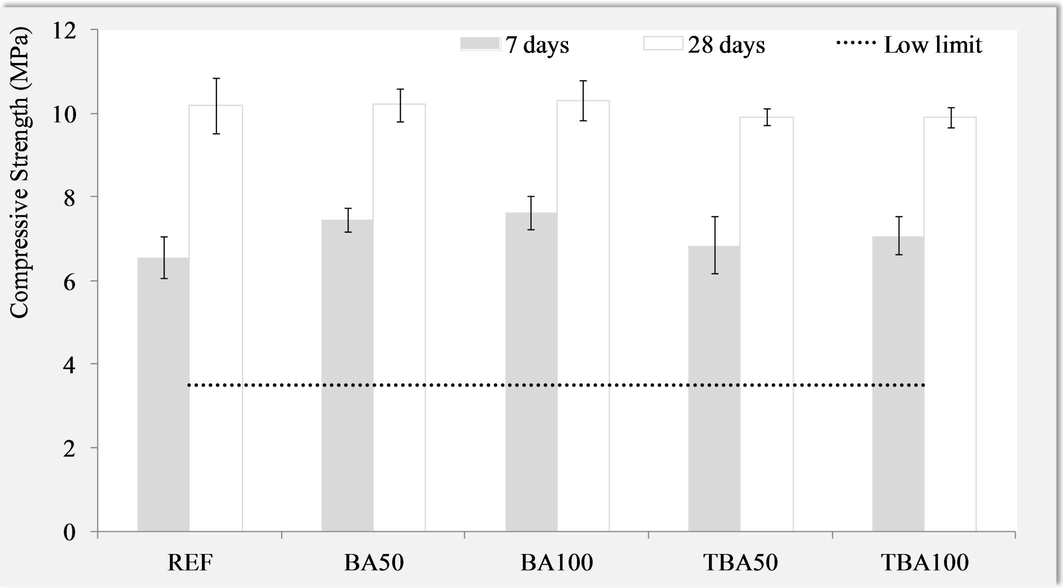


Figure 6. 7. Compressive strength of mortars cured for 7 and 28 days.

The water:cement and cement:aggregates ratios are also obviously important [Atahan et al., 2009; Atahan et al., 2011]. Variation of elasticity modulus was not very expressive (9.1-10.65 GPa) but tends to increase in ash-containing mortars (BA and TBA). This tendency follows the observed relative differences in the compressive strength.

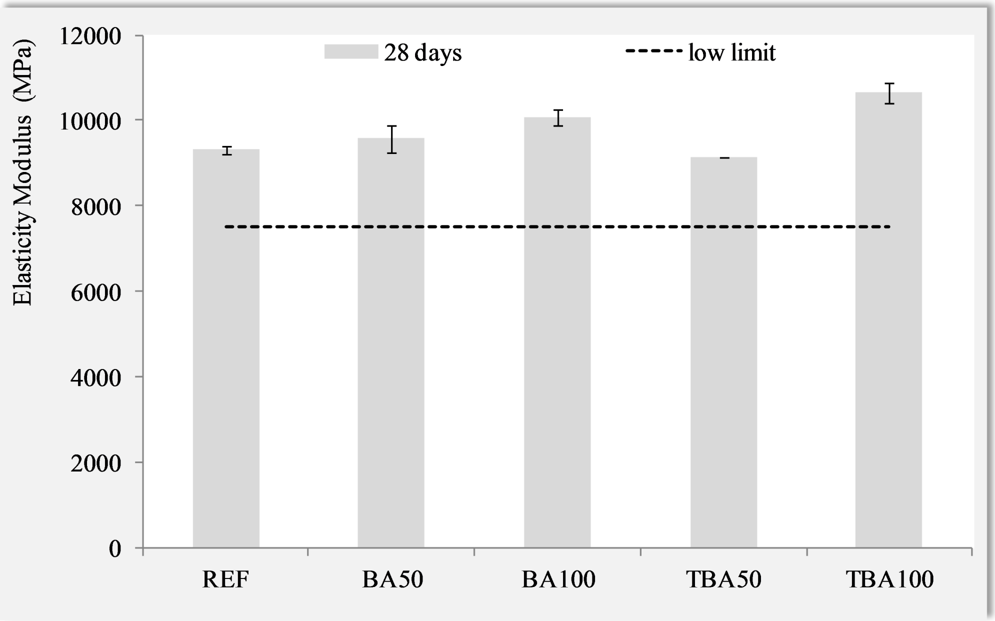


Figure 6. 8. Elasticity modulus of mortars cured for 28 days. The dotted line gives the required minimum value.

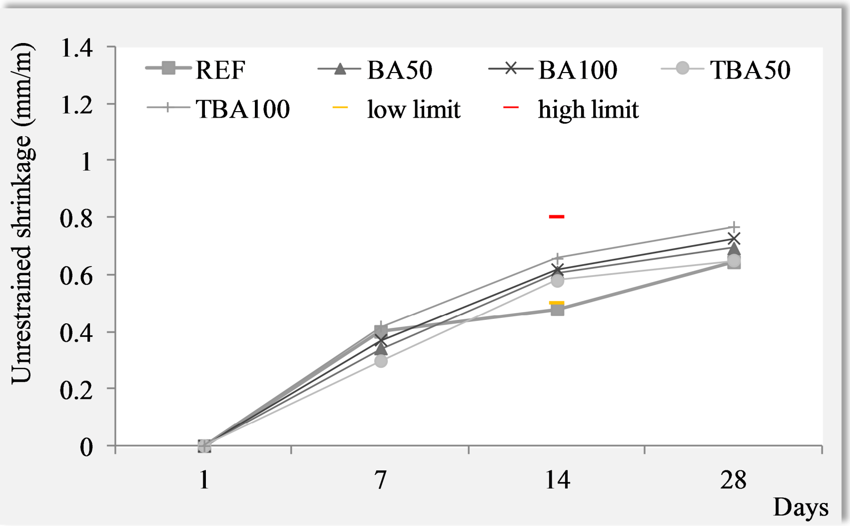


Figure 6. 9. Values of unrestrained shrinkage of mortars along the time. Minimum and maximum values are shown at 28 days curing.

Finally, the unrestrained shrinkage of mortars registered upon curing was also evaluated (see Figure 6. 9), since the control of this parameter is relevant to avoid cracking. Values are strongly dependent on the microstructure development upon curing [Thomas & Jennings, 2003; Jennings & Xi, 1994; Garboczi, 1993]. The measured shrinkage is the resultant of autogenous and drying contributions. The autogenous shrinkage is due to the self-desiccation of the mixture during hydration, while the drying shrinkage occurs due to the evaporation of water from the mixture to the environment. Registered values after 28 days curing give the following sequence: TBA100>BA100>BA50>TBA50>REF (Figure 6. 9) meaning that the use of ashes as S2 replacement tends to induce stronger dimensional changes. Shrinkage of TBA100 and BA100 mortars is, respectively, ~19% and ~13% higher than that of REF formulation, but even so they stay below the specified limit. In comparison to S2 aggregate, the ashes might show (incipient) hydraulic characteristics due to the Ca-rich surface layer and to the presence of calcium silicates. This means that ash particles are not as inert as the conventional sand.

6.4 Conclusions

The use of bottom ash generated by burning biomass in bubbling fluidized combustors as replacement of conventional sand used as coarse aggregate of industrial rendering-mortars is technologically feasible. In general this substitution does not induce negative impact on the relevant properties and formulations accomplish with required specifications. The as-collected ash shows suitable particle size distribution and only the chlorides content deserve control and potential treatment. The simple washing process industrially tested revealed to be very effective in reducing the amount (by about 60%) of soluble chlorides in the ash. This application could avoid sending thousand tons of ashes for landfilling, with obvious environmental advantages. Moreover, economic savings might be achieved by mortar producers, due to the replacement of treated and calibrated sand. Further tests covering durability issues of formulations produced under optimized conditions (including the ash content) should be performed in the future to validate this recycling alternative.

ACKNOWLEDGMENT

The authors acknowledge Foundation for Science and Technology (FCT- Portugal) for the financial support (SFRH/BD/75182/2010 - PhD grant and the project PTDC/AAC-AMB/098112/2008 - Bias-to-soil - Biomass ash: Characteristics in relation to its origin, treatment and application to soil) and Saint Gobain/Weber-cimenfix company for laboratory and materials support.

7 BOTTOM ASH FROM BIOMASS COMBUSTION IN BFB AND ITS USE IN ADHESIVE-MORTARS

R.C.E. Modolo*, T. Silva, V.M. Ferreira, L.A.C.Tarelho, J.A. Labrincha, L.Senff, L.Silva

Published in **Fuel Processing Technology** 129 (2015) 192-202 (2015)
DOI: http://dx.doi.org/10.1016/j.fuproc.2014.09.015
Impact Factor (5-year): 3.493; ISSN: 0378-3820
WebQualis: A1

Abstract

Bottom bed ash (BA) from forest biomass residues combustion generated in bubbling fluidised bed combustor (BFBC) was chemically, mineralogically and physically characterized and evaluated according to Decision 2003/33/CE and its landfill classification was determined based on criteria established by European and Portuguese legislation. Aiming to investigate its potential for being used as alternative aggregate in cementitious-adhesive mortar (CAM), formulations were produced by replacing commercial sand by equivalent mass of 25, 50 and 100 wt% of bottom ash. CAM properties were measured in fresh and hardened conditions. The bottom ash effect on the tensile adhesion strength (TAS) was investigated on samples cured under four distinct conditions. Macro and microstructural analysis were carried out to identify the influence of wetting capability and transference area in the TAS. Results revealed that high ashes levels cause relevant changes in TAS, particularly those evaluated after 30 minutes of open time. However, within reasonable limits, the effects are minor and acceptable. This recycling route seems feasible, since it combines environmental benefits with economic advantages for the adhesive mortar producers in the sense they can use BA as raw material, saving a natural resource; this recycling option is also important since can avoid one waste landfilling.

7.1 Introduction

To supply the demand for energy of national power grid, Portugal has been operating forestry biomasses fuelled thermal power plants (TPP) and forestry biomass co-fired power plants. This country has an important set of biomass TPP and cogeneration plants, mostly with bubbling fluidized bed combustors (BFBC, 30 to 120 MWth). Most of these industrial units are using as fuel a mixture of residual forest biomass (RFB – resultant from activities of industries, i.e. pulp and paper mill, such as the preparation of feedstock and forest maintenance) acquired to local or regional forestry harvesting operators working around the location of the TPP. However, most of this RFB is delivered to the thermal plants and used as fuel without a proper quality control of the biomass, and related to inappropriate practices during RFB harvesting at the forest.

The main thermal and cogeneration power plants in Portugal use bubbling fluidized bed combustion and a variety of forest biomass residues is mainly derived of Eucalyptus globulus and Pinus pinaster [Tarelho et al., 2012]. The combustion of forest biomass generates ashes as solid wastes. Presently, most of the biomass ash produced in thermal power plants is either disposal of in landfill or recycled on agricultural or forest fields, and most times those go on without any form of control. On the other hand, concerning that disposal cost of biomass ashes is arising, and that biomass ash volumes are also increasing worldwide, a sustainable ash management has to be established [Rajamma et al., 2009]. A schematic view of the ash flows generated in a bubbling fluidised bed combustor is presented in figure 1. This same figure also describes the basic operations implemented for potential further valorization of generated wastes. According to Obernberger et al (1997), for achieving a sustainable biomass to energy strategy it is essential to close the material fluxes and to integrate the biomass ashes within the natural cycles. Approximately 480 million tons of ash from biomass combustion is being generated worldwide annually [Vassilev et al., 2012]. This quantity is becoming comparable to that of coal ash, namely 780 million ton produced per year at present [Izquierdo and Queirol, 2012]. Due to the strict environmental regulations imposed by the environmental regulatory bodies, landfilling of forest biomass ashes has becoming more difficult and this scenario is an opportunity to study and perspective diverse recycling ways for such waste [Cheah and Ramli, 2012]. The ash characteristics are influenced by biomass characteristics, the soil conditions where the biomass has been collected, the combustion techniques, the operation conditions during combustion (temperature, stoichiometry, air staging, and additives) and the gas cleaning systems [Vassilev et al., 2010; Latva-Somppi et al., 1998; Dahl et al., 2009; Steenary and Fedje, 2010].

The specific ash researched in this work has been generated when periodic discharges of the bed are performed, namely bottom ash. The periodic discharges are performed to maintain the bed particle size distribution and to avoid bed agglomeration (a phenomenon associated with inappropriate fluidization which could lead to the fluidised bed collapse [Bartels et al., 2008]). In general, the relative high level of inert material present in the biomass used in Portuguese BFBC plants enhances the frequency of bed discharges, meaning that bottom ashes have low residence time (<5 days) in the BFBC when compared with results reported for other installations using BFBC [Latva-Somppi et al., 1998; Tarelho et al., 2011]. The bottom ash from BFBC has the code 100124 according to European List of Wastes and the search for recycling or reuse alternatives of such residue is an hot topic and a serious need. A reasonable number of recent investigations report the use of ashes for distinct applications: masonry products, low and medium-strength concrete, road pavement, blended cements, adsorbents, and ceramics [Rajammaet al., 2009; Menéndez et al., 2014; NCASI, 1993; Wang et al., 2008; Alonso and Palomo, 2001; Rajamma et al., 2012; Yip et al., 2005; Wang and Baxter, 2007; Siddique, 2010]. However, as far as we know, the use of bottom ash in CAM is not well documented.

Cementitious-adhesive is a technical product, namely a mixed-binder mortar specially made from a combination of lime, sand, and water, as well as from other types of cementitious products, mainly composed of sand and different mineral fillers, inorganic or organic binders, and additives depending on the use. This product must assure the adhesion between tiles (ceramic or ornamental stones) and the concrete wall. Cementitious-adhesive mortars (CAM) role is particularly challenging for the fixation of large and dense samples, as occurred in the last decades due to the evolution on tile industry [Ançid et al., 2005; Wetzel et al., 2012]. Their performance depends on the content, quality and the interaction between the components [Mansur et al., 2009; Öhama, 1995; Jenni et al., 2005; Jenni et al., 2006]. CAM hold up well to outdoor temperatures, but dries hard and may be prone to cracking or expansion if not applied properly or if subjected to temperature extremes or ground heave.

Schulze (1999) tested the influence of water-cement ratio and of the cement content on the properties of polymer-modified mortars. Within certain limits, the water-cement ratio exerts a smaller effect on the adhesion strength of the material, but the relative amount of cement in the mixture is a crucial parameter. In the fresh state condition, the generation of a skin (film) on the external surface of the mortar having suitable gluing properties drastically influences the bond strength between the adhesive and the tile [Bühler et al., 2013]. This mechanism is rather complex and its study is far from its conclusion.

In the present work, raw bottom ash from forest residues combustion was characterized as received and its particle size distribution was compared with 2 bottom ashes generated in Thermal Power Plants (TPP) with the same type of technology (BFBC). The aim of this part of the work was to assess the influence of biomass characteristics in the bottom ash quality, namely particle size distribution and also to report the significant bottom ash high level amount generated when compared to other plants and finally emphasizes the need of treatment of bottom ash to be used as replacement material in the construction sector. After, the tested bottom ash was evaluated according to Decision 2003/33/CE and Decree-Law nº 152/2002 (Decree-Law nº 152/2002 was repealed by Decree-Law nº 183/2009 and rectified by Decree-Law nº 84/2011). The waste classification for landfilling purposes was then established.

In general, the bottom bed ash from a BFBC are composed mostly by silica (quartz) sand particles, with particle size from the few micrometers until some millimeters, being the mean particle size (around 0.950 mm) very similar to that of conventional silica sand used in CAM formulations. Considering this fact, the bottom ash from a BFBC was treated (by sieving) and tested as partial replacement of the conventional sand used in CAM. The bottom ash treatment consisted in sieving in order to remove coarse (> 1.00 mm) and fine (< 0.25 mm) particles, that are often introduced in the combustor mixed with the biomass fuel, that can contain important amounts of inert material (soil and little stones) mixed. The tests were performed in the fresh and hardened state. The wetting capability and transference capacity of fresh mortars, as well as the ultimate tensile adhesion strength (TAS) developed upon curing in distinct conditions, was evaluated. Economic savings might be achieved by cementitious-adhesive producers, due to the replacement of expensive calibrated sand, considering that at least four thousand tonnes per year of this sand is used only by one mortar producer [Modolo et al., 2013].

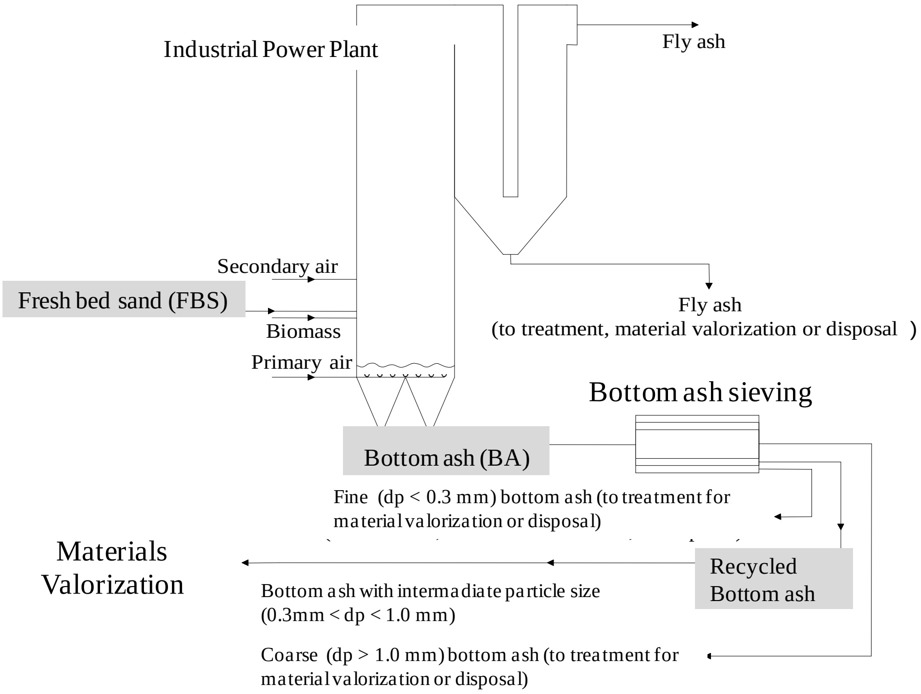


Figure 7. 1. Schematic view of the ash flows generated in the BFBC, including the basic operations implemented for potential further valorization.

7.2 Methodology

Raw bottom ash here studied was collected from a 90 MWth BFBC (bubbling fluidised bed combustor, namely Thermal Power Plant 3 (TPP_3)) located in the centre of Portugal. It burns forest biomass residues, namely eucalyptus bark and remains from logging activities. The temperature of the bubbling bed ranges from 800ºC to 900ºC. The raw BA was directly collected in the ashtray of the combustor, schematically represented in Figure 7.1.

7.2.1 Characterization of raw BA

Particle size distribution of BA from TPP_1, 2 and 3 were obtained by manually sieving according to EN 933-1: 2000. The chemical composition of raw BA from TPP_3 was determined by X-Ray Fluorescence Spectroscopy –XRF (Panalytical Axios spectrometer), while the crystalline phases were detected by X-ray diffraction – XRD (RIGAKU-Geiger flex diffractometer). Raw BA was observed by optical microscopy

(Leica EZ4 HD). Laser diffraction using Coulter LS analyzer was also used to obtain the particle size distribution. Gravimetric and differential thermal analyses (TG/DTA – Setaram, Labsys) were used to evaluate the amount of unburnt (organic) components. Concerning the presence of metals, the hazardous potential of BA was determined by using two techniques: (i) digestion with aqua-regia ($HCl:HNO_3$, 3:1, v/v) and (ii) leaching according to DIN 38414-S4. In this case the as received waste was used to prepare an eluate (100 g of dried material was immersed in 1 liter of distilled water). The suspension was stirred for 24 hours and then filtered. Then, 100 mL of such cleaned eluate was titrated. Metal contents were determined by ICP (Inductively Coupled Plasma) in an apparatus Jobin Yvon - Sequential NSPL upgrade model (J4/200). Chlorides were estimated by the Argentometric method (CHLORIDE, 4500-Cl^-; Standard Methods Committee, 1997), while sulphates were estimated by gravimetry (SULFATE, 4500-SO_4^{-2}; ignition of residue, Standard Methods Committee, 1997). In this case, sample was dried, weighed and dissolved in diluted HCl. Barium chloride solution was added in excess to precipitate barium sulphate, and the precipitate was digested in the hot solution (between 80 – 90ºC). The precipitate was filtered through a paper filter and was then ignited (at 800 ºC for 4 hours) for complete combustion. Difference between the weight of the sample and of the precipitate gives the percentage of sulphates.

7.2.2 Characterization of materials used in cementitious-adhesive application

Raw BA from TPP_3 was sieved (between 250 and 1000µm) in a lab-scale equipment to adjust the particle size distribution to the one of the commercial aggregate (sand) that will be replaced normally used in this type of mortars; Raw Bottom Ash was here identified as BA. Particle size distribution of CAM components were obtained by manually sieving according to EN 933-1: 2000. The chemical composition of BA, Ordinary Portland Cement type I, S1 (finer sand) and S2 (coarse sand) particles was also determined using were also X-Ray Fluorescence Spectroscopy –XRF (Panalytical Axios spectrometer), while the crystalline phases were detected by X-ray diffraction – XRD (RIGAKU-Geiger flex diffractometer).

7.2.3 CAM formulations and characterization

The formulations studied are presented in Table 7.1. The raw materials brand and content were suggested by the company which intents to improve forward the valorization solution using its own specific formulations. The copolymer powder is a vinyl acetate and ethylene which is dispersible in water and has good saponification resistance. CEM II/A-L 42.5R is used in lower quantity and its function is to improve the cementitious-adhesive behaviour in aggressive environments. Apart from CEM I, the fine sand (S1) is the aggregate with highest content used in these cementitious-adhesive formulations and its function is related with the final product texture and type of application. The water content of samples was defined according to the workability of the adhesives observed through the slip (results comprehended from 0 to 1.0 mm). The adhesive's preparation was developed according to EN 12004: 2007+A1 (Adhesives for tiles - Requirements, evaluation of conformity, classification and designation). It includes:

(a) Hand mixing the water with the solids for 15 seconds;
(b) Mixing for 30 seconds at low rotation speed (60 rpm);
(c) Stopping for 1 minute;
(d) Mixing again for 1 minute under the same low speed and,
(e) Keep the mixture in stand by for 2 minutes;
(f) Mixing for the last 15 seconds at low rotation speed. After mixing, the fresh paste was applied on concrete plates in two steps: as a first contact layer with a thickness corresponding to the surface base layer (approximately 2 mm), which then was trowelled repeatedly with a toothed notched trowel (profiled 6x6x6 mm). The standards used in the characterisation of mortars are presented in Table 7.2.

Table 7. 1. Cementitious-adhesive mortars formulations and their respective components content.

Sample ID	BA (% wt of S2 substituiton)	Water	S2	BA	S1	CEM I 42.5	CEM II/A-L 42.5	Polymer powder
		% wt						
REF	0	26.5	9.6	0.0	25.7	30.9	3.7	3.7
BA25	25	26.0	7.2	2.4	25.9	31.1	3.7	3.7
BA50	50	26.0	4.8	4.8	25.9	31.1	3.7	3.7
BA100	100	26.0	0.0	9.6	25.9	31.1	3.7	3.7

Slip

This parameter determines the resistance to slip of tiles applied to combed adhesive layer on a vertical surface. It is measured through the downward movement of the tile (weight = 200g), corresponding to a 20kg/m^2. The distance between the top (where the tile was applied) and the place where the tile stopped after 10 minutes of testing is considered the final result, given in millimetres [EN 1308: 2007].

Wetting capability and transference

The wetting capability is estimated as the contact area (%) between the mortar/adhesive and a glassy sheet of 25 cm^2. It gives a qualitative estimation of the capacity shown by the adhesive mortar to embed the surface of a ceramic or glass tile. A squared piece of glass (5x5x0.5 cm) is pushed by a metal piece of 2 kg against the combed adhesive during 30 seconds; afterwards and before removing the glass, the area covered by the adhesive is visually inspected and determined by an image editing software that allows the calculation of specific selected areas. The test is repeated 10, 20 and 30 min after the adhesive layer has been combed. This test is described by the European Standard EN 1347:2007.

Transference measurements

After removal the glassy piece from the substrate with the adhesive, the quantity of mortar that was transferred to the tile is measured given the so called transference value. The evolution of the tiles surface coverage by the adhesive mortar with the curing time gives an estimation of the adhesion loss due to hardening process. Values were correlated with tensile adhesion strength evaluated after an open time of 30 minutes. Again, the area values were estimated by using the same imaging software.

Tensile Adhesion Strength – pull-off test

The adhesive strength is determined as the maximum tensile strength supported by the material under a load that is applied perpendicular to the surface being tested. The pull-off test is classified as a near-to-surface, partially destructive method [Ramos et al., 2012]. The tensile load is applied by means of a defined pull-head plate glued to the testing surface.

A thin layer of the adhesive is applied on the concrete slab (substrate) with a straight edge trowel. On the top of this first layer another thicker layer of the adhesive is deposited and combed with a notched trowel (having 6 x 6 mm notches at 12 mm centers). It was hold at an angle of approximately 60° to the substrate at a right angle to one edge of the slab and drawn across the slab parallel to that edge (in a straight line). After 5 min, the ceramic tiles (of porcelain type, having water absorption ≤ 0,5 % by mass, unglazed and covered with plain, matt glaze, with dimensions of 5x5x0.5 cm) were laid in, loaded with 2 kg for 30 seconds one by one. The minimum adhesion defined by CEN specifications (EN 1348: 2007) is ≥ 0.5 MPa for samples cured under distinct conditions (see below).

(i) *Dry curing (28d, 23ºC, 50%RH)*: samples are cured for 28 days in a climate chamber (23ºC±2 and 50%±5 relative humidity). These conditions are considered the standard ones. Then, pull-head plates are bonded (square metallic plates, with dimensions of 50 x 50 mm and thickness of 10 mm) to the tiles by using a proper high strength adhesive resin (epoxy). After more 24 h storage in standard conditions the tensile adhesion strength is evaluated under a load that is applied at constant rate of 250 N/s.

(ii) *Wet curing (7d, 23ºC, 50%RH + 21d, inside water at temperature of 20ºC±2)*: now the samples cured for 7 days in standard conditions were then immersed in water (at 20ºC ±2) for another 21 days. Before testing the adhesion, according to the conditions already described, pieces are wiped with a cloth.

(iii) *Heat curing (14d, 23ºC, 50%RH + 14d, 70ºC +1d, 23 º C, 50% RH)*: samples are previously cured for 14 days in standard conditions and then are placed inside an air-circulating oven at 70 ± 3°C for another 14 days.

(iv) *TAS after 30' open time (28d, 23ºC, 50%RH)*: the open time is defined as the period during which the tiles might be applied to the adhesive (i.e., the time during which the adhesive surface remains “tacky” to the touch) [Bentz et al., 2008; Oberste-Padtberg and Sieksmeier, 2007]. Measurements were performed according to the EN1346:1999 standard. This means that samples are cured for 28 days in standard conditions, then the adhesive mortar is applied and samples are tested after 30 minutes (the designated open time).

Failure patterns

The failure patterns of tested samples were also observed. AF-T indicates failure between tile and adhesive, CF-S is used to define the cohesive failure at the interface between adhesive and substrate and CF-A defines the failure within the adhesive layer as specified by EN 12004: 1999. Failure patterns are schematically illustrated in Figure 7.2.

Table 7. 2. Standards used to characterize the cementitious adhesives mortars.

State	Test	Unit	Standard
Fresh	Apparent Density		EN 1015-6:1998
	Slip	mm	EN 1308:2007
	Wetting capability	%	EN 1347:2007
	Tranference	%	
Hardened	Tensile Adhesion Strength (after 7, 14 and 28 days)	MPa	EN 1348:2007
	Tensile Adhesion Strength after water immersion		
	Tensile Strength after heat ageing		
	Tensile Adhesion Strength (OT-Open time 30')		EN 1346:1999

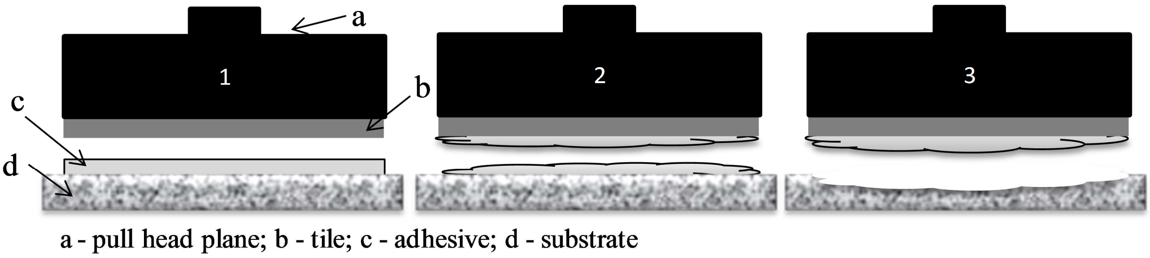


Figure 7. 2. Failure patterns observed in this study (as specified by EN 12004). (1) Failure pattern AF-T, failure in tile adhesive-tile interface. (2) Failure pattern CF-A, failure within tile adhesive layer. (3) Cohesive failure in substrate CF-S.

7.3 Results and Discussion

7.3.1 Characterization of raw BA

Figure 7.3 presents the particle size distribution of raw BA (before sieving), BA (sieved) and the other two sands used in the whole work. S1 is the finest sand used in the formulations and S2 the coarse one, having the mean size around 400 μm and 1025 μm, respectively, while BA (before sieving) and BA (before sieving) is 900 μm and 950 μm, respectively. In case of BA (before sieving) the existence of almost 60% of particles diameter between 0.25 – 1.0 mm is reasonable in the light of the fact that, in fluidized bed boiler furnaces, the combustion bed material, silica sand, consists of calibrated sand which must be kept constant to guaranty the height of bed. From the utilization point of view, these particles (between 0.25 and 1.0 mm) can be of great potential because of their similar particle size with the calibrated sand used as aggregate for the tested type of cementitious-adhesive. Other types of bottom ash [Dahl et al., 2009; Dahl et al., 2010] can differ significantly in particle size range compared with the BA tested here, thus suggesting that in those cases lower amounts of particles from those ashes can be used for this application. The percentage of material (particles) retained in the sieve with 2 mm mesh is in the order of 1% and in the sieve 0.25 mm mesh is in order of 65%wt [Dahl et al., 2009]. Nevertheless, an appropriate treatment (sieving) could guarantee the use of a fraction of bottom ash from bubbling fluidised bed combustors in mortars formulations by replacement of the conventional sand as aggregate, because they contain always an important fraction of particles with size range between 0.25 and 1.0 mm, and thus of interest for these formulations. Also, considering the typical operating conditions of bubbling fluidised bed combustors using residual forest biomass as fuel, the chemical composition of bottom ash, for example, in terms of organic matter, soluble salts, chlorides, seems to be within the standard specifications of the material to be used as aggregate and it is not expected the promotion of deleterious effects in this type of products (cement-based mortars) [Modolo et al., 2013]. Considering this fact, raw BA was sieved, characterized and tested as aggregate partially replacing S2 in CAM formulations (figure 7.3). The enrichment with fine and coarse particles relative to the original sand bed in the Portuguese TPPs can be explained in result of characteristics of forest biomass residues used as fuel, namely the inert material. So, this fact is completely associated with the biomass quality, mainly related with stones and soil particles contamination of forest residues during harvesting transport and their handling [Modolo et al., 2014]. Another concern when compare both scenery is about ashes amount. Dahl et al (2010)] referred that TPP (246MW) produced about 15.430 tonnes of ashes in 2009, which 2580 tonnes was bottom ash. Meanwhile, the specific Portuguese TPP (90MWth) where the studied BA is generated produces around 6.000 tonnes/year what demonstrates the strong influence of biomass quality on the bottom ash characteristics mainly in terms of amount. Decision 2003/33/CE establishes for waste acceptance in each landfill type (inert, non-hazardous and hazardous) based on both the characteristics of the waste and leachate acquired by EN 14405 and refers that each member state must define which L/S ratio to use. In Portugal, the criteria for landfill deposition of inert and hazardous wastes are those of Decision 2003/33/CE with ratio L/S of 10l/kg. For non-hazardous waste, the criteria are defined on

Decree-Law 152/2002 with leachate obtained by DIN 38414-S4 (L/S=10 l/kg). Neither Decision 2003/33/CE nor Decree-Law 152/2002 establish legal limits for Mn and Fe, but both elements were quantified together others minor elements objectifying information report. The results for minor elements are presented in figure 7.4 and legal limit for waste acceptance in each landfill type and BA results are presented in table 7.3.

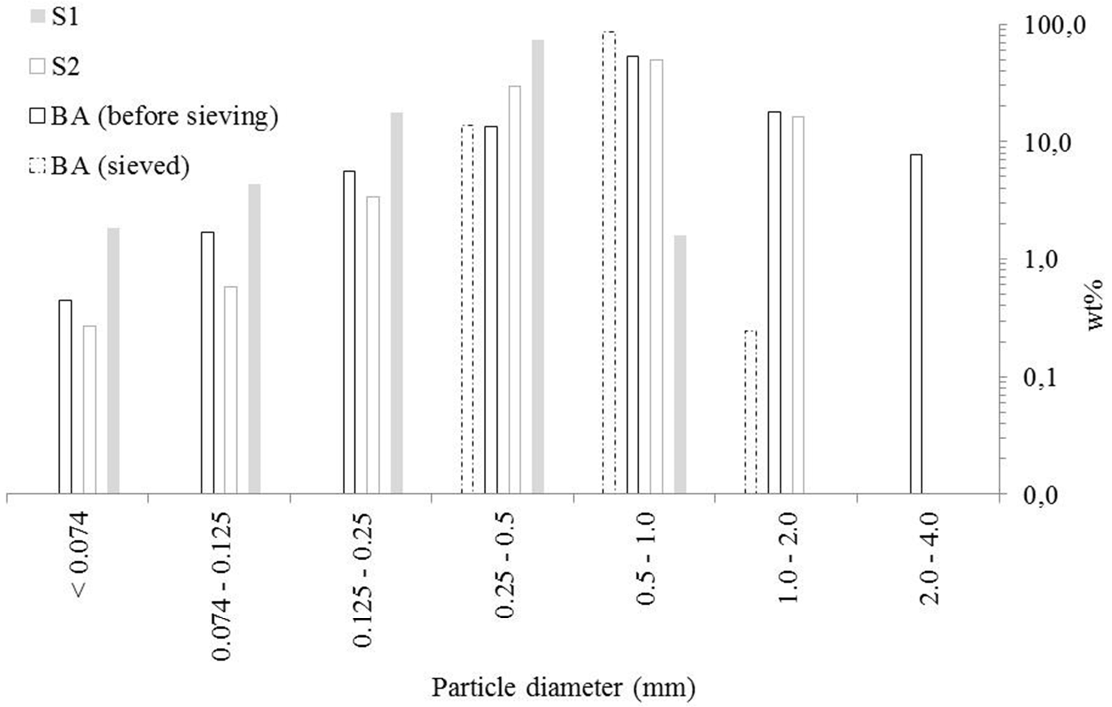


Figure 7. 3. Grain size distribution determined according to EN 933:1/2000.

Comparing values obtained with the limits stated in Decision 2003/33/CE, can verify that values of Cd (0.77 mg/kg), Cr total (9.1 mg/kg), Ni (3.85 mg/kg) and Zn (17.8 mg/kg) exceed the legal limit for inert wastes. The pH (12) and nitrates concentration (2.5 mg/l) are near the limits defined for non-hazardous wastes, so deserves control and precaution to not be surpassed. Recycling this waste in cement- based mortars/concrete, as a replacement of natural aggregates, might be an interesting alternative, since it is perfectly aligned with EU directives recommending solutions to transform the waste into a resource [Horizon 2020, 2014; Schiessler et al., 2007]. The use of cementitious-adhesive mortars might additionally constitute an added-value valorisation solution.

S2 and BA particles are microscopically illustrated in figure 7.5. Images “a” and “b” emphasize the main physical differences between the two materials in terms of dimension, shape and surface. In general, S2 particles show smoother contours and have more rounded and homogeneous shapes, while are larger in size than BA grains. These last ones show clearly a large diversity of shapes. Images "c" and "d" present BA images focusing the surface of the particle. It is possible to observe that BA presents some crystals spread out on the surface, certainly attached upon burning or as impurities during the ash manipulation.

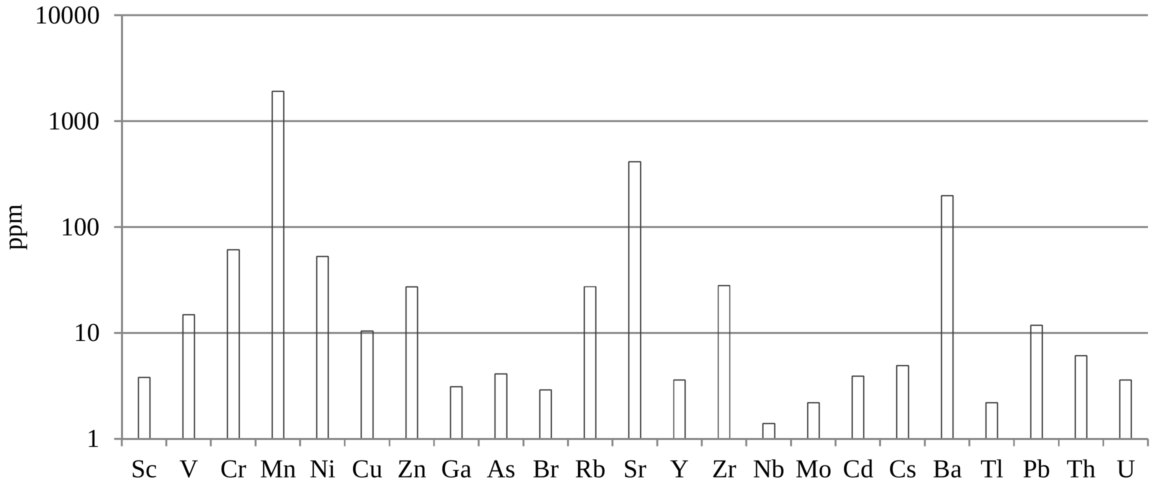


Figure 7. 4. Concentration of minor chemical elements and heavy metals in the raw bottom ash (particle < 2.00 mm).

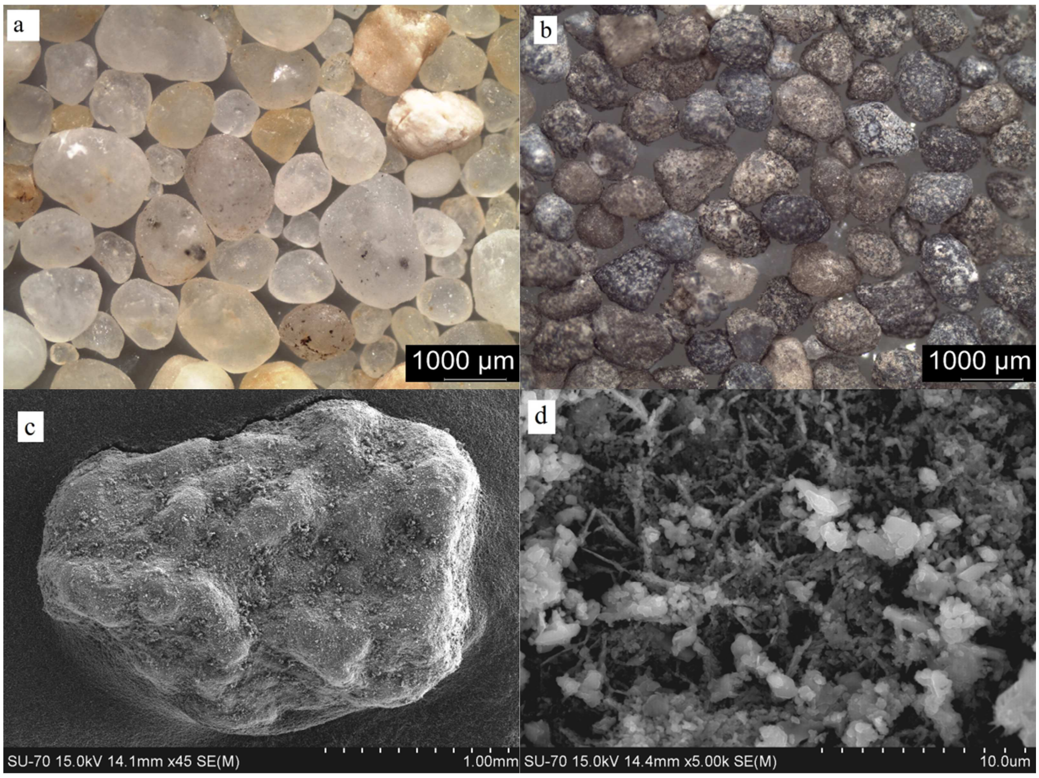


Figure 7. 5. Magnifying glass microscopy images; (a) Conventional sand (S2); (b) BA; (c) BA scanning electron microscopic (SEM) image; and (d) BA surface (SEM).

Table 7. 3. Bottom ash characterization and comparison of the values obtained with the limits stated on Decision 2003/33/CE for L/S= 10l/kg and DL 152/2002.

Parameter/Substance		Standard/Proceedure	Legal limit of Decision 2003/33/CE for L/S ratio of 10 l/kg (mg/kg dry weight) Legal limit of Decree-Law 152/2002 (mg/l)			
			Inert	Non-hazarduos	Hazarduos	BA (average of 2 samples collected during one year)
Moisture	105ºC (%wt)	EN 12880: 2000				<1
As	mg/kg dry weight	ICP - JY Inductively Coupled Plasma - Instrumental analysis technique based on atomic emission spectrometry. Model: J4/200 - ISO 11885	0.5	2	25	< 4.3 LQ
	mg/l		0.1	0.5	1	< 0.04 LQ
Cd	mg/kg dry weight		0.04	1	5	0.77
	mg/l		0.1	0.2	0.5	< 0.01 LQ
Cu	mg/kg dry weight		2	50	100	< 3.65 LQ
	mg/l		2	5	10	< 0.03
Cr total	mg/kg dry weight		0.5	10	70	9.1
	mg/l		0.5	2	5	< 0.04
Hg	mg/kg dry weight		0.01	0.2	2.0	< 0.08 LQ
	mg/l		0.02	0.05	0.1	< 0.001
Ni	mg/kg dry weight		0.4	10	40	3.85
	mg/l		0.5	1	2	< 0.03 LQ
Pb	mg/kg dry weight		0.5	10	50	< 3.3 LQ
	mg/l		0.5	1	2	< 0.03 LQ
Zn	mg/kg dry weight		4	50	200	17.8
	mg/l		2	5	10	0.07
Cr VI	mg/l		0.1	0.1	0.5	< 0.02
pH		EN 12176: 1998	5.5 - 12	4 - 13	4 - 13	12.0
Conductivity	mS/cm	NP EN 27888: 1996	6 - 50		100	2.6
Chlorides	mg/l	4500D-Cl^-, Standard Methods, Potenciometric method, 4-69	500	5000	10000	107
Sulfates	mg/l	4500D-SO_4^{-2}, Standard Methods, Gravimetric with drying of residue method, 4-177	500	1500	5000	154
Nitrates	mg/l	4500D-NO3, Standard Methods, Nitrate-selective-electrode method, 4-86	3	10	30	2.5
Ammonium	mg/l	NP 730/1978 - Portuguese Standard - Determination of Ammonia Nitrogen.	5	200	1000	0.4
Cyanides	mg/l	4500D-CN-, Standard Methods, Cyanide-ion-selective electrode method, 4-86	0.1	0.5	1	0.02
*AOH	mg/Cl/l	ISO 9562 - Water Quaity - Determination of adsorbable organically bound halogens (AOX)	0.3	1.5	3	0.15

*Adsorbable organic halogens; LQ - Limit of quantification

The chemical composition of raw BA, BA, S1, S2 and Ordinary Portland Cement type I is given in table 7.4. Mineralogical composition of BA, S1 and S2 is presented on figure 7.6. The bottom ashes are basically composed by a mixture of the original bed (silica sand - quartz) and by inorganic impurities (forest soil and small stones) included in the biomass. These respond for the presence of Al, Na and K oxides, introduced as feldspars (i.e., microcline – figure 7.6), or micas. In the TGA, the highest weight loss was registered between 600 and 800 ºC, resulting from decarbonatation reactions.

Table 7. 4. Chemical and mineralogical composition of used components.

Parameters	Raw material				
	[a]Raw BA	[b]BA	CEM I 42,5R	S1	S2
LOI (%wt)	1,97	2,08	2,26	0,09	0,24
Na (%wt)	0,94	0,65	0,13	0,03	0,05
Mg (%wt)	0,98	1,18	1,37	0,04	0,01
Al (%wt)	1,64	1,21	2,55	[c]<QL	0,64
Si (%wt)	34,84	33,74	9,42	46,48	45,59
Cl (%wt)	0,14	0,12	0,02	[c]<QL	[c]<QL
K (%wt)	0,92	0,63	1,23	0,03	0,40
Ca (%wt)	9,62	12,26	42,82	0,05	0,20
Ti (%wt)	0,07	0,05	[c]<QL	0,08	0,01
Mn (%wt)	0,22	0,28	0,03	0,08	[c]<QL
Fe (%wt)	0,82	0,55	2,17	[c]<QL	0,07
O (%wt - by difference)	47,3	46,6	35,6	53,1	52,8

[a] Particles < 2.00 mm;

[b] Particles between 0.25 to 1.00 mm

[c] <QL - Lower than the quantification limit

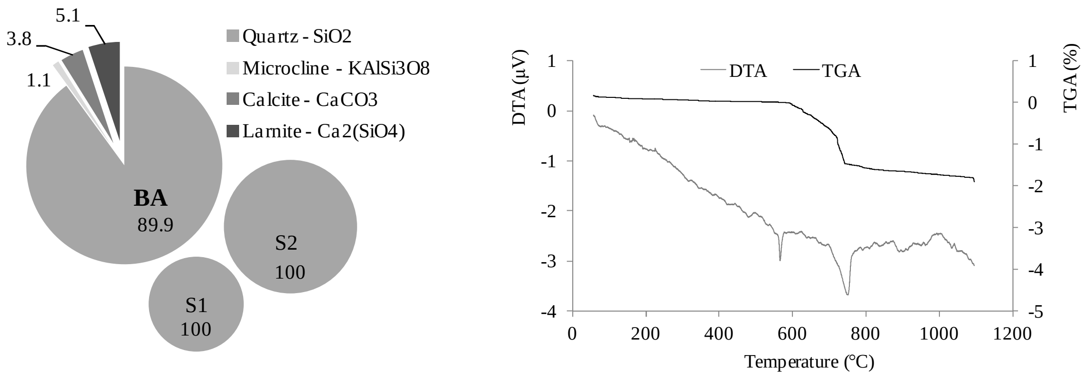


Figure 7. 6. DTA and TGA profile of BA and XRD of BA, S1 and S2.

XRD revealed the existence of calcite and CaO, one of the major components of the ash, apart from SiO_2. In addition to this endothermic reaction observed in DTA curve, another endothermic event was detected at 573 °C and can be attributed to the α-β quartz polymorphic change. The total mass loss reached about 2%. This relatively low value and the absence of expressive exothermic reactions in the range 250-500 °C confirm the absence of organic matter. Otherwise, the remaining unburnt matter should decompose in that temperature region.

7.3.2 Characterization of materials used in cementitious-adhesive application

Ozkahraman and Isik (2005) highlighted that the fundamental requirement of the tile adhesive mortar is its adherence and durability and proved that the properties of adhesives are affected by the chemical and mineralogical composition of the aggregates. In figure 7.6 (XRD results) It can be observed that S1 and S2 are basically quartz-sand and Ba presented approximately 90% SiO_2 in its composition. Other 10% of crystalline substances are minerals which do not represent a negative aspect on the proposed application, calcite i. e., is a material frequently used in several types of cements and cement-mortars, as filler or as raw material used in clinker production. The calcium silicate mineral Larnite found is vestiges.

7.3.3 Characterization of CAM

Values of slip and apparent density determined on adhesive mortars are presented in table 7.5.The apparent density tends to slightly increase with BA content in the mortars. This fact can be associated to the particle size distribution of the ash-containing mixtures, that when S2 is replaced by BA produces mixtures that require less amount of water to assure a similar workability (see BA50 and BA100 formulations) leading to a better final compactness.

Figure 7.7 illustrates the wetability of the glassy surface shown by the tested formulations as a function of exposure time (10, 20, 30 and 40 min after application). It is quite evident the gradual weatability lost along the time. According to Bühler et al (2013) there is the formation of a top skin that hardens quickly than the interior of the material and it will reduce its deformation and gluing capacity. The formation of such layer depends on the mortar formulation, nature of the substrate, application technique, and also by the climatic. It is found that after 20 minutes REF sample already denotes deficiencies in covering the tile surface, while BA-containing mortars show good wettability. The homogeneous particle size distribution of BA associated with the roughness of its surface might explain this increase. Indeed, less finer particles demanding less water retard skin formation, leading to better transference capability. Bühler et al (2013) also confirmed this fact by testing different mortar formulations and observing that water content could retard the skin formation.

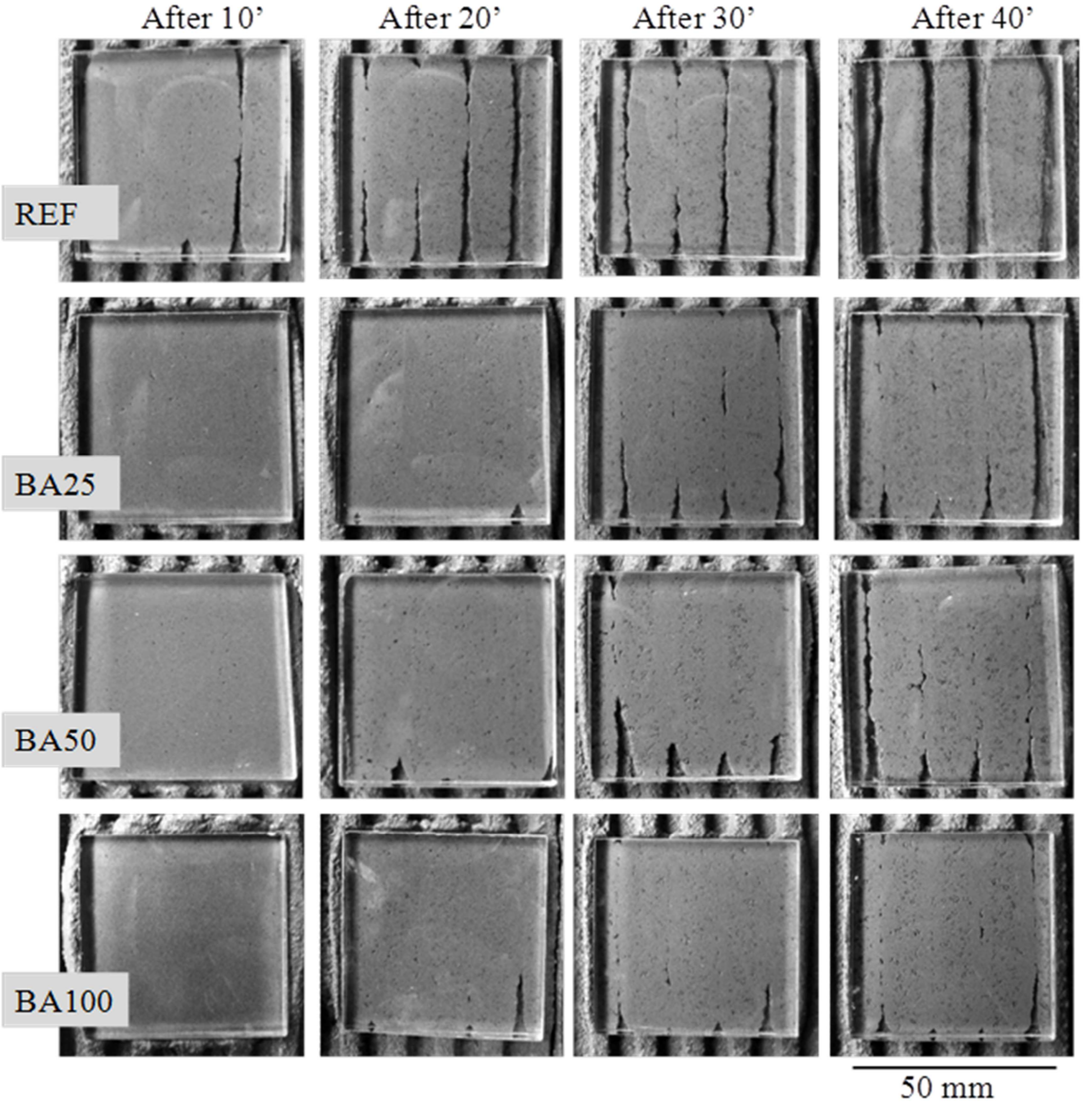


Figure 7. 7. Photograph of glass plate embedded during the wetting capability test of cementitious-adhesives as a function of exposure time (10, 20, 30 and 40 min after the mortars were combed).

On the other hand, in terms of fresh state behavior, these mortars should present a slip value close to 0 mm. So, looking at the slip results, the fact that less water is needed when BA is introduced leads to lower slip values in BA50 and BA100 (0 to 1 mm) together with a good wetting capability along the exposure time after combed.

Figure 7.8 shows pictures of the tile surface covered by the mortars, used to estimate the transference capacity. This same figure was analyzed by image software, which enabled the quantification of the areas covered by the mortar. In figure 8 the area calculation was made on the basis of the total area of each tile (25 cm^2). What is observed is a steady decreasing in the transference capacity of the mortar with open time. REF presents very high loss of transference capacity at 30 and 40 minutes of the test (in order of 46 and 85% of loss respectively). However, BA25, BA50 and BA100 showed values even higher than 70% transference capacity after 40 minutes of the open time test. The loss of transference capability of the material 20 minutes after the application could have serious implications in the TAS, or as longer is the exposure time of the mortar, the lower is the adhesion of the ceramic piece to the mortar.

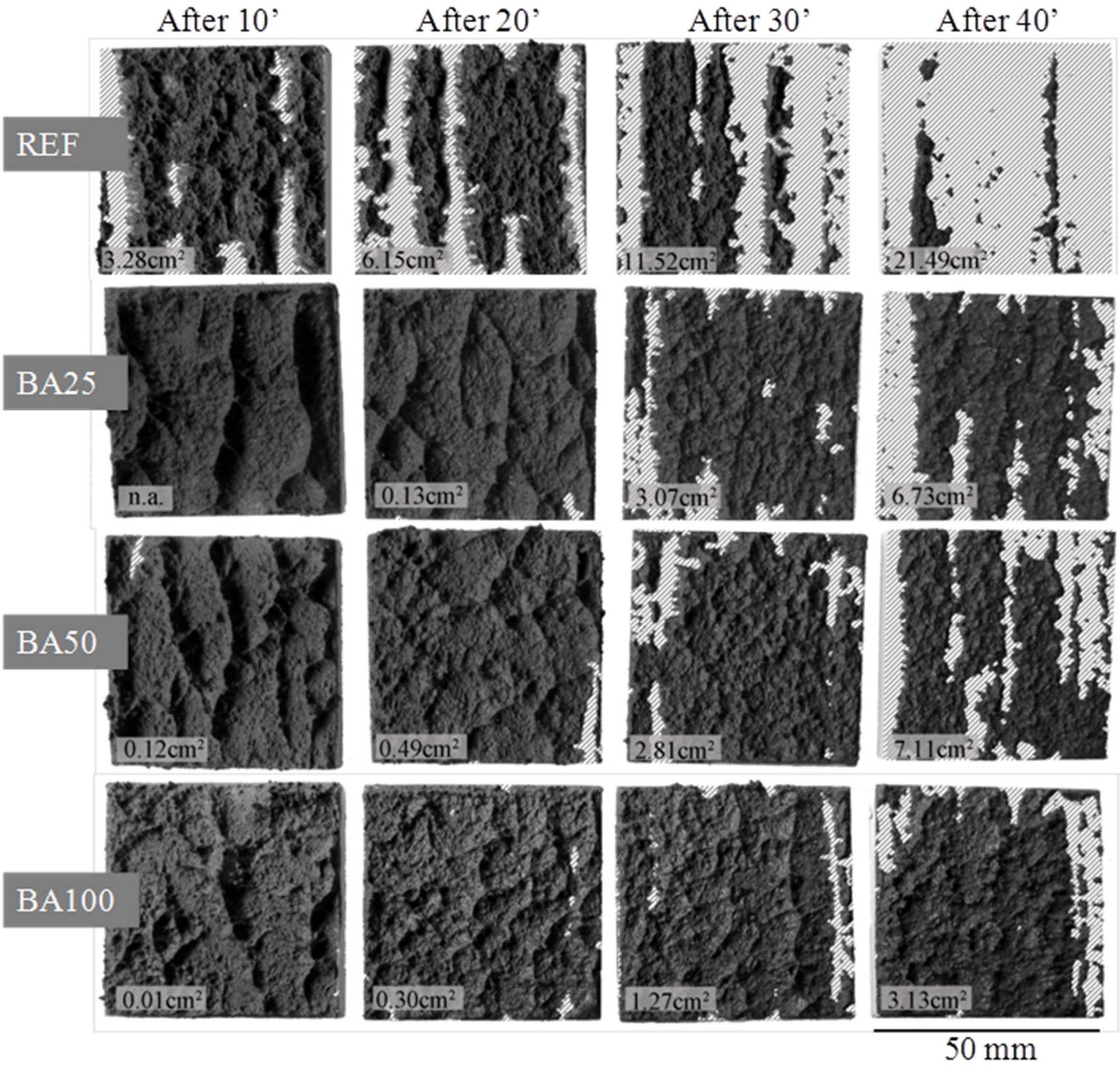


Figure 7. 8. Ceramic-tiles after transference test of cementitious-adhesive and calculated non-filled area of tiles (Considering 25 cm^2 of total area per each ceramic tile).

What could justify the difference between the reference mortar (REF) and other formulations containing BA is the fact that its surface presents a roughness and an overall number of smaller particles compared to S2, which may have promoted a better distribution of the cement paste in the aggregate particles surface increasing the interfacial contact between mortar and ceramic tile.

Table 7. 5. Slip of cementitious-adhesive mortars.

Sample	Slip (mm)	Apparent density (g/cm^3)
REF	0.0	1.484
BA25	0.0	1.487
BA50	0.0 - 1.0	1.506
BA100	0.0 - 1.0	1.525

Hardened state properties

The tensile adhesion strength of samples cured in distinct conditions (standard, wet and heat) is given in table 6. The increase of adhesion with the incorporation of BA may be justified by two factors: (i) the increase of interfacial contact between the adhesive and the ceramic tile; (ii) the slight lower water content of BA-containing samples (water/cement ratio is 0.55 while the one of REF is 0.56).

Upon curing in standard conditions (28d, 23ºC, 50%RH) we can observe that adhesion tensile strength proportionally increases with BA content, despite some uncertainty on the evolution given by the expressive standard deviation of measurements of REF and BA50 samples.

The adhesive strength of the entire system is dominated by the properties of the tile-mortar interface [Jenni et al., 2005]. According to Chew (1999) the reduction of the capillary water, especially in the region near the interface between the adhesive and the substrate, will cause the flocculation of polymer particles and the appearance of a continuous close-packed layer of these particles at the surface of cement gel-hydrates. With water withdrawal caused by cement hydration (accelerated upon curing at higher temperature), the closed-packed layer of polymer particles tends to coalesce into continuous films or membranes, that will efficiently bind the cement hydrated particles together and form a monolithic network in which the polymer phase interpenetrates throughout the cement hydrate phase [Öhama et al., 1986]. Table 7.6 also presents the tensile adhesion strength of samples cured in water for 21 days, after being 7 days placed under the same standard conditions (23° C, 50% RH). The immersion in water strongly diminishes the adhesion of samples. The results obtained show that BA formulations presented a slightly increase of TAS in immersion conditions when compared to REF. Developed studies [Jenni et al., 2006] focused in changes in physical properties of immersed adhesive-mortars, revealed that the strength decrease is attributed to causes related not only to cement hydration but also to volume changes of mortar and reversible swelling of latex films. These authors proved that in water the cellulose ether structures are completely dissolved. Furthermore, the adhesion strength of adhesive-mortars containing polymers is mainly dependent on the polymer content but it is less affected by the cement content or the water-cement ratio. Indeed, according to Schulze (1999) the adhesion strength can be increased with high levels of cement but the influence of the polymer is still much higher.

Table 7. 6. Cementitious-adhesive adhesion strength results (MPa).

Sample ID	7 days	SD	14 days	SD	28 days	SD	H_2O	SD	Heat	SD
REF	1.7	0.04	1.7	0.13	1.7	0.32	0.7	0.13	1.8	0.16
BA25	1.7	0.08	1.7	0.09	1.7	0.17	0.9	0.08	1.9	0.31
BA50	1.8	0.12	1.9	0.09	2.0	0.33	1.1	0.03	2.1	0.08
BA100	1.9	0.05	1.9	0.24	2.1	0.05	1.1	0.06	2.1	0.18

SD - Standard Deviation

In opposition to the behaviour observed in water (wet cure condition), samples tend to gain adhesion when submitted to heat curing. This gain is not very significant but there is, under this curing condition, a positive trend in tensile adhesion strength as it was also observed by Jenni et al (2006), under prolonged storage of samples at 70 ºC and even at 100 ºC. On the other hand, the evaluation of bond strength should always take into account not only the adhesive strength values but also the type of rupture (failure patterns), in order to effectively understand the behaviour of adhesive mortars.

Samples cured for 7 and 14 days in standard conditions showed predominantly AF-T rupture (adhesive failure in the ceramic tile). However, upon prolonging the cure for 28 days in standard conditions it was found that samples BA50 and BA100 revealed partial adhesive failure pattern [BA50 (35% AF-T and 65% CF-A), BA100 (60% AF-T and 40% CF-A)], while REF and BA25 ones only show AF-T rupture. This change is related to the observed increase on the values of tensile adhesion strength in both higher BA content formulations, cured in this condition.

Differences between failure patterns of samples cured in water and under heat can be observed in figure 7.9. AF-T is dominant in wet conditions while CF-A is more common on samples cured under heat. According to Jenni et al (2006), the resulting failure patterns can be correlated to the final adhesive strength achieved by the tile adhesive-mortar, leading to an interface failure pattern in wet conditions or a failure trough the adhesive mortar (cohesive failure pattern) under heat curing conditions.

Figure 7. 9. Examples of cementitious-adhesives failure patterns commonly observed in the actual study (left image – AF-T observed on samples cured in water; right image – CF-A observed on samples cured under heat).

Figure 7.10 shows the relation between the adhesion strength (after 28 days of curing in standard conditions under 30 minutes of open time) of the samples and transference capacity results after 30 minutes of open time. Bentz et al (2008) emphasizes that tackiness is lost due to the formation of a skin/film and reinforce the idea that a key property of adhesive-mortars is their open time. TAS increase with BA content increasing on open time test (30’). It means that there is a higher adhesive capability of the adhesive mortar that can be also related to their wetting capability and transference capacity (figures 7.7 and 7.8). Formulations with BA present transference and wetting capability higher than REF not only at 30 minutes, but also at 10, 20 and 40 minutes of open time. This fact could justify the highest value of TAS obtained for this formulation in the open time test. The addition of BA retards the adhesive film formation leading to an increasing of workability time of the product; BA also promotes an increase in the interfacial contact between adhesive and tile, consequently increasing the tensile adhesion strength of formulations with BA in their composition.

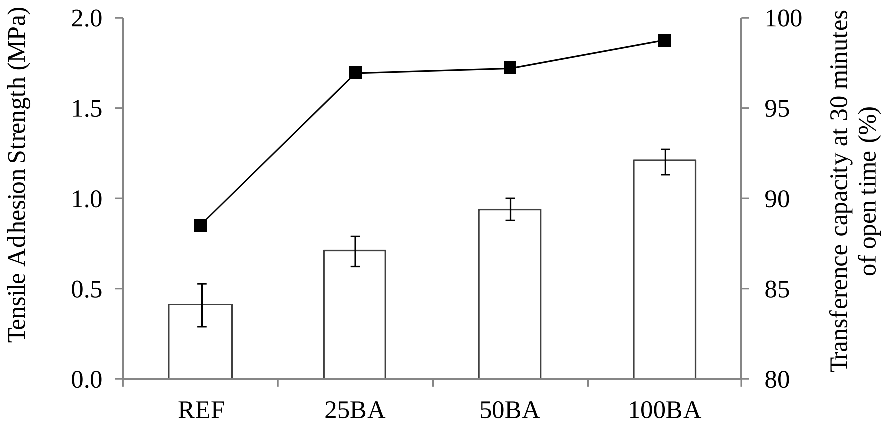


Figure 7. 10. Tensile-adhesion strength of cementitious-adhesive formulations and Transference capacity results after 30 minutes of Open Time results.

7.4 Conclusions

1) BA landfilling classification

The bottom ash from the studied bubbling fluidized bed combustor using residual forest biomass as fuel is considered a non-hazardous material according to legal limits established in Decision 2003/33/CE and the Portuguese Decree-Law 152/2002.

2) BA as a replacement aggregate in CAM formulations

About the fresh properties of the formulations tested, the replacement of coarse sand by BA led to a decrease on water demand by formulations, and the results in fresh state showed that adhesive-mortars could keep interesting values of wetting capability, even with lower water content. Increasing on the replacement amount of conventional sand by BA proportionally increases the tensile adhesion strength of the formulations in every storage conditions (standard wet and heat curing). This result could be mainly related with the increase of interfacial contact between the adhesive and the ceramic tile. The developed tests of wetting capability and transference demonstrate that the conventional sand (S2) replacement by BA lead to a considerable increasing in both parameters.

About the hardened properties of the formulations tested, the evaluation of adhesion also involved the follow up of the failure adhesion patterns. Introduction of BA led to a shift from typical adhesive failure pattern in the tile-adhesive interface to a cohesive failure pattern inside the mortar. This effect can be attributed to the increase on tensile adhesion strength of the adhesive mortar containing BA. Another advantage in incorporating BA in these mortars was observed in the open time test that gives indication on the tackiness of the adhesive mortars. BA contributes to delay the adhesive film formation, thus leading to better adhesion results.

Particle size distribution of BA could be properly adjusted to replace the conventional coarse sand aggregates used in this type of cementitious adhesive-mortar formulations. Hence, recycling of BA in adhesive mortar was found to be suitable for this kind of application without detrimental implications in terms of major chemical or physical effects on the product. It was shown that this process constitutes a valid waste valorization solution in a construction material, also reducing the use of an important natural resource (raw coarse sand) which, in turn, contributes to increase the level of sustainability of the industrial processes involved. Furthermore, this waste recycling solution is also important for the pulp and paper industry and energy industry, because it contributes to avoid the landfill disposal of one of its industrial process residues (the bottom ash from biomass combustion), thus minimizing related environmental and economic costs.

Acknowledgements

The authors acknowledge Foundation for Science and Technology (FCT Portugal) for the financial support (SFRH/BD/75182/2010-PhD grant, PTDC/AAC-AMB/ 116568/2010 - BiomAshTech - Ash impacts during thermo-chemical conversion of biomass) and also Saint-Gobain Weber company for laboratory and materials support.

8 TREATMENT AND USE OF BOTTOM BED WASTE IN BIOMASS FLUIDISED BED COMBUSTORS

Regina C.E. Modolo*, Luis A. Tarelho, Elisabete R. Teixeira, Victor M. Ferreira, João A. Labrincha

Published in **Fuel Processing Technology** 125 (2014) 170–181
DOI: http://dx.doi.org/10.1016/j.fuproc.2014.03.040
Impact Factor (5-year): 3.493; ISSN: 0378-3820
WebQualis: A1

Abstract

Bottom bed waste (BBW) from combustion of forest biomass residues was characterized aiming its use as partial substitute of fresh bed sand (FBS) in industrial bubbling fluidized bed combustors (BFBC). BBW particle size distribution, elemental composition (mainly Si, Ca, Al, Na, K, P and Mg) and mineralogy were evaluated considering also the influence of the characteristics of the biomass used as fuel. Biomass combustion experiments were developed using a pilot-scale bubbling fluidized bed combustor. The operating conditions during the experiments were monitored, namely the flue gas composition (CO_2, O_2 and CO), temperature and pressure, and compared with data collected from BFBC located in two industrial biomass thermal power plants. Physical, chemical and mineralogical characteristics of the FBS and BBW revealed that practices related with biomass handling at the forest strongly influence the BBW properties, not only in terms of coarse soil particles addition (> 1.0 mm) but also mineralogically. However, the results obtained here indicate that by sieving of BBW it is possible to recover almost 60% of the original BBW particles (size between 0.3 to 1.0 mm), which have properties that allow its reuse as substitute of FBS for bed make-up in industrial BFBC.

8.1 Introduction

Fluidized bed combustion (FBC) is recognized as the most suitable technology for biomass combustion. FBC plants can deal with distinct fuel mixtures (e.g. different types of biomass) but might show some operating problems when the particle size distribution and type/amount of impurities in the fuel are not adjusted (Mitsui, 1997). The combustion temperature inside the bed must be kept relatively low (usually 700–900°C) in order to prevent ash sintering. Even so, this technology assures high conversion efficiency [(McKendry, 2002; Khan et al., 2009]. Problems that might appear during biomass combustion are related to the amount of ashes being generated and their properties, with potential reflex on the energy conversion efficiency. Slagging, fouling, corrosion, and bed agglomeration are unwanted episodes. Additionally, the generated ash also requires a proper environmental [Werkelin et al., 2010; Rajamma et al., 2009].

Several authors consider agglomeration of bed particles as the major problem during biomass combustion in FBC [Ohman et al., 2005; Zevenhoven-Onderwater et al., 2006; Elled et al., 2013; Nuutinen et al., 2004]. According to Bartels et al. (2008) the inappropriate fluidization caused by agglomeration could lead to the fluidized bed collapse. The bed material agglomeration and sintering are related with the sticky coatings on bed particles formation. These coatings are formed by multiple layers of ash or ash-rich compounds. The internal layers seem to be a sign of the composition of the bed material (sand), while the outer layers are essentially defined by the ash characteristics [Ohman et al., 2000]. In addition, certain elements segregation to the ash layers on bed sand particles has been observed [Åmand and Leckner, 2004]. The volume of ashes, their characteristics and management has been considered one of the most important issues during thermochemical conversion of biomass to energy. The type of biomass in use (i.e., forest wastes, wood, herbaceous, domestic wastes), the amount/nature of impurities (i.e., soil, inorganics), the technology and the operating conditions (e.g., bed material residence time, temperature, etc.) determine the amount and characteristics of the ashes produced during combustion. According to Vassilev et al. (2012) approximately 480 million ton. of ash from biomass combustion could be generated worldwide annually. This quantity is becoming comparable to that of coal ash, namely 780 million ton produced per year at present [Izquierdo and Querol, 2012].

During biomass combustion in bubbling fluidized bed combustors (BFBC) two main types of ashes are produced: bottom bed and fly ashes. The bottom bed ashes are basically composed by a mixture of sand (mainly quartz) particles from the original bed, and by inert/inorganic components (forest soil and small stones) included in the biomass. Additionally unburnt organic components might also be present in the ash. The components of the fly ashes are similar to the previous ones, but finer enough to be aspired by the exhaustion system of the combustor. The bed sand fraction is normally much lower than in the bottom ash, since only the original finer particles or the ones resulting from attrition and abrasion phenomena are present. During BFBC, the bottom bed ashes often represent the lower fraction of the total ashes produced: around 5 %wt. [Latva-Somppi et al., 1998a; Latva-Somppi et al., 1998b], 10 %wt. [Dahl et al., 2010], and 17 %wt. [Tarelho et al., 2012]. However, in some Portuguese thermal plants with BFBC, the relative amount of bottom bed ashes can be as high as 50-60 %wt. [Tarelho et al., 2012].

The bottom bed waste is generated when periodic discharges of the bed are performed: i) trying to maintain the particle size distribution and to avoid agglomeration, in order to assure the suitable fluidity and hydrodynamic conditions of the bubbling bed; ii) to discharge the excess of solids (ash) and keep the height constant. In general, the relative high level of inert material present in the biomass used in Portuguese BFBC plants (Tarelho et al., 2011) enhances the frequency of bed discharges, meaning that bottom bed ashes have low residence time (<5 days - *see* Tables 8.1 and 8.2) in the BFBC when compared with results reported for other installations using BFBC [Latva-Somppi et al., 1998a; Latva-Somppi et al., 1998b]. Since around 60 wt.% of discharged bottom bed waste is composed by sand particles having sizes in the range of 0.5 – 1.0 mm, the mentioned increase of discharge frequency will imply a stronger make-up with fresh sand, while increases the volume of waste being generated.

The bottom bed waste from BFBC have the code 100124 according to European List of Wastes [Decree n.º 209/2004] and the search for recycling or reuse alternatives of such residue is an hot topic and a serious need. We should also look to other relevant environmental indications like the one given by Hoffman (2013) that concluded that around 90% of the beaches in the world are losing ground due to excessive sand extraction for distinct uses.

Previous studies demonstrated that the use of bottom bed waste from biomass burning in BFBC as substitute of the conventional sand used as coarse aggregate in the formulation of industrially-prepared rendering-mortars is technologically feasible [Modolo et al., 2013]; in general this substitution does not induce negative effects on the relevant properties and material accomplishes with required specifications. However, other applications for such waste must be found and one obvious option is the recirculation or reuse of the material in the same BFBC. Apparently easy, this way requires the pre-adjustment of particle size distribution, with removal of fines and agglomerates by screening. This pre-treatment might also help to minimize the concentration of inorganic alkali elements that tend to constitute the agglomerates. Nevertheless, other chemical impurities might not be removed by this simple process, and additional leaching/washing processes might be required to reach the purity level of the bed make-up.

The main aim of the actual work is improving the knowledge on the characteristics of bottom bed waste from fluidized bed combustion of residual forest biomass in Portuguese thermal plants and cogeneration plants. Based on them, physical pre-treatment processes were applied aiming to regenerate the material to be recirculated in the bed of a pilot-scale combustor.

8.2 Materials and methods

8.2.1 Characterization of industrial bottom bed waste

The sampling schematic diagram of the ashes here studied is shown in Figure 8.1. The bottom bed waste (BBW) studied were sampled in two BFBC, with nominal capacities of 50 MWh and 100 MWth, denominated TPP_1 and TPP_2 respectively. They both use a mixture of forest biomass residues as fuel. In each installation, the typical operating temperature of the bubbling bed ranges from 750ºC to 940ºC; while the O_2 concentration in the flue gas varies between 4 vol.% and 8 vol.% (dry gases). Bottom bed wastes from TPP_1 (BBW_1) and from TPP_2 (BBW_2) were collected and characterized simultaneously during one year (monthly).The particle size distributions of the fresh bed sand (FBS) and of bottom bed wastes were obtained by sieving, following the NP EN 933-1:2000 standard. For this determination, the waste was collected from the BFBC and used as discharged. Further characterization tests were performed with sieved fraction below 2 mm. The chemical composition was obtained by X-ray fluorescence spectroscopy (XRF), using a Panalytical Axios spectrometer. X-ray diffraction (XRD) patterns of the wastes were taken using an X-ray diffractometer (RIGAKU-Geigerflex, power 40kV/30mA) and the semi-quantitative analysis determined by MDI Jade9 software using WPF (Whole Pattern Fitting) method, in the scan mode continuous/speed-3 2◦ϴ/min. Simultaneous gravimetric and differential thermal analyses (TG/DTA – Setaram, Labsys) were used to complement the chemical characterization, namely to detect unburnt organic components.

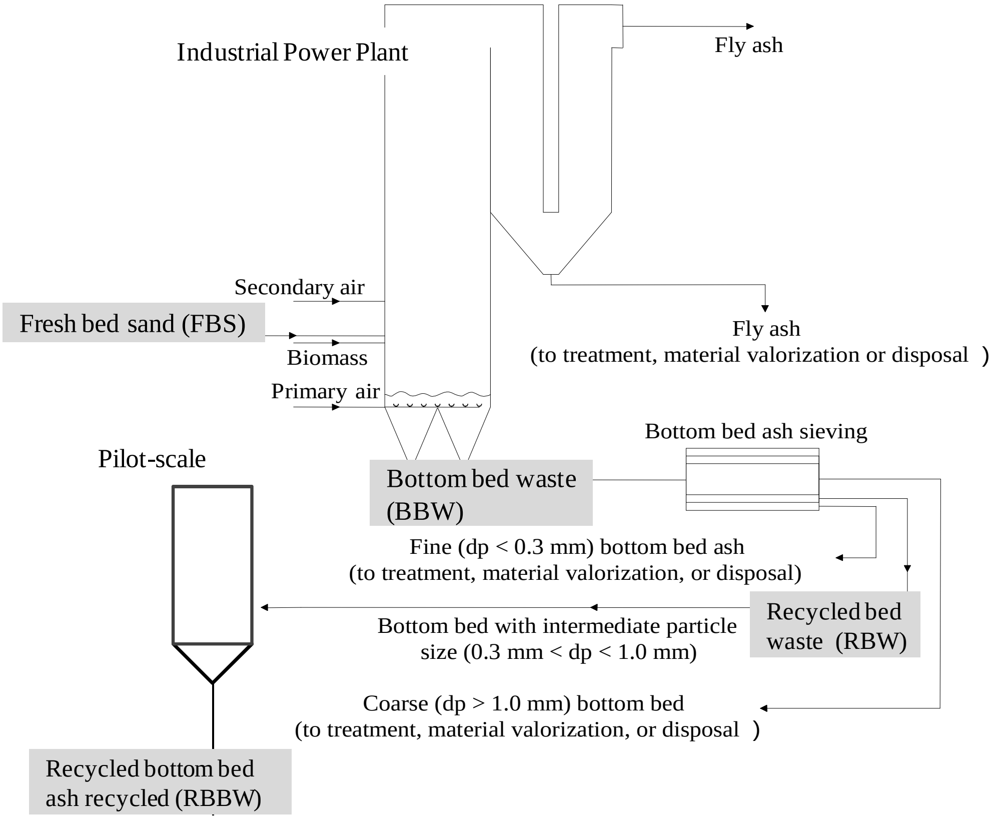


Figure 8. 1. Schematic diagram of the main ashes flows in a thermal plant with BFBC and the respective samples used in this study.

8.2.2 Use of recycled bed waste (RBW) as sand bed replacement in BFBC

From a third TPP with nominal capacity of 90MWth, which operates in similar conditions of TPP_1 and TPP_2, in terms of temperature and pressure, but using eucalyptus bark as major fuel, another BBW sample (~50kg) was collected and sieved, having particles ranging from 0.3 mm and 1.0 mm. This sample is here named recycled bed waste (RBW) since it was reused as fluidized bed in a pilot-scale combustor. The combustion experiments were performed in a pilot-scale bubbling fluidized bed (0.2 m height); the reactor is a thermally insulated AISI 310 SS tube with 0.25 m internal diameter and 3 m height. The facility layout is shown in Figure 2 and is better described elsewhere

[Tarelho et al., 2011; Tarelho et al., 2004; Tarelho et al., 2005). The combustion air is staged with primary air during the distributor plate whereas secondary air goes into a vertical tube located inside the freeboard. The solid fuel is fed together the secondary air and discharged constantly at the bed surface (Figure 8.2). Eight water-cooled probes are located at the bed level. They allow the bed temperature control between the desired ranges. Pressure and temperature along the reactor are supervised by means of nine water-cooled sampling probes located at several heights; two are immersed in the dense bed and the others are situated along the freeboard. Each probe is equipped with a cooled particle filter at the stern of the probe, a K-type thermocouple, and a cerablanket (ceramic fiber refractory) cap at the tip located inside the combustion chamber with the purpose of holding the particles present in the flue gas. The combustion flue gas composition was monitored continuously at the exit of the combustion chamber in terms of O_2, CO and CO_2; the online gas analyzers included a paramagnetic sensor for O_2 (ADC model 02-700 with a Servomex Module) and non-dispersive infra-red sensors for CO_2 and CO (ADC model SB-300). Residual forest biomass from eucalyptus logging activities was used as fuel; it was air dried, chopped and sieved to the size range of 1-5 mm. The main thermochemical characteristics of the biomass used as fuel are shown in Table 8.1. The pilot-scale BFBC operated with a bed temperature in the range of 790-840 ºC, and with an excess air of 50%. The fuel was continuously fed to the reactor at a rate of approximately 3.8 kg/h. The combustion air was staged, with primary air accounting for 80% of the total combustion air. The combustion experiments lasted approximately 10 hours. After that, the bottom bed ash was discharged/quenched and conditioned for further characterization.

Table 8. 1. Characteristics of the residual forest biomass used as fuel in the combustion experiments.

Proximate analysis	(%wt, as received)	Ultimate analysis	(%wt dry basis)
Moisture	5.82	Ash	1.41
Volatile matter	73.01		
Fixed C	19.84	C	51.7
Ash	1.33	H	6.72
Heat value	M*kg^{-1}	N	0.29
LHV	20.34	S	0.02
HHV	21.81[a]	O (by difference)	39.86

[a][Thipkhunthod et al., 2005]

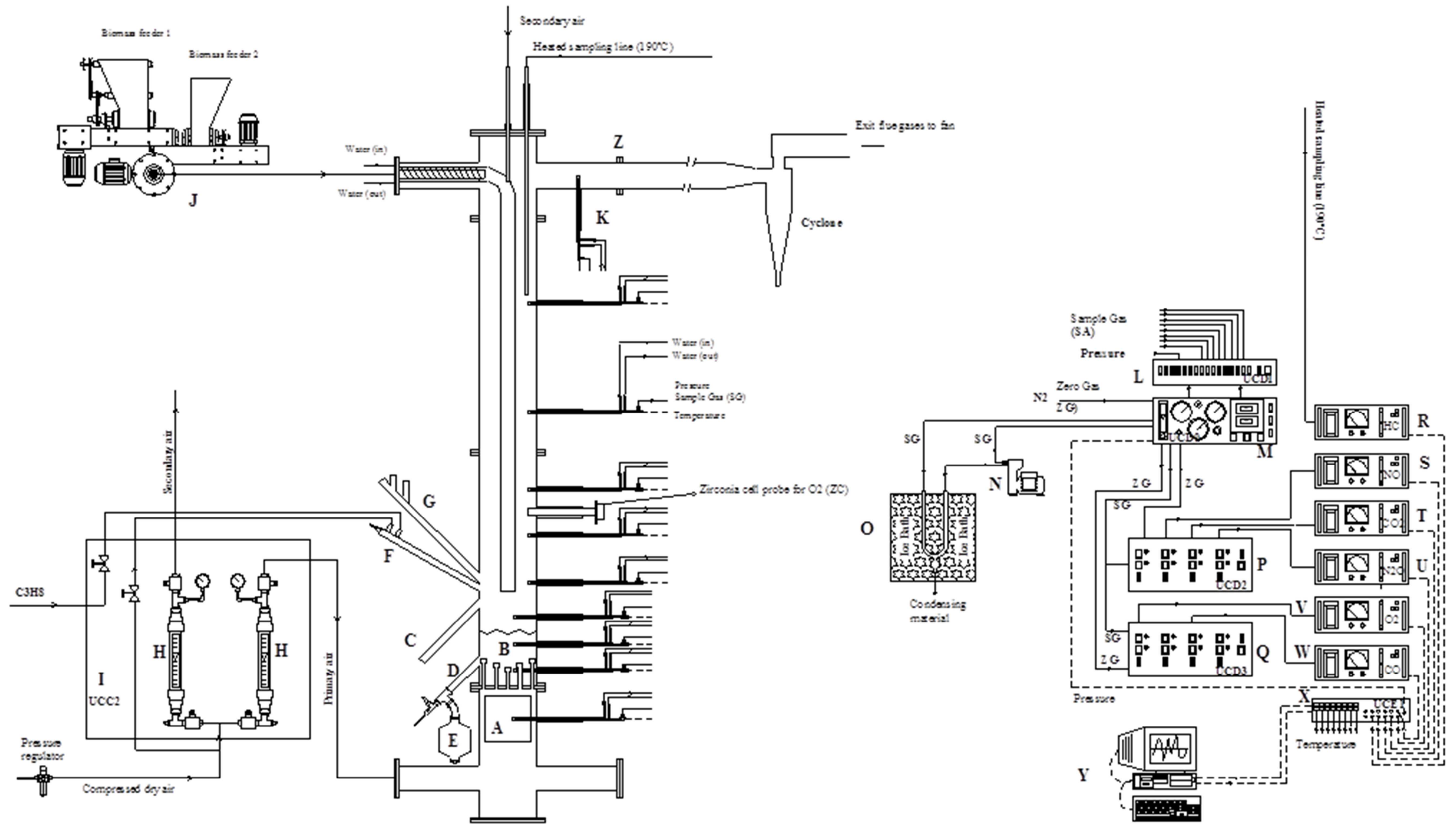


Figure 8. 2. Schematic diagram of the bubbling fluidized bed combustor. Dashed line - Electric circuit, Continuous line - Pneumatic circuit, A - Primary air heating system, B - Sand bed, C – Control of the bed solid levels, D – Discharge of bed solids, E - Bed solids discharge silo, F - Propane burner system, G - Port for visualization of bed surface, H – Combustion air flow meters, I – Command and control unit, Z- Exhaust duct to cyclone; J – biomass feeder set, K - Water-cooled gas sampling probe, L – Command and distribution unit, M - Command and distribution unit, N – Gas sampling pump, O - Ice cooled bath, P - Command and distribution unit, Q - Command and distribution unit, R, S, T, U, V, W – Online gas analyzers for total hydrocarbons, NO, CO_2, N_2O, O_2, CO.

That characterization involved scanning electron microscopy (Hitachi S2300 SEM with EDX25KV) analyses performed to evaluate the morphology and elemental composition of bed ash particles collected. Samples of forest biomass residues used as fuel in the industrial thermal power plants were collected in the fuel feeding system of the plants in order to characterize the impurities (forest soil and stones) fed mixed. Those impurities were separated from branches, grounded in agate mill (<0.100 mm) and characterized in terms of chemical composition and mineralogy.

8.3 Results and Discussion

8.3.1 Industrial bottom bed waste

Figure 8.3 illustrates the macroscopic view of the fresh bed sand particles “a”, and particles of the two wastes (BBW_1 “b” and BBW_2 “c”). Color differences are very notorious between the two wastes, reflecting the type of biomass used as fuel (TPP_1 burns a large variety of residual forest biomass residues, whereas TPP_2 uses mainly eucalyptus bark), and the presence of unburnt material (that tend to assume dark hue). In both residues, the presence of coarse particles is evident, reflecting the presence of inorganic impurities (forest soil particles, coarse and small stones) fed mixed with the biomass fuel. The macroscopic view of these impurities is shown in Figure 8.4 “a” and their mineralogical and chemical composition in Figure 8.4 “b” and “c” respectively. The presence of this type of impurities fed mixed in biomass evidences bad practices applied during biomass handling at forest before delivering to the BFBC installations. In terms of mineralogy, quartz and kaolinite are the most abundant crystalline phases present in this material, followed by common mica (muscovite) and feldspars (microcline and albite). Consequently, Si, Al and K are the most abundant chemical elements present in these impurities, as detected in the chemical analysis (Figure 8.4 “c”).

Figures 8.5 and 3.6 show the particle size distributions of FBS and BBW. The wastes have wide particle size distributions when compared to the FSB, being the presence of fines (particles under 0.25 mm) relatively more abundant than the amount of coarse grains (> 1 mm). This is an indication that agglomeration is not too severe in the actual burning conditions, being the fines introduced as impurities in the fuel feed or resulting from the breakdown of larger particles of the sand bed. Dimensional changes between samples collected in consecutive months are broader in BBW_2, reflecting less stable operating conditions in the TPP_2. Nevertheless, the fraction of particles within the desirable size range (0.3-1 mm) is rather similar in the two wastes, representing around 60 wt.% of the material.

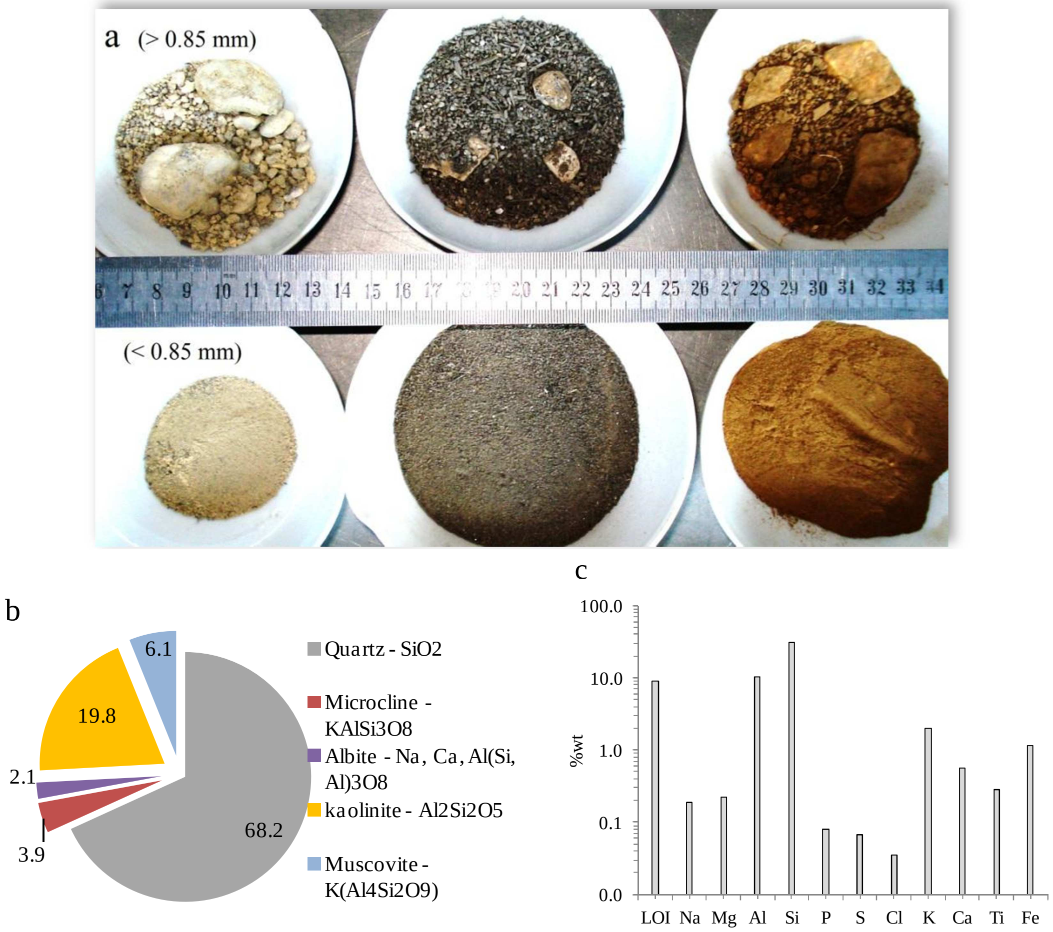


Figure 8. 3. Impurities (forest soil and stones) fed mixed with the biomass, macroscopic view (a), X-ray diffraction semi-quantitative analysis (b), and X-ray fluorescence results (c).

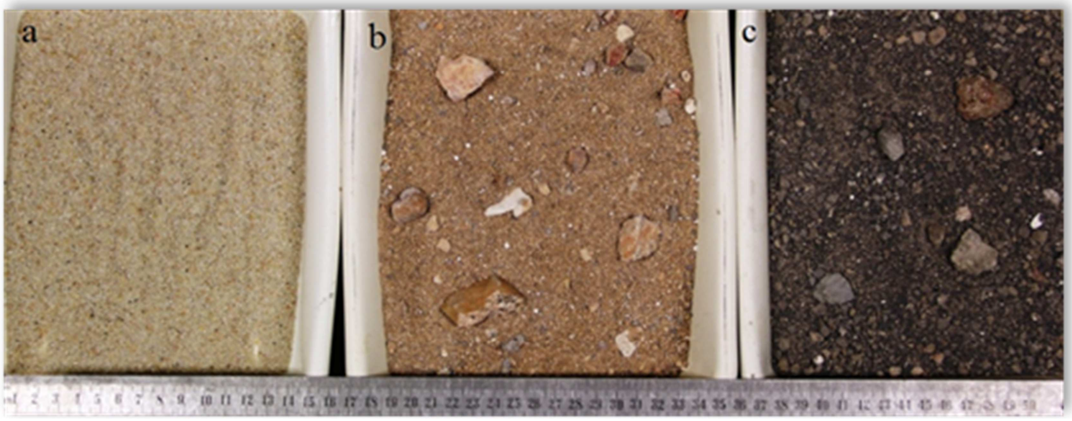


Figure 8. 4. Macroscopic aspect of fresh bed sand (FBS) (a), bottom bed waste (BBW_1) from TPP_1 (b) and bottom bed waste (BBW_2) from TPP_2 (c).

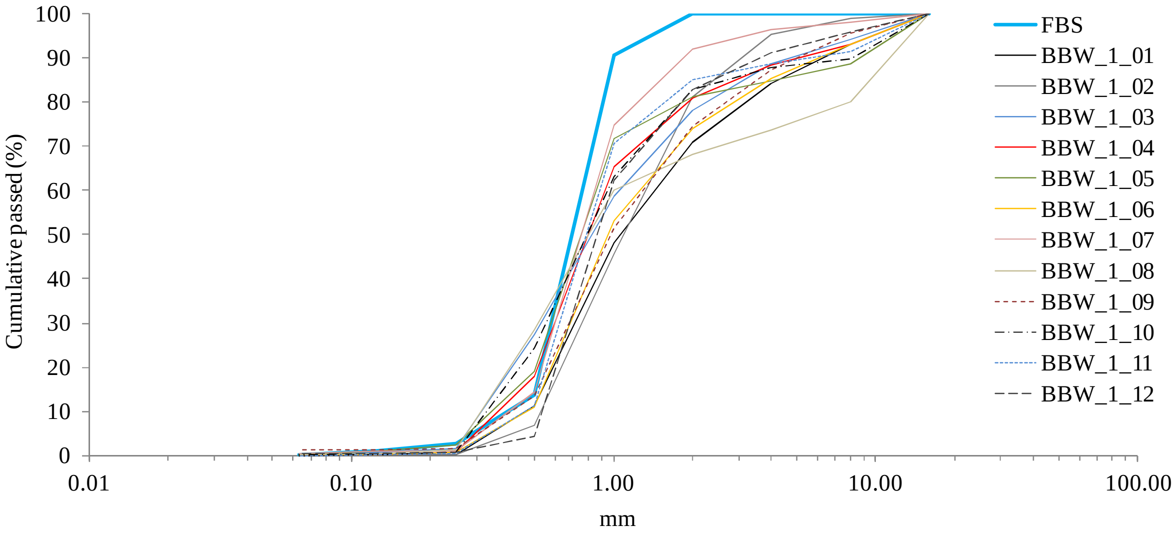


Figure 8. 5. Particle size distribution of BBW samples from thermal power plant 1.

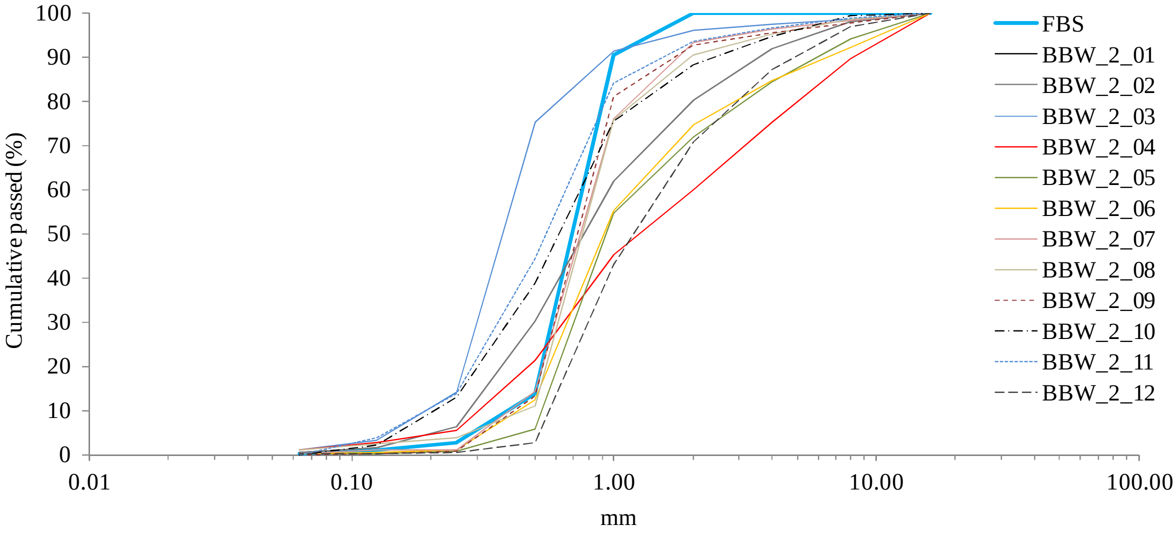


Figure 8. 6. Particle size distribution of BBW samples from thermal power plant 2.

Figure 8.7 and Figure 8.8 show the chemical compositions of the wastes and FSB, while their semi-quantitative mineralogical constitution is given in Figure 8.9. In general, changes on the composition of BBW collected in consecutive months are not expressive, apart some punctual fluctuations in minor elements (e.g. Cl, S, Ti). Anyway, BBW_1 seems to show higher variability, certainly related with stronger changes is the fuel feed, as previously mentioned. Both BBW samples show Si as major element (between 35 and 40 %wt.), being mostly present as quartz. FBS is even richer in Si, because is mainly composed by quartz sand, as can be seen in Figure 8.10 and also as will be showed by

SEM-EDX analyses. Contributing to the high Si content in the BBW samples is the original fresh bed sand, and also the forest soil particles fed mixed with the residual forest biomass resulting from bad practices during biomass harvesting and handling previously to combustion in the industrial BFBC installations, as also referred in other studies [Steenari et al., 1999]; the impurities (forest soil particles) fed mixed with the residual forest biomass also contribute to the Al and K content (present in the microcline and albite mineral composition). Calcium (and magnesium) tend to react with Si or to generate carbonates, while these last components might also be present since the beginning as contaminant of the sand or in the biomass. Those additional elements/phases detected in the wastes were certainly introduced by the inorganic impurities present in the biomass (Figure 8.4), as reported in the literature [Åmand and Leckner, 2004; Aho et al., 2008; Dayton et al., 1999]. While few and small, mullite peaks seem also to be present, certainly as a result of reactions that occurred at high temperature. Loss on ignition is below 2% in all BBW samples, but changes along the time are relatively high, particularly for BBW_2. This is another indication of higher operational fluctuations on the TPP_2 unit.

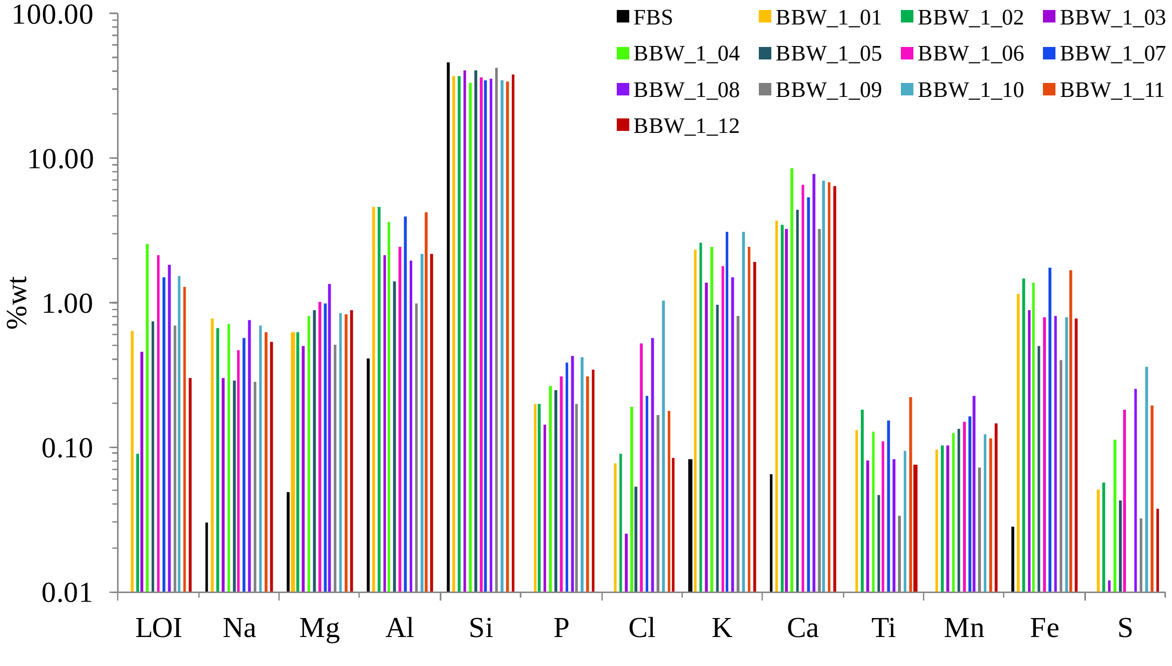


Figure 8. 7. Loss on ignition (LOI) and chemical composition (major elements determined by XRF) of FBS and BBW samples collected on thermal power plant 1 along a year. Chemical element without value in the table means that its concentration is zero.

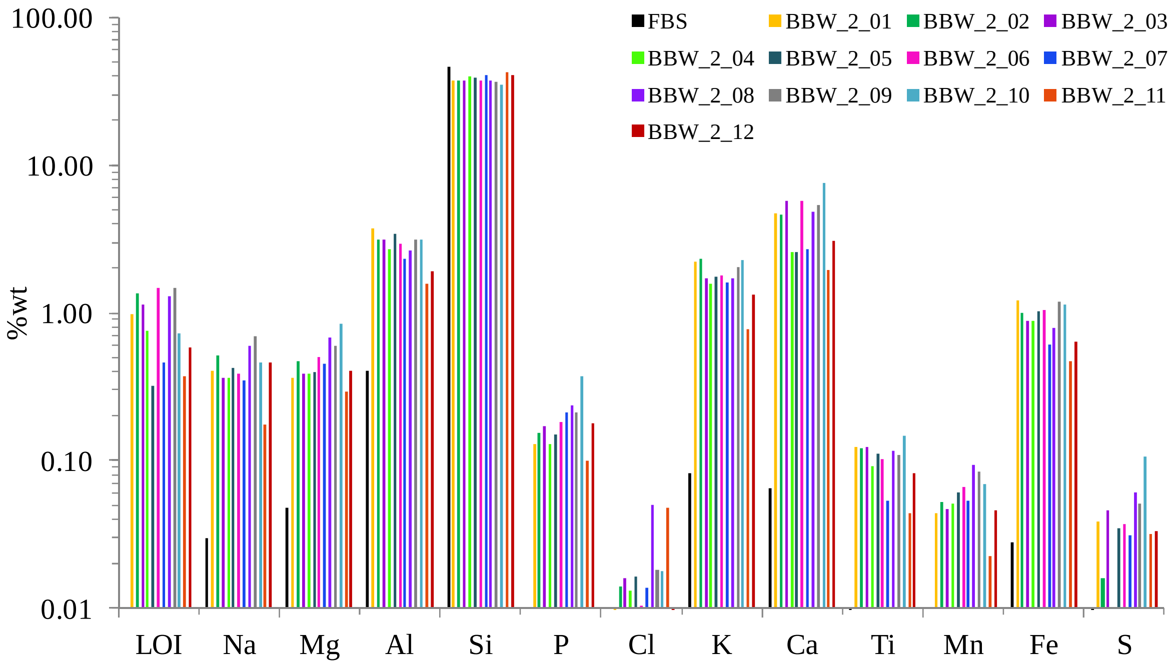
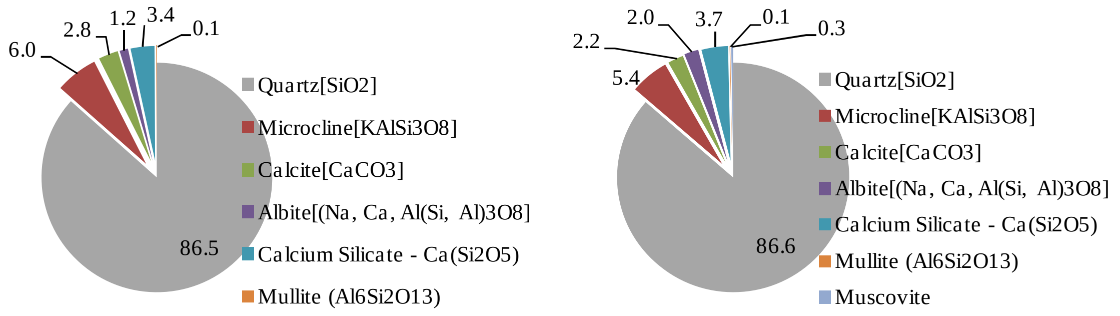


Figure 8. 8. Loss on ignition (LOI) and chemical composition (major elements determined by XRF) of FBS and BBW samples collected on thermal power plant 2 along a year. Chemical element without value in the table means that its concentration is zero.



BBW_1

BBW_2

Figure 8. 9. X-ray diffraction semi-quantitative analysis of BBW samples from thermal power plants 1 (TPP_1) and 2 (TPP_2); average of 12 samples collected during one year (monthly sampled).

Thermal analyses (TG/DTA) are shown in Figure 8.11 and confirm the overall inert characteristics of BBW samples. The most noticeable weight loss was registered between 600 and 800 ºC and results from the release of CO_2 of the carbonates (mainly calcite). This reaction is also denoted by the endothermic peak registered in the DTA curve at about 750 °C. The other endothermic reaction, detected at 573 °C, is attributed to the α-β quartz polymorphic transformation. The total mass loss reached about 4%, above the LOI values given in Figure 8.7 and Figure 8.8. The absence of expressive exothermic peaks in the range 250-500 °C, particularly on BBW_1 sample, confirms that biomass burning was rather complete. Otherwise, the remaining unburnt/organic matter should decompose in that temperature region.

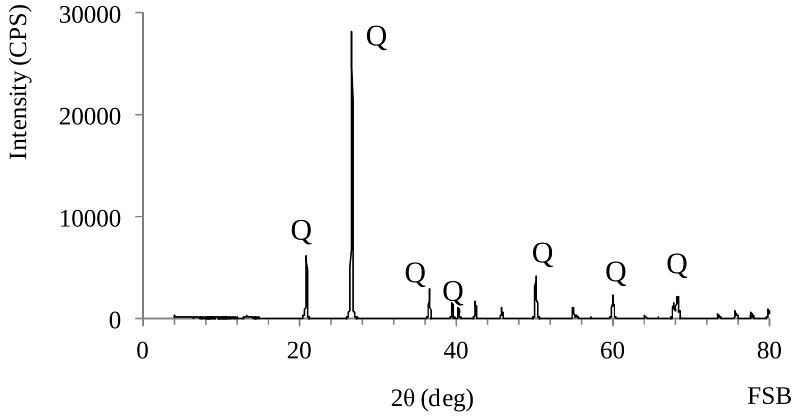


Figure 8. 10. X-ray diffraction of FBS; Q = Quartz.

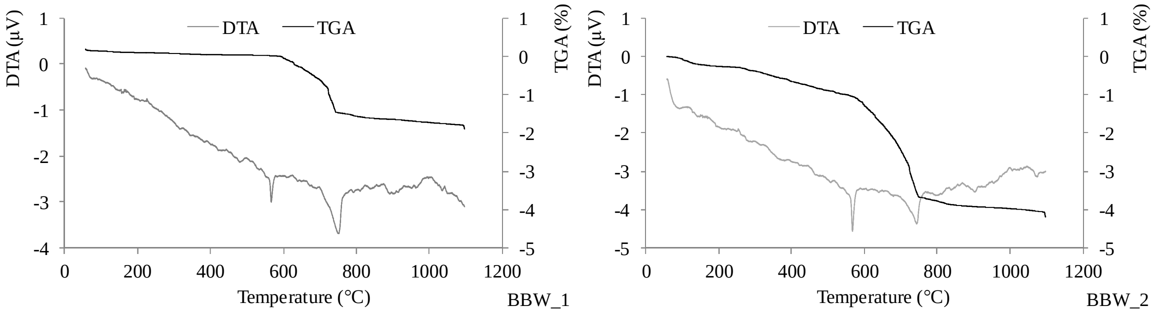


Figure 8. 11. DTA and TGA profiles of BBW thermal power plants 1 (TPP_1) and 2 (TPP_2).

8.3.2 Use of recycled bed waste (RBW) as sand bed replacement in BFBC

As observed in previous sections, during biomass combustion, the original sand bed particles become enriched in chemical compounds that correspond to the inorganic contaminants in the biomass. This enrichment occurs as a coating layer of the sand particles. This process is shown in Figure 8.12 and Figure 8.13, where the SEM-EDS of the cross-section of a particle from the fresh sand bed (FSB) and a particle from the RBW are presented. In these figures, we also show the distribution and qualitative abundance of some of those chemical elements, namely Ca, K, Mg, Al, P, and Na. The increasing of such elements in the outer layer of the bottom bed particles has been documented in the literature and appears to establish the particle agglomeration [Zevenhoven-Onderwater et al., 2006; Nuutinen et al., 2004; Ohman and Nordin, 2000; Lin et al., 2003; Lin and Wey, 2004; Scala and Chirone, 2006]. At the same time as expressive upon operation, this phenomenon is unwanted, since it will modify the fluidizing conditions through the bed [Ohman et al., 2000; Ohman, A. Nordin, 2000; Lyn and Wey, 2004; Kuo et al., 2008; Lin et al., 2009; Skrifvars et al., 1998; Zevenhoven-Onderwater et al., 2001]. Attempting to prevent its occurrence, some authors suggested the use of certain additives [Bartels et al., 2008; Ohman and Nordin, 2000; Kuo et al., 2008; Lin et al., 2009; Llorente et al., 2006]. According to Lin et al. (2009) the coating layer formed around the particles is composed by infusible fine waste particles embedded in the melted phases. These authors concluded that melts contain potassium, sodium, and sulfur, while the infusible components are rich in calcium and magnesium. Based on SEM-EDS determinations, distinct authors [Nuutinen et al., 2004; Ohman et al., 2000] demonstrate that the coating layer of sand particles is rich in alkali and Si. The melting point of certain silicates can be as low as 720ºC, being the reaction also affected by the particle size. Tendency for agglomeration is proportional to the specific surface area of the particles [Langston and Stephens, 1960], so the relative amount of finer grains should be limited. Combustion experiments conducted with RBW lasted for 6-7 hours (constant period of data registration).

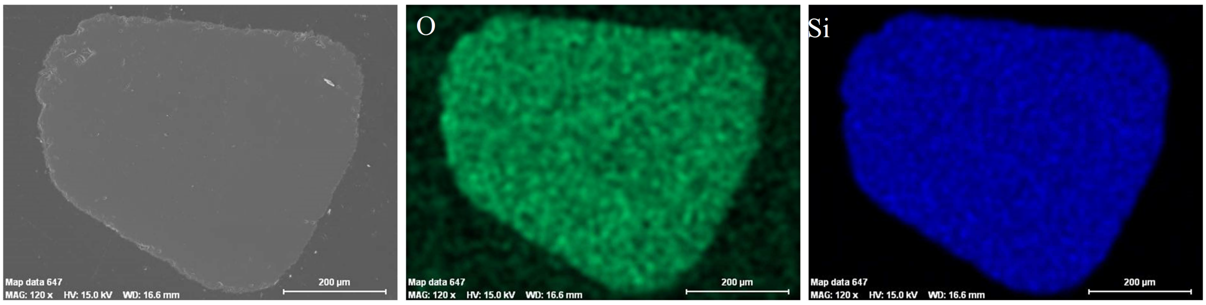


Figure 8. 12. Scanning electronic microscopic (SEM) view of cross section of Fresh bed sand (FBS) particles and EDS images.

Average values for the pressure and temperature profiles along the reactor height are shown in Figure 8.14. The pressure is higher at the base of the bed (109 kPa), tends to decrease along the bubbling fluidized bed height, and stabilizes along the freeboard height (107 kPa). The temperature has a minimum value (around 380ºC) at the base of the bed (measured below the level of the fluidizing air injectors, that is, in the fixed bed region), then it increases in the fluidized bed section and achieves its maximum (960ºC) just above the place where fuel feeding and secondary air ingress occurs.

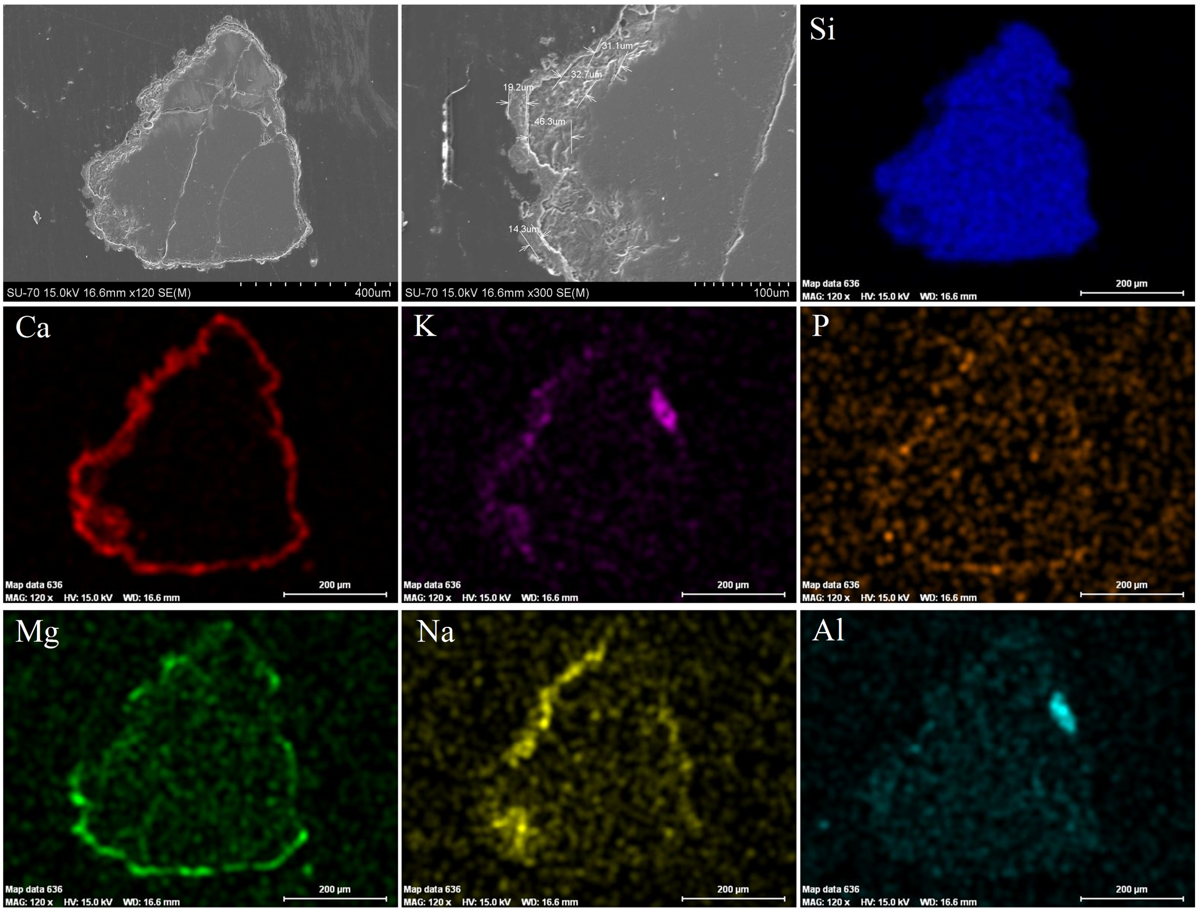


Figure 8. 13. Scanning electron microscopy (SEM) view of cross section of BBW particles and respective EDS images for the distribution of several chemical elements (Si, Na, Al, P, K, Ca, Mg).

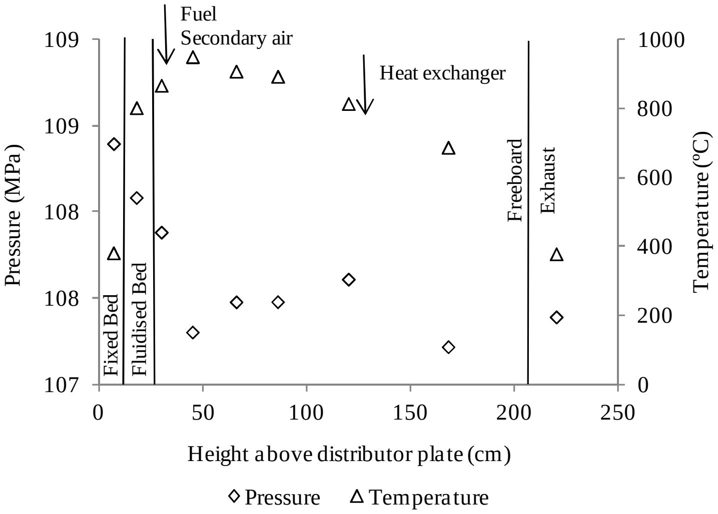


Figure 8. 14. Longitudinal pressure and temperature profiles along the pilot-scale BFBC during the biomass combustion experiments with the recycled bed.

This higher temperature in the freeboard is related to the release of a significant amount of heat as a result of volatile mater combustion at this location; biomass fuels have a significant amount of volatile matter (typically higher than 75 %wt in dry basis) and it is recognized that the release and combustion of this volatile matter occurs mostly near the location where the fuel is feeding [Tarelho et al., 2011]. After that, the temperature decreases along the freeboard due to heat losses through furnace walls (Figure 8.2).

The operating temperature is an important parameter to be controlled in order to guarantee an efficient fuel conversion, and also to control the bed fluidization conditions. Figure 8.15 shows typical flue gas composition profile measured during the experiment; CO_2, O_2, and CO average concentrations (by %vol. of dry gases) were around 13%, 8% and 0.005%, respectively.

During the pilot-scale combustion experiment no expressive particle agglomeration was observed, and so no changes on the bed fluidizing conditions were registered. The waste discharged from the pilot-scale BFBC, thereafter denoted as recycled bottom bed waste (RBBW), looked just slightly darker than the used RBW.

Nevertheless it was observed the occurrence of some sand particles linked, corresponding to less than 0.1% of bed mass [value founded through the sieving (retained mass in 1.00 mm) of bottom bed waste total mass]. Industrially, this 0.1% can represent around 50kg of agglomerates total mass, considering a bed capacity of 50 tones.

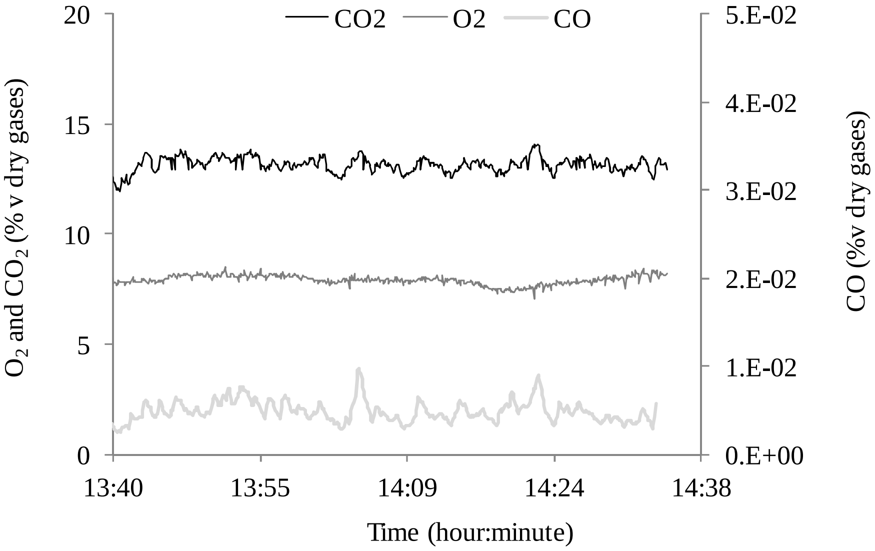


Figure 8. 15. CO_2, O_2 and CO concentration profiles along the pilot-scale BFBC during the combustions experiments.

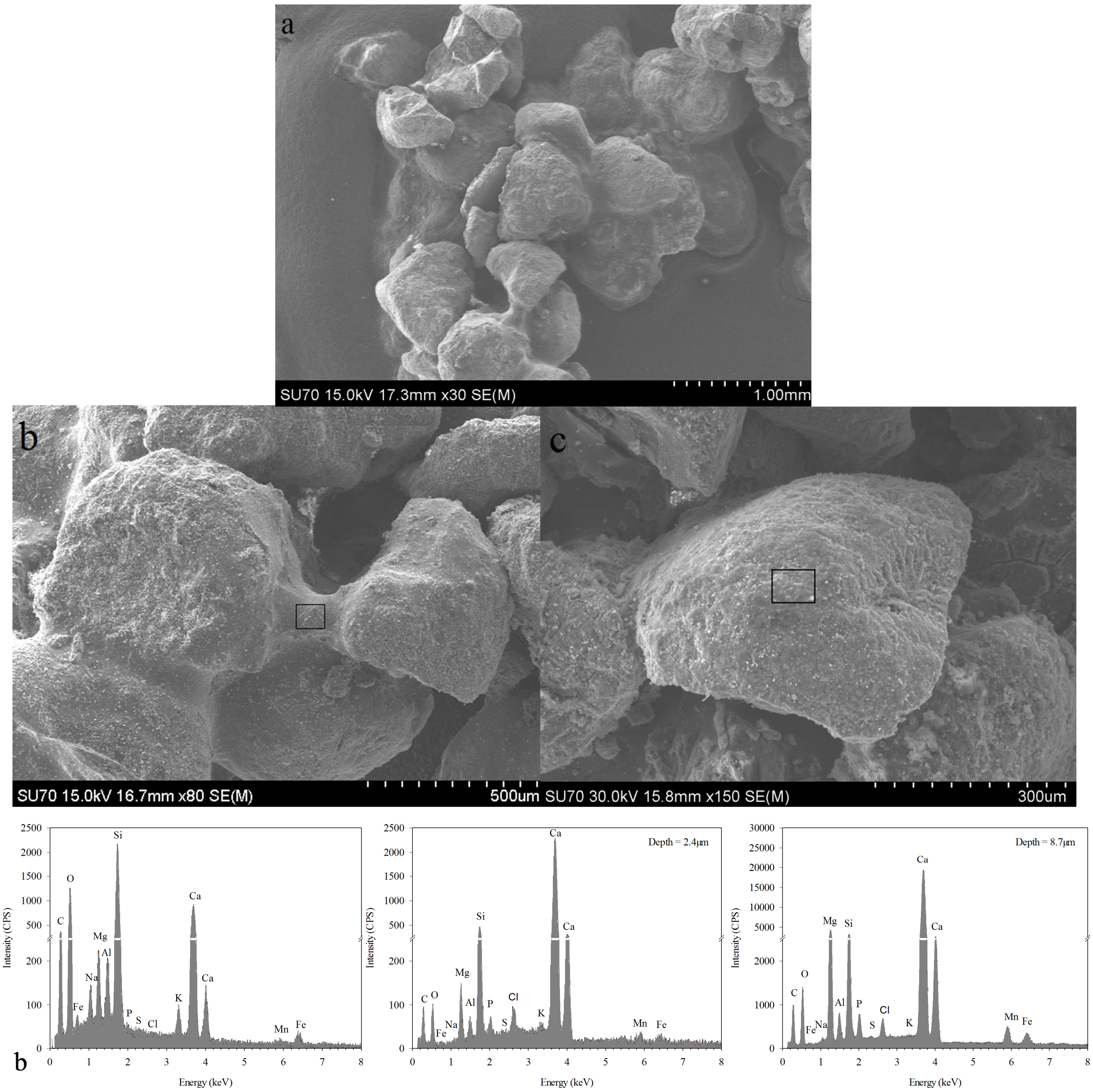


Figure 8. 16. (a) Small agglomerated particles from the recycled bottom bed waste (RBBW) after the pilot-scale combustion experiments; (b) Scanning electron microscopy (SEM) image of agglomerate from RBBW, and respective EDS results of the particle surface (pointed section); and (c) Scanning electronic microscopic (SEM) image of the connecting bridge between particles of RBBW, and respective EDS results (pointed section).

Figure 8.16 “a” illustrates small agglomerated bed particles from the pilot-scale combustion experiments. It is observed that some particles are linked by a kind of connective bridge with distinct texture when compared to the surrounding particles. According to many developed studies already referred, this phenomenon is related with the occurrence of melting in the outer layer of the sand particles, and associated with the relative content of some chemical elements (mainly sodium, potassium) present in this ash layer [Bartels et al., 2008; Lin et al., 2003; Lin et al., 2009; Langston and Stephens, 1960; Manzoori and Agarwal, 1994].

Figure 8.16 “b” shows a detail (determined by SEM-EDS analysis) of a particle surface and connection layer between particles from 8.16 “a”. From Figure 8.16 “b” it is observed that the main elements present in the particle surface (measured at 2.4 and 8.7 µm depths) are Ca, Si, Mg, Al, P, Cl, Mn and Fe. The EDS from the particle surface at 2.4 µm depth indicate mainly the presence of Ca, Si and Mg. With increasing depth in the particle surface, e.g. at 8.7 µm (also in the typical outer ash layer of the bed particles (Figure 8.12), it is observed an increasing intensity in the abundance of Mg and K. In fact, it is reported in the literature, a characteristic dual ash layer around the bed particles that consists of an inner layer rich in potassium (typically potassium silicate) and an outer layer rich in calcium where calcium silicate is dominant [Ohman et al., 2005; Elled et al., 2013; Nuutinen et al., 2004]. In this case, calcium is dominant in both depths.

8.3.3 Economic evaluation of the recirculation scenario

Figure 8.16 “c” shows the detail (determined by SEM/EDS analysis) of the connection bridge formed between two adjacent sand particles. It is confirmed the enrichment in sodium, potassium and silicon, and the relative decrease in calcium, in the bridge connecting the two bed particles when compared with the particle surface EDS (Figure 8.16 “b”). This chemical composition explains the lowering on the melting temperature of the ash layer around the sand particles and the consequent connection bridge formation between adjacent particles, as has been reported in the literature [Lin et al., 2003; Zevenhoven-Onderwater et al., 2001]. The interaction between alkali metals and oxygen can result in the formation of oxide-eutectics with a low melting point, for example Na_2O, causing particle agglomeration [Lin et al., 2009; Atakül et al., 2005]. Also, the importance of potassium in this process is recognized, e.g., Elled et al. (2013) found potassium silicate (K_2SiO_9) in the inner ash layer and using a thermodynamic equilibrium modeling approach suggested that it can originate a melt at typical temperatures of fluidized bed combustion. They suggest that this melted form of K_2SiO_9, which can also be present as $K_2O.4SiO_2$ probably leads to a sticky coating of the quartz sand particles which induce agglomeration if this inner ash layer is not covered by non-sticky as particles consisting of calcium silicate.

Nevertheless, it should probably be noted that these problems of agglomeration may become minimized considering, in addition to the physical treatment, a chemical treatment of recycled bottom bed waste through an efficient washing system in order to decrease part of the alkali and soluble salts concentration [Tarelho et al., 2012; Modolo et al., 2013], thus decreasing the risk of bed particles agglomeration. However, in that circumstance it will be needed to consider proper management options for the washing solution.

Table 8.3 presents real inputs and outputs of biomass fuel, fresh sand bed, bottom bed waste and fly ash mass flows for the two thermal power plants (TPP_1 and TPP_2). In general, inputs are similar for the two power plants, but significant differences exist in the relative amount of produced bottom bed waste and fly ash; TPP_1 generates higher amount of BBW (~ 6900 ton) when compared to TPP_2 (5819 ton).

Estimated values were also obtained (see Table 8.3), based on experimental data collected in field, and on bench and pilot-scale trials. In this analysis, we approached the decreasing of mass flow sent to landfill while saving costs associated with partial replacement of fresh sand for bed make-up were anticipated (Table 8.2). The fresh sand used in these BFBCs has particle sizes comprehended in the range of 0.3-1.0 mm. As it has been shown, BBW contains ~60% particles within that size range.

Table 8. 2. Thermal power plants mass flows of biomass fuel, FBS, BBW and FA quantities and associated costs.

	Input		
Estimated data	TPP_1	TPP_2	Unit
Inerts fed with biomass (dry base)**	31.7	29.0	t/day
Biomass ash content (Loss on 550ºC - dry base)	10.8	14.0	t/day
Mass of fresh bed sand input (dry base)*	2.6	4.4	t/day
Total	**45.1**	**47.3**	**t/day**
	Output (a)		
Real data supplied by the industry	TPP_1	TPP_2	
BBW - Discharge (dry base)*	20.9	17.6	t/day
FA - Discharge (dry base)*	20.5	29.8	t/day
FA - Discharge (dry base)**	24.2	29.7	t/day
Total*	**41.4**	**47.4**	**t/day**
Total**	**45.1**	**47.3**	**t/day**

*Industry data

**Estimated values based on bench tests and Industry values

If no material valorization is considered, a total of 12719 ton of BBW is landfilled, with an associated cost of around 400.000,00 €/year [the landfill cost is estimated and variable based on industry data; the values are calculated in €/waste ton/km]. Adding to this value the costs associated with acquisition of fresh sand to make-up the bed (FSB) (approximately 65.000,00 €/year), the total costs approach half million €/year. On the other hand, by assuming 60 wt% reuse of BBW as bed make-up, predicted savings are over 200.000,00 €/year (X in Table 8.3). This estimation does not consider potential costs associated with physical BBW treatment operations, since in the actual circumstances the screening facilities already exist in the industrial unit and then no additional investment costs are required for its acquisition.

Table 8. 3. Database and equations used to estimate biomass fuel, FBS, BBW and FA quantities and associated costs.

		TPP_1	TPP_2	Unit	Formula
A	Biomass (dry base)*	264	241	t/day	
B	Inerts fed with biomass**	0.12	0.12	%	
C	Inerts fed with biomass (dry base)**	31.7	29.0	t/day	A*B
D	Biomass ash content (Loss on 550ºC - dry base)	4.1	5.8	%	
E	Biomass ash content (Loss on 550ºC - dry base)	10.8	14.0	t/day	(A*D)/100
F	Mass of fresh bed sand input (dry base)*	2.6	4.4	t/day	
G	BBW - Discharge (dry base)*	20.9	17.6	t/day	
H	BBW useful fraction (0.3-1.0 mm)**	59.5	59.2	%	
I	BBW useful fraction (0.3-1.0 mm)	12.4	10.4	t/day	(H*G)/100
J	FA - Discharge (dry base)*	20.5	29.8	t/day	
L	FA - Discharge (dry base)**	24.2	29.7	t/day	(C+E+F)-G
M	Landfill (dry base)*	32		€/t	
N	FBS unitary costs (dry base)*	28		€/t	
O	TPP Operating period	330		days/year	
Costs before solution					
P	BBW Landfill (dry base)*	220800	186202	€/year	G*M*O
Q	FBS aquisition (dry base)*	23864	40476	€/year	F*P*O
R	Subtotal	244664	226678	€/year	P+Q
S	Total	471342		€/year	
Costs and savings after solution					
T	BBW useful fraction for FSB total substitution (dry base)	23947	40616	€/year	[(F*M)+(F*N)]*O
U	BBW useful fraction for storage (dry base)***	104163	63912	€/year	(I-F)*M*O
V	BBW Landfill unusufull fraction (~ 40% of "G") (dry base)*	89363	76031	€/year	(G-I)*M*O
X	Total savings	232639		€/year	T+U

* Industry data

** Estimated values based on bench tests and Industry values

*** Estimated value (The costs related with storage must be reduced for this value and added to "V")

8.4 Conclusions

Some conclusions based on the present work about the use of a fraction of sand particles from the bottom bed ash discharged from fluidized bed combustion of biomass can be made:

1 - Bottom bed wastes (BBW) produced during biomass combustion in fluidized bed combustors are mostly composed by quartz, and this is related with the characteristics of

the sand used as original bed in the BFBC, and other components that came from biomass contaminants (forest soil particles) and inorganic content of biomass (ash).

2 - The characterization of the BBW from two different biomass thermal power plants not only demonstrated the influence of the inorganic content of the biomass in the BBW chemical and mineralogical properties when compared with the original sand bed, but also emphasized the strong influence of the original bed sand in those properties, mainly in terms of quartz amount.

3 - Combustion experiments in a pilot-scale BFBC proved the potential of using RBBA as raw material in substitution of fresh sand for bed make-up in BFBC.

4 - Cost-benefit analysis could help to enlight the industry about the importance of using a fraction of the sand present in this waste as raw material, leading not only to the decrease of costs related with landfilling, but also saving costs with raw fresh bed sand acquisition, both important for the efficient use of resources.

ACKNOWLEDGEMENT

The authors acknowledge Foundation for Science and Technology (FCT – Portugal) for the financial support (SFRH/BD/75182/2010 – PhD Grant, and the Projects PTDC/AAC-AMB/098112/2008 - Bias-to-soil - biomass ash: characteristics in relation to its origin, treatment and application to soil, and PTDC/AAC-AMB/ 116568/2010 - BiomAshTech - Ash impacts during thermo-chemical conversion of biomass).

9 PRACTICAL IMPLEMENTATION OF WASTE MANAGEMENT SOLUTIONS STUDIED: VIABILITY AND LIMITATIONS

9.1 Wastes amounts and tested solutions

This chapter exemplifies and discusses some important aspects related to the valorization solutions tested mainly in terms of wastes generated amount, conventional raw-materials consumption, industrial process operations viability and limitations. The amount of wastes generated is referred to a ton of processed pulp. Table 9.1 presents the amount of some solid wastes generated in the pulp mill during 2012 year based on 330 working days in Portugal. Fly ash from biomass combustion was not studied in this thesis work, but its generated amount is also presented.

Table 9. 1. Amount of wastes generated in Kraft mill based on pulp ton processed.

Wastes	Production (kg dry basis/pulp ton)(1)	Moisture (%)	t/year (dry basis)(2)
Dregs	12	40	30000
Grits	7	30	17500
Fly ash	20	0	50000
Primary sludge	10	74	25000
Lime mud(3)	15	34	6750
Bottom ash	12	0.7	28750

(1) Data supplied by industry

(2) Considering 2012 total pulp Portuguese production of approximately $2.5*10^6$ tons (CELPA, 2012)

(3) Considering one factory which the pulp production is around 400 thousand tons per year

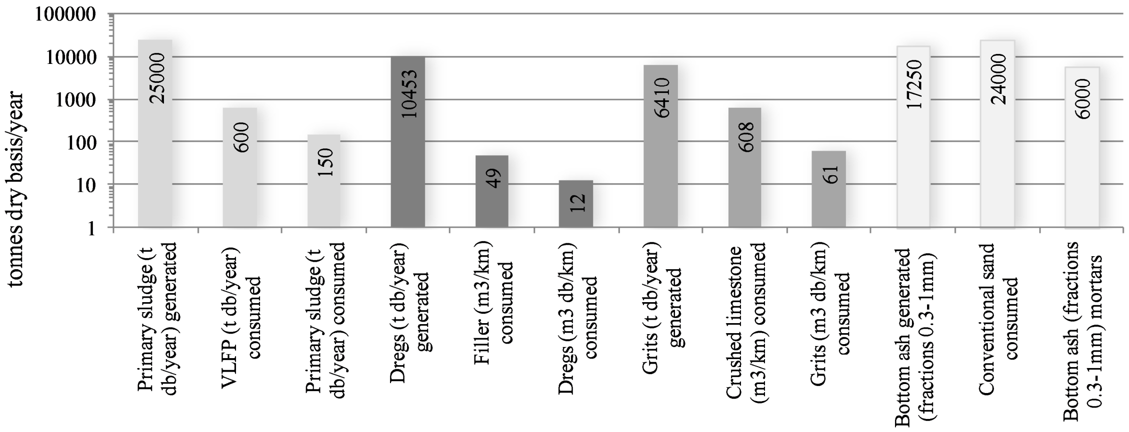


Figure 9. 1. Estimation of wastes amount generation, conventional material consumption and wastes potential consumption in the applications studied.

The estimated amount of wastes generated by Portuguese pulp and paper industry was based on $2.5*10^6$ tonnes of pulp, and the ratio of wastes produced by ton of pulp is shown on table 9.1. This estimative and respective recycling capacity is presented in Figure 9.1 and discussed in the section 9.2.

Considering the developed study-cases in this thesis, it was possible to summarize the solutions discussed in section 9.2 for the waste material valorization.

9.2 Material valorization solutions

9.2.1 Fiber-cement (Chapter 3)

Virgin long fiber pulp (VLFP) represents 2.6% of total fiber-cement composition in proportion of dry raw materials. Conventionally the used fiber in fiber-cement production is from softwood (*Pinus*). In this work, these softwood long fibers were replaced by hardwood fibers existing in the primary sludge (PS) that is generated in pulp and paper mill effluent treatment; the fixed replacement level studied was 25%. The primary sludge composition includes around ~70% hardwood fibers and fillers (~5% sand and 25% precipitated calcium carbonate), as already referred on chapter 3. Figure 9.1 presents the absorption/consuming flow of the fiber-cement application.

It is important to consider the following aspects related not only with the waste characteristics but also with the process itself:

- Sludge transportation and storage

The specific characteristics of PS, namely its high moisture content and odour, lead to special care in terms of transportation and storage. First, PS needs to be transported in big bags which will facilitate its weight measurement before being introduced into refinement tank for beating. After, these big bags can easily be storage in a place where they don’t disturb workers due to its unpleasant smell. It is also important to consider the storage time which will depend on the weather and storage conditions, trying to avoid PS decomposition and consequent loss of quality.

- Energy - Sludge disintegration (beating process)

The *Eucalyptus* fibers achieve the same Schopper Riegler degree consuming less energy comparing to *Pinus* fibers. Lower refinement time represents low energy consumption compared to the standard process containing only virgin pulp composed of long fibers. A

30% time saving was estimated during the industrial test procedure, consequently, leading to costs reduction.

- Water quality control (total suspended solids and dissolved salts)

The VLFP represents 2.6% of dry material in fiber-cement production. 25% of this amount can be substituted by primary sludge. Knowing that 40% of primary sludge is composed by inorganic material, the amount of suspended solids introduced by the sludge is estimated in 26 kg per ton of dried fiber-cement produced. This solids might be retained on fiber-cement sheets or drained to the process water together conventional solids. This fact can lead to two opposite aspects, a positive and a negative one. The positive aspect is related to the fiber-cement sheet density increase that was evaluated as appropriated in the final product specification. The negative one is related with the cumulative discharge of solid matter presented in the waste composition, in the water process. This fact might deserve more frequent monitorization of the water in order to avoid problems as vats obstruction and/or corrosion of equipment and consequently improvement of maintenance costs. General costs associated with this waste management solution were shown on Chapter 3.

9.2.2 Bituminous mixtures (Chapter 4)

The amount of aggregates in a bituminous mixture represents between 90 to 95% in mass and 70 to 75% in volume [Pereira e Santos, 2002]. It was estimated that the amount of crushed limestone and filler (represents around 50%wt of 4%wt total aggregates, respectively) consumed per one kilometre of dense bituminous layer - with 6 cm of thickness (DBL) from a highway with 27 meters width. Assuming those figures, the amount of grits and dregs used as replacement of the primary components can be estimated. The substitution of 5%wt of crushed limestone by grits represents to save 10% of that conventional material extracted. The construction of at least 200 kilometres of DBL is necessary to incorporate all grits generated per year. In case of dregs, replacing 1% of the filler represents to avoid more than 25% of this conventional material extraction.

However, not only the saving of non-renewable materials extraction makes part of this recycling option and other aspects must be considered and researched in order to improve this solution, including both environment and industrial issues.

For instance, two wastes characteristics, moisture and soluble salts content are examples of these aspects to be assessed. The need for drying is one of the most relevant issues, due to energy demand and cost. Dregs and grits have high moisture content (~50% and 40%, respectively) requiring proper pre-drying before composing the bituminous mixture. Additionally, dregs require a washing treatment to reduce the level of soluble salts. According to experimental indications given in chapter 5, a minimum of 10 tons of hot water (~80ºC) per ton of dregs is required to reach an acceptable level of soluble salts in their composition, allowing then their use in bituminous mixtures. In addition, the wastewater from the washing process should be properly treated before discharge in the environment, and this enhances costs.

9.2.3 Industrial Mortars (Chapters 6 and 7)

Two types of industrial mortars were analyzed in this work, namely renders and cementitious-adhesive formulations. In both products, the used of conventional calibrated sand was replaced by treated bottom ash generated in a bubbling fluidized bed combustor using forest residues as fuel. In general, these applications seemed to be technologically feasible. The substitution did not induce negative impact on the relevant properties and formulations accomplish with the industry required specifications. However, the waste treatment (sieving to remove coarse and fine particles and/or washing to diminish soluble salts content) before utilization seems to be needed in order to guarantee the success of this solution.

Figure 9.2 presents the estimation of the amounts of bottom ash with interest for this specific application in terms of conventional sand replacement, bottom ash generated amount and bottom ash surplus; it is also shown the amount of conventional sand consumed. According to the results presented and discussed in detail on chapters 6 and 7 it is possible to replace over 50%wt of conventional calibrated sand by a fraction of bottom ash without compromising the final products quality. In order to improve this waste management solution, it is important to consider aspects related with the waste characteristics and to the process itself.

According to industry data (value supplied by one factory) at least 24000 tonnes of calibrated sand has been consumed every year. They are generated around 28750 tonnes of raw bottom ash per year in which 60% (~17250t) is useful for being utilized as aggregate in these types of mortars. For example, if consider 25% (value tested in bench scale) of conventional calibrated sand replacement by treated (just sieved) bottom ash, it has been verified that at least 6000 tonnes of this waste (fractions between 0.3 – 1.00 mm) would be valorized (Figure 9.2). The treated bottom ash surplus (~11250t) could be used in other applications i.e. its reuse in as raw material as substitute of fresh sand for bottom bed make up in fluidized bed combustors where it is generated (see Chapter 8).

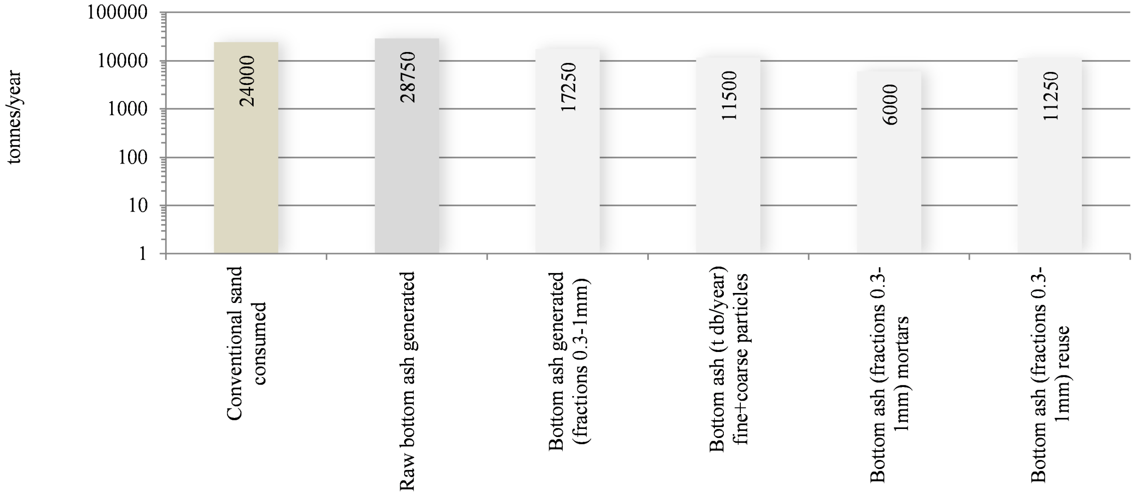


Figure 9. 2. Estimated amount of total bottom ash generated, bottom ash fraction with interest for industrial mortars, conventional sand consumption and bottom ash surplus.

9.3 Concluding remarks

The involved partners will have to be aware about the advantages and concerns related with the above referred processes of waste valorization. In case of the waste producer, by avoiding landfilling it contributes to environment protection; and also economic costs related with to this waste management option are saved. Part of the savings related to the avoiding of waste landfilling can be used by the waste producer to transport and deliver the waste to the unit where its pre-treatment will be performed. In case of the unit that treats the waste to sell or to valorize it, if he receives the waste on its location, the economic benefits are higher considering that he gets an additional product to be treated and commercialized without raw material acquisition. However, the need for investment will depend on the industrial unit where the waste will be treated, as for, place to storage the waste, the need for specific sieving, liquid effluent treatment and monitoring and this will influence the costs of the recycling operation. At least, the benefit in terms of decreased costs related to conventional sand acquisition will avoid the extraction of the natural resource thus contributing to environmental protection, and sustainability of process.

The success of those recycling solutions will depend on how the intervenient have capacity to integrate the operations and to minimize the related costs with the whole process.

10 CONCLUSION AND FUTURE WORKS

10.1 Conclusions

The design of correct waste management plans could avoid the landfilling of several by-products/wastes and, if recycling alternatives are searched, the consumption of primary non-renewable resources will diminish. Impacts associated to their extraction and treatment will be avoided. However, to fully accomplish with environmental and technical aspects of each recycling solution, multidisciplinary issues must be considered.

Novel recycling alternatives for several wastes generated by the pulp and paper industries were defined in this work, as is summarized in this chapter.

Fiber-cement composites can be produced with 25% of primary sludge in substitution of conventional cellulose long fibers without affecting the required properties of the material or the productive process. The controlled parameters of the processing water, such as COD, chlorides, sulphates, dissolved salts and metals of process water are acceptable when compared with the conventional process. The mechanical and physical properties of the sludge-containing composites were improved. Fiber-cement sheets with primary sludge achieved a bending moment higher than conventional ones (5267 N and 4695 N, respectively) and a load at rupture was also higher and acceptable according to the final product quality control.

Grits could easily be used as aggregates in dense bituminous mixtures for regularization layers of road pavements. Physical and mechanical properties that define the stability of the material are suitable. This waste is compatible with natural crushed stone normally used as aggregate for similar applications. By contrast, the use of dregs in the same application requires pre-treatment operations, namely washing to remove soluble salts, and then further studies are required to prescribe a better way to treat/adapt this waste (cost effective). The soluble salts influence is clearly demonstrated when mixes MBDC1%, MBG5% and MBG10% presented a good behaviour in terms of conserved strength (up to 75%), but formulations with more than 2%wt of dregs (MBDC2%, MBDC3% and MBDC4%) presented water sensitivity. After dregs washing, the tests showed that it is possible to obtain a very good performance of formulations with until 4%wt of filler replacing by dregs in terms of conserved strength, even with voids content lower than the allowed value. This problem could be easily solved by a particle size adjustment of the aggregate. The problem with water sensitivity had been solved with the washing procedure.

Precipitated calcium carbonate ($CaCO_3$) mud is an avoidable by-product when the industrial unit is working properly, since it might be reused and fully consumed in the lime kiln to regenerate the causticizing agent for the regeneration of digestion liquor. If available, as occurred during this work, its properties are compatible with those of primary/natural calcium carbonate and it might be used in cement-based products, like mortars. The ones prepared and characterized is this thesis show technological properties that fulfill the standard requirements. Specifically in terms of bulk, the filler effect is obvious, whereby mortar densifies up to an optimum value situated between 10 and 20% of LM amount. LM formulations presented compressive strength values between 22 and 23 MPa at 90 days of curing while reference presented similar results. In general, their characteristics are similar to the ones of current industrial formulations and preparation conditions are also not much affected. The high moisture content of the mud is the main drawback, in terms of transportation for a potential mortar producer. Viable ways to minimize it should be search.

The bottom ash generated in bubbling fluidized bed combustors used to burn the biomass wastes was here studied in two distinct directions: (i) recycling in rendering or adhesive mortar formulations, as sand substitute (used as aggregate); (ii) reuse in regenerated beds for further combustion steps.

For using in mortar formulations the as-collected ash shows suitable particle size distribution but the high chlorides content deserve control and the potential use of cleaning treatment. The simple washing process tested in industrial-scale trials revealed to be effective in reducing the amount (by about 60%) of soluble chlorides in the ash. Once treated (sieved), the increasing amount of bottom ash as sand substitute for both products, rendering-mortars and cementitious-adhesive mortars. In case of rendering-mortars, been ash particles relatively smaller than conventional sand replaced, the thicker mixes had as consequence, the flowability of ash-containing mixes decreased. Anyway differences were minor and can easily adjustable if required.

The tensile adhesion strength at 28 days of curing in standard conditions incresed at about 23% (sample with 100% of substitution) when compared with reference (sample without BA). A considerable increase of wetting capability and transference values was observed, probably associated with the homogeneous particle size distribution of BA and with the roughness of its surface. These BA characteristics might explain this increase. Indeed, less finer particles demanding less water retard skin formation, leading to better transference capability.

Considering the relevance of the bottom ash characteristics on its application in the recycling processes studied here, the monitoring of bottom ash characteristics in a biomass thermal power plant confirms that significant variations can occur along the year, namelly in terms of chemical elements composition. The chemical element present in higher concentration (oxygen is not considered) in the bottom ashes is Si. The amount of Si, expressed as SiO_2, varied from 79 wt% to 91wt%. The high concentration of Si is related with the natural (mostly quartz) sand (>98.5wt% SiO_2) used as original bottom bed in the BFBC. Considering the relatively high content of inert material (forest soil particles and small stones) fed mixed with the biomass, it is expected also that the bottom ash composition is influenced by the composition of that inert material. The bottom bed ashes are also enriched in chemical elements that can be found in the inorganic fraction of biomass, when compared to the original sand bed. That enrichment is noticed also as a coating layer around the sand particles of the bed. It was observed that the coating layer around the sand particles was not completely removed by water leaching, although a decrease on the coating layer thickness occurred after industrial treatment (for example, by leaching) of bottom ash particles. The presence of Na and Ca in the coating layer is responsible for the formation of a glassy phase that promotes the agglomeration even at relatively low bed operation temperature (around 870ºC). Attempting to reuse a fraction of the discharged bottom bed sand from the fluidized bed combustor for bed make-up, the content of fluxing elements such as Ca, Na and K must be carefully controlled, in order to avoid potential agglomeration.

Regarding the environmental aspects related with the industrial solid wastes valorization, this work contributes with results about several possibilities of recycling these wastes as substitute of some raw natural minerals in industrial applications. The wastes intensive characterization contributes to industry and research giving important information about potential raw materials, the tested applications and results obtained from produced and tested formulations demonstrated that it seems to be possible to obtain final products with similar characteristics of conventional products. These solutions could avoid a significant decrease on wastes landfilling and consequently its recycling could contribute to decrease the extraction of non-renewable resources as it is the case of some minerals.

10.2 Future works

As proposals for future works it would be interesting to design integrated treatment stations in the paper and pulp industries, attempting to optimize washing, sieving and drying operations eventually required to adapt certain wastes for future valorization. This solution is a step forward in comparison to the existing waste treatment facilities that basically involve the wastewater treatment before safety discharge. Moreover, such industrial units normally have heat and power available for the requirements of some of the novel operation. This concept of circular processes will contribute to fastly achieve sustainable indicators that are associated to near zero-waste production. As examples, the washing of dregs and bottom ash might be, at least partially, conducted by the treated water that is now discharged. Drying of dregs and primary sludge should use the wasted heat generated by biomass burning.

All the applications suggested for wastes recycling still deserve assessment of durability issues, due to the punctual character and temporal limitations of runned tests. In particular, formation of efflorescence and other chemical-related pathology should be carefully checked.

Development of a systematic assessment of the environmental consequences associated with the tested wastes. This study should involve the quantification and analysis of environmental balances (gains and losses) associated with them. Through this evaluation it is important to quantify the most relevant environmental discharges involved in all stages of life cycle of this ash, from origin, transport, use, and disposal. It would be assessed valuation of the waste solutions for comparative analysis with the current destination. To achieve the above would be essential to select the tool to perform the LCA (Life Cycle Analysis), and analysis of the benefits and limitations of the chosen methodology.

An economic analysis about the waste management solutions here tested could be also remarkable considering the industry potential interest.

REFERENCES

Ahmadi B, Al-Khaja W. Utilization of paper waste sludge in the building construction industry. Resour.Conser. Rec.32 [2] (2001),105–113. http://dx.doi.org/10.1016/S0921-3449(01)00051-9.

Ahmaruzzaman M. A review on the utilization of fly ash. Progress in Energy and Combustion Science 36 (2010) 327-363.

Aho M, Gil A, Taipale R, Vainikka P, Vesala H. A pilot-scale fireside deposit study of co-firing Cynara with two coals in a fluidized bed. Fuel 87 (2008) 58–69.

AIFF. Relatório de caracterização da fileira florestal 2010. Portugal, 2010.

Akbulut H, Gürer G. Use of aggregates produced from marble quarry waste in asphalt pavements. Building and Environment 42 (2007) 1921-1930.

Akers SAS, Studinka JB, Meier P, Dobb MG, Johnson DJ, Hikasa J. Long term durability of PVA reinforcing fibers in a cement matrix. International Journal of Cement Composites and Lightweight Concrete, 11 (1989) 79-91.

Ali MB, Saidur R, Hossain MS. A review on emission analysis in cement industries. Renew Sustain Energy Rev 15 (2011) 2252–61.

Alonso S, Palomo A. Alkaline activation of metakaolin–calcium hydroxide solid mixtures: Influence of temperature, activator concentration and metakaolin/$Ca(OH)_2$ ratio. Mater Lett 47 (2001) 55–62.

Åmand L-E, Leckner B. Metal emissions from co-combustion of sewage sludge and coal/wood in fluidized bed. Fuel 83 (2004) 1803-1821.

Ampadu OK, Torii K. Chloride ingress and steel corrosion in cement mortars incorporation low-quality fly ashes. Cemenet and Concrete Research 32 (2002) 893-901.

Andiç O, Ramyar K, Korkut Ö. Effect of fly ash addition on the mechanical properties of tile adhesive. Construction and Building Materials 19 (2005) 564-569.

Andrade LB, Rocha JC, Cheriaf M. Influence of coal bottom ash as fine aggregate on fresh properties of concrete. Construction and Building Materials 23 [2] (2009) 609–614.

Antão, A. Caracterização de materiais calcários. Aplicação à pedreira de Sangardão. Universidade Coimbra, 1994. Tese de Mestrado.

APREN. Roteiro Nacional das Energias Renovaveis - Aplicacao da Directiva 2009/28/CE. Portugal 2010.

Argiz C, Menéndez E, Sanjuán MA. Effect of mixes made of coal bottom ash and fly ash on the mechanical strength and porosity of Portland cement Mater. Construcc. 63 [309] (2013) 49-64. http://dx.doi.org/10.3989/mc.2013.03911.

Atahan HN, Oktar O, Tasdemir MA. Effects of water–cement ratio and curing time on the critical pore width of hardened cement paste. Construction & Building Materials 23 [3] (2009) 1196–200.

Atahan HN, Oktar O, Tasdemir MA. Factors determining the correlations between high strength concrete properties. Construction & Building Materials 25 [3] (2011) 2214-2222.

Atakül H, Hilmioğlu B, Ekinci E. The relationship between the tendency of lignites to agglomerate and their fusion characteristics in a fluidized bed combustor. Fuel Processing Technology 86 (2005) 1369–1383.

Ban CC, Ramli M. The implementation of wood waste ash as a partial cement replacement material in the production of structural grade concrete and mortar: an overview. Resource Conservation and Recycling 55 (2011) 669–685.

Banfill PFG. The rheology of fresh cement and concrete – a review, Proc. of 11th Intern. Congr. Chem. Cem. (2003) 50–62.

Barnett H, Morse C. Scarcity and growth: Baltimore, Johns Hopkins Press, Resources for The Future (1963).

Bartels, B., Lin, W., Nijenhuis, J., Kapteijn, F., Ommen, R. Agglomeration in fluidized beds at high temperatures: Mechanisms, detection and prevention, Progress in Energy and Combustion Science 34 (2008) 633-66.

Bédérina M, Khenfer MM, Dheilly RM, Quéneudec M. Reuse of local sand: effect of limestone filler proportion on the rheological and mechanical properties of different sand concretes. Cement and Concrete Research 35 [6] (2005) 1172–1179.

Beers van D, Bossilkov A, Lund C. Development of large scale reuses of inorganic by-products in Australia: The case study of Kwinana, Western Autralia. Resources Conservation and Recycling Journal 53 (2009) 365-378.

Benachour Y, Davy CA, Skoczylas F, Houari H. Effect of a high calcite filler addition upon microstructural, mechanical, shrinkage and transport properties of a mortar. Cement and Concrete Research 38 (2008) 727–736.

Bentz DP, Haecker CJ, Peltz MA, Snyder KA. X-ray absorption studies of drying of cementitious tile adhesive mortars. Cement and Concrete Composites 30 (2008) 361-373.

Bhattacharjee U, Kandpal TC. Potencial of fly ash utilization in India. Energy 27 (2002) 151-166.

Binici H, Shah T, Aksogan O, Kaplan H. Durability of concrete made with granite and marble as recycle aggregates. Journal of Materials Processing Technology 208 (2008) 299-308. http://dx.doi.org/10.1016/j.jmatprotec.2007.12.120

Bleischwitz R, Bahn-Walkowiak B. Aggregates and construction markets in Europe: Towards a sectoral action plan on sustainable resource management. Minerals and Energy 22 (2007) 159-176.

Bleischwitz R, Bahn-Walkowiak, B. Sustainable developed in European aggregate industry – A case for sectoral strategies. Wupertal Institute for Climate, Environment and Energy, Germany 2006. ISBN 978-1-4398-0130-7.

Brunauer S, Emmet PH, Teller E. Adsorption of Gases in Multimolecular Layers. Journal of the American Chemical Society 60 [2] (1938) 309-319. ISSN 0002-7863.

Bühler TH, Zurbriggen R, Pieles U, Huwiler L, Raso RA. Dynamics of early skin formation of tiling mortars investigated by microscopy and diffuse reflectance infrared Fourier transformed spectroscopy. Cement and Concrete Composites 37 (2013) 161-170.

Cabral F, Vasconcelos E, Goss M, Cordovil C. The value, use, and environmental impacts of pulp-mill sludge addition to forest and agricultural lands in Europe. Environmental Reviews 6 (1998) 55–64.

Celpa. Indústria Papeleira Portuguesa. Boletim Estatístico, Ed. Associação da Indústria Papeleira 2008, Lisboa.

Cernec F, Zule J, Moze A, Ivanu A. Chemical and microbiological stability of waste sludge from paper industry intended for brick production. Waste Management and Research 23 (2005) 106–112. http://doi.10.1177/0734242X07079188

Cernec F, Zule J. Chemical stability of papermill sludges. COST Action E26. Effective solutions to reduce the impact of waste arisings from papermaking. In: Workshop on Solid Waste Management in the Papermaking Prevention, Creation of New Products and Energy Recovery, Milan, 2005.

Cheah CB, Ramli M. Mechanical strength, durability and drying shrinkage of structural mortar containing HCWA as partial replacement of cement. Construction and Building Materials 30 (2012) 320-329.

Cheerarot R, Jaturapitakkul C. A study of disposed fly ash from landfill to replace Portland cement. Waste Management 24 (2004) 701-709.

Chew MYL, Factors affecting ceramic tile adhesion for external cladding. Construction and Building Materials 13 (1999) 293-296.

Cicek T, Tanriverdi M. Lime based steam autoclaved fly ash bricks. Construction and Building Material 21 (2007) 1295–300.

Cioffi R, Colangelo F, Montagnaro F, Santoro L. Manufacture of artificial aggregate using MSWI bottom ash. Waste Management 31 (2011) 281–288.

Coelho AMSL. (2010) Gestão de cinzas produzidas em centrais de cogeração operadas com biomassa. Dissertação de Mestrado, Universidade de Aveiro, Portugal.

Cordeiro GC, Toledo Filho RD, Tavares LM, Fairbairn EMR. Pozzolanic activity and filler effect of sugar cane bagasse ash in Portland cement and lime mortars. Cement and Concrete Composites 30 [5] (2008) 410-418.

Coutinho JS, Garcia ML. Investigação inicial de resíduos da indústria de pasta de papel. In Inovação na Construção Sustentável. Ed. Plataforma para a Construção Sustentável 1 173 – 184, 2008. ISBN 978-989-95978-0-8.

Coutts Robert SP, Kightly P. Bonding in wood fiber cement composites. Journal of Materials Science 19 (1984) 335-339.

Coutts Robert SP. A review of Australian research into natural fiber-cement composites. Cement and Concrete Composites 27 (2005) 518-526.

Dahl O, Nurmesniemi H, Pöykiö R, Watkins G. Comparison of the characteristics of bottom ash and fly ash from a medium-size (32MW) municipal district heating plant incinerating forest residues and peat in fluidised-bed boiler. Fuel Processing Technology 90 (2009) 871-878.

Dahl O, Nurmesniemi H, Poykio R, Watkins G. Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values. Fuel Processing Technology 91 (2010) 1634-1639.

Dahl O, Nurmesniemi H, Pöykiö R, Watkins G. Heavy metal concentrations in bottom ash and fly ash from a large-sized (246MW) fluidised bed boiler with respect to their Finnish forest fertilizer limit values. Fuel Processing Technology 91 (2010) 1634-1639.

Davis ML, Cornweel DA. Introduction to Environmental Engineering. Third ed. WCB, McGraw-Hill, 1998.

Dayton DC, Jenkins BM, Turn SQ, Bakker RR, Williams R B, Belle-Oudry D, et al. Release of inorganic constituents from leached biomass during thermal conversion. Energy and Fuels 13 (1999) 860–870.

Decree n.º 209/2004. Portuguese legislation about the European list of wastes in accordance with Commission Decision 2000/532/EC of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.

Decree-Law 152/2002 – Solid wastes. Landfills classification – Portuguese Legislation (*in Portuguese*).

Decree-Law 183/2009 - Solid wastes landfilling – Portuguese Legislation (*in Portuguese*).

Demir I, Baspınara MS, Orhanb M. Utilization of kraft pulp production residues in clay brick production. Building and Environment 40 (2005) 1533-1537.

Demirbas A. A discussion of the paper ‘‘Influence of natural pozzolan, colemanite ore waste, bottom ash, and fly ash on the properties of Portland cement’’ by Targan S.¸ Olgun A., Erdogan, Y., and Sevinc, V. Cement and Concrete Research 34 (2004) 1949–1950.

Demirbas A. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues, Progress in Energy and Combustion Science 31 (2005) 171–192. DGEG. Renovaveis - Estatisticas Rapidas 2013, http://www.dgeg.pt/ 2013, accessed December 2013.

Edvardsson E, Amand LE, Thunman H, Leckner B, Johnsson F. Measuring the External Solids Flux in a CFB boiler. In: Proceedings of the 19th International Conference on Fluidized Bed Combustion, Vienna, Austria, 2006.

Elled AL, Amand LE, Steenari B-M. Composition of agglomerates in fluidized bed reactors for thermochemical conversion of biomass and waste fuels, Experimental data in comparison with predictions by a thermodynamic equilibrium model. Fuel 111 (2013) 696-708.

EN 1015-10: 1999. Methods of test for mortar for masonry – Part 10: Determination of dry bulk density of hardened mortar.

EN 1015-11: 1999. Methods of test for mortar for masonry – Part 11: Determination of flexural and compressive strength of hardened mortar.

EN 1015-18: 2002. Methods of test for mortar for masonry. Water absorption by capillary.

EN 1015-2:1998. Methods of test for mortar for masonry Part 2: Bulk sampling of mortars and preparation of test mortars.

EN 1015-3:2007. Methods of test for mortar for masonry: determination of consistence of fresh mortar (by flow table).

EN 12004: 1999. Adhesives for tiles definitions and specifications. CEN, European standards.

EN 12176:1998 - Characterization of sludge. Determination of pH value - Sludge, Sewage, pH measurement, Water testing, Control samples, Test equipment, Test specimens, Specimen preparation, Safety measures.

EN 12880:2000 - Chemical Analyses. Determination of dry matter and water content on a mass basis in sediment, sludge, soil, and waste – Gravimetric method.

EN 1308: 2007. Adhesives for tiles - Determination of slip.

EN 13139: 2003. Aggregates for Mortars.

EN 1346: 1999. Adhesives for tiles - Tensile adhesion strength for tiles with open time. CEN, European standards.

EN 1347: 2007. Adhesives for tiles – Determination of wetting capability. CEN, European standards.

EN 1348: 2007. Adhesives for tiles – Tensile adhesion strength for tiles. CEN, European standards.

EN 14405:2004. Technical Specification - Characterization of waste - Leaching behaviour tests - Up-flow percolation test (under specified conditions).

EN 933-1: 2000. Tests for geometrical properties of aggregates, Part 1: Determination of particle size distribution.

EN 998-2: 2003 (E). Specific for mortar for mansonry. Part 2: Mansonry mortar.

EPA 2000. Pulp and Paper Combustion Sources National Emission Standards for Hazardous Air Pollutants: A Plain English Description. United States Environmental Protection Agency. EPA-456/R-01-003.September 2001.

EPA 2009. Technical Support Document for the Pulp and Paper Sector: Proposed Rule for Mandatory Reporting of Greenhouse Gases. Office of Air and Radiation, United States Environmental Protection Agency. February 2009.

Eroğlu H, Acar Uçüncü HH, İmamoğlu O. Soil stabilization of roads sub-base using lime-mud waste from the chemical recovery process in alkaline pulp mill. Journal of Applied Science 6 [5] (2006) 1199-1203. ISSN 1812-5654.

Eroğlu H, Acar Uçüncü HH, İmamoğlu O. The effect of dry sludge addition supplied from pulp mill on the compressive strength of cement. Journal of the University of Chemical Technology and Metallurgy 42 [2] (2007) 169-174.

Esteves TC, Rajamma R, Soares D, Silva AS, Ferreira VM, Labrincha JA. Use of fly ash for mitigation of alkali-silica reaction of cement mortars. Construction and Building Materials 26 (2012) 687-693.

Etiegni L.Wood ash recycling and land disposal. Department of Forest Products, University of Idaho at Moscow, Idaho, USA, 1990. PhD thesis.

Felekoglu B. Utilisation of high volumes of limestone quarry wastes in concrete industry (self-compacting concrete case). Resources Conservation and Recycling 51 [4] (2007) 770-791. http://dx.doi.org/10.1016/j.resconrec.2006.12.004.

Ferraris CF, Brower L, Ozyıldırım C, Daczko J. Workability of self-compacting concrete. In: Intern. Symp. High Perform. Concr. Proceedings. Florida: National Institute of Standards and Technology (2000) 398–407.

Ferraris CF, Hackley VA, Aviles AI. Measurement of particle size distribution in Portland cement powder: Analysis of ASTM round robin studies. Cement Concrete and Aggregates 26 [2] (2004) 71-81. ISSN 0149-6123.

Ferraris M, Salvo M, Ventrella A, Buzzi L, Veglia M. Use of vitrified MSWI bottom ashes for concrete production. Waste Management 29 (2009) 1041–1047.

Flatt RJ, Roussel N, Cheesenman CR. Concrete: an ecomaterial that needs to be improved. J Eur Ceram Soc 32 (2012) 2787–98.

Forteza R, Far M, Segu C, Cerd V. Characterization of bottom ash in municipal solid waste incinerators for its use in road base, Waste Management 24 (2004) 899–909.

Frederico LM, Chidiac SE. Waste glass as a supplementary cementitious material in concrete – critical review of treatment methods. Cement Concrete and Composites 31 (2009) 606–610.

Fujimori E, Minamoto K, Iwata S, Chiba K, Haraguchi H. Enrichment of elements in industrial waste incineration bottom ashes obtained from three different types of incinerators as studied by ICP- AES and ICP-MS. Journal of Material Cycles and Waste Management 6 (2004) 73–79.

Garcia ML, Coutinho JS. Strength and durability of cement with forest waste bottom ash. Constr Build Mater 41 (2013) 897–910.

Gaskin, J. Land application of pulp mill lime mud. University of Georgia, College of Agriculture and Environmental Sciences, Cooperative Extension Service along with the Pollution Prevention Assistance Division. Bulletin 1249, Georgia, USA, 2004.

GeGerven T. Van, Geysen D, Stoffels L, Jaspers M, Wauters G, Vandecasteele C. Management of incinerator residues in Flanders (Belgium) and in neighboring countries. A comparison. Waste Management 25 (2005) 75–87.

Gjorv, OE. High strength concrete. In Malhotra VM editor. Advances in concrete Institute Montreal Canada (1992) 21-77.

Gomes CF. Raios X no estudo de materiais, Universidade de Aveiro, 1979.

Harila P, Kivilinna VA. Biosludge incineration in a recovery boiler. Water Science and Technology 40 (1999) 195–200.

Hassani A, Ganjidoust H, Maghanaki AA. Use of plastic waste (poly-ethylene terephthalate) in asphalt concrete mixture as aggregate replacement. Waste Management & Research 23 (2005) 322-327.

Henglein A. Q-particles: Size quantization effects in colloidal semiconductors. In: HOFFMANN, H. - New Trends in Colloid Science. Springer Berlin/Heidelberg, 1-3, 1987.

Hoffman D. Allert aux pilleurs de sable. Magazine Du Vendredi, 23 Août (2013) 52-57.

Horizon 2020., 2014. http://www.h2020.net/en/the-h2020-initiative.html.
http://dx.doi.org/10.1016/j.cemconres.2008.02.007.

http://dx.doi.org/10.1016/S0008-8846(02)00721-4
http://dx.doi.org/10.3989/mc.2014.06312.

http://www.epa.gov/ttn/atw/pulp/chapters1-6pdf.zip

Huang C, Yang W, Song Y. The potential of recycling and reusing municipal solid waste incinerator ash in Taiwan. Waste Management 26 (2006) 979–987.

Huang Y, Bird N, Heidrich RO. A review of the use of recycled solid waste materials in asphalt pavements. Resources, Conservation and Recycling 52 (2007) 58-73.

Huet RJ. Disposal of primary paper mill sludge on sandy cropland soil. University of Wisconsin, Madison, 1982. PhD. Thesis.

IPPC - Integrated Pollution Prevention and Control. Reference Document on Best Available Techniques in the Pulp and Paper Industry, European Commission, December 2001.

ISO 5267-1: 1999. Pulps - Determination of drainability - Part 1: Schopper-Riegler method. This standard specifies a method for the determination of the drainability of a pulp suspension in water in terms of the Schopper-Riegler (SR) number.

ISO/TS 17892-3: 2004. Geotechnical investigation and testing laboratory testing of soil. Determination of particle density – Pycnometer method.

IZF Seminar. Brick making raw materials - properties, treatment, product quality, Part 1. Ziegelindustrie International 2 [11] (1994) 779–790.

Izquierdo M, Querol X. Leaching behaviour of elements from coal combustion fly ash: an overview. International Journal of Coal Geology 94 (2012) 54–66.

Jackson MN, Schultz S, Sander P, Schopp L. Beneficial use of CFB ash in pavement construction applications. Fuel Journal 88 (2009) 1210-1215.

Jenni A, Holzer L, Zurbriggen R, Herwegh M. Influence of polymers on microstructure and adhesive strength of cementitious tile adhesive mortars. Cement and Concrete Research 35 (2005) 35 – 50.

Jenni A, Zurbriggen R, Holzer L, Herwegh M. Changes in microstructures and physical properties of polymer-modified mortars during wet storage. Cement and Concrete Research 36 (2006) 79 – 90.

Jennings HM, Xi Y. In Creep and Shrinkage of Concrete; Baant, Z.P; Carol, I, Ed. E&FN Spon: London (1994) 85-102.

Jornal Oficial das Comunidades Europeias, 2003. Decision 2003/33/CE.

Joshi RC, Lothia RP. Fly ash in concrete: production, properties and uses. Advances in concrete technology, Gordon and Breach Science Publishers 2 (1997).

Junta Autónoma das Estradas, JAE, Construção, S.A. – JAE, Lisboa (1997).

Kaci A, Bouras R, Phan VT, Andréani PA, Chaouche M, Brossas H. Adhesive and Rheological properties of fresh fibre-reinforced mortars. Cement and Concrete Composites 33 (2011) 218-224.

Kaushik SK, Islam S. Suitability of sea water for mixing structural concrete exposed to a marine environment. Cement and Concrete Composite 17 (1995) 177-185. http://dx.doi.org/10.1016/0958-9465(95)00015-5.

Khan AA, Jong. de W, Jansens PJ, Spliethoff H. Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel Processing Technology 90 (2009) 21-50.

Kim HK, Jeon JH, Lee HK. Flow, water absorption, and mechanical characteristics of normal-and high-strength mortar incorporating fine bottom ash aggregates. Construction and Building Materials 26 (2012) 249-256.

Kim HK, Lee HK. Use of power plant bottom ash as fine and coarse aggregates in high-strength concrete. Construction and Building Materials 25 [2] (2011) 1115-1122.

Krigstin S, Sain M. Characterization and potential utilization of recycled paper mill sludge. Pulp Paper Canada 107 [5] (2006) 29-32.

Kuo J-H, Wey M-Y, Lin C-L, Chiu H-M, The effect of aluminium inhibition on the defluidization behavior and generation of pollutants in fluidized bed incineration. Fuel Processing Technology 89 (2008) 1227-1236.

Langston BG, Stephens FMJr. Self agglomerating fluidized bed reduction. Journal of Metals 12 (1960) 312-316.

Larsson A, Thunman H, Neves D, Pallares D, Seemann M. Zero-dimensional modelling of indirect fluidized bed gasification. In Proceedings of the XIII Fluidization Conference. Gyeong-ju, Korea, 2010.

Latva-Somppi J, Kauppinen EI, Valmari T, Ahonen P, GuravS AS, Kodas TT, Johanson B. The ash formation during co-combustion of wood and sludge in industrial fluidized bed boilers. Fuel Processing Technology 54 (1998) 79-94b.

Latva-Somppi J, Moisio M, Kauppinen EI, Valmari T, Ahonen P, Tapper U, Keskinen J. Ash formation during fluidized-bed incineration of paper mill waste sludge. Journal Aerosol Science 4 (1998) 461-480a.

Leckner B. Fluidised bed combustion: Mixing and pollutant limitation, PII: S0360 – 1285 (97) 00021 – X, Prog. Energy Combustion Science 24 (1998) 31-61.

Li YJ, Sun RY, Liu CT et al. CO_2 capture by carbide slag from chlor-alkali plant in calcination/carbonation cycles. International Journal of Greenhouse Gas Control 9 (2012) 117–123. http://dx.doi.org/10.1016/j.ijggc.2012.03.012

Lin C-L, Kuo J-H, Wey M-Y, Chang S-H, Wang K-S. Inhibition and promotion: The effect of earth alkali metals and operating temperature on particle agglomeration/defluidization during incineration in fluidized bed. Powder Technology 189 (2009) 57-63.

Lin C-L, Wey M-Y. The effect of mineral compositions of waste and operating conditions on particle agglomeration/defluidization during incineration, Fuel 83 (2004) 2335-2343.

Lin W, Dam-Johansen K, Frandsen F. Agglomeration in bio-fuel fired fluidized bed combustors. Chemical Engineering Journal 96 (2003) 171-185.

Liu, JN Stregth and hydration of an activated alumino-silicate mineral. Pennsylvania State University, USA, 1998.

Llorente MJF, Cuadrado RE, Laplaza LMM, García JEC. Combustion in bubbling fluidized bed with bed material of limestone to reduce the biomass ash agglomeration and sintering. Fuel 85 (2006) 2081-2092.

Llorente MJF, Garcia JEC. Concentration of elements in wood and herbaceous biomass as a function of dry ashing temperature. Fuel 85 (2006) 1273-1279.

Loo, S.V., Koppejan, J.Handbook of Biomass Combustion and Co-firing, Twente University Press, The Netherlands, 2003.

Lopes E, Dias A, Arroja L, Capela I, Pereira F. Application of life cycle assessment the Portuguese pulp and paper industry. Journal of Cleaner Production 11 (2003) 51–59.

Lynde-Mass MK, Unwin JP, Miner RA. Preliminary results from the NCASI 1995 wastewater and solid waste survey. In: Environmental Conference and Exhibit. TAPPI Proceedings, Book 1. Minneapolis Convention Centre, p. 239-241, 1997.

Mahmonoudkhani M. Recycling inorganic residues from wood-based industries to the forest – Study of Treatment Techniques and Leaching Characteristics. Chalmers University of Technology, Göteborg, Sweden, 2005. PhD Thesis.

Makaratat N, Jaturapitakkul C, Namarak C, Sata V. Effects of binder and CaCl2 contents on the strength of calcium carbide residue-fly ash concrete. Cement & Concrete Composites 33 (2011) 436-443.

Mansur AAP, do Nascimento OL, Mansur HS. Physico-chemical characterization of EVA-modified mortar and porcelain tiles interfaces. Cement and Concrete Research 39 (2009) 1199-1208.

Manzoori AR, Agarwal PK. Agglomeration and defluidization under simulated circulating fluidized-bed combustion conditions. Fuel 73 (1994) 563–568.

Martins FM, Martins JM, Ferracin LC, Cunha, da CJ. Mineral phases of green liquor Dregs, slaker grits, lime mud and wood ash of a Kraft pulp and paper mill. Journal of Hazardous Materials 147 (2007) 610-617.

Maschio S, Tonello G, Piani L, Furlani E. Fly and bottom ashes from biomass combustion as cement replacing components in mortars production: Rheological behaviour of the pastes and materials compression strength. Chemosphere 85 (2011) 666–671.

Masia AAT, Buhre BJP, Gupta RP, Wal TF. Use of TMA to predict deposition behaviour of biomass fuels. Fuel 86 (2007) 2446 – 56.

Matjie RH, Li Z, Ward CR, French D. Chemical composition of glass and crystalline phases in coarse coal gasification ash. Fuel 87 (2008) 857–869

Matos MAA. Formacao e reducao de NOx na combustão de coque em leito fluidizado. Aveiro, Portugal: University of Aveiro, 1995. PhD Thesis.

McKendry P. Energy production from biomass (part 2): conversion technologies. Review paper, Bioresource Technology 83 (2002) 47–54

Meadows D, Randers J, Maedows D. The limits to Growth: a 30-year update. Chelsea Green Publishing, 2004. ISNB: 9781931498586.

Menéndez, E., Álvaro, A.M., Hernández, M.T., Parra, J.P., 2014. New methodology for assessing the environmental burden of cement mortars with partial replacement of coal bottom ash and fly ash Journal of Environmental Management 133, 275-283.

Mitsui Babcock Ltd. Studies on the Thermal Processing of Biomass and Waste Materials, 1997. ETSU, B/T1/00358/Rep.

Modolo R, Benta A, Ferreira VM, Machado LM. Pulp and paper plant wastes valorisation in bituminous mixes. Waste Management 30 (2010) 685 – 696.

Modolo R, Benta A, Machado L, Labrincha JA, Ferreira VM. Solutions development for pulp and paper process solid wastes – from laboratory bench to industrial scale. In Inovação na Construção Sustentável, Ed. Plataforma para a Construção Sustentável 1 (11-22), 2008. ISBN 978-989-95978-0-8 2008.

Modolo R, Ferreira VM, Machado LM, Rodrigues M, Coelho I. Construction materials as a waste management solution for cellulose sludge. Waste Management 31 (2011) 370–377.

Modolo R, Machado L, Labrincha JA, Ferreira VM. Use of cellullose sludge in the production of fiber-cement building materials. In Proceedings of Sustainable Construction – Materials and Practices, Ed. By L. Bragança et al., Lisbon, IOS press 2 (918-923), 2007.

Modolo R.C.E., L.A.C. Tarelho, E.R. Teixeira, V.M. Ferreira, J.A. Labrincha, Treatment and use of bottom bed waste in biomass fluidized bed combustors, Fuel Processing Technology 125 (2014) 170–181. http://dx.doi.org/10.1016/j.fuproc.2014.03.040.

Modolo RCE, Ferreira VM, Tarelho LA, Labrincha JA, Senff L, Silva L, Mortar formulations with bottom ash from biomass combustion. Construction and Building Materials 45 (2013) 275–281. http://dx.doi.org/10.1016/j.conbuildmat.2013.03.093

Monte M.C, Fuente E, Blanco A, Negro C. Waste management from pulp and paper production in the European Union. Waste Management and Research 29 (2009) 293-308. http://dx.doi.org/10.1016/j.wasman.2008.02.002

Monteiro C, Tarelho L, Lopes M, Monteiro A, Cascao P, Miranda AM. Air pollution impacts from logistics related to forest biomass to energy chain. In World Bioenergy 2012, Conference & Exhibition on Biomass for Energy, Jonkoping, Sweden, 2012.

Moosberg-Bustnes H, Lagerblad B, Forssberg E. The function of filers in concrete. Materials Structure 37(2004) 74-81.

Morton JH, Akers SAS, Cooke T. Performances of slash pine fibers in fiber-cement products. In 10th International Inorganic-Bonded Fiber Composites Conference. University of São Paulo & University of Idaho, Brazil, p. 168 – 177, 2006.

Naik TR, Kraus RN, Siddique R. CLSM containing mixtures of coal ash and a new pozzolanic material. ACI Materials Journal 100 (2003) 208-215.

Naik TR. Tests of wood ash as a potential source for construction materials. Report no. CBU-1999-09. UWM Center for By-Products Utilization. Department of Civil Engineering and Mechanics, University of Wisconsin-Milwaukee, Milwaukee, p. 61, 1999.

Narodoslawsky M, Obernberger I. From waste to raw material –the route from biomass to wood ash for cadmium and other heavy metals. Journal of Hazardous Materials 50 (1996) 157–168.

NCASI, Beneficial use of industrial by-products. Identification and review of material specifications, performance standards, and technical guidance. RTM, Inc. NCASI. Working Copy, December 2003.

Ngoc NU, Schnitzer H. Sustainable solutions for solid waste management in Southeast Asian countries. Waste Management 29 (2009) 1982-1995.

Nilforoushan MR, Sharp JH. The effect of additions of alkaline-earth metal chlorides on the setting behaviour of refractory calcium aluminate cement. Cement and Concrete Research 25 [7] (1995) 1523-1534.

NP 4220: 2010. Pozzolans for concrete, mortar and grout. Definitions, requirements and conformity criteria. Ed. IPQ, Lisbon, Portugal.

NP EN 196-3: 2005. Methods of testing cement. Determination of setting times and soundness.

NP EN 27888:1996 – Water quality. Determination of electric conductivity (based on ISO 7888: 1985).

NP EN 450-1: 2012. European committee for standardization, fly ash for concrete, part 1, definition, specification and conformity criteria.

NP EN 933-1: 2000. Tests for geometrical properties of aggregates, Part 1: Determination of particle size distribution, Sieving method.

Nurmesniemi H, Pöykiö R, Keiski RL. A case study of waste management at the Northern Finnish pulp and paper mill complex of Stora Enso Veitsiluoto Mills. Waste Management 27 (2007) 1939–1948.

Nuutinen LH, Tiainen M, Virtanen ME, Enestam SH, Laitinen RS. Coating layers on bed particles during biomass fuel combustion in fluidized-bed boilers. Energy and Fuels 18 (2004) 127-139.

Obernberger I, Biedermann F, Widmann W, Riedl R. Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions, Biomass and Bioenergy 12 (1997) 211–224.

Oberste-Padtberg R, Sieksmeier J. Factors influencing the open time of building mortars. Drymix Mortar Yearbook (2007) 44-49.

OECD. Road Transport Research: Recycling Strategies for Road Works. Organization for Economic Co-operation and Development (OECD), Paris, France, pp. 140–148, 1997.

Ohama Y, Demura K, Nagao H. Adhesion of polymer modified mortars to ordinary cement mortar by different test methods. Adhesion between polymer and concrete. Symposium organised by Rilem Technical Committee 52, 1986.

Ohama Y. Handbook of polymer-modified concrete and mortars. Properties and Process Technology. Noyes Publications. Park Ridge, New Jersey, 1995.

Ohlström MO, Lehtinen KEJ, Moisio M, Jokiniemi JK. Fine-particle emissions of energy production in Finland. Atmospheric Environment 34 (2000) 3701-3711.

Ohman M, Nordin A. The role of kaolin in prevention of bed agglomeration during fluidized bed combustion of biomass fuels. Energy and Fuels 14 (2000) 618-624.

Ohman M, Pommer L, Nordin A. Bed agglomeration characteristics and mechanisms during gasification and combustion of biomass fuels. Energy and Fuels 19 (2005) 1742-1748.

Older I. Lea’s chemistry of cement and concrete. Arnold, London, 1998.

Ozkahraman HT, Isik EC. The effect of chemical and mineralogical composition of aggregates on tensile adhesion strength of tiles. Construction and Building Materials 19 [4] (2005) 251–255.

Paiva H, Esteves LP, Cachim PB, Ferreira VM. Rheology and hardened properties of single-coat render mortars with different. Construction and Building Materials 23 [2] (2009) 1141–1146. http://dx.doi.org/10.1016/j.conbuildmat.2008.06.001

Pandey SP, Sharma RL. The influence of mineral additives on the strength and porosity of OPC mortar. Cement and Concrete Research 30 (2000) 19-23.

Patrao G. The Portuguese Energy Strategy and the role of Biomass, Workshop BIOGAIR. Aveiro, Portugal, 2011.

Pereira P, Oliveira J, Picado-Santos L. Pavimentos Rodoviários. Barbosa & Xavier, Lda, Braga, 2002. ISBN 972-8692-02-1.

Pérez-Carrión M, Baeza-Brotons F, Payá J, Saval JM, Zornoza E, Borrachero M, Garcés P. Potential use of sewage sludge ash (SSA) as a cement replacement in precast concrete blocks Materiales de Construcción 64 [313] (2014), e002.

Pingoud K, Lehtila A. Role of forest sector and bioenergy in limiting the carbon emissions of Finland. Biomass and Bioenergy 14 (1997) 33–56.

Podobnik E, Zule F. Paper mill sludges. A secondary raw material, not waste. Papir 34 [1] (2006) 25-27.

Pöykiö R, Taskila E, Perämäki P, Nurmesniemi H, Kivilinna VA, Kuokkanen T, Virta P. Sediment, Perch (Perca fluviatilis L.) and bottom fauna as indicators of effluents discharged from the pulp and paper mill complex at Kemi, Northern Finland. Water, Air, and Soil Pollution 158 (2004) 325–343.

Rajamma R, Labrincha JA, Ferreira VM. Alkali activation of biomass fly ash–metakaolin blends. Fuel 98 (2012) 265–271.

Rajamma R, Tarelho LAC, Alen GC, Labrincha JA, Ferreira VM. Characterisation and use of biomass fly ash in cement-based materials. Journal of Hazardous Materials 172 (2009) 1049-1060. http://dx.doi.org/10.1016/j.jhazmat.2009.07.109

Ramos NMM, Simões ML, Delgado JMPQ, de Freitas VP. Reability of the pull-off test for in situ evaluation of adhesion strength. Construction and Building Materials 31 (2012) 86-93.

Ramos T, Matos AM, Coutinho JS. Mortar with wood waste ash: Mechanical strength carbonation resistance and ASR expansion. Construction and Building Materials 49 (2013) 343–351.

Ravina D. Properties of fresh concrete incorporating a high volume of fly ash as partial fine sand replacement. Materials and Structures/ Matèriaux et Constructions 30 (1997) 473-479.

Redemann K, Hartge J, Werther J. Ash management in circulating fluidized bed combustors. Fuel 87 (2008) 3669–3680.

Renewable energy in Portugal 2007. Communication from the Portuguese Ministry of Economy and Innovation.

REP, Renewable Energy in Portugal. Communication from the Portuguese Ministry of Economy and Innovation, 2007.

RISI, Japan in the World (according to the figure in Annual Review of Global Pulp and Paper Statistics by RISI). Japan Paper Association, 2012.

RISI, The leading information provider for the global forest products industry; www.risi.com, 2011.

Rocha JC, John MW. Utilização de resíduos na construção habitacional. Coletânea Habitare 2 [4] (2003).

Rosário J, Castelo Branco F. Agregados para a construção civil e obras públicas. A indústria e a qualidade. Revista Portugal Mineral 34, Lisboa, 1994.

Sales A, Lima SA. Use of Brazilian sugarcane bagasse ash in concrete as sand replacement Waste Management 30 (2010) 1114–1122.

Saltan M, Findik SF. Stabilization of subbase layer materials with waste pumice in flexible pavement. Building and Environment 43 (2008) 415-421.

Sanjuan MA. Formation of chloroaluminates in calcium aluminate cements cured at high temperatures and exposed to chloride solutions. J. Mat. Sci. 32 [23] (1997) 6207–6213.

Santos P. O mercado da energia verde e as mecanismos de apoio aos projetos de biomass. Associacao de Produtores de Energia e Biomassa. Expo Energia, 2011.

Scala F, Chirone R. Characterization and early detection of bed agglomeration during the fluidized bed combustion of olive husk. Energy and Fuels 20 (2006) 120-132.

Scherer GW. Internal stress and cracking in stone and masonry. In Measuring, Monitoring and Modeling Concrete Properties, Proc. 16th European Conf. Fracture. Konsta-Gdoutos MS (ed.). Springer, Berlin (2006) 669–673.

Schiessler N., E. Thorpe, W. Jones, L. Philips, LIFE and waste recycling, Innovative waste management options in Europe Environment Directorate-General (LIFE Unit - BU-902/1), 2007.

Schiessler, N., Thorpe, E., Jones, W., Philips, L., 2007. LIFE and waste recycling: Innovative waste management options in Europe Environment Directorate-General (LIFE Unit - BU- 902/1).

Schulze J. Influence of water-cement ratio and cement content on the properties of polymer-modified mortars. Cement and Concrete Research 29 (1999) 909–915.

Scrivener KL, Kirkpatrick RJ. Innovation in use and research on cementitious material. Cement and Concrete Research 38 (2008) 128–136.

Senff L, Hotza D, Labrincha JA. Effect of red mud addition on the rheological behaviour and on hardened state characteristics of cement mortars. Construction and Building Materials 25 (2011) 163-170.

Senff L, Labrincha JA, Ferreira VM, Hotza D, Repette LW. Effect of nano-silica on rheology and fresh properties of cement pastes and mortars. Construction and Building Materials 23 (2009) 2487-2491.

Senff L, Tobaldi DM, Lucas S, Hotza D, Ferreira VM, Labrincha J.A. Formulation of mortars with nano-SiO_2 and nano-TiO_2 for degradation of pollutants in buildings. Comp. Part B, Eng. 44 [1] (2012) 40-47. doi.org/10.1016/j.compositesb.2012.07.022.

Senff, L, Hotza D, Labrincha JA Effect of lightweight aggregates addition on the rheological properties and the hardened state of mortars. Applied Rheology 21 [1] (2011) 13668 (8 pages). doi:10.3933/ApplRheol-21-13668.

Shao Y, Qui J, Shah SS. Microstructure of extruded cement bonded fiberboard. Cement and Concrete Research 31 (2001) 1153–61.

Siddique, Rafat., 2010. Utilization of municipal solid waste (MSW) ash in cement and mortar Resources, Conservation and Recycling 54, 1037–1047.

Sipula O. Fine Particle formation and emissions in biomass combustion. Report series in aerosol science, University of Eastern Finland, Nº108, Helsinki, 2010, ISBN 978-952-5822-15-1, Academic dissertation.

Skrifvars B-J, Backman R, Hupa M. Characterization of the sintering tendency of ten biomass ashes in FBC conditions by a laboratory test and by phase equilibrium calculations. Fuel Processing Technology 56 (1998) 55–67.

Snelson DG, Kinuthia JM, Davies PA, Chang S-R. Sustainable construction: Composite use of tyres and ash in concrete. Waste Management 29 (2009) 360–367.

Sorlini S, Abbà A. Collivignarelli C.Recovery of MSWI and soil washing residues as concrete aggregates. Waste Management 31 (2011) 289–297.

Soroka I, Stern N. Calcareous fillers and the compressive strength of portland cement. Cement and Concrete Research 6 [3] (1976) 367-376. http://dx.doi.org/10.1016/0008-8846(76)90099-5

Soroka I; Setter N. The effect of fillers on strength of cement mortars. Cement and Concrete Research 7 [4] (1977) 449-456. doi.org/10.1016/0008-8846(77)90073-4.

Standard of Procedure. Process Procedure of Waste Management Operations Simplified Licensing, Commission for Regional Coordination and Development – Lisbon and Tejo's Valey, CCDR-LVT. October, 2012.

Steenari B-M, Karlfeldt Fedje, K. Addition of kaolin as potassium sorbent in the combustion of wood fuel – Effects on fly ash properties. Fuel 89 [8] (2010) 2026–2032

Steenari BM, Linqvist O. Stabilisation of biofuel ashes for recycling to forest soil. Biomass and Bioenergy 13(1997) 39–50.

Steenari B-M, Schelander S, Lindqvist O. Chemical and leaching characteristics of ash from combustion of coal, peat and wood in a 12 MW CFB — a comparative study. Fuel 78 (1999) 249–258.

Suslick S, Machado I. Non-Renewable Resources in Earth system: History and Natural Variability. Ed. V. Cilek & R. Smith, Encyclopedia of Life Support Systems (EOLSS), EOLSS Publishers – UNESCO, Oxford, UK, 2009.

Tapkin Sercan. The effect of polypropylene fibers on asphalt performance. Building and Environment 43 (2008) 1065-1071.

Tarelho LAC, Coelho AMSL, Teixeira ER, Rajamma R, Ferreira VM. Characteristics of ashes from two Portuguese biomass co-generation plants. Proceedings of the 19th European Biomass Conference & Exhibition, Berlin, Germany (2011) 1041-1053.

Tarelho LAC, Matos MAA, Pereira FJMA. Axial and radial CO concentration profiles in an atmospheric bubbling FB combustor. Fuel 84 (2005) 1128-1135.

Tarelho LAC, Matos MAA, Pereira FJMA. Axial concentration profiles and NO flue gas in a pilot-scale bubbling fluidized bed coal combustor. Energy Fuel 18 (2004) 1615-1624.

Tarelho LAC, Neves DSF, Matos MAA. Forest biomass waste combustion in a pilot-scale bubbling fluidized bed combustor. Biomass and Bioenergy 35 (2011) 1511–1523.

Tarelho LAC, Teixeira ER, Silva DFR, Modolo RCE, Silva JJF, Characteristics, management and applications of ashes from thermochemical conversion of biomass to energy, in World Bioenergy 2012, Conference & Exhibition on Biomass for Energy, 2012.

Tarelho LAC, Teixeira ER, Silva DFR, Modolo RCE. Treatment by leaching of bottom bed ash from biomass combustion in bubbling fluidized bed. In Proceedings of Ash utilisation Conference, Stockholm, Sweden, 2012.

Tarelho LAC. Controlo de emissoes gasosas poluentes resultantes da conbustao de carvao em leito fluidizado. University of Aveiro, Aveiro, Portugal, 2001, PhD Thesis.

Targanş, Olgun A, Erdogan Y, Sevinc V. Influence of natural pozzolan, colemanite ore waste, bottom ash, and fly ash on the properties of Portland cement. Cement and Concrete Research 33 (2003) 1175-1182.

Tarnawski W. Emission factors for combustion of biomass fuels in the pulp and paper mills. Fibres and Textiles in Eastern Europe 12 (2004) 91–95.

Taylor PC, Tait RB. Effects of fly, ash on fatigue and fracture properties of hardened cement mortars. Cement and Concrete Composites 21 [3] (1999) 223-232. http://dx.doi.org/10.1016/S0958-9465(99)00005-0

Thipkhunthod P, Meeyoo V, Rangsunvigit P, Kitiyanan B, Siemanond K, Rirksomboon T, Predicting the heating value of sewage sludges in Thailand from proximate and ultimate analyses. Fuel 84 (2005) 849–857.

Thomas JJ, Jennings HM. Changes in the size of pores during shrinkage (or expansion) of cement paste and concrete. Cement and Concrete Research 33 (2003) 1897-1900.

Thompson G, Swain J, Kay M, Forster C. The treatment of pulp and paper mill effluent: a review. Bioresource Technology 77 (2001) 275-286.

Thy P, Jenkins BM, Grundviig S, Shiraki R, Lesher CE. High temperature elemental losses and mineralogical changes in common biomass ashes. Fuel 85 (2006) 783-95.

Torgal FP, Jalali S. A sustentabilidade dos materiais de construção. TecMinho, 2010. 460 p. ISBN: 978-972-8600-22-8.

Türkel S. Strength properties of fly ash based controlled low strength materials. Journal of Hazardous Materials 147 (2007) 1015-1019.

UMTC. Use of recycled materials and recycled products in highway construction. University of Massachusetts Transportation Center Report, UMTC-95-1, US, p. 238–245, 1995.

United Nations Economic and Social Council. Executive summary report of the status report on the management of by-product/residue containing persistent organic pollutants. Report Number: EB.Air/Wg.5/2001/9 (12–3).

Van Loo S, Koppejan J. Handbook of Biomass Combustion and Co-firing. Twenty University Press, 2003.

Van Loo S, Koppejan J. The Handbook of Biomass Combustion and Co-firing. Ed. Sjaak van Loo and Jaap Koppejan Earthscan, London, 2008. ISBN 978-1-84407-249-1.

Vassilev S. V., D. Baxter, L.K. Andersen, C.G. Vassileva, T.J. Morgan, An overview of the organic and inorganic phase composition biomass, Fuel 94 (2012) 1-33.

Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the composition and application of biomass ash. Fuel 89 [5] (2012) 913-933.

Vaysburd AM, Emmons PH. Corrosion inhibitors and other protective systems in concrete repair: concepts or misconcepts. Cement and Concrete Composites 26 (2004) 255-263. http://dx.doi.org/10.1016/S0958-9465(03)00044-1

Vuk T, Tinta V, Gabrovšek R, Kaučič V. The effects of limestone addition, clinker type and fineness on properties of Portland cement. Cement and Concrete Research 31(2001) 135-139. doi.org/10.1016/S0008-8846(00)00427-0.

Wang S, Baxter L. Comprehensive study of biomass fly ash in concrete: strength, microscopy, kinetics and durability. Fuel Process Technology; 88 [11] (2007)1165-70.

Wang S, Miller A, Llamazos E, Fonseca F, Baxter L. Biomass fly ash in concrete: mixture proportioning and mechanical properties. Fuel 87 [3] (2008) 365-71.

Werkelin J, Skrifvars B, Zevenhoven M, Holmbom B, Hupa M, Chemical forms of ash-forming elements in wood biomass fuels. Fuel 89 (2010) 481-493.

Werther J, Saenger M, Hartge EU, Ogada T, Siagi Z. Combustion of agricultural residues. Progress in Energy and Combustion Science 26 (2000) 1–27.

Wetzel A, Herwegh M, Zurbriggen R, Winnefeld F. Influence of shrinkage and water transport mechanisms on microstructure and crack formation of tile adhesive mortars. Cement and Concrete Research 42 (2012) 39-50.

Wetzel A., M. Herwegh, R. Zurbriggen, F. Winnefeld, Influence of shrinkage and water transport mechanisms on microstructure and crack formation of tile adhesive mortars, Cement and Concrete Research 42 (2012) 39-50.

Yin C, Rosendahl LA, Kaer SK. Grate-firing of biomass for heat and power production, Progress in Energy and Combustion Science 34 (2008) 725–754.

Yip C.K., G.C. Lukey, J.S.J. Deventer, The coexistence of geopolymeric and calcium silicate hydrate at the early stage of alkaline activation, Cement & Concrete Research 35 (2005) 1688–97.

Yip CK, Lukey GC, Deventer JSJ. The coexistence of geopolymeric and calcium silicate hydrates at the early stage of alkaline activation. Cement & Concrete Research 35 (2005) 1688-97.

Zampini D. Future developments of concrete in the construction materials industry. In: Forde M, editor. ICE manual of construction materials, vol.1. Thomas Telford; 2009, p. 251–8 [chapter 21]. Pereira P, Santos LP. Pavimentos Rodoviários. ISBN 972-8692-02-1, 2002.

Zevenhoven-Onderwater M, Backman R, Skrifvars B-J, Hupa M. The ash chemistry in fluidized bed gasification of biomass fuels. Part I: predicting the chemistry of melting ashes and ash-bed material interaction. Fuel 80 (2001) 1489–502.

Zevenhoven-Onderwater M, Ohman M, Skrifvars B-J, Backman R, Nordin A, Hupa M. Bed agglomeration characteristics of wood-derived fuels in FBC. Energy and Fuels 20 (2006) 818-824.

APPENDIX I

Bottom ash from biomass combustion as aggregate for mortars

R.C.E. Modolo[1], V.M. Ferreira[1], L.A. Tarelho[2], J.A. Labrincha.[3], D.F.R. Silva[2]

[1]Dpt.of Civil Engineering/CICECO, University of Aveiro , Aveiro, Portugal, regina.modolo@ua.pt
[2]Dpt. of Environment and Planningt, University of Aveiro , Aveiro, Portugal
[3]Dpt. Ceramics and Glass Engineering/CICECO, University of Aveiro , Aveiro, Portugal

Abstract

The quality of mortars depends firstly on the characteristics of raw materials. Criteria are defined and controlled to guaranty the final product established specifications. Bottom ash from eucalyptus bark combustion in a bubbling fluidized bed was tested in partial substitution of the standard aggregate (granulometric calibrated sand) used in industrial mortars. The relevant characteristics of the new mortars were then evaluated and compared with those of the reference (ash-free formulations). Results revealed that bottom ash has potential to be recycled in these products, but pre-treatment operations are needed to the ash, particularly to remove soluble salts.

Keywords: Biomass, bottom ash, fluidized bed combustion, mortars.

INTRODUCTION

The solid biomass combustion is a proven technology for heat and power generation, and fluidized bed and grate furnace equipments are the most common [1; 2]. Fluidized bed combustion (FBC) has been used due its economic and environmental benefits in burning low-grade coals, biomass and organic wastes, and thereby mixtures of them [1; 3]. These furnaces have been applied since 1960 for combustion of municipal solid wastes and industrial wastes. Since 1980, more than eight hundred commercial circulating fluidised bed boilers have been put into operation in China [4]. In Portugal, the first installation started running 20 years ago, in pulp and paper producing industries and also to burn tires [3]. Nowadays, Portugal has several plants operating with the fluidized bed technology and the future scenario predicts the construction of more units [5]. As a consequence, the amount of ashes generated from the process will increase considerably. The high level of inert material (soil and little stones from the forest) fed together with the biomass in the Portuguese BFBC plants [6] implies a relatively high frequency of bottom bed discharge.

The production of industrial pre-mixed mortars exceeds one million tons in Portugal, consuming then a huge amount of natural pre-treated raw materials (e.g. quarried sand) as aggregates. This activity can be looked as a target for the incorporation of ashes, as currently happens with the fly ashes from the coal combustion in concrete [7].

In this work, the coarse sand fraction used in mortars formulations was (partially and completely) substituted by the bottom ash produced during fluidized (bubbling) bed combustion of biomass. The ash was used in two conditions: (i) as collected and just sieved to obtain a compatible grain size distribution; (ii) and pre-washed (to diminish the amount of chlorides) and then sieved. The leaching of chlorides from the components of mortar mixes is mandatory, since they cause deleterious effects [8; 9; 10]. The control of grain size distribution of the aggregates is crucial to adjust the fresh (e.g. workability) and hardened (e.g. mechanical strength) properties of the mortars.

METHODOLOGY

Material

The ordinary Portland cement used was CEM I 42.5 R, while the bottom-ashes were collected in an industrial fluidized (bubbling) bed combustor using biomassa as fuel in a paper-pulp producer (BA – sieved and used as collected) or BAT pre-treated –The industrial leaching was performed in continuous and under typical conditions used in an industry that makes treatment of natural sand for the construction industry. The leaching procedure includes a continuous shower like process using a L/S (liquid to solid) ratio equal to 2, and a processing capacity of 10 ton/h; the process includes treatment of the leaching solution by sedimentation in order to reuse the liquid solution on the leaching process.The chemical composition of ashes was analyzed for some chemical elements using X-Ray Fluorescence Spectroscopy –XRF (using a Panalytical Axios spectrometer) and the results are expressed in terms of metal oxides, while the crystalline phases were detected by X-ray diffraction – DRX (equipment RIGAKU-Geiger flex diffractometer). Results are presented in Table 1. The grain size distribution was determined by sieving according to NP EN 933:1/2000. The fine grain sand fraction (S1) has particles between 63 and to 250 µm, while the coarse fraction (S2) is constituted by larger particles, as shown in Figure 1; in the figure it is also presented the grain size distribution of BA and BAT. Finally, the Limestone Filler (LSF) has particles between 0.41 to 19.50 µm, as determined by laser interference (Coulter LS230 – measurement interval of 0.04; 2000mm).

Table 1. Raw materials chemical and mineralogical analysis.

Parameters	Raw material					
	BA	BAT	S1	S2	LSF	CEM 42,5 I
SiO_2 (%)	72,17	85,00	99,43	97,53	0,60	20,16
CaO (%)	17,16	8,60	0,07	0,28	56,37	59,91
Na_2O (%)	0,88	1,00	0,04	0,07	0,05	0,17
Cl (%)	0,12	0,04	0,00	0,00	0,04	0,02
L.O.I (%)	1,97	0,60	0,09	0,24	41,26	2,26
Mineralogy (by DRX)	Quartz, Calcite, Larnite and Microcline	Quartz, Calcite and Larnite	Quartz and Microcline	Quartz and Microcline	Calcite	NQ*

*Not Quantified

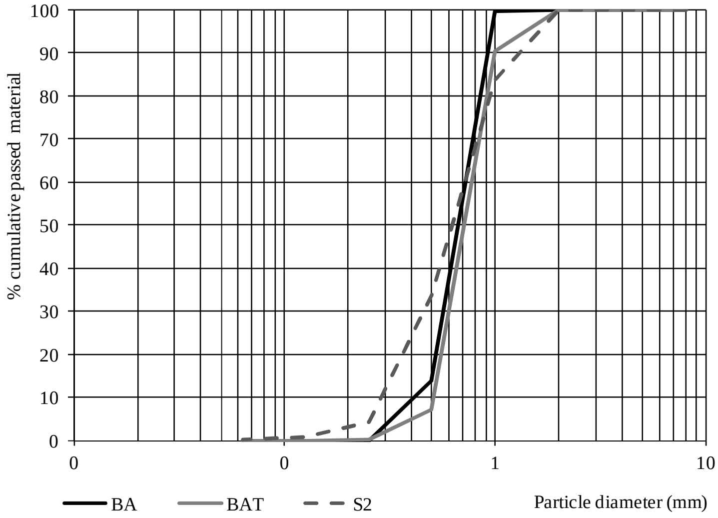


Figure 1. Grain size distribution of BA, BAT and S2, determined according to EN 933:1/2000.

Mortars formulations and characterization

Specific rendering mortars with different amounts of BA and BAT (0, 25, 50 and 100%) were produced and tested. BA and BAT were introduced replacing in the formulations the coarser sand (S2). Portland cement (type I 42.5R) was used as binder and the binder to aggregates mass ratio was kept at 1:6. The amount of water for mixing was fixed (16.5% of total mass).

The particle size distribution of powdered and dried mortars (dust) was controlled according to EN 933-1:2000 standard [11]. The preparation of samples included: (i) water weighting and addition to the solids; (ii) mixing for 30s at a low rotation speed (60 rpm); (iii) stopping for 1 min; (iv) mixing again for 1 min at the same low speed and, (v) keep the mixture in stand by for 10 minutes before testing. Fresh state properties were also assessed. Workability was evaluated by the spread diameter on the flow table (according to EN 1015-3:1999) [12] and setting time was measured according to EN 196-3:2005 standard [13] (Vicamatic - Automatic Recording Vicat Apparatus). Regarding the hardened state mortar properties, specimens with 40×40×160 mm were produced and tested after 7 and 28 days of curing, according to EN 1015-11:1999 [14]. Compressive and flexural strength were evaluated with these samples. Table 2 gives the basic requirements for a suitable rendering mortar.

Table 2. Rendering mortars specific requirements.

State	Characteristics		Minimum	Maximum
Dust	Grain size distribution (%)	1.600 mm	0.0	0.0
		1.250 mm	0.0	1.0
		0.630 mm	9.0	17.00
		0.315 mm	16.0	43.0
		0.160 mm	12.0	35.0
		0.080 mm	2.0	15.0
		< 0.080 mm	23.0	33.0
Fresh	Water/Cement (%)		1.1	1.2
	Density (g/cm3)		1.65	1.80
	Flow table (mm)		150	180
	Setting time (min)	Beggining	300	450
		End	400	550
Hardened at 28 days	Flexural Strength (MPa)		1.5	--
	Compressive Strength (MPa)		3.5	--

RESULTS AND DISCUSSION

The decrease of Cl^- content in BAT ashes (see Table 1), when compared to BA, reveals the efficiency of the washing process. In particular, the reduction of chlorides (about 60%) is very important for this application. Their presence usually has an effect of anticipation of setting time, but deleterious effects are mostly observed on hardened bodies.

Table 3 gives the particle size distributions of the prepared formulations, obviously related with the size distribution of each single component (Figure 1).

S2 aggregate present a broader size distribution: below 0.1 mm and up to 1.25 mm, with 50 vol. % of particles comprised in the 0.5 mm upper fraction. By contrast, BA has a narrower distribution (~90 vol. % between the 1mm and 0,5 mm fractions). The washing process seems to destroy some agglomerates of BA, and then BAT contains more particles below 0.5 mm. Its distribution approaches that of S2 size distribution. The control of particle size is crucial to define the compactness of the mixtures, then affecting physical and hydration behaviour of cementitious mortars.

In

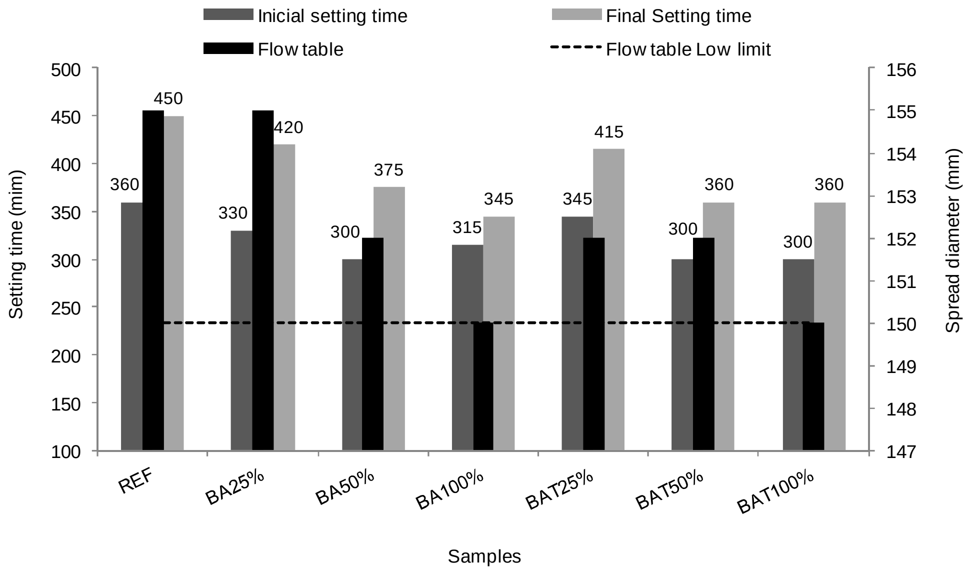


Figure 2 it is shown the setting time and values of spread diameter on the flow table for the mixtures. According to the requirements (see Table 2), the minimum limit for the initial setting time is 300 min. The use of BA and BAT tends to diminish setting time, as a possible consequence of the presence of chlorides in the ash. This effect is more pronounced with the use of BA since it has more chlorides.

Table 3. Rendering mortars mixtures grain size distribution.

mesh (mm)	% retained material								
	REF	BA25%	BA50%	BA100%	BAT25%	BAT50%	BAT100%	Low limit	High limit
1,6	0	0	0	0	0	0	0	*0*	*0*
1,25	1	0	0	0	0	1	0	*0*	*1*
0,63	10	9	13	15	11	13	15	*9*	*17*
0,315	40	37	35	33	35	33	34	*16*	*43*
0,16	16	19	17	17	20	19	17	*12*	*35*
0,08	9	9	9	9	9	9	9	*2*	*15*
Bottom	25	25	25	26	25	25	24	*23*	*33*

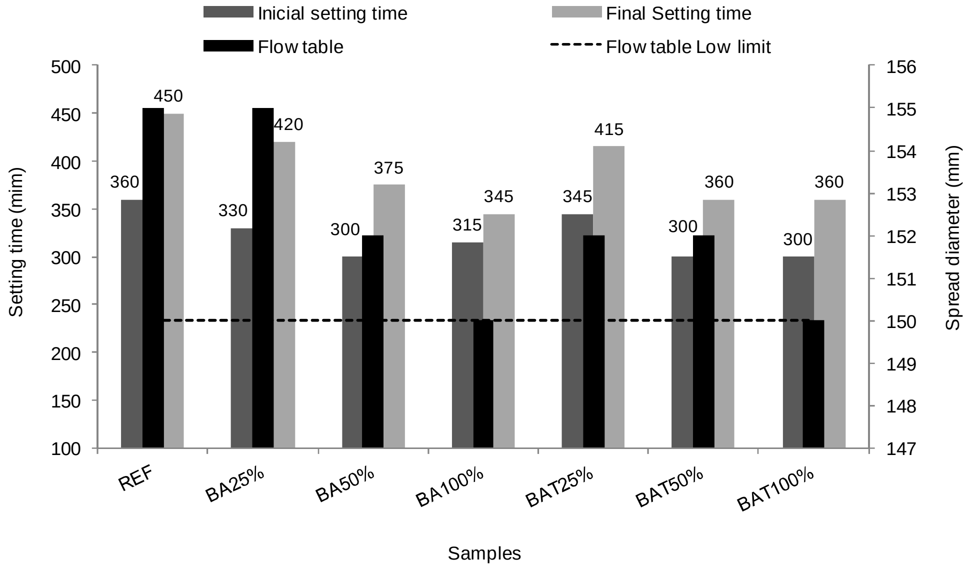


Figure 2. Setting time and spread diameter (flow table) of prepared mortars.

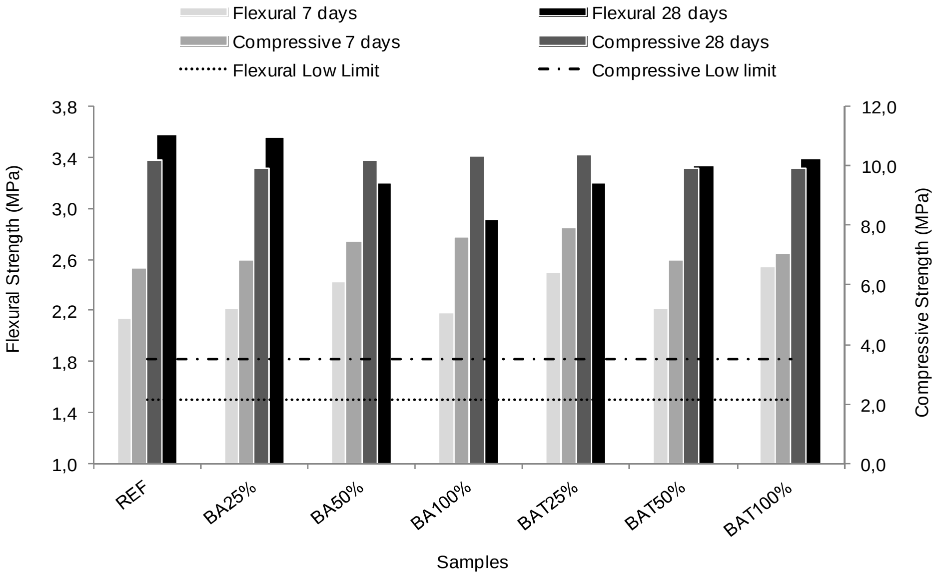


Figure 3. Rendering mortars mechanical strength results at 7 and 28 days.

The workability of the mortars also tend to diminish when the ash is used (the spread diameter is lower) and mortars in which the S2 aggregate was fully replaced by BA or BAT, workability reached the lower limit. Specifications recommend spread diameters between 150 and 180 mm. The lack of fluidity in ash-containing samples might also result from a poor particles arrangement and a need for kneading water content adjustment.
Figure 3 gives the mechanical strength of mortars cured for 7 and 28 days. All samples show values well above the required limits: 1.5 and 3.5 MPa, respectively on flexion and compression strength. Differences between distinct compositions are not relevant and the replacement of S2 by ashes did not degrade the mechanical behavior.

CONCLUSIONS

Apart the concern about the presence of chlorides in the ashes, this study suggests that the use of the waste in the formulation of rendering mortars, as a substitute of sand, is promising. Workability and mechanical strength in mortar containing ashes could be controlled and kept on the range for required values for conventional mortars. However, further tests should be conducted to prove the sustainability of the proposed solution. Long-term or durability tests are also recommended.

ACKNOWLEDGMENTS

The authors want to acknowledge the financial support by Fundação para a Ciência e a Tecnologia (FCT), Portugal, through the project with reference PTDC/AAC-AMB/098112/2008 (Bias-to-soil - Biomass ash: Characteristics in relation to its origin, treatment and application to soil) and SFRH/BD/75182/2010.

REFERENCES

[1] Van Loo, S., J. Koppejan, *Handbook of Biomass Combustion and Co-firing*, Twente University Press, The Netherlands, 2003.

[2] Yin C., Rosendahl LA., Kaer S.K., Grate-firing of biomass fort heat and power production, Progress in Energy and Combustion Science 34 (2008) 725–754.

[3] Tarelho LAC., (2001). Controlo de emissões gasosas poluentes resultantes da combustão de carvão em leito fluidizado, Dissertação de Doutoramento, Departamento de Ambiente e Ordenamento, Universidade de Aveiro, Portugal.

[4] Van Loo, S., Koppejan, J. *The Handbook of Biomass Combustion and Co-firing, Earthscan*, London, 2008.

[5] Coelho AMSL. Management of ashes produced in thermoelectric and cogeneration plants operated with biomass. MSc Thesis in Environmental Engineering (in Portuguese) University of Aveiro, Aveiro, Portugal, 2010.

[6] Tarelho LAC, Coelho AMSL, Teixeira ER, Rajamma R, Ferreira VM. Characteristics of ashes from two Portuguese biomass co-generation plants. Proceedings of the 19th European Biomass Conference & Exhibition, 6-10 June 2011, Berlin, Germany, pg 1041-1053.

[7] Silva L, Modolo R, Ferreira VM, Labrincha JA, Sequeira P. Utilização e Valorização de Resíduos de Areias de Leito Fluidizado e de Lamas de Corte de Pedra em Argamassas. Exemplos de Aplicação. 1º Congresso Nacional de Argamassas de Construção, pesquisa de 14/10/2009. ,www.apfac.pt

[8] Goudie, A.; Viles, H. Salt Weathering Hazard. Chichester, John Wiley & Sons, 1997.

[9] Harris, S.Y. Building pathology. New York, John Wiley & Sons, 2001.

[10] Scherer, G.W. Internal stress and cracking in stone and masonry. In Measuring, Monitoring and Modeling Concrete Properties, Proc. 16th European Conf. Fracture. Konsta-Gdoutos MS (ed.). Springer: Berlin, 2006, 669–673.

[11] NP EN 933-1: 2000. Tests for geometrical properties of aggregates, Part 1: Determination of particle size distribution, Sieving method.

[12] EN 1015-3:2007. Methods of test for mortar for masonry: determination of consistence of fresh mortar (by flow table).

[13] NP EN 196-3: 2005. Methods of testing cement. Determination of setting times and soundness.

[14] EN 1015-11:1999. Methods of test for mortar for masonry – Part 11: Determination of flexural and compressive strength of hardened mortar.

APPENDIX II

USE OF LIME-MUD FROM PULP MILL PLANT IN CEMENT-MORTARS

R. Modolo[1], L.Senff [2], V.M. Ferreira[1], J.A.Labrincha[2] and L.A. Tarelho[3]
1 Dpt. Civil Engineering/CICECO, University of Aveiro, Aveiro, Portugal, regina.modolo@ua.pt , victorf@ua.pt
2 Dpt. Ceramics and Glass Engineering/CICECO, University of Aveiro , Aveiro, Portugal, lsenff@gmail.com, jal@ua.pt
3 Dpt. Environment and Arrangement, University of Aveiro, Aveiro, Portugal, ltarelho@ua.pt

ABSTRACT

Lime-mud is a solid waste generated in pulp mill plants in considerable amounts. Its homogeneous chemical and physical characteristics allow valorization opportunities in the construction materials sector, namely in mortars. In this paper, a potential waste management solution was evaluated regarding the viability of this waste incorporation with a clear benefit in terms of natural raw materials savings.

The lime-mud characterization and its incorporation in cement-based mortars were appraised. The lime-mud effect on fresh and hardened state properties in different mortars formulations was assessed. Workability and mechanical strength were some of the critical features evaluated in this work.

Due to the high moisture content of this waste, the work was developed with the waste in its natural state, saving water and energy costs, taking into account environmental and economic factors by avoiding the waste pre-treatment.

Keywords: Lime-mud; cement-mortars; waste management.

INTRODUCTION

Large amounts of industrial wastes have been stabilized with cement or used as an additive material in cement related manufacturing sector [1;2;3]. The pulp and paper industry is a source of a wide range of solid residues. Both inorganic (ash, dregs and grits) and organic (sludges) solid wastes are generated during the different stages in bleached kraft pulp production. The chemical composition of the sludge, dregs and grits is dependent on the manufacturing and effluent treatment processes and raw materials, and the composition of the ash is dependent on the fuels and combustion techniques used at individual mills [4]. Alternative ecological and economic waste recovery techniques have been developed and implemented in pulp and paper industry due to the increase in the amount of waste and the pressure from public opinion in the last decade. Waste handling is a concern in pulp and paper mills as well as in all industrial plants [5]. Best available techniques for reducing waste involve minimizing the generation of solid waste or to reuse these materials, whenever practicable [6]. Building construction industry is a valid option to drain large quantitative of solid wastes and, as a consequence, avoid natural resources use. Several authors have been studying several alternatives of pulp and paper wastes valorisation replacing partially or completely conventional raw materials. Ahmadi and Alkhaja (2001) [7] tested with success primary sludge as a replacement filler material in concrete mixes. Eroglu H. *et al* (2007) [8] studied lime mud in composite cement manufacturing and the results suggested that the waste is practically an additive for this application. Considering limestone one of the most used raw materials in the construction sector, this work intends to assess a solid waste with similar characteristics of limestone powder, namely as a standard filler. In this work, lime-mud (LM), a solid waste mainly composed by calcium carbonate and small amount of magnesium carbonate [9] generated from pulp and paper mill in the chemical recovery process, was studied as a replacement to a standard limestone mineral filler (SF) in cement-mortars. Both LM and SF were chemically, mineralogical and physically characterized and the results compared. Cement based mortars were produced and tested.

In the case of mortars, workability parameters in the fresh state were measured using a flow table. Flow table is a traditional method to determine the workability of mortars. Although it is easy to use and widespread around the world, this technique does not discriminate the yield stress and plastic viscosity, which are important parameters to define the rheological behavior of mortars [10,11]. For that reason, a rheometer has been used for this purpose. In terms of the rheological behaviour, mortars typically behave as a Bingham fluid, being characterized by a yield stress and a plastic viscosity. The rheological behaviour was studied with a specific mortar rheometer (Viskomat PC, Schleibinger) that is able to quantify those factors. This apparatus automatically measures torque, up to a limit of 300 N.mm, following a preset speed-time program. The Bingham behaviour can be expressed as the torque (T) to rotation speed (N) relation, $T = g + hN$, where g and h are coefficients directly proportional to yield stress and plastic viscosity, respectively [12-15]. Additionally, the mechanical strength up to 28 days of curing, the apparent density, water absorption and porosity were measured.

EXPERIMENTAL

Materials

The ordinary Portland cement (PC) used in this study was a CEM II 32.5 R type produced by Secil (Portugal). The lime-mud was collected from paper pulp mill, where 420.000 t/year of this waste in dry base is produced. It is an industrial solid waste obtained from re-causticizing process inserted in the chemical recovery process circuit. The calibrated standard limestone mineral filler was a commercial one. This material is conventionally used as filler in industrial mortars. PC has an average particle size of 14 μm and a Blaine fineness of $0.47 m^2/g$, LM has a particle size distribution between 0.5 to 26 μm (average 10 μm) and a surface area of $5.17 m^2/g$ (BET) and the SF has a particle size distribution between 0.5 to 9 μm (average 2.8 μm) and a surface area of $3.44 m^2/g$ (BET). The sand particle size was below 1,2 mm (EN 933-1: 2000) [16]. The chemical composition data (determined by X-ray fluorescence spectroscopy) of LM and SF are illustrated in Table 1.

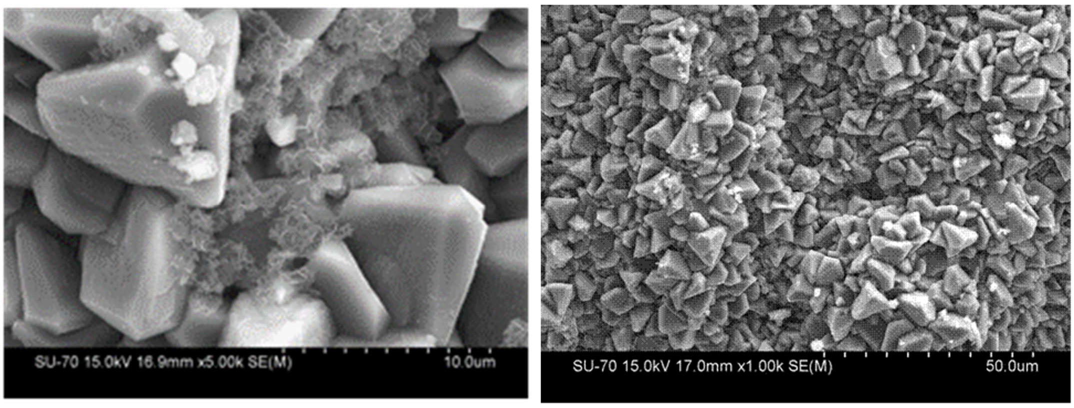


Figure 4.Lime-mud (scanning electronic microscope photograph).

Table 4. Chemical composition of lime-mud (LM) and standard filler (SF).

Sample	CaO	MgO	Al_2O_3	SiO_2	K_2O	Na_2O	Fe_2O_3	LOI
	%							
LM	51.80	0.48	0.20	0.29	0.06	**1.85**	0.03	43.7
SF	55.1	0.37	0.35	0.20	0.01	0.01	0.05	44.3

Methods

Mortars using different amounts of lime-mud and standard lime filler (0, 6, 12 and 18 %) were produced and tested (Table 2). Lime-mud was used in its natural condition, as-received from the paper pulp mill with 34% of moisture. This LM water was discounted from nominal water content used to produce the mortars. The total water and the superplasticiser used in the mortars mixtures were 62% and 0.07% in relation to cement content, respectively. The LM and SF were used as fillers in substitution of sand by weight in dry base. The formulations were evaluated through rheology and flow table measurements, assuring that all the samples exhibited an adequate condition to be tested in both equipments. In this way, it was possible to obtain a complete characterization of their fresh state behavior. A complementary study of these mortars in the hardened state was also developed.

The procedures used to prepare the formulations included: (i) placing lime-mud and the rest of mortar components into water; (ii) mixing for 1 min at a low rotation speed of 60 rpm; (iii) stopping for 1 min; (iv) mixing again for 1 min at a higher rotation speed (120 rpm). The rheometer measured the rheological behavior of fresh mortars, with a maximum speed rotation of 100 rpm during 60 minutes of total test time. The workability of mortars was measured through the “slump” on flow table, according to EN 1015-3:1999 [17]. Mortars specimens with 40 × 40 × 160 mm were produced for the mechanical test and tested after 28 curing, according to EN 1015-11:1999 [18]. Specific density, apparent porosity and water absorption were also determined with two flexural specimen remains by the immersion technique.

Table 5. Cement-mortars formulations.

Mortars	Cement	Sand	Free Water	LM Water	LM (d.b.)	SF (d.b.)	Ratio (Filler/Cement/Sand)
	(g)						
0%	445	1335	276	0	0	0	0 / 25 / 75
LM6%	445	1255	232	44	80	0	4.5 / 25 / 70.5
LM12%	445	1175	189	87	160	0	9 / 25 / 66
LM18%	445	1095	145	131	240	0	13.5 / 25 / 61.5
SF6%	445	1255	276	0	0	80	4.5 / 25 / 70.5
SF12%	445	1175	276	0	0	160	9 / 25 / 66
SF18%	445	1095	276	0	0	240	13.5 / 25 / 61.5

Results and Discussion

The high content of CaCO3 in LM makes this waste an interesting material to be used as filler, although LM and SF exhibited some significant differences like the particle size, specific surface area and Na2O content. For that reason, such differences may be the main responsible for distinct performance on the mortars.

Fig. 2 exhibits the torque values of mortars containing LM, SF and control (0%). In general, the torque values of samples with LM reached the highest results if compared to the SF substitution.

When very fine particles with higher surface area are added in the mortars, they can modify the fresh state behavior, since the free water available in the mixture tend to decrease. Thus, particle friction in such samples is higher than those samples without additions. Moreover, in the control sample, the superplasticiser can act exclusively on the cement particles increasing the free water, responsible for keeping particles separate by a certain distance. In addition, describing mortars rheological behavior as a Bingham fluid means that the material acts as a rigid body at low stresses but flows, as a viscous fluid, at high stress having a linear relationship between shear stress and strain rate once the threshold shear stress is exceeded [12]. The vertical lines above the torque line of the mixtures (fig. 2) indicate intense structural formation during the test stop period (when rotation speed goes to zero rpm). Such behavior was more evident on the samples with higher content of LM and at the end of the test.

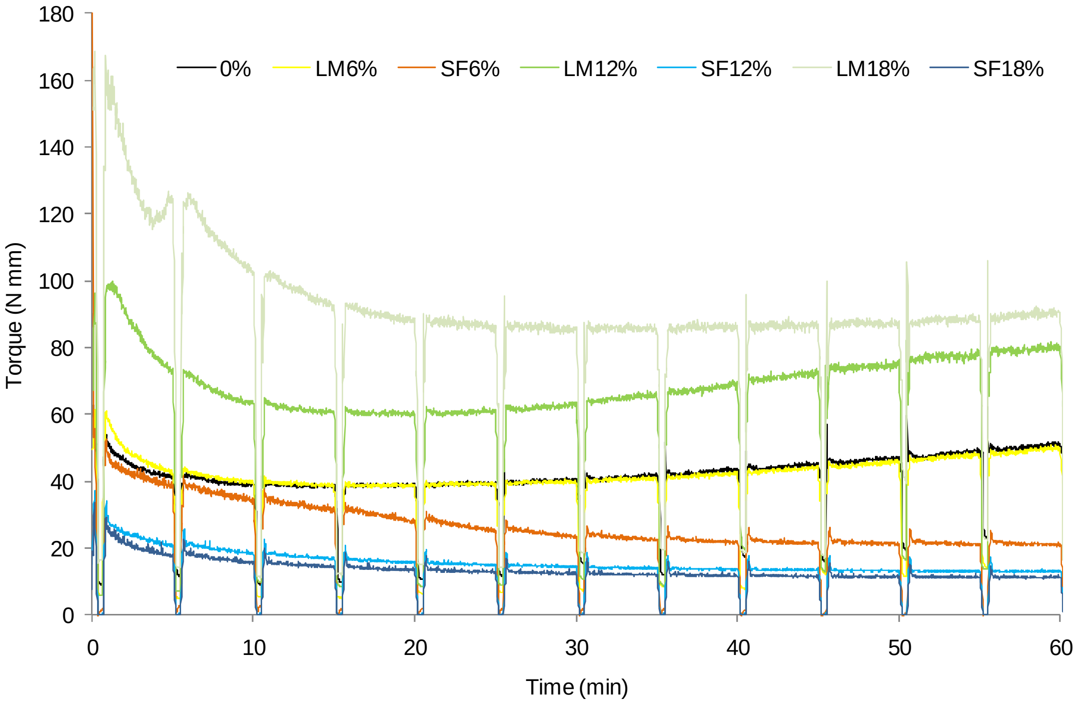


Figure 5. Torque vs. time of lime-mud and standard filler mortars.

Fig. 3 and 4 present the results concerning the effect of fine particles introduction on the plastic viscosity and yield stress on mortars, respectively. In general, samples with LM exhibited the highest results if compared to the LM at the beginning of the test. However, such differences decreased along time.

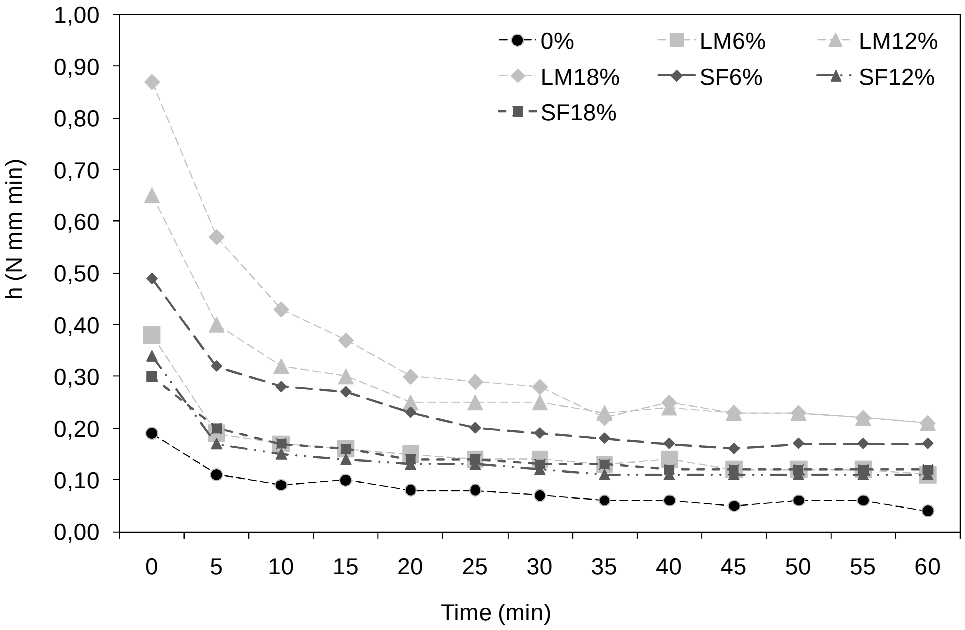


Figure 6. Plastic viscosity of mortars with lime-mud and standard filler.

This LM mortars behaviour make sense if the waste-water has not been available in the beginning of the test as discussed before. This remaining water starts getting free of the mixture after 30 minutes of test, making the LM mixtures more fluid and keeping the registered values constant. LM mortars plastic viscosity can also be confirmed through the flow table (spread diameter) results on Table 3. The spread decreases with the LM content increase. The maximum yield stress was observed in LM18% samples when compared to the control sample, while low constant values were registered on samples with 12% and 18% of SF.

Table 6. Mortars flow table spread results.

Samples	0%	LM6%	LM12%	LM18%	SF6%	SF12%	SF18%
Spread (mm)	206	200	191	151	238	260	260

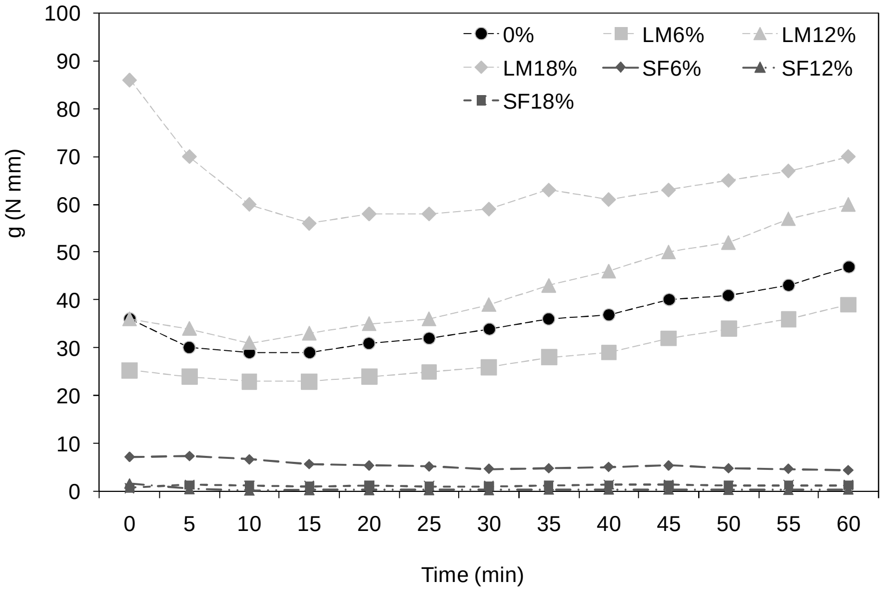


Figure 7. Yield stress of mortars with lime-mud and standard filler.

Table 4 presents the mortars hardened state characterization. The results show that LM does not affects significantly mortars density and strength, as well as the porosity or water absorption when compared to SF samples. The standard limestone filler (SF) containing mortars presents slightly higher values of the compressive strength and lower porosity, which might be related to its particle size distribution that might improve compaction.

Table 7. Mortars hardened state characterization.

Samples	Specific Density	SD	Porosity	SD	Water Absorption	SD	Flexural Strength	SD	Compressive Strength	SD
	(g/cm^3)		(%)		(%)		(Mpa)		(Mpa)	
0%	1.92	0.0	24	0.2	13	0.1	5.5	0.2	17	0.9
LM6%	1.90	0.0	24	0.0	13	0.1	4.9	0.4	19	1.8
LM12%	1.88	0.0	24	0.2	13	0.1	5.1	0.2	20	0.4
LM18%	1.89	0.0	25	0.1	13	0.1	5.5	0.3	21	2.4
SF6%	2.06	0.0	18	0.5	9	0.3	6.0	0.2	26	0.8
SF12%	2.04	0.0	18	0.2	9	0.1	5.8	0.3	26	0.3
SF18%	2.02	0.0	19	0.1	9	0.1	6.3	0.1	25	2.7
*SD - Standard Deviation										

CONCLUSIONS

The characterization results indicate that lime-mud from pulp and paper mill represents a waste with similar chemical and physical properties.

The use of this waste (lime-mud) in mortars affects significantly their rheology when compared to SF mortars results and the control sample:

(i) The increase of LM content decreases the mortars fluidity, improving the cohesion between the material particles in fresh state;
(ii) LM addition is equivalent to removing water from the system causing torque and yield stress increase and plastic viscosity decrease.

The hardened properties of mortars are not hindered with LM addition when compared to control samples. The LM waste use in cement-based materials as mortars can represent a good alternative for thousands of tonnes of this waste per year. This application avoids waste landfilling and also saves of natural resources as lime.

References

[1] B. Batchelor, Overview of waste stabilization with cement. Waste Management, 26 (2006) 689-698.
[2] M.C. Monte, E.Fuente, A. Blanco, C. Negro, Waste management from pulp and paper production in the European Union. Waste Management & Research, 29 (2009) 293-308.
[3] B.J. Mohr, H. Nanko, K.E. Kurtis, Durability of kraft pulp fiber-cement composites to wet/dry cycling. Cement and Concrete Composites, 27 (2005) 435-448.
[4] H. Nurmesniemi, R. Pöykio, L.R. Keiski, A case study of waste management at the Northern Finnish pulp and paper mill complex of Stora Enso Veitsiluoto Mills, Country Report, Waste Management 27 (2007) 1939–1948.
[5] H. Eroglu, U. Acar, O. İmamoğlu, O, Soil stabilization of roads sub-base using lime-mud waste from the chemical recovery process in alkaline pulp mill. Journal of Applied Sciences 6 (5) (2006) 1199-1203; ISSN 1812-5654.
[6] A. Hassani, H. Ganjidoust, A.A. Maghanaki, Use of plastic waste (poly-ethylene terephthalate) in asphalt concrete mixture as aggregate replacement. Waste Management & Research; 23 (2005) 322-327.
[7] B. Ahmadi, and W. Al-Khaja, Utilization of paper waste sludge in the building construction indusry. Resources Conservation Recovery 32 (2) (2001) 105-113.
[8] H. Eroglu, H.H. Acar Uçüncü, O. İmamoğlu, The effect of fry sludge addition supplied from pulp mill on the compressive strength of cement. Journal of the University of Chemical Technology and Metallurgy 42 (2) (2007) 169-174.
[9] J. Gaskin, Land application of pulp mill lime mud. University of Georgia, College of Agriculture and Environmental Sciences, Cooperative Extension Service along with the Pollution Prevention Assistance Division. Bulletin 1249, Georgia, USA, 2004.
[10] L. Senff, D. Hotza, W.L. Repette, V.M. Ferreira, J.A. Labrincha, Influence of added nanosilica and/or silica fume on fresh and hardened properties of mortars and cement pastes Advances in Applied Ceramics, 108 (2009).
[11] R. Modolo, V.M. Ferreira, L.M. Machado, M. Rodrigues, I. Coelho, Construction materials as a waste management solution for cellulose sludge. Waste Management 31 (2011) 370–377.
[12] H. Paiva et al., Effects of a water retaining agent on the rheological behaviour of a single-coat render mortar. Cement Concrete Res 36 (2006) 1257–62.
[13] C.F. Ferraris, Measurement of rheological properties of cement past: a new approach. J Res Natl Inst Standard Technology 104 (1999) 461–78.
[14] P.G. Banfill, Rheological methods for assessing the flow properties of mortar and related materials. Construction Building Materials 8 (1994) 43–50.
[15] P.G. Banfill, Structure and rheology of cement based systems. Proc Mater Res Society Symp 289 (1993) 149-60.
[16] EN 933-1: 2000. Tests for geometrical properties of aggregates. Part 1: Determination of particle size distribution – Sieving method.
[17] EN 1015-3: 2007. Methods of test for mortar for masonry: determination of consistence of fresh mortar (by flow table).
[18] EN 1015-11: 1999. Methods of test for mortar for masonry – Part 11: Determination of flexural and compressive strength of hardened mortar.

APPENDIX III

Ornamental stone sludge Valorisation in mortars

Regina Modolo[1, a*], Luciano Senff[2,b], Victor M. Ferreira[3,c], João A. Labrincha[4,d]

[1,3]Department of Civil Engineering/CICECO, University of Aveiro (UA), 3810-193 Aveiro, Portugal

[2,4]Department of Ceramics and Glass Engineering/CICECO, University of Aveiro (UA), 3810-193 Aveiro, Portugal

[a] regina.modlo@ua.pt, [b]lsenff@gmail.com, [c]victorf@ua.pt, [d]jal@ua.pt

*****Correspondent author

Keywords: ornamental stones, waste, valorisation, mortars.

Abstract

Sludges obtained as marble and granite waste sawing and polishing production process was characterized from chemical and physical point of view in order to use them as mineral addition for mortars. The formulations were prepared using two types of sludges (LS – Loom sludge and PS – Polishing sludge) in 5 and 10% (wt %) of cement replacement with water/cement ratio of 0.6. The sludges were also tested in cement paste replacement in 10% (wt%) with water/cement ratio of 0.45. The mortars formulations were defined through the flow table and rheometer behavior purposing to achieve a suitable workability. The appraised properties were rheology, spread, heat of hydration, physics (density, porosity and water absorption) and compressive strength (at 28 days). Results obtained showed that 10% cement replacement by the sludge provided mortars production without associated damages to the final product. This waste valorisation represents an important waste outflow for the ornamental stones sector, avoiding wastes landfill disposal.

Introduction

In recent years, the environmental damage and the wastes generated from industrial activity, increased significantly worldwide. Thus, the raw natural materials have become scarce and the adverse impacts on the environment are visible [1, 2, 3]. The ornamental stones production (including extraction, cutting, sawing and stone blocks polishing) generates about 30 to 40% of loses [4]. In the natural stone sector, the processors convert the quarries extracted blocks in intended pieces for floor coverings, household applications, the funerary art, sculpture and more. The subsector includes extracting and processing companies, mainly limestone and granite, whose production is intended primarily for the construction sector (inert or granules and gravel), and also to the chemical, steel-metallurgy and food processing. This is an important activity in Portugal. There are over 1250 companies in this sector and 11,000 over employees. The global production in terms of raw material processed is mentioned in more than 1.6 million tonnes [5]. The extraction and processing involves essentially two natural stone types, marble and granite. The sludges are the main generated waste (LER 01 05 04). Generally, their composition is stone waste, sand, lime and sometimes steel balls (due to the abrasive material recirculation). Sawing, cutting and polishing operations produce about 0.10 m^3 of sludge per ton of processed stone: 0.08 m^3 of sawdust in the operation and 0.02 m^3 in grinding and cutting. (one cubic meter of sludge is equivalent to 2,7 tonnes). [6]. The ornamental stone sludge is a fine particle with high tendency to agglomerate, difficulty a homogenous distribution in the mixtures. The fine particles can act as micro filler in the matrix, but at same time decreases the workability of mortars. Although, the sludge is not considered a hazardous waste (Class I), in many cases, there is no concern in these tailings reutilization and, therefore, they are dumped in lakes and rivers directly without any pre-treatment.

Nowadays, the final disposal or the reutilization of fine powder from ornamental stones industry as industrial wastes are considered one of the biggest environmental problems worldwide [7]. In this way, many attempts [8, 9, 10, 11, 12, 13] have been testing such wastes, especially in the construction industry, as tile, asphalt aggregate, brick, cement, concrete, clay products. So, it is possible to minimize the waste environmental negative impact and at same time add it some value. Although, some authors [10, 7, 8] have been tested the stone marble sludge in mortars, the use of rheology and spread on table are rarely used as considered parameters to define the mortars formulations. The flow table is a traditional method used in mortars to determine workability. It does not measure the yield stress and plastic viscosity separately due its constant load application. So, the rheometer has been used for this purpose. Traditionally, mortars, cement paste and concrete rheological behavior has been measured by the Bingham model.

The rheometer is capable of measures the rheological parameters for a wide values range at same time. The cement mixtures rheological behavior is described by the Bingham equation:

$$\tau = \tau_o \ \mu_p \gamma \qquad (1)$$

where τ (Pa) is the shear stress, τ_o (Pa) is the yield stress, μ_p (Pa*s) is the plastic viscosity and γ (s^{-1}) is the shear rate. Some rheometers measures torque T as a function of rotational speed N then the Bingham model has been also expressed by the following equation:

$$T = g + hN \qquad (2)$$

where g (N mm) and h (N mm min) are directly proportional to the yield stress and plastic viscosity respectively.

Systematic studies applying a methodology of experimental design are not frequently used in cement based materials. However, they can assist to identify the main effects and their interactions of the constituents [chemical admixtures, mineral additions and W/B (water/binder) ratio][14].

This paper aims to reuse the ornamentals stone sludge, as cement partial replacement (0, 5 and 10 wt %) to produce mortars based on mixtures formulation according to flow table and rheology performance.

Experimental

Materials

The Portland cement used in this paper was a CEM I 42.5 R. It has an average particle of 14 μm and the Blaine fineness 0.35 m^2/g, while the chemistry composition is showed in Table 1. Loom sludge (LS) and polishing sludge (PS) were used in dried condition as replaced of Portland cement. LS has a particle size distribution between 1.50 to 77.8 μm and average 15.7 μm and surface area of 3.7 m^2/g (BET), while PS has between 1.23 to 55.6 μm and average 11.2 μm and 7.2 m^2/g, respectively. The chemistry compositions was obtained by X-ray fluorescence spectroscopy (Shimadzu, EDX-700), while the pozzolanicity was determined by Standard EN 196-5:2005 [15].

Mortars and paste testing procedures

Mortars and pastes were produced, using different amounts (5 and 10 wt%) of ornamental sludge. Mortars with 1:3 cement/aggregate weight ratio and 0.6 water/cement weight ratio (w/c) were produced to rheology, flow table, compressive strength, water absorption and apparent porosity. Meanwhile, the cement paste with 0.45 w/c was utilized to the temperature of hydration. The components were weighed and mixed in the mechanical mixing (CONTROLS, 65-LS). The procedures included: (i) Water addition to the dry powder mix; (ii) Mix for 1 min at a low rotation speed of 60 rpm; (iii) Stop for 1 min to gather the mix into the centre; (iv) Mix again for 1 min at a higher rotation speed (120 rpm). The rheological behaviour of fresh mortars was measured by a rheometer (Viskomat PC). It was used a maximum speed rotation (100 rpm) and 250 minutes of test time. The workability of mortar was measured through "spread" on flow table according to EN 1015-3:1999 [16]. For the mechanical test, mortars specimens with 40 × 40 × 160 mm were performed. The moulds were covered with plastic bags for 24 h to avoid water loss. After 24 h, all the samples were immersed in water for curing during 27 days and the compressive strength was determined by EN 1015-11:1999 [17]. Water absorption, porosity and apparent density were also determined by the immersive techniques [18]. The heat of hydration was tested in cement paste samples during 24 h. This parameter was measured in a quasiadiabatic calorimeter (Langavant). The cement pastes were thermally isolated in boxes stored in a curing chamber at 20 °C of temperature and 65% of relative humidity.

Table 8. Chemical composition of Portland cement CEM I – 42.5R.

Material	PS	LS	Binder
Characteristics	Sludge from polishing process	Sludge from cutting (loom) process	Portland Cement (CEM I 42,5) Secil (Maceira)
Moisture (%)	37,4	38,4	<1
SiO_2 (%)	65,9	57,7	20,4
Al_2O_3 (%)	12,1	16,0	5,2
Fe_2O_3 T (%)	11,0	6,1	3,1
MgO (%)	0,1	2,5	2,0
CaO (%)	3,2	6,3	65,7
Na_2O (%)	2,1	2,3	nd
K_2O (%)	5,1	4,4	1,4
TiO_2 (%)	0,2	1,4	0,3
P_2O_5 (%)	0,1	0,6	0,1
L.O.I. (%)	0,1	2,6	2,1

Results and Discussion

Rheology and flow table measurements

When ultra fines particles with higher surface area than Portland cement are used in mortars, they can modify the fresh and hardened properties. If flow table and rheometer are used to define a set of formulations of mortars, the maximum amount to be added is reduced, since the minimum plasticity requires for such equipments are different. On the other hand, it permits to achieve a better characterization. In general, the torque values and yield stress changed markedly when the Portland cement was replaced to sludges (Fig. 1

and Fig. 2). However, the plastic viscosity did not show a noticeable difference (Table 2). Such additions exhibit higher surface area than particle cement and consequently, the free water available in the mixture decreased. As consequence, the particle friction and three-dimensional structures formation tend to increases.

Table 9. Water absorption, bulk and porosity, flow table, torque, yield stress and plastic viscosity, heat of hydration mortars results.

Sample	Flow Table	Torque	Yield stress	Viscosity	Heat of hydration	Bulk	Water absorption	Porosity	Compressive Strengh (28 days)
	mm	N mm min (*)	N mm	N mm	ºC (105')	g/cm3	%	%	MPa
Control	218	58,45	29,5	0,14	23,62	2,01	9,82	19,78	34,35
PS5%						2,00	10,16	20,34	33,19
PS10%	205	72,35	34,8	0,14	24,20	2,00	10,18	20,28	32,59
LS5%						1,99	9,94	19,83	32,91
LS10%	207	79,47	43,7	0,13	24,00	1,99	10,29	20,44	31,53

(*) Registered value at minute 105 of the rheology test.

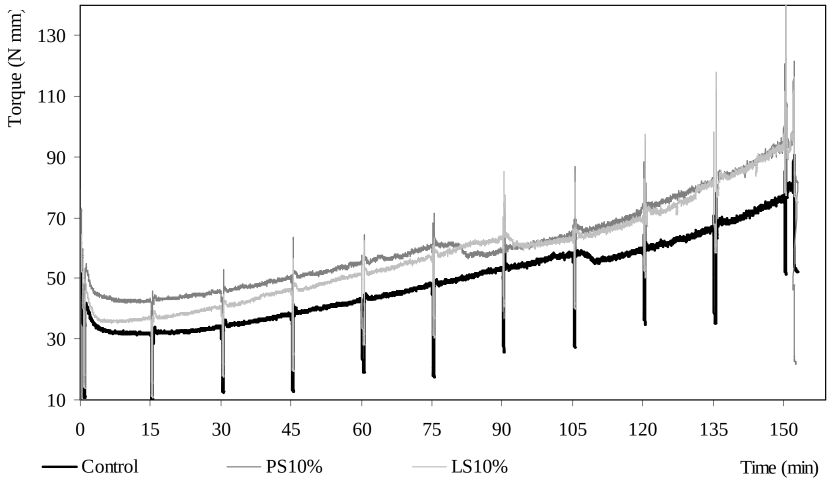


Figure 8. Ornamental stones sludges and control mortars rheological behaviour (Torque).

The torque values of sludge samples increased compared to the control samples. As PS has a higher surface area than LS, a high value of initial torque was obtained. On the other hand, such characteristic was not enough to keep the results above the LS level after 75 min. In addition, both sludges samples showed low plasticity and the Bingham model accuracy became poorer, while the vertical line above of the torque line shows intense structures formation during the test stop period.

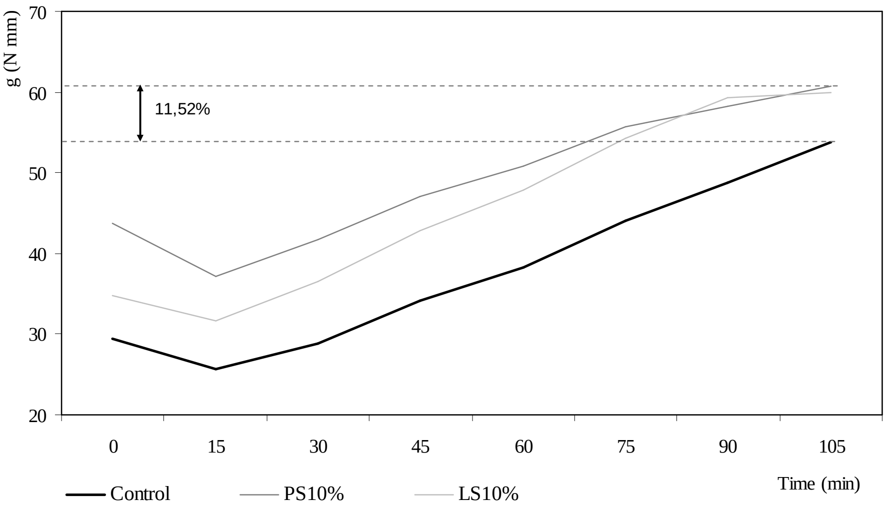


Figure 9. Ornamental stones sludges and control mortars rheological behaviour (Yield stress).

Heat of hydration

In general, when the Portland cement is mixed with water, two main peaks can be observed. The first peak occurs few minutes after contact with water, where several Ca^{2+}, SO_4^{2-}, Na^+, K^+, and OH^- ions are releases to the aqueous solution from gypsum, C_3S, C_3A and C_4AF phases. Meanwhile, the second peaks occur after dormant period finished, caused by faster crystallization of CH and C-S-H.

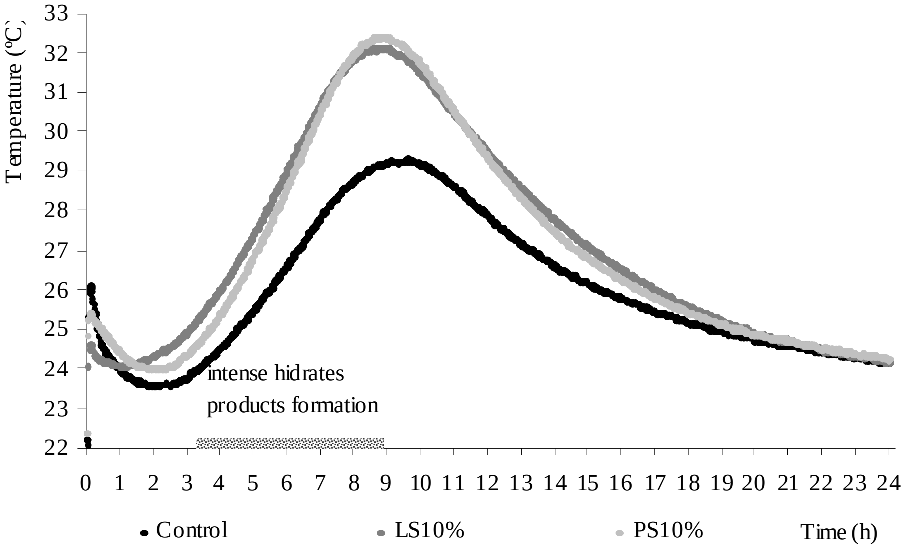


Figure 10. Cement and Ornamental stones paste heat of hydration results.

In general, the presence of sludges influenced significantly the results in both of cases. In the first peaks, the cement replaced by PS and LS seems that was determinate to the results. However, such formulations showed lower dormant period, as well as, increased faster the temperature in relation to the control (Fig. 3). Thus, the hydraulic charter of sludges can be appointing as responsible for the results. In addition, the heterogeneous chemical activation nuclei can be also considered to the results. The fast temperature increasing might induce micro cracking to material due to internal stress. Such formulation, showed the highest values of torque in relation to the control samples, suggesting that there is a relationship between them.

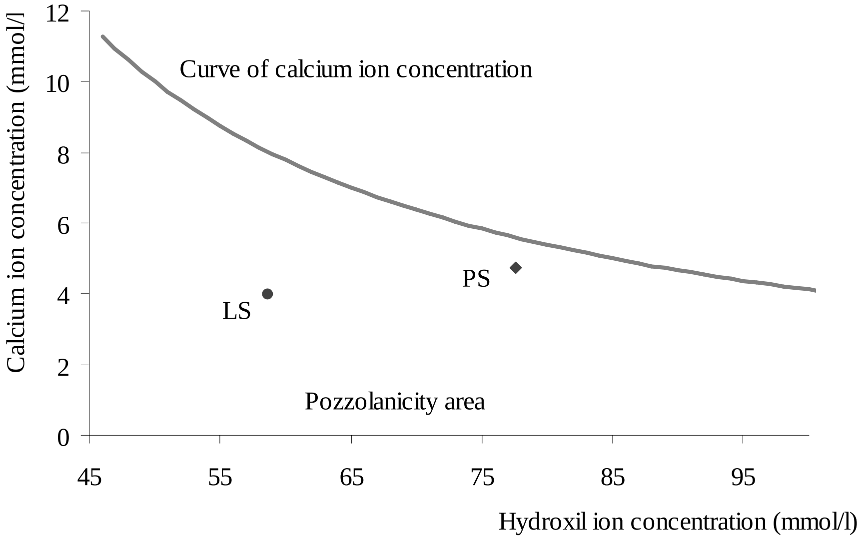


Figure 11. Ornamental stones sludges pozzolanicity results.

Water absorption, apparent porosity and compressive strength

The addition of ultrafine particles in cement based materials can contribute to fill out the space (physical effect – Table 2) or react with calcium hydroxide (pozzolanic effect – Fig. 4), resulting in calcium silicate hydrates (C-S-H). In general, the results showed that up to 10% of sludge incorporation doesn’t modify significantly the physical properties of mortars. Probably, the microfiller effect can contribute to the results, despite the reduction of cement in the material. However, the compressive strength was reduced significantly, despite the material exhibits pozzolanic effect. In this case, this characteristic was attenuate by cement replaced (Table 2).

Conclusions

The optimal working interval definition for fresh mortars based on simultaneous information obtained from flow table and rheometer tests is complex. The reduction of plasticity of mortars is denoted by enhance of applied torque, while there is a spread reduction in the flow table test. In both cases, this tendency could be explained by an increasing friction between surface grains and plasticity lost. It is feasible to use the rheometer to evaluate the mortars rheological parameters. Increasing finer mortars content thought ornamental stone sludge addition increases the torque and the yield stress. A verified advantage was to replace 10% of cement by ornamental stones sludge without bringing material damages. 10% of theses sludges addition doesn’t modify significantly the mortars physical and mechanical properties. According to the exposed, cement can be 10% replaced in mortars production without associated damages to the final product. This waste valorisation represents an important waste outflow for the ornamental stones sector, avoiding wastes landfill disposal.

References

[1] Binici, H., Shah T., Aksogan, O., Kaplan H., Durability of concrete made with granite and marble as recycle aggregates, Journal of Materials Processing Technology 208 (2008) 299–308.

[2] UMTC, Use of recycled materials and recycled products in highway construction, University of Massachusetts Transportation Center Report UMTC-95-1, US, 1995, pp. 238–245.

[3] OECD, Road Transport Research: Recycling Strategies for Road Works. Organization for Economic Co-operation and Development (OECD), Paris, France, 1997, pp. 140–148.

[4] NITES - Núcleo Regional de Informação Tecnológica do Espírito Santo, "Desperdício na Indústria de Mármore e Granito. Rochas de Qualidade"(Marble and Granite Industry Waste: Stones Quality), Ed.118 (Jul-Ago-Set 1994).

[5] INPRI, Estudo de inventariação de resíduos, Instituto dos resíduos. CAE 26, Relatório Síntese – Classificação Portuguesa das Actividades Económicas, Fabricação de outros produtos minerais não metálicos. (2003)

[6] Figueiredo, J. M., Rodrigues, F.,Correia, A. E., Chambino, M. T, 2001. *Sector daPedra Natural*. INETI,Lisboa,2001.

[7] Corinaldesi V., Moriconi G., Naik, T.R., Characterization of marble powder for its use in mortar and concrete Construction and Building Materials 24 (2010), 113–117.

[8] Alyamaç, K. E., Ince R., A preliminary concrete mix design for SCC with marble powders. Construction and Building Materials 23 (2009), 1201–1210.

[9] Akbulut, H., Gürer, G., Use of aggregates produced from marble quarry waste in asphalt pavements. Building and Environment 42 (2007), 1921–1930.

[10] Segadães, A.M., Carvalho, T, M.A., Acchar, W., Using marble and granite rejects to enhance the processing of clay products. Applied Clay Science 30 (2005), 42– 52.

[11] Hwang, E., Soo Ko Y., Jeon, J., Effect of polymer cement modifiers on mechanical and physical properties of polymer-modified mortar using recycled artificial marble waste fine aggregate Journal of Industrial and Engineering Chemistry 14 (2008), 265–271.

[12] Karaşahin, M., Terzi, S., Evaluation of marble waste dust in the mixture of asphaltic concrete. Construction and Building Materials 21 (2007), 616–620.

[13] Karasahin, M. and Terzi, S., 2004. Use of Marble Waste Dust in the Mixture of Asphaltic Concrete As Mineral Filler. Euro Bitume, Viyana.

[14] L. Senff, D. Hotza, W. L. Repette, V. M. Ferreira, J. A. Labrincha., Influence of added nanosilica and/or silica fume on fresh and hardened properties of mortars and cement pastes Advances in Applied Ceramics, 108, n.º 7 (2009).

[15] EN 196-5: 2005, Methods of testing cement—part 5: pozzolanicity test for pozzolanic cements.

[16] EN 1015-3:2007. Methods of test for mortar for masonry: determination of consistence of fresh mortar (by flow table).

[17] EN 1015-11:1999. Methods of test for mortar for masonry – Part 11: Determination of flexural and compressive strength of hardened mortar.

[18] EN 197-1:2004. Cement: composition, specifications and conformity criteria for common cements.

APPENDIX IV

The rheological behaviour and hardened properties of mortars with red mud addition

SENFF L[1,a], MODOLO RCE[2,b], HOTZA D[3,c], FERREIRA VM[2,d], LABRINCHA JA[4,e]

[1]Mobility Engineering Center, Federal University of Santa Catarina, Joinville, SC 89218-000, Brazil

[2]Department of Civil Engineering/CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

[3]Department of Chemical Engineering (EQA), Federal University of Santa Catarina (UFSC), 88040-900 Florianópolis, SC, Brazil

[4]Department of Ceramics and Glass Engineering/Centre for Research in Ceramics and Composite Materials (CICECO), University of Aveiro, 3810-193 Aveiro, Portugal

[a]lsenff@gmail.com, [b]regina.modolo@ua.pt, [c]dhotza@gmail.com, [d]victorf@ua.pt, [e]jal@ua.pt

Keywords: Red mud, mortar, rheology

Abstract

The use of solid wastes in the building industry can contribute to achieve the sustainable development of this sectorial activity, while it might help to reduce production costs. In this way, the experimental research here presented evaluates the influence of Red Mud particles (RM) on the fresh and hardened properties of cured mortars up to 28 days. Portland cement was replaced up to 50 wt.% RM, adjusting the relative amount of water (36–48 wt.%) in order to get mortars with suitable workability as defined by rheometry and flow table measurements. Temperature of hydration, water absorption and compressive strength were also determined. RM decreases the workability and increases the yield stress of the material. Mortars with similar spread on table showed different behaviour along the rheology test. RM did not change significantly the dormant period, but the magnitude of exothermic peak is reduced when the Portland cement was replaced by RM above 20 wt.%. The water absorption increased when the cement was replaced by RM, while the compressive strength exhibited an opposite tendency.

Introduction

The red mud is a residue generated in large scale from the Bayer process used to produce alumina. Through this process, bauxite is digested in a concentrated caustic soda (NaOH) solution at high pressure and moderate temperatures (~270 ºC), in order to obtain the alumina trihydrate ($Al_2O_3.3H_2O$) [1][2]. This process leads to the formation of insoluble hydroxides where the impurities are concentrated, after proper washing, settling, and filtration operations. Such is the case of the red mud, containing goethite (α-FeOOH), hematite (α-Fe_2O_3), bohemite (γAlO(OH)), quartz (SiO_2), sodalite ($Na_4Al_3SiO_{12}Cl$), and gypsum ($CaSO_4.2H_2O$) as major phases, and calcite ($CaCO_3$), whewellite ($CaC_2O4.H_2O$), gibbsite ($Al(OH)_3$), and TiO_2 as minor components [1]. In general, the production of 1 ton alumina generates 1-2 ton (dry basis) of red mud. Thus, the storage of these massive amounts is economically and environmentally problematic, due to the risk of contamination of natural resources and living organisms [3][4]. Therefore, the main purpose of this work is investigating the impact of red mud on the rheological properties of mortars. Complementary fresh and hardened state properties of mixtures are also evaluated.

Materials and Methods

Portland cement (PC - type I 42.5R, according to EN 197-1 [5] was used as binder. It has a specific area of 0.35 m^2/g (Blaine fineness), average particle size of 14 μm and its chemical composition is given in Table 10. Red mud (RM) slurry (Alcoa, Spain), here used as partial substitute of Portland cement, contains about 61 wt.% solids, specific area of 20 m^2/g, particle size distribution between 0.1 to 7 μm (average 0.78 μm), and chemical composition illustrated in Table 10. Superplasticizer (SP) used to adjust the plasticity of fresh mortars is based on a polycarboxylic acid (Glenium 52, Basf), with density between 1.067-1.107g/cm³. The sand used as aggregate is composed by three particle size fractions (1.2, 0.6 and 0.3 mm), each one corresponding to 33.33 wt.%.

Table 10 Chemical composition of Portland cement CEM I – 42.5R as red mud determined by XRF.

Component	Portland Cement (wt.%)	Red Mud (wt.%)
SiO_2	20.37	5.54
CaO	63.05	3.27
Al_2O_3	4.78	18.76
Fe_2O_3	2.96	51.8
SO_3	3.70	0.23
MgO	2.02	-
Cl^-	0.02	-
Na_2O	-	6.84
K_2O	-	0.08
TiO_2	-	11.18
MnO	-	0.04
Loss On Ignition	2.37	0.16

Testing procedures

The RM particles were used as partial substitute of Portland cement, in levels up to 50 wt% (Table 11 and Figure 1). An extra dosage of water (W) was required in mixtures containing more than 15 % RM to keep the spread value in 200 mm. In addition, the SP was fixed in 0.25 wt.% and binder-to-aggregate weight ratio was also fixed (1:3). Red mud was used in the as-received condition (as a paste), and the quantity of water incorporated by the RM was considered to reduce the volume required to prepare each mixture. The solid components of the blends were mixed inside a plastic bag for 1 min, while the superplasticizer was mixed into water, before addition to the solids. The mixing of the paste was conducted for 3.5 min.

Table 11 Mortar formulations.

Wet basis (wt.%)			Dry basis (wt.%)	
Cement	RM	Water	Cement	RM
64.0	0.0	36.0	100	0
59.4	4.7	36.0	92.7	7.3
52.7	9.3	38.0	85	15
49.5	12.4	38.1	80	20
42.0	18.0	40.0	70	30
34.0	22.7	43.3	60	40
26.0	26.0	48.0	50	50

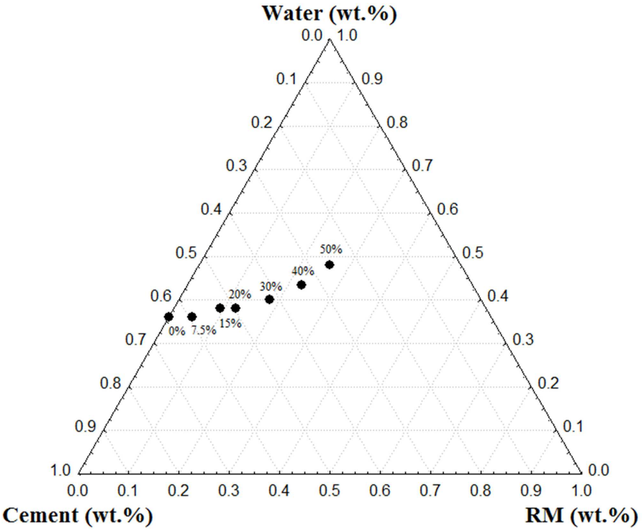


Figure 1 Experimental space showing the prepared mixtures.

The rheological behaviour of fresh mortars was measured in a rheometer (Viskomat PC, Germany) for testing cement pastes and mortars (Figure 2a), while the flow table (Figure 2b) was performed immediately after mixing, following the EN 1015-3 [6].

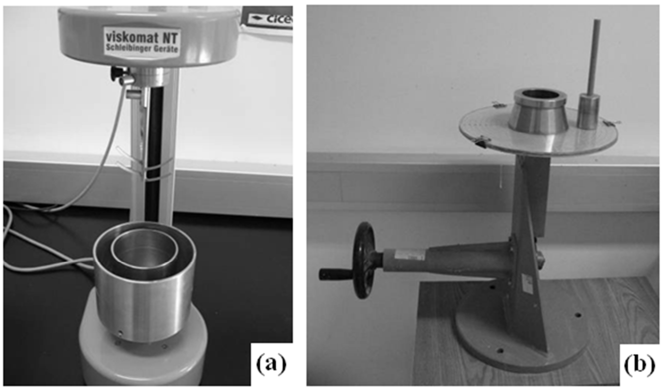


Figure 2 (a) Rheometer and (b) flow table test.

The maximum rotation speed was 100 rpm and at every 15 min the speed was brought to zero, kept as that for 30 s, and was then increased to 100 rpm during 30 s. The rheological parameters, namely, plastic viscosity (*h*) and yield stress (*g*) were obtained from Bingham model [7].

The temperature of hydration was monitored in a quasi-adiabatic calorimeter (Langavant), while the water absorption of hardened mortars was determined by an immersive technique [8]. The compression strength was determined according to the EN 1015-11 standard [9]. Samples with 40 × 40 × 160 mm were used, as prescribed by EN 196-1 [10]. The curing was firstly conducted in room conditions with samples placed inside the moulds (covered by plastic bags and for 24 h), followed by immersion in water for 28 days.

Results and Discussion

Rheometry and flow table measurements

When the flow table and rheometer were used as parameters for determining the composition of mixtures, an additional difficulty in defining the experimental plan was observed. Such equipments differ in terms of minimum plasticity required. To evaluate the effect of higher levels of RM in mortars, it was necessary to fix the value of spread on table (200 mm), in a condition that permits their evaluation in the rheometer and flow table, simultaneously.

In general, RM particles increased the yield stress and plastic viscosity regardless the water content added (Figure 3). As RM particles are smaller and have higher surface area than PC grains, they reduce the amount of free water required to lubricate the solid particles. As a result, the internal friction of particles increased and the plasticity of mixture diminished. In addition, the ultra-fine particles in suspension have a stronger tendency to agglomerate, which hampers the adequate flow of the mixture.

The yield stress also increased by prolonging the measurements. Particle collisions, formation of a three-dimensional structure upon hydration, and concomitant reduction of free water available are possible causes for that variation. The evolution of plastic viscosity does not show a defined tendency and, therefore, the effect of RM is better accounted by looking to the yield stress. Although the values of the initial yield stress are similar for samples with 20, 30 and 40 wt.% RM, they exhibited significant differences during the rheology test.

Temperature of hydration

Samples showed two main peaks on curves representing the temperature variation upon curing (Figure 4). The first peak occurred in the first moments after contact with water, while the second peak has its maximum at 11-13 h but starts after 4-6 h.

The presence of RM particles did not accelerate the hydration process. As expected from the slight hydraulic character of RM, its use as binder (PC replacement) should delay the hydration reactions. However, when used up to 15% differences are small when compared with REF mortar (RM-free). The fineness of RM particles might be responsible for their action as heterogeneous chemical activation nuclei for the hydration of cement [11]. In addition, samples containing higher RM levels reached lower maximum temperature.

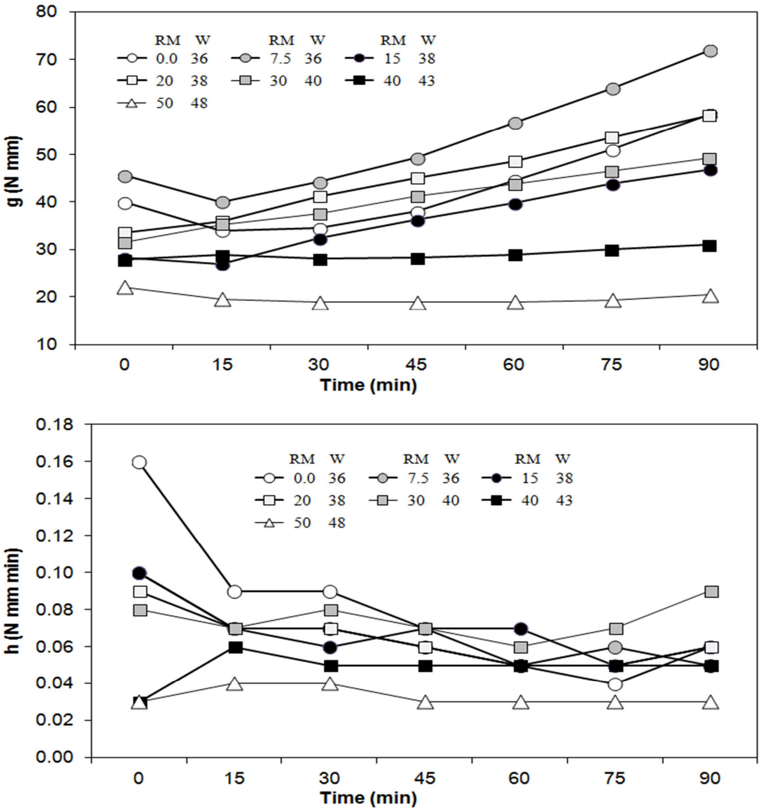


Figure 3 Rheological parameters of fresh mortar mixtures containing up to 50 wt.% RM

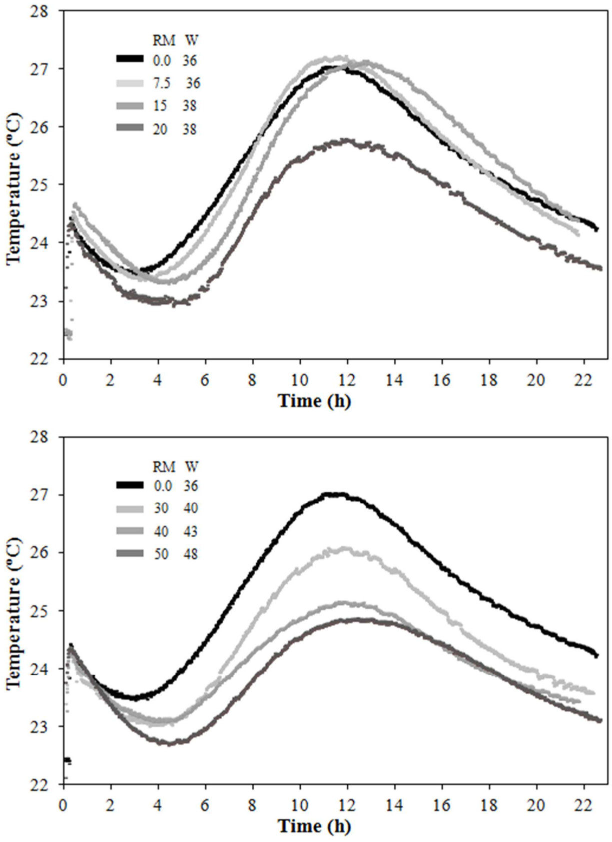


Figure 4 Temperature of hydration of mortars containing up to 50 wt.% RM

Water absorption and compressive strength of hardened samples

Samples showed higher water absorption when red mud and water levels increased (Figure 5). The combined effect of RM and W strongly increased the water absorption, confirming again the non-hydraulic character of the mud. Hardened samples will show higher volume of open pores. Despite the possible capacity of RM particles to fill in the pores of the material, due to their fineness, this effect is not sufficient to compensate the lower extent of chemical reactivity and hydrates formation. As a consequence, the compression strength of samples will diminish when RM level is higher (Figure 6).

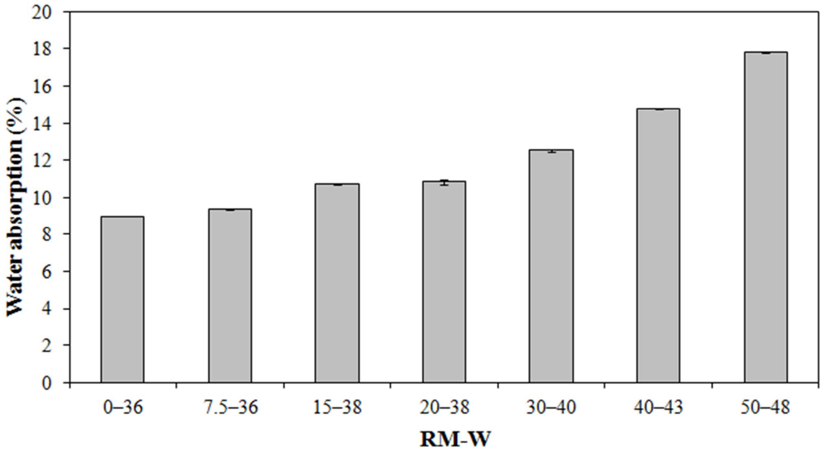


Figure 5 Water absorption (%) of mortar after curing at 28 days.

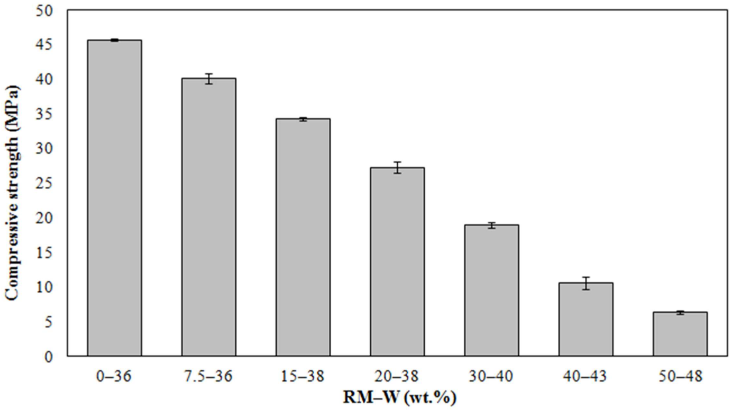


Figure 6 Compression strength (MPa) of mortars after curing at 28 days

The compressive strength of samples 7.5RM + 36W, 15RM + 38W and 30RM + 40W reduced respectively 12, 25 and 59% regarding the REF. RM particles can adsorb some water, and then the available amount for cement hydration become insufficient to complete the reactions. Mortars with 20, 30, 40 and 50 wt.% RM showed a successive loose of mechanical resistance, since the relative amount of cement diminished. Moreover, the required amount of water to reach suitable workability of the mixtures tends to increase, leaving pores after drying/curing.

Conclusions

The differences (relative to REF) of initial yield stress for mixtures with RM are not constant and also depend on W. By contrast, the plastic viscosity does not change too much. Mortars with 20, 30 and 40 wt.% RM exhibited similar values of initial yield stress, but during the rheology test the behaviour of such mixtures tend to be distinct. RM does not significantly delay the hydration process. However, for high RM amounts (above 20 wt.%) the maximum temperature decreased. Hardened samples show higher water absorption and lower mechanical strength when RM level increases. This also confirms the non-hydraulic character of the mud. Such tendencies are also affected by the W added.

References

[1] R.A. Hind, S.K. Bhargava, S.C. Grocott: Colloids and surfaces A: Physicochemical Engineering Aspects Vol. 146 (1999), p. 359–374.
[2] M.J. Matteson, L. Orr: Marcel Dekker Inc, New York (1987).
[3] L.G. Mason: Nova Science Publishers Inc, New York (2007).
[4] A.T. Hubbard: Marcel Dekker Inc, New York (2002).
[5] EN 197-1:2004. Cement: composition, specifications and conformity criteria for common cements.
[6] EN 1015-3:2007. Methods of test for mortar for masonry: determination of consistence of fresh mortar (by flow table).
[7] Banfill PFG: Constr Build Mater Vol. 8 (1994), p. 43–50.
[8] E.C.M. Pennings, W. Grellner: J Am Ceram Soc Vol. 72 (1989); p. 1268–1270.
[9] EN 1015-11:1999. Methods of test for mortar for masonry – Part 11: Determination of flexural and compressive strength of hardened mortar.
[10] EN 196-1:2005. Methods of testing cement: determination of strength.
[11] P. Lawrence, M. Cyr, E. Ringot: Cem Conc Res Vol. 33 (2003), p. 1939-1947.

APPENDIX V

LIME MUD AS RAW MATERIAL IN LIGHTWEIGHT AGGREGATE PRODUCTION

R.C.E. Modolo[1], V.M. Ferreira[2], J.A. Labrincha[2], L.A.C. Tarelho[3], L. Senff[2], N. Costa[4]
1 University of Aveiro/CICECO, Dep. Eng. Civil, 3810-193 Aveiro, Portugal, regina.modolo@ua.pt
2 University of Aveiro/CICECO, 3810-193 Aveiro, Portugal, victorf@ua.pt; jal@ua.pt; lsenff@gmail.com
3 University of Aveiro/CESAM, 3810-193 Aveiro, Portugal, ltarelho@ua.pt
4 Argex – Argila Expandida, SA.

ABSTRACT

Lime-mud is a solid waste generated in pulp mill in considerable amounts. It is a waste chemical and physically homogeneous, basically composed by calcium carbonate which allows valorization opportunities in the construction materials sector and, in this specific case study, in lightweight aggregates (LWA).

In this paper, a potential management solution was evaluated regarding the viability of using lime mud at industrial scale. The test was developed using lime mud as raw material with total substitution of conventional limestone powder on fabrication of lightweight aggregates. The industrial process was evaluated considering some limitations on operations logistic due to the lime mud moisture content. Involved costs were estimated for the waste management solution and the impact on final product basic characteristics was assessed.

The obtained results indicate that lime mud presents high potential of utilisation as raw material in lightweight aggregate production but, in what basic characteristics are concerned, the waste moisture content must be taken into consideration.

Keywords: lime mud, lightweight aggregate, waste management

INTRODUCTION

According to several authors, pulp mill industry generates various potential solid wastes that could easily be used as raw material in construction sector due its basic chemical and physical characteristics and, in some cases, even improve some of their properties 0[2],[3],[4],[5],[6],[7].

The extraction of natural aggregates for use in construction is associated with significant adverse environmental effects [8]. In recent years, the environmental damage and the wastes generated from industrial activity increased significantly worldwide. Thus, natural raw materials have become scarce and the adverse impacts on the environment are visible [9][10],[11]. Construction sector is able to drain large solid wastes and in consequence avoid natural resources consumption [12],[13],[14]. Several types of wastes have been exhaustively tested in lightweight aggregates (LWA) production, but most of them have been used to replace an expansive material. Sarabèr et al (2012)[15] for example, tested fly ash from coal fired power in this application. The results showed that adequate LWA can be produced. Meanwhile, Wang et al (2009) [16] also tested coal fly ash but blended with dry sewage sludge.

In terms of raw material, this product can be manufactured by thermally treatment of clays, shale, siliceous rock or slate and also uses in its composition, water and limestone coating powder (LSCP). The LSCP specific function in the LWAs is related with covering the LWA pellets surface avoiding their agglomeration in the rotary kiln and also contributes to the formation of a denser external surface to avoid water absorption.

Considering limestone one of the most used raw-material in the construction sector, this work intends to assess a solid waste from pulp mill process, namely a lime mud (LM), with similar chemical, physical and mineralogical characteristics with limestone filler, as replacement material for standard LSCP conventionally used in LWAs production. LM is a solid waste generated from pulp and paper mill in the chemical recovery process mainly composed of calcium carbonate and small amount of magnesium carbonate and it is estimated that about $0.47m^3$ of lime mud is generated to produce 1 ton of pulp [17][18],[5],[19]. In this specific study, the pulp mill generates approximately 360ton/month (in dry base).

From a waste management perspective, the focus of this study is to evaluate the replacement potential of LM in lightweight aggregate production as a substitute material of LSCP at industrial scale. This paper presents the research work developed in industrial scale (process stages and final product). The comparative study of the raw-materials was used as criteria decision for industrial test. Energy costs related to drying lime mud process was also assessed. In terms of waste flow capacity and related economic aspects of the application, as well as logistic and technical problems due to LM properties (mainly related to moisture content) some parameters were registered and also compared. In industrial scale approximately 25 tons of LM in LWA production was tested. Process parameters as machine stream, operation time, energy costs related to LM moisture elimination and the waste transportation were measured or calculated and compared with the conventional process.

The consumption of LSCP is around 300 $\text{tons}_{\text{dry base}}$/month only in one LWA mill. This fact implies that the process could drain large amount of LM per year. It would permit the drainage of approximately 80% of the lime mud produced in this pulp mill located around 30km of the LWAs mill installation. This waste management option as a valorization solution could avoid the waste landfilling, the reduction of natural resources extraction and also to save costs for both sectors, lightweight aggregate and pulp paper industries.

Assuming the agreement with the involved companies, this work uses the denominations “factory X” for the pulp mill which generates the lime mud and “factory Y” for the LWA mill with the waste final application.

EXPERIMENTAL

Materials

Raw-materials were characterized in terms of chemical, physical (grain size distribution and bulk density) and mineralogical properties. LM used in this research was collected in the washing stage as illustrated in Fig 1.

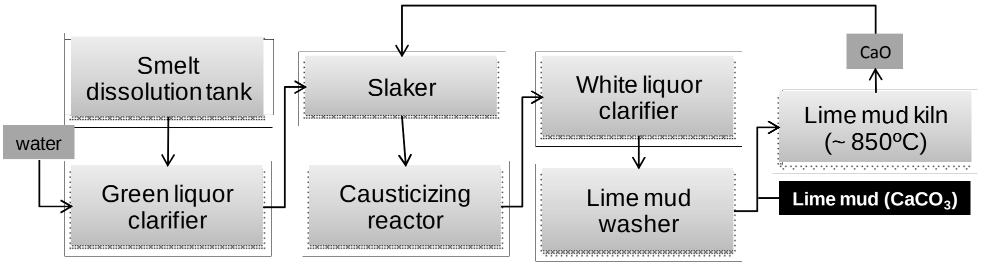


Fig.1. Scheme of caustification zone from Kraft process under study. Lime mud collection spot.

This LM presents approximately 20% of moisture content. The raw-material main characteristics are presented in Table 1. The particle size distribution was determined by laser diffraction in the range between 0.04 and 2000 µm (Beckman Coulter LS230). The crystalline phases present in dried materials were determined by X-ray diffraction (XRD) and the chemical composition was determined by X-ray fluorescence spectroscopy (XRF). Raw materials weight and energy changes were also analysed by thermogravimetry and differential thermal analysis (TG/DTA). SEM (Scanning electron microscope) observation was used to assess LM and LSCP microstructures. LSCP and clay pellets (CP) were supplied by factory Y.

Table 1. Raw materials characterization results.

Parameter	Unit	LM	LSCP	Clay Pellets
Na_2O	%	1.12	0.08	0.18
MgO	%	0.48	0.27	3.2
Al_2O_3	%	0.16	0.55	20.7
SiO_2	%	0.3	0.76	56.3
P_2O_5	%	1.19	0.02	0.13
SO_3	%	0.04	0.53	0.39
K_2O	%	0.01	0.02	3.13
CaO	%	54	56.4	25.5
TiO_2	%	*ND	0.02	0.58
Fe_2O_3	%	0.04	0.10	4.2
MnO	%	0.02	*ND	0.11
LOI	%	42.6	41.3	7.95
Moisture	%	~30	<1.0	**NQ
Particle Size	µm	0.79 - 25	0.28 - 8.0	**NQ
Mineralogy		Calcite and Calcium Silicon	Calcite	Quartz Muscovite Kaolinite Montmorilonite Microline

Methods

LWA industrial test

Conventional data process was registered during 4 hours before the industrial test with LM. The lime mud was incorporated in wet base. The data were collected each 15 minutes during all period of the test. The LSCP flow (kg/h) in the entrance of rotary drum and the kiln average exit temperature (ºC) were monitored. The standard lightweight aggregate is referred as LWAs and the one incorporating lime mud is named as LWAw. In both cases density and flow rate were controlled and registered. The industrial test with the lime mud waste was developed in 2,5 hours.

Valorization solution limitations

To assure the proper functioning stages of the process, considering the high level moisture content of LM, costs related to a silo and drying equipment were also estimated.

Industrial scale - Logistic

A truck with 25 tons of capacity conducted the waste as collected to the LWA mill (factory Y) and stored during half day. The waste was placed near the production line equipment to be used in the same day in total substitution of the conventional LSCP. The LM was introduced in the system by two ways. The first, in the conveyors belt through the worn straw and in the second, it was introduced manually into the rotary drum.

LWA industrial test database

Factory Y supplied the estimated costs related to raw-material consumption, drying process and investment for assessment. In this research the investment amortization period considered was about 10 years. Table 2 presents the database for assessment of the valorization solution. The first calculation was based on the energy flows, to vaporize water (M) in Kcal/kg of water and drying LM (N) in kcal/kg of Lime Mud, where:

$$M = (D+E)*(100+(100-F))/100 \quad \text{(Eq. 1)}$$

Where, D= Vaporization latent heat; E= Water heating energy (until 100ºC); F= Dryer efficiency; and,

$$N = (C/100)*M \quad \text{(Eq. 2)}$$

Where, C= Lime mud moisture content.

The fuel need to dry the lime mud (O) in kg fuel/kg LM was calculated through the following equation:

$$O = N/G \quad \text{(Eq. 3)}$$

Where, G= Calorific power of fuel.

Table 2. Data for assessment of LWA valorization solution.

Data Base		Estimated Values	Unit
A	LSCP	270	ton/month
B	LMw (LSCP equivalent amount - humid base)	242	ton/month
Drying process			
C	LMw moisture content	20	%
D	Vaporization latent heat	597	kcal/kg of water
E	Water heating energy (until 100ºC)	80	kcal/kg of water
F	Drying efficiency	65	%
G	Calorific power of fuel	9.600	kcal/kg of fuel
Investiment			
H	Dryer + silo + assembly	52.000	€
I	Amortization (10 years)	5.200	€/year
Costs			
J	LSCP	17.5	€/ton
K	Energy (fuel)	0.25	€/kg
L	Labour (one employee)	10.500	€/year

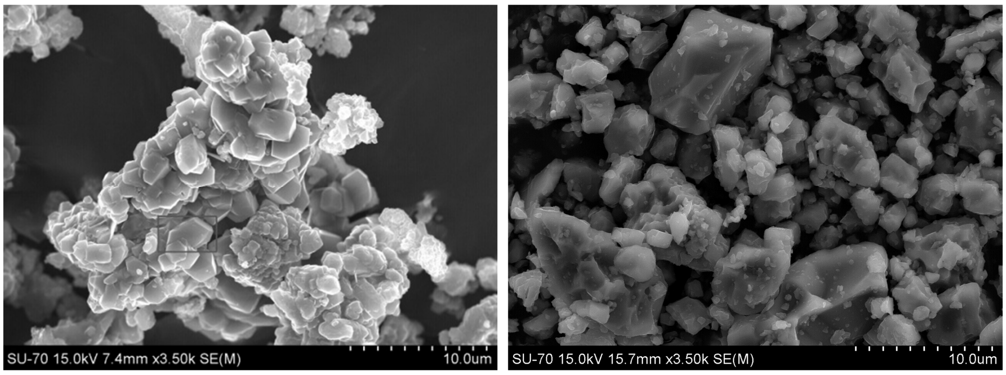


Fig. 2. SEM micrographs of LM (left) and LSCP (right).

RESULTS AND DISCUSSION

Calcite is the main crystalline phase in both materials (LSCP and LM) as can be seen in Table 1. Thermal gravimetric and differential analyses (TG/DTA) of raw materials were performed up to 1000ºC with a heating rate of 10ºC/min. The results are presented on Figure 4. Before performing the analysis, the raw materials were dried at 105ºC. The weight loss exhibited by both materials, between 800ºC and 900ºC is related with the decomposition of calcium carbonate.

Although LM presents higher level of sodium than LSCP the chemical analysis confirms how similar they are. The differences of other oxides contents are not relevant between these materials and for the application.

Observing Table 3, the average flow of production during the test with LM is not different from the conventional LWA production result (average from 8:00 to 12:00h). The density of LWA_w seems to be slightly lower than LWA_s (~5%) but negligible looking at the standard deviation of 11 kg/m^3. According to factory Y reports, the same variation happens in the conventional production process.

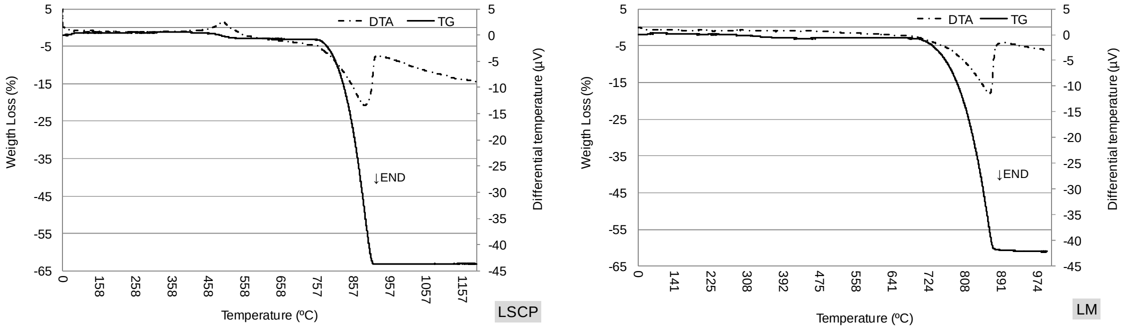


Fig 4. TG/DTA analyses for LM and LSCP samples.

Table 3. Industrial test results with and without LM.

Time	Flow	Density of the LWA	Temperature (kiln exit)
H:min	m^3/h	kg/m^3	ºC
Average of data collected between 8:00 to 12:00h)	21.2	331	745
Average of data collected between 13:30 to 15:00h (Test)	22.4	319	783

The first concern about introducing LM in the production process of factory Y would be drying it. Technically any drying process implicates energy consumption. In this specific case, assuming the involved costs (see Table 2) provided by factory Y, the estimated total costs for the drying and processing of the LM is around 10.17€/ton. Transportation costs are not included in this value, only investments in drying equipment, employee and energy costs. The factory X would transport the LM waste to factory Y to warranty this estimated total cost. Assuming this as the implemented management solution, the benefits for factory Y would be the saved costs with the conventional raw material (around 7.33€/ton). Assuming 89% of LSCP replacement level (Table 4) for LM and an amount of 2904 ton/year in total used material, the factory Y could save approximately 21.000,00€/year as liquid benefit.

Table 4. Cost-benefits analysis of the solution according to factory Y.

Variable		Equations	Result	Unit
M	Energy to vaporise water		913.95	kcal/kg of H_2O
N	Energy to dry LM		183	Kcal/kg of LM
O	Fuel to dry LM		0.019	kg fuel/kg of LM
P	Fuel unitary cost	K*O*1000 (Eq. 4)	4.76	€/ton of LM
Q	Energy cost of drying	P*B*12 (Eq. 5)	13,823.5	€/year
R	Dryin and processing LM costs	(I+L+Q)/(B*12) (Eq. 6)	10.17	€/ton of LM
S	Transport costs - from company X to company Y (31 - 50km)	variable	3.6	€/ton
T	Replacement level of LSCP	B/A*100 (Eq. 7)	89.6	%

According to cost-benefits assessment estimated here for factory X, and considering the actual landfill tax estimated in 30€/ton of waste dry base, the savings would be in the order of 26.4€/ton of LM (194 ton of LM d.b.), more than 60.000€/year. But, in another perspective, if factory X assumes the transportation and drying costs related to the waste management, instead of saving 26.4€/ton, the factory would save 16.24€/ton of LM [30€ (LM landfilling) – 3,6 (LM transport) – 10.17 (LM drying and processing) = 16.24). In this situation, the total saving amount would be around 38.000€/year.

CONCLUSIONS

The high content of $CaCO_3$ in LM makes this waste an interesting material to be used as mineral aggregate in this application. The characterization results indicate that lime mud from pulp and paper mill represents a waste with similar chemical and physical properties comparing with LSCP used in LWA production. Technically the industrial test with LM was successfully performed. The industrial test showed that LM represents a potential material for being used in LWA production as alternative raw material. According to the estimated values, factory X would avoid landfilling around 3.000 tons of LM a year. This fact, combined to saving costs and natural resources extraction saving permits to conclude that this valorization solution is a viable one generating savings on both sides.

Acknowledgements

The authors would like to thank RAIZ, Portucel Soporcel group, ARGEX S.A. for their valuable help and contribution in this work. The authors also acknowledge FCT -

Fundação para a Ciência e Tecnologia (grant SRFH/BD/75182/2010) for financial support for this work.

References

[1] B.Ahmadi, and W. Al-Khaja, Utilization of paper waste sludge in the building construction indusry. Resources Conservation Recovery 32 (2) (2001) 105-113.

[2] M.C. Monte, E. Fuente, A.Blanco, C.Negro. Waste management from pulp and paper production in the European Union, Waste Management & Research 29 (2009) 293-308 (Review).

[3] R. Modolo, A. Benta, V.M. Ferreira, L.M. Machado. Pulp and paper plant wastes valorisation in bituminous mixes. Waste Management 30 (2010) 685–696.

[4] R.Modolo, A.Benta, L.Machado, J.A.Labrincha, V.M.Ferreira. Solutions development for pulp and paper process solid wastes – from laboratory bench to industrial scale", in "Inovação na Construção Sustentável, Ed. Plataforma para a Construção Sustentável, ISBN 978-989-95978-0-8 (2008) 11-22.

[5] H. Eroglu, H.H.Acar Uçüncü, O. İmamoğlu. The effect of fry sludge addition supplied from pulp mill on the compressive strength of cement. J. of Uni. of Chemical Tech.and Metallurgy 42 (2) (2007) 169-174.

[6] A.Hassani, H.Ganjidoust, A.A.Maghanaki. Use of plastic waste (poly-ethylene terephthalate) in asphalt concrete mixture as aggregate replacement. Waste Management & Research 23 (2005) 322-327.

[7] B.J.Mohr, H.Nanko, K.E.Kurtis. Durability of kraft pulp fiber-cement composites to wet/dry cycling. Cement and Concrete Composites 27 (2005) 435-448.

[8] C.R.Cheeseman and G.S.Virdi. Properties and microstructure of lightweight aggregate produced from sintered sewage sludge ash. Resources, Conservation and Recycling 45 (2005) 18-30.

[9] H.Binici, T.Shah, O.Aksogan, H.Kaplan. Durability of concrete made with granite and marble as recycle aggregates. Journal of Materials Processing Technology, 208 (2008) 299–308.

[10] UMTC, 1995. Use of recycled materials and recycled products in highway construction. University of Massachusetts Transportation Center Report UMTC-95-1, US, 238–245.

[11] OECD, 1997. Road Transport Research: Recycling Strategies for Road Works. Organization for Economic Co-operation and Development (OECD), Paris, France, pp. 140–148.

[12] L.B.Andrade, J.C.Rocha, M.Cheriaf. Evaluation of concrete incorporation bottom ash as natural aggregate replacement. Waste Management 27 (2007) 1190-1199.

[13] R. Modolo, V.M. Ferreira, L.M. Machado, M. Rodrigues, I. Coelho, Construction materials as a waste management solution for cellulose sludge. Waste Management 31 (2011) 370–377.

[14] S.P. Pandey, R.L.Sharma. The influence of mineral additives on the strength and porosity of OPC mortar. Cement and Concrete Research 30 (2000) 19-23.

[15] A.Sarabèr, R.Overhof, T.Green, J.Pels. Artificial lightweight aggregates as utilization for future ashes – A case study. Waste Management 32 (2012) 144-152.

[16] X.Wang, Y.Jin, Z.Wang, Y. Nie, Q.Huang, Q.Wang. Development of lightweight aggregate from dry sewage sludge and coal ash. Waste Management 29 (2009) 1330-1335.

[17] W.Wirojanagud, N.Tantemsapya and P.Tantriratna. Precipitation of heavy metals by lime mud waste of pulp and paper mill. Songklanakarin Journal of Science Technology, 26 (2004) 45–53.
[18] J. Gaskin. Land application of pulp mill lime mud. Uni. of Georgia, College of Agriculture and Environmental Sci., Cooperative Extension Service along with the Pollution Prevention Assistance Division. Bulletin 1249, Georgia, USA, 2004.
[19] F.M. Martin, J.M.Martins, L.C.Ferracin, C.J.Cunha. Mineral phases of green liquor dregs, slaker grits, lime mud and wood ash of a kraft pulp and pepr mill. J. of Hazardous Materials 147 (2007) 610-617.

APPENDIX VI

Treatment by leaching of bottom bed ash from biomass combustion in bubbling fluidized bed

L.A.C. Tarelho[1], E.R. Teixeira[1], D.F.R. Silva[1], R.C.E. Modolo[2]

[1]Department of Environment and Planning, CESAM, University of Aveiro, Portugal, ltarelho@ua.pt
[2]Department of Civil Engineering, CICECO, University of Aveiro, Portugal, regina.modolo@ua.pt

Abstract

The management of bottom bed ashes from biomass combustion in bubbling fluidized bed combustors (BFBC) is a major issue, namely considering operating problems and environmental aspects.

Bottom bed ashes from combustion of forest biomass residues in BFBC were studied. The ashes were characterized considering particle size distribution, chemical composition, and water leaching.

Compared to the original sand bed, the bottom bed ashes have a wider distribution of particle sizes; the inert material fed mixed with the biomass is responsible for this result.

The bottom bed ashes studied have distinct physical-chemical properties.

The treatment by water leaching and screening improves the quality of the ashes in order to allow its material valorization. After leaching, the concentration of some chemical elements in the ashes decreased in distinct percentages, depending on the chemical element and the origin of the ashes. The higher percentage of concentration decrease was observed for Cl and S.

Keywords: Ash, leaching, combustion, fluidized bed, biomass

INTRODUCTION

Fluidized bed combustion (FBC) technology is recognized as the most appropriate technology for biomass combustion, due to the inherent advantages of low process temperatures, isothermal operating conditions, and fuel flexibility. The existing FBC technology at industrial scale includes the bubbling fluidized bed combustors (BFBC) and the circulating fluidized bed combustors (CFBC). Among other characteristics, these technologies differ in the pattern of gas-solid hydrodynamics in the reactor, the size of the bed particles, the heat and mass transfer rates in the reactor, the temperature and flue gas composition profile along the reactor. This in turns influences the characteristics of the ashes produced during biomass combustion, and thus, flows of ashes with distinct properties will be produced in these installations.

During biomass combustion in BFBC two main types of ashes are produced: the bottom bed ashes and the fly ashes. The bottom bed ashes are composed by the sand particles from the original (mainly quartz) sand bed, the inert material (forest soil and small stones) fed together with the biomass, and the biomass ash. The fly ashes are composed by the smaller size particles from the original sand bed, particles resulting from attrition and abrasion of the original sand bed particles, inert material fed with the biomass, and the biomass ash. In opposition to a grate furnace, where the bottom ashes represent the higher percentage of the total ashes produced in the installation, during BFBC the bottom bed ashes often represent the lower fraction of the total ashes produced in the plant; the bottom bed ash fraction can be of the order 5%wt [1,2], 10%wt [3], 17%wt [4], or as high as 50%wt to 60%wt as often observed in some Portuguese thermal plants with BFBC.

The bottom bed ashes during BFBC result from periodic discharges of the bed, among other reasons, related to: i) the need of bed renovation and replacement in order to avoid bed agglomeration and defluidization, ii) discharge of excess bed solids in order to maintain bed height, iii) the replacement by fresh natural sand with appropriate particle size distribution in order to guarantee proper hydrodynamic conditions of the bubbling bed. The discharge of bottom bed ashes originates a significant amount of solid wastes to be managed. The ashes from biomass combustion in thermal plants are classified as a waste according to the European List of Wastes [5], and the bottom bed ashes from BFBC are classified with code 100124. Most of the published research work dealing with bottom bed ashes from BFBC is related with the phenomena of bed agglomeration and defluidization, and less related with the environmental management and material valorization of the bottom bed ashes.

The phenomenon of bed agglomeration and defluidization is an issue of major concern during BFBC. The reasons behind this phenomenon are associated with the formation of an ash coating layer around the bed particles, and are related with the Na and K and their combination with the Si, resulting in compounds with a relative lower melting point present on those layers, achieved at the low temperatures of BBFC (800ºC to 900ºC), thus promoting the agglomeration of the particles and subsequent defluidization of the bed [6-20]. Nevertheless, in general, the bottom bed ash in a BFBC are composed mostly of silica (mostly quartz) sand particles, with particle size from the few micrometers until some millimeters, often containing a relatively thin (with a few micrometers) coating layer mainly composed of inorganic material that is found in most of the typical biomass fuels [21].

In this work are analyzed some physical-chemical properties of bottom bed ashes from combustion a variety of forest biomass fuels in industrial BFBC existing in Portugal. Are also evaluated some results of the physical-chemical treatment applied to the bottom bed ashes from the BFBC, in order to produce a material that can be used in industrial applications, as for example, in substitution of natural silica sand.

EXPERIMENTAL METHODOLOGY

The experimental work developed in this study is included in a wider research project [22] aimed to study the characteristics of ashes produced in industrial thermal plants in Portugal, and to evaluate solutions for their management. The work includes the characterization of the ash flows in industrial thermal plants using biomass as fuel, the treatment of the ashes considering is material valorization, and the environmental management of the ashes.

In the study presented here are analyzed results about the characteristics of bottom bed ashes sampled in some Portuguese industrial thermal plants with BFBC. The ashes were characterized for particle size distribution, chemical composition and leaching.

It was studied the raw bottom bed ash and the mass fraction of bottom bed ash with particle size in the range 0.3 to 1.0 mm. The interest in this particle size fraction (0.3 to 1.0 mm) is related with the possibility of its recycling, namely to be utilized as: i) substitute of part of the natural sand used for bottom bed replacement in the BFBC, and ii) as aggregate in construction materials.

Figure 1 shows the main flows of ashes in thermal plants with BFBC, and also the proposed bottom bed ash treatment and material valorization approach under evaluation.

Thermal Plant Characteristics

The bottom bed ashes studied were sampled in five BFBC, with nominal thermal capacity in the range 50 MW_{th} to 100 MW_{th}, using forest biomass residues as solid fuel. Among the biomass fuels used, the eucalyptus bark and the residues from logging activities are the major component. The typical operating conditions of the industrial BFBC include temperature of the bubbling bed in the range 800ºC to 900ºC, and O_2 concentration in the flue gas in the range 4%v(dry gases) to 7%v(dry gases).

The ash samples were collected at the discharge location of the bottom bed ash in the industrial BFBC plants. Each bottom bed ash sample had a mass of about 30 kg.

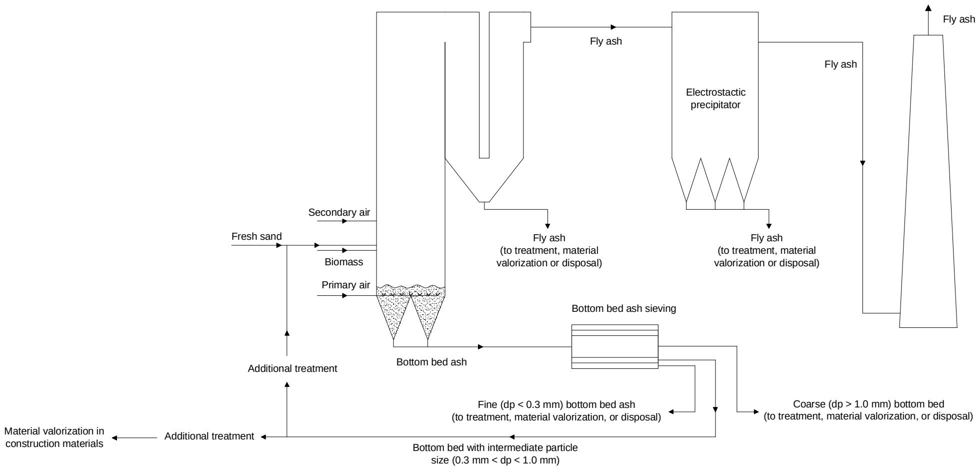


Figure 1 – Schematic of the main flows of ashes in a thermal plant with BFBC, and bottom bed ash treatment for further material valorization.

Bottom Bed Ash Characterization

The bottom bed ashes samples collected were characterized for particle size distribution by sieving. For chemical characterization, it was selected the bottom bed ash fraction with particle size in the range 0.3 to 1.0 mm from three BFBC installations, considering the applications to be studied, as stated before. The mass fraction of the bottom bed with particle size in this range 0.3 to 1.0 mm can represent from 40%wt to 60%wt of the bottom bed ash discharged in the BFBC analyzed. It was also characterized the raw bottom bed ashes (with particle size below 2 mm) from one industrial BFBC. The chemical characterization of the bottom bed ash was performed for major and minor chemical elements by X-Ray Fluorescence (XRF), using a Panalytical Axios spectrometer. Prior to analysis, the bottom bed ash samples were subjected to a grinding process in an Agatha mill, followed by drying at 101 ºC ± 1 ºC for 12 h. The chemical analysis was performed considering: i) Loss on ignition (LOI), and ii) XRF analysis on a pressed pellet previously prepared. For LOI determination, approximately 1.5 grams of the sample, milled and dried, were heated to 1100 ºC for 3 hours in a Carbolite furnace; the LOI was obtained based on the loss of weight after the heating at 1100 ºC. The pressed pellet for XRF analysis was prepared with about 10 grams of milled and dried ash sample. The ash sample was mixed with 4 or 5 drops of polyvinyl alcohol and homogenized in a plastic recipient, and further pressed in a standardized form. After drying the pressed pellet is then submitted to X-Ray analysis.

Some particles from the raw bottom bed ash of one BFBC and the respective particles resulting from its industrial leaching with water were prepared for further analysis of their cross section by Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS), using an ultra-high resolution analytical scanning electron microscope HR-FESEM Hitachi SU-70.

Bottom Bed Ash Leaching

The bottom bed ash leaching was evaluated using two procedures: i) water leaching in laboratory, and ii) industrial water leaching. The leaching in laboratory was applied to three bottom bed ashes with particle size in the range 0.3 to 1.0 mm. The industrial leaching was applied to the raw bottom bed ashes from one industrial BFBC.

The laboratorial leaching tests were performed according to the European Norm EN 12457-2 [23]. Before leaching, the solid samples were pre-dried for 12 h at 105ºC ± 5ºC. According to this procedure, 100 grams of dry bottom bed ash sample were transferred to a polypropylene stopper flask and then 1 L distilled water was added; that is, leaching with an L/S ratio (liquid to solid ratio) equal to 10 was used. It was a batch leaching test with duration of 24 hours under continuous stirring in an orbital shaker (250 rpm).

The industrial leaching was performed in continuous and under typical conditions used in an industry that makes treatment of natural sand for the construction industry. The leaching includes a continuous shower like process using a L/S (liquid to solid) ratio equal to 2, and a processing capacity of 10 ton/h; the process includes treatment of the leaching solution by sedimentation in order to reuse the liquid solution on the leaching process.

RESULTS

The results presented here include: i) the particle size distribution of the original sand bed of the BFBC (OB_1, OB_4, OB_6), and the particle size distribution of the raw bottom bed ashes (BA_1_R, BA_2_R, BA_4_R, BA_5_R, BA_6_R) from five industrial BFBC, ii) the chemical composition (determined by XRF) of the original natural sand bed (OB_4, OB_6), of the bottom bed particles with particle size in the range 0.3 to 1.0 mm before (BA_4, BA_5, BA_6) and after (BA_4_L, BA_5_L, BA_6_L) laboratorial leaching with water, of a raw bottom bed ash (BA_6_R) and the respective bottom bed ash after industrial leaching and screening (BA_6_IL).

After industrial leaching and screening the material (BA_6_IL) to be valorized in industrial applications has the following particle size cumulative (lower) mass distribution: 100%wt<2.0 mm, 94.9%wt<1.0, 18.9%wt<0.50 mm, 0.027%wt<0.25 mm, 0%wt<0.063 mm, and the chemical analysis by XRF was made on samples prepared from this particle size distribution.

It is presented information about the SEM-EDS analysis of the cross section of some bottom bed ash particles before (BA_6_R) and after industrial leaching (BA_6_IL).

Bottom Bed Ash Characteristics

From the macroscopic point of view, the bottom bed ashes from BFBC that use (mainly) eucalyptus bark as biomass fuel are dark in color, whereas the bottom bed ash from BFBC that use a variety of forest biomass residues (e.g., from logging activities) are brown in color. The bottom bed ashes from the BFBC analyzed showed no agglomerated particles.

The particle size distribution of the natural sand utilized as original bed and the bottom bed ashes discharged is shown in Figure 2, for the industrial BFBC installations studied. It is observed that the bottom bed ashes show a particle size distribution that is enriched with fine and coarse particles when compared with the original natural sand bed. Other studies in industrial BBFC [1,2,3,4] do not show this pattern characterized by a wide particle size distribution. The enrichment in fine and coarse particles relative to the original sand bed, observed in these Portuguese BFBC installations, can be explained by the quality of the forest biomass residues used as fuel. The biomass used can have considerable amounts of inert material (forest soil particles and small stones) as has been shown in a study conducted in a Portuguese industrial thermal plant using similar biomass fuel [24]; this contamination of the biomass fuel by inert material results from bad practices during the biomass residues collection and management before delivering to the BFBC installation. In fact, the increasing mass fraction of coarse particles in the bottom bed ashes observed here is not related with agglomeration phenomena, because no signs of agglomeration were observed in the samples studied.

From the operating perspective, there are some negative implications from the bottom bed enrichment in lower particle size material. For example, the lower particle size material fed with the biomass is composed mostly of particles from the forest soil, and its lower terminal velocity enhances the entrainment along the freeboard and the corresponding erosion of the heat exchange equipment (e.g. super-heaters). The higher particle size material is composed of coarse soil particles and small stones from the forest, that have much higher fluidization velocities than that of the particles from the original sand bed. This enrichment in coarse particle size influences the quality of bed fluidization, affecting negatively the heat and mass transfer inside the bed, and the whole performance of the BFBC.

The high level of inert material (soil and small stones from the forest) fed mixed with the biomass in the Portuguese BFBC plants [24] implies a relatively high frequency of bottom bed discharge, and consequently these bottom bed ashes have low residence time (<3 days) in the BFBC when compared with other practices in industrial installations using BFBC [1,2].

The composition of bottom bed ashes samples is shown in Figure 3, considering the loss on ignition (LOI) and major chemical elements, and in Figure 4 considering some minor chemical elements. The characteristic low value of LOI reveals the low content of organic matter in the bottom bed ashes, as it is usual in BFBC due to the relatively efficient combustion inside the bed and the low solid carbon content inside the bed during the combustion of high volatile matter content solid fuels as the biomass. For the bottom bed particles BA_4 and BA_5, the unburned material determined at 550ºC [25] was found to be lower than 0.40%wt (dry basis) and 0.09%wt (dry basis), respectively. The major chemical element present in the bottom bed ashes is Si; Oxygen not considered. The Si expressed as SiO_2 represent about 74%wt, 72%wt, 83%wt and 85%wt of the bottom bed ashes with reference BA_6_R, BA_6, BA_4 and BA_5. This abundance of Si it is related with the natural (mostly quartz) sand (>98.5%wt SiO_2) used as original bottom bed in the BFBC. The bottom bed ashes are enriched in chemical elements (Figures 3 and 4) that can be found in the inorganic content of biomass [21], when compared to the original (quartz) sand bed. Considering the relatively high content of inert material (forest soil particles and small stones) fed mixed with the biomass [24], it is expected also that the bottom bed ash composition is influenced by the composition of that inert material.

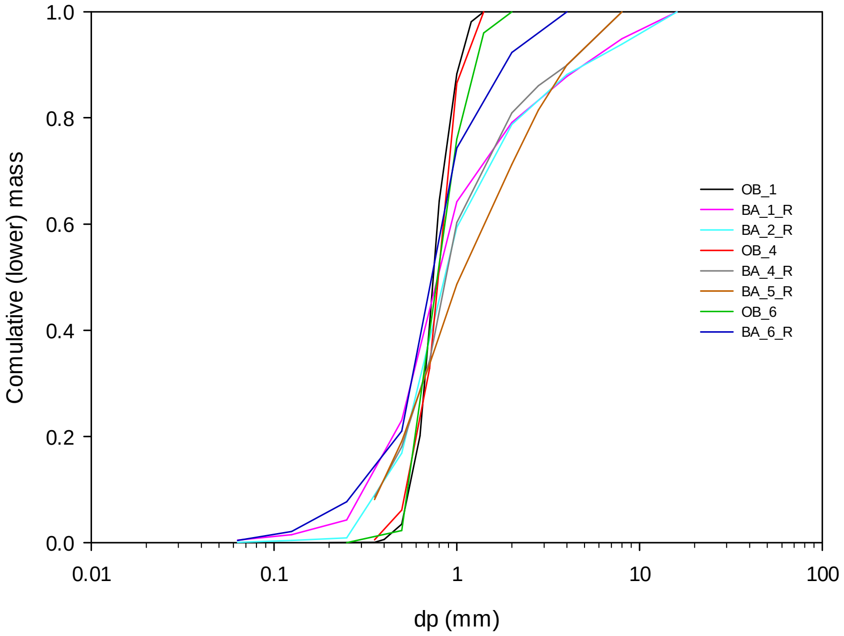


Figure 2 – Cumulative (lower) mass size distribution of particles from: original sand bed of plants 1 and 2 (OB_1), original sand bed of plants 4 and 5 (OB_4), original sand bed of plant 6 (OB_6), and raw bottom bed ashes from plants 1, 2, 4, 5 and 6 (BA_1_R, BA_2_R, BA_4_R, BA_5_R, BA_6_R).

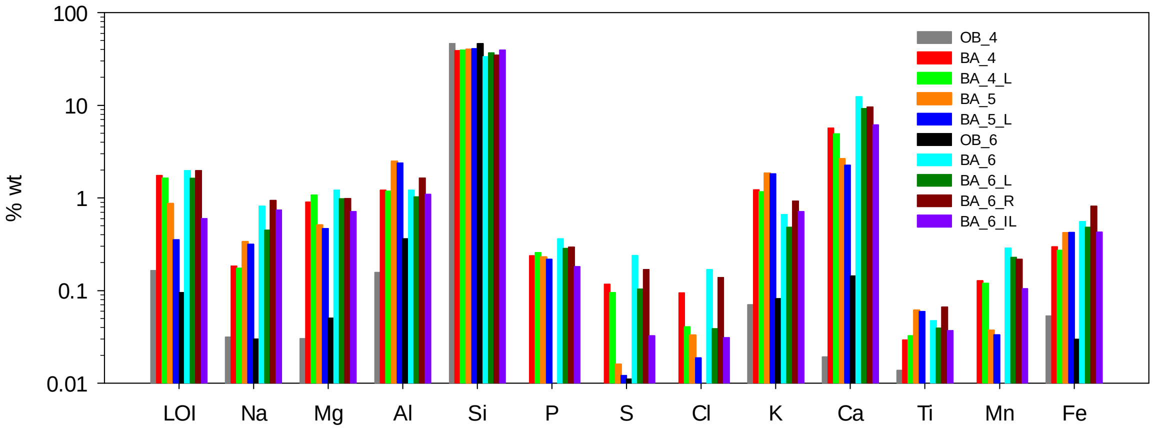


Figure 3 – Chemical composition (LOI and major elements determined by XRF, except Oxygen) of the original sand bed from three BFBC (OB_4=OB_5, OB_6), bottom bed ashes (0.3 to 1.0 mm) from three BFBC (BA_4, BA_5, BA_6) and the respective bottom bed ashes after laboratory leaching (BA_4_L, BA_5_L, BA_6_L), raw bottom bed ashes from a BFBC (BA_6_R) and the respective bottom bed ashes after industrial leaching (BA_6_IL). Chemical elements without value in the figure mean that the concentration it is below the detection level of the XRF. Y-axis in logarithmic scale.

Nevertheless, each bottom bed ash analyzed has its own particular chemical composition, among other factors, influenced by: i) the biomass fuel characteristics, ii) the operating conditions, namely the stoichiometry and temperature, and iii) the residence time of the bottom bed ashes. With exception of Ca, present in concentrations in the range 2.5%wt to 10%wt, the other chemical elements are present in concentrations lower than 2%wt. By a descending order in concentration, the general pattern of abundance of major chemical elements in the bottom bed ashes is:

Si>Ca>Al≈K>Mg>Fe>P>Na>Mn≈S>Cl>Ti, for BA_4;
Si>Ca≈Al>K>Mg>Fe>Na>P>Ti>Mn>Cl>S, for BA_5;
Si>Ca>Al≈Mg>Na≈K>Fe>P>Mn>S>Cl>Ti, for BA_6;
Si>Ca>Al>Mg≈Na≈K>Fe>P>Mn>Ti>S≈Cl, for BA_6-R.

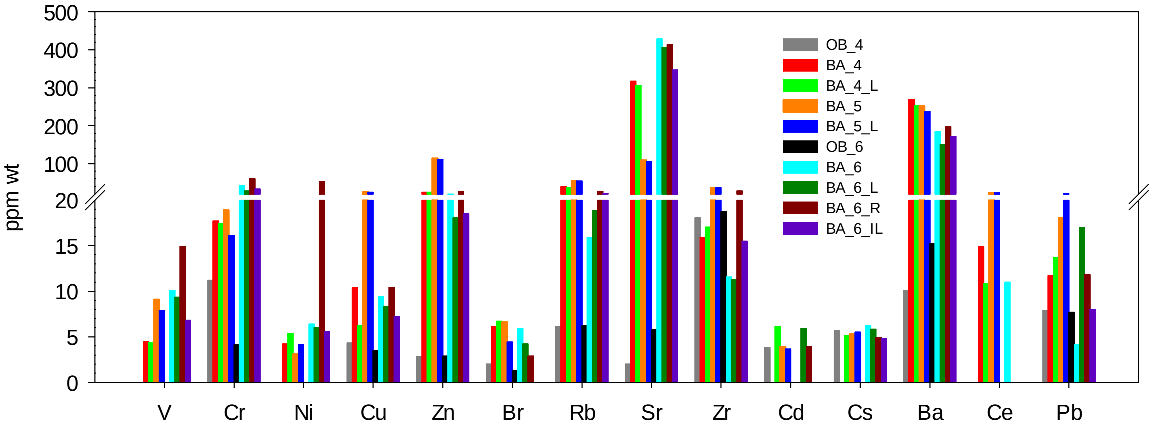


Figure 4 – Chemical composition (some minor elements, with concentration > 5 ppm wt, determined by XRF) of the original sand bed from three BFBC (OB_4=OB_5, OB_6), bottom bed ashes (0.3 to 1.0 mm) from three BFBC (BA_4, BA_5, BA_6) and the respective bottom bed ashes after laboratory leaching (BA_4_L, BA_5_L, BA_6_L), raw bottom bed ashes from a BFBC (BA_6_R) and the respective bottom bed ashes after industrial leaching (BA_6_IL). Chemical elements without value in the figure mean that the concentration it is below the detection level of the XRF.

Three bottom bed ashes samples (BA_4, BA_6, and BA_6_R) show Sr followed by Ba as the most abundant minor chemical elements; the bottom bed ashes BA_5 show Ba as the most abundant minor chemical element, followed by Zn, Sr and Rb. By a descending order in concentration, the general pattern of abundance of minor chemical elements in the bottom bed ashes is:

Sr>Ba>Rb>Zn>Cr>Zr>Ce>Pb>Cu>Br>V≈Ni, for BA_4;
Ba>Zn>Sr>Rb>Zr>Cu Ce>Cr≈Pb>V>Br>Cs>Cd>Ni, for BA_5;
Sr>Ba>Cr>Zn>Rb>V≈Ce>Zr≈Cu>Br≈Ni>Cs>Pb, for BA_6;
Sr>Ba>Cr>Ni>Zr>Rb≈Zn>V>Pb>Cu>Cs>Cd>Br, for BA_6-R.

During biomass combustion the original (mostly quartz) sand bed particles become enriched in chemical compounds typical of the inorganic content of the biomass. This enrichment occurs as a coating layer of the sand particles. This process is shown in Figures 5 and 6, where the SEM-EDS of the cross-section of a particle from the original sand bed

(OB_6), a particle from the raw bottom bed ashes discharged (BA_6_R), and from the leached (industrial procedure) bottom bed ashes (BA_6_IL) are presented. The coating layer was measured as to have less than 50 μm thickness in particles with equivalent diameter higher than 0.4 mm. Some of the chemical elements typical of the inorganic content of the biomass [21] were found in that coating layer in distinct amounts, namely the Si, Ca, Mg, P, Na, Al, S. In Figure 6 it is presented the location and qualitative abundance of some of those chemical elements in that layer, namely the Ca, K, Mg and Na. This enrichment in the outer layer of the bottom bed particles has been documented in the literature and it is related with the bed agglomeration and defluidization phenomena [6,7,8,9,11,12,13]. The relative amount of some of these chemical elements, namely Si, Ca, K, Na and Al, and it relation to the melting temperatures of some inorganic compounds present in that layer has been used to explain the agglomeration and defluidization phenomena during BFBC [6,7,17,18], and to develop measures for its prevention, as for example the use of additives [7,14,16,17,18].

Leaching of Bottom Bed Ash

When comparing the chemical composition of the bottom bed ash samples not leached (BA_4, BA_5, BA_6, and BA_6_R) and leached (BA_4_L, BA_5_L, BA_6_L, and BA_6_R_L) it is observed that the concentration of some chemical elements, among them the Cl, S, Na and K, is lower in the leached samples (Figures 3 and 4); this result is important in the context of material valorization of the bottom bed ashes. It was calculated the percentage of variation in the concentration of chemical elements present in the bottom bed ashes samples in result of leaching; for that purpose it was used the ratio between the difference in concentration of (major) chemical elements in the samples not leached and in the leached samples, and (relative to) their concentration in the samples not leached. That percentage of variation reflects a decrease in concentration of some chemical elements present in the bottom bed ashes after leaching. The percentage of decrease in concentration of some chemical elements in the bottom bed ashes in result of leaching is shown in Figure 7. This decrease in concentration can also be regarded as an indicator of the chemical elements removal in result of leaching. It is observed that the percentage of decrease in concentration is different for the distinct bottom bed ashes studied. In general, the percentage of decrease in concentration of (major) chemical elements in the bottom bed ashes with reference BA_6_L is higher than that observed for the bottom bed ashes BA_4_L and BA_5_L.

As well, differences in the percentage of decrease in concentration of some chemical elements between the laboratorial (BA_6_L) and industrial (BA_6_IL) leaching of bottom bed ashes were observed; the industrial leaching shows higher percentages of decrease in concentration, except for Na and K. However, it is important to refer that the laboratorial and industrial leaching procedures had differences on: i) the particle size distribution of the bottom bed ashes leached, ii) the L/S ratio, iii) the pattern of solid-liquid contact, and iv) the leaching time.

The chemical elements removal by leaching is influenced by the form according which the elements are bonded in the ashes, including the coating layer around the sand bed particles, and by the physical-chemical properties of the leaching solution, among them, the pH [26,27,28]. Distinct chemical compounds have distinct solubility.

The chemical (major) elements that show higher percentage of decrease in concentration are the Cl and S (Figure 7), despite these elements are present in low concentration

(<0.25%wt) in the bottom bed ashes. A concentration decrease in the range 20% to 80% is observed for S, and in the range 40% to 80% for Cl. The presence of these chemical elements bound in soluble salts in the bottom bed ashes can explain the high removal level by leaching [26].

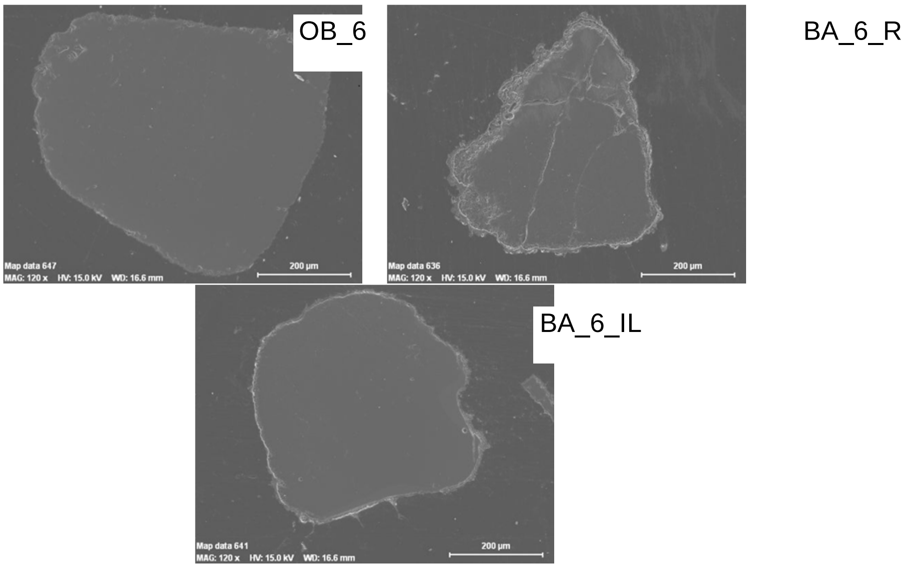
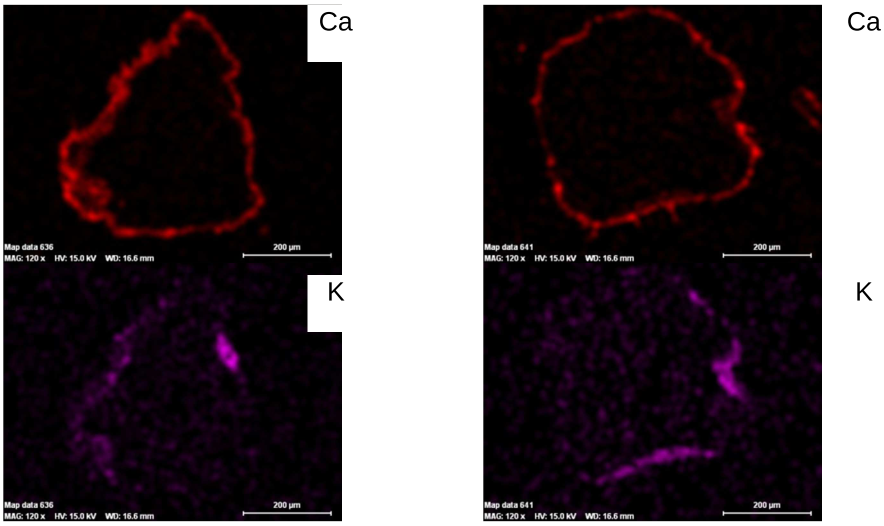
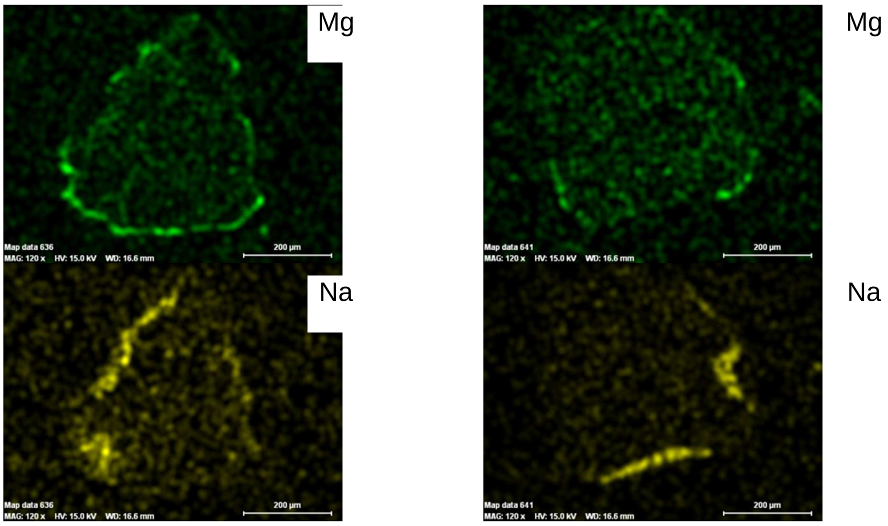


Figure 5 – Microscopic view of cross section of bed particles: original sand bed (OB_6), raw bottom bed (sand) particle (BA_6_R), bottom bed (sand) particle after industrial water leaching (BA_6_IL).

The decrease in concentration of other (major) chemical elements important considering the material valorization of the bottom bed ashes, as for example the Na and K, was relatively low (<7%wt) for the samples BA_4_L and BA_5_L, and in the range 20% to 50% for BA_6_L and BA_6_IL, respectively. The samples resulting from laboratorial leaching showed a higher percentage of decrease in concentration of Na and K when compared with the industrial leaching; when analyzing the laboratorial and industrial leaching it is important to refer that the experimental conditions are distinct.



continue



BA_6_R BA_6_IL

Figure 6 – Composition (Ca, K, Mg, Na) of the coating layer of a bed particle determined by SEM-EDS: bottom bed particle (BA_6_R), bottom bed particle after industrial leaching (BA_6_IL).

The relatively low percentage of decrease in concentration of K and Na could be related with the fact that those compounds are not present mainly in the form of soluble salts, like the KCl or K_2SO_4 [26], but instead should be present as compounds with low solubility as for example the sodium and potassium feldspars [26], also with origin in the inert material (forest soil) fed mixed with the biomass. To a better understanding of this process there is ongoing work dealing with Energy-Dispersive X-Ray spectroscopy (EDX) analysis of the bottom bed ashes.

The concentration of Mg, P and Ti in the leached sample BA_4_L was higher than in the non-leached sample BA_4 (Figure 3). Among other reasons, the relative lower leachability of these chemical elements in comparison to the other chemical elements present in the bottom bed ashes can explain this result; thus, after leaching the sample become enriched in these elements. Considering that sample replicates were used in chemical characterization, before and after leaching, the representativeness of the replicates is another issue to be considered. This subject has to be confirmed with further experiments.

The higher concentration of Si in all the leached samples, relative to the non-leached samples, is justified by the lower leachability of this chemical element relative to the other chemical elements present; thus, after leaching the sample become enriched in this element.

It was observed that the coating layer around the bottom bed sand particles it is not removed by water leaching, as shown in Figure 5 and 6; nevertheless, by SEM it was observed that the particles show a coating layer with lower thickness after leaching, as shown in the example of Figure 5 for a particle resulting from industrial leaching.

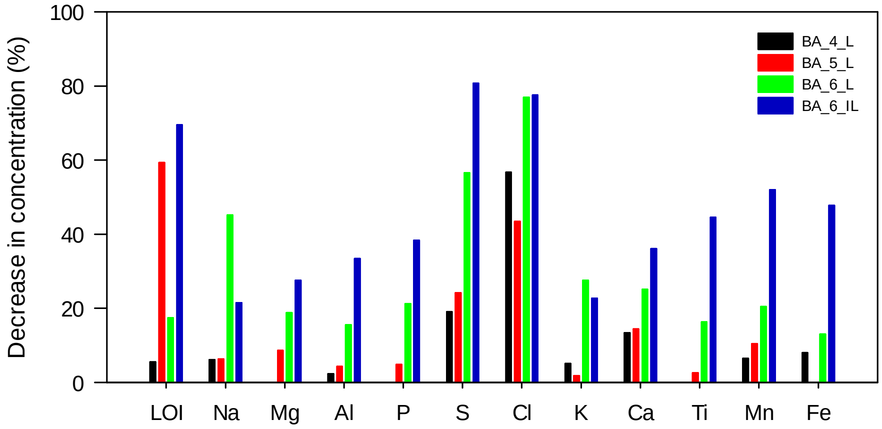


Figure 7 – Percentage of decrease in concentration of (major) chemical elements in the bottom bed ashes in result of leaching. Determined based on the chemical composition (by XRF) of bottom bed ashes before and after water leaching. The percentage of decrease is calculated in relation to the concentration of chemical element in bottom bed ashes not leached.

Characteristics of Leaching Solutions (pH and conductivity)

The pH and conductivity values of the solutions from (laboratorial and industrial) leaching of bottom bed ashes are shown in Figure 8. The laboratorial leaching solutions had pH values in the range 11.5 to 13.0, with the higher value observed in the solution from leaching BA_6 (sample BA_6_L in Figure 8). The pH value of the solution from the industrial leaching has a lower value (pH=9.5) than those observed in the laboratorial leaching solutions. The high pH values are related to the alkaline characteristics of the ashes, and results from its content in alkali chemical elements, as for example the Na, K, Ca, that become dissolved in the leaching solutions. High values of pH are common of bottom bed ashes from industrial BFBC using biomass as fuel [3,4].

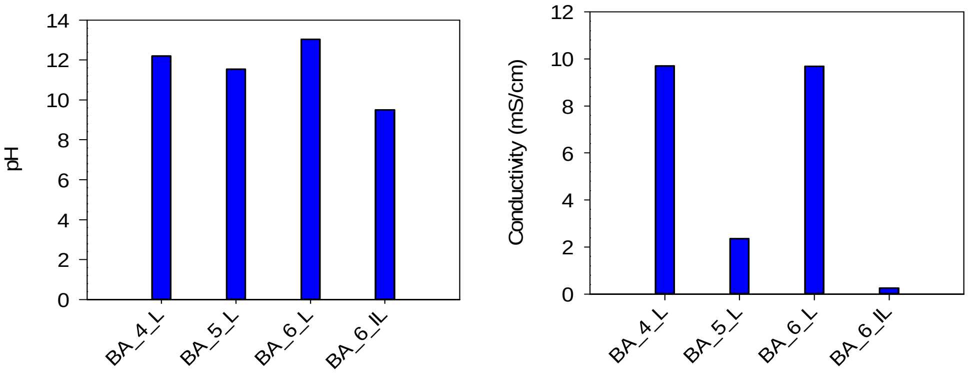


Figure 8 – pH and conductivity of the leaching solutions. Temperature of the solution during measurement: 28ºC for BA_4_L, 25ºC for BA_5_L, 21ºC for BA_6_L, 25ºC for BA_6_IL.

The conductivity of the leaching solutions was in the range 0.25 mS/cm to 9.7 mS/cm; the lower value was observed in the solution from industrial leaching of bottom ashes BA_6 (sample BA_6_IL in Figure 8), and the higher values in the solutions from leaching bottom ashes BA_4 and BA_6 (samples BA_4_L and BA_6_L in Figure 8). The conductivity is related with the concentration of dissolved ions, among those, the ions derived from alkali elements like Na, K, Ca, and also ions derived from Cl and S. High conductivity reveals high ionic strength of the solution and this is associated with high concentration of ions, and reflects a higher removal of alkali elements, chlorine and sulphur from the bottom bed ashes. In the laboratorial leaching experiments, the higher values of pH and conductivity where observed for the solutions from leaching bottom bed ashes from the two BFBC using mainly eucalyptus bark (samples BA_4_L and BA_6_L in Figure 8). For the bottom bed ashes from the BFBC that uses forest residues from several forest management activities a relatively lower value of conductivity was observed (sample with reference BA_5_L in Figure 8).

When analysing the values of pH and conductivity of the solution from industrial leaching with those from laboratorial leaching, BA_6_L and BA_6_IL, it is important to remember that are distinct leaching procedures, as described previously.

CONCLUSIONS

In this work, bottom bed ashes from combustion of forest biomass residues in industrial BFBC where studied. The bottom bed ashes were characterized considering particle size distribution, chemical composition, and water leaching.

Compared to the original sand bed, the bottom bed ashes have a wider distribution of particle sizes. The inert material fed mixed with the biomass has a major role in this process. In this context, the quality of the forest biomass residues used as fuel has to be improved, namely by removing the inert material (forest soil and small stones) that arrives to the thermal plant mixed with the biomass.

It was observed that the treatment by screening and water leaching can improve the quality of the bottom bed ashes in order to allow its material valorization in some industrial applications, namely as substitute of natural sand, thus saving natural resources.

After the leaching process the concentration of some chemical elements in the bottom bed ashes decreased in distinct percentages, depending on the chemical element and the origin of the ashes. The higher percentage of concentration decrease was observed for Cl and S.

ACKNOWLEDGMENTS

This work was financially supported by *Fundação para a Ciência e a Tecnologia*, Portugal, through the project with reference PTDC/AAC-AMB/098112/2008 (Bias-to-soil - Biomass ash: Characteristics in relation to its origin, treatment and application to soil).

REFERENCES

[1] Latva-Somppi J, Moisio M, Kauppinen EI, Valmari T, Ahonen P, Tapper U, Keskinen J. Ash formation during fluidized-bed incineration of paper mill waste sludge. Journal Aerosol Science 1998; 4:461-480.

[2] Latva-Somppi J, Kauppinen EI, Valmari T, Ahonen P, Gurav AS, Kodas TT, Johanson B. The ash formation during co-combustion of wood and sludge in industrial fluidized bed boilers. Fuel processing Technology 1998; 54:79-94.

[3] Dahl O, Nurmesniemi H, Poykio R, Watkins G. Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler. Fuel Processing Technology 2009; 90:871-878.

[4] Dahl O, Nurmesniemi H, Poykio R, Watkins G. Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values. Fuel Processing Technology 2010; 91:1634-1639.

[5] Portaria n.º209/2004. Portuguese legislation about the European list of wastes.

[6] Ohman M, Nordin A, Skrifvars B-J, Backman R, Hupa M. Bed agglomeration characteristics during fluidized bed combustion of biomass fuels. Energy and Fuels 2000; 14:169-178.

[7] Ohman M, Nordin A. The role of kaolin in prevention of bed agglomeration during fluidized bed combustion of biomass fuels. Energy and Fuels 2000; 14:618-624.

[8] Lin W, Dam-Johansen K, Frandsen F. Agglomeration in bio-fuel fired fluidized bed combustors. Chemical Engineering Journal 2003; 96:171–185.

[9] Nuutinen LH, Tiainen MS, Virtanen ME, Enestam SH, Laitinen RS. Coating layers on bed particles during biomass fuel combustion in fluidized-bed boilers. Energy and Fuels 2004; 18:127-139.

[10] Lin C-L, Wey M-Y. The effect of mineral compositions of waste and operating conditions on particle agglomeration/defluidization during incineration. Fuel 2004; 83:2335-2343.

[11] Ohman M, Pommer L, Nordin A. Bed agglomeration characteristics and mechanisms during gasification and combustion of biomass fuels. Energy and Fuels 2005; 19: 1742-1748.

[12] Scala F, Chirone R. Characterization and early detection of bed agglomeration during the fluidized bed combustion of olive husk. Energy and Fuels 2006; 20:120-132.

[13] Zevenhoven-Onderwater M, Ohman M, Skrifvars B-J, Backman R, Nordin A, Hupa M. Bed agglomeration characteristics of wood-derived fuels in FBC. Energy and Fuels 2006; 20:818-824.

[14] Llorente MJF, Cuadrado RE, Laplaza JMM, García JEC. Combustion in bubbling fluidised bed with bed material of limestone to reduce the biomass ash agglomeration and sintering. Fuel 2006; 85:2081-2092.

[15] Shao J, Lee DH, Yan R, Liu M, Wang X, Liang DT, White TJ, Chen H. Agglomeration Characteristics of Sludge Combustion in a Bench-Scale Fluidized Bed Combustor. Energy and Fuels 2007; 21:2608-2614.

[16] Bartels M, Lin W, Nijenhuis J, Kapteijn F, Ommen JR. Agglomeration in fluidized beds at high temperatures: Mechanisms, detection and prevention. Progress in Energy and Combustion Science 2008; 34:633-666.

[17] Kuo J-H, Wey M-Y, Lin C-L, Chiu H-M. The effect of aluminum inhibition on the defluidization behavior and generation of pollutants in fluidized bed incineration. Fuel Processing Technology 2008; 89:1227-1236.

[18] Lin C-L, Kuo J-H, Wey M-Y, Chang S-H, Wang K-S. Inhibition and promotion: The effect of earth alkali metals and operating temperature on particle agglomeration/defluidization during incineration in fluidized bed. Powder Technology 2009; 189:57-63.

[19] Liu H, Feng Y, Wu S, Liu D. The role of ash particles in the bed agglomeration during the fluidized bed combustion of rice straw. Bioresource Technology 2009; 100:6505-6513.

[20] Grimm A, Skoglund N, Bostrom D, Ohman M. Bed agglomeration characteristics in fluidized quartz bed combustion of phosphorus-rich biomass fuels. Energy and Fuels 2011; 25:937-947.

[21] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the chemical composition of biomass. Fuel 2010; 89:913-933

[22] PTDC/AAC-AMB/098112/2008. Biomass ash: Characteristics in relation to its origin, treatment and application to soil. Project financed by *Fundação para a Ciência e a Tecnologia*, Portugal.

[23] EN 12457-2 (2002) - Characterisation of waste — Leaching - Compliance test for leaching of granular waste materials and sludges — Part 2.

[24] Tarelho LAC, Coelho AMSL, Teixeira ER, Rajamma R, Ferreira VM. Characteristics of ashes from two Portuguese biomass co-generation plants. Proceedings of the 19th European Biomass Conference & Exhibition, 6-10 June 2011, Berlin, Germany, pg. 1041-1053.

[25] CEN/TS 14775:2005. Solid biofuels – Method for the determination of ash content.

[26] Steenari B-M, Karlsson LG, Lindqvist O. Evaluation of the leaching characteristics of wood ash and the influence of ash agglomeration. Biomass and Bioenergy 1999; 16:119-136.

[27] Mahmoudkhani M, Wilewska-Bien M, Steenari B-M, Theliander H. Evaluating two test methods used for characterizing leaching properites. Waste Management 2008; 28:133-141.

[28] Mellbo P, Sarenbo S, Stalnacke O, Claesson T. Leaching of wood ash products aimed for spreading in forest floors – Influence of method and L/S ratio. Waste Management 2008; 28:2235-2244.

APPENDIX VII

PHYSICAL-CHEMICAL CHARACTERISTICS OF ASH FLOWS IN A BIOMASS THERMAL POWER PLANT

E.R.Teixeira[1], L.A.C. Tarelho[1], T.C.S.R. Silva[1], D.F.R. Silva[1], R.C.E. Modolo[2]
[1]Department of Environment and Planning, CESAM, [2]Department of Civil Engineering, CICECO
University of Aveiro, 3810-193 Aveiro, Portugal

ABSTRACT: In this work it was made the characterization of distinct ash flows in a biomass thermal power plant using bubbling fluidised bed technology. Bottom bed ashes differ significantly from fly ashes, in concern of both physical characteristics and chemical composition. It was observed a modification in some physical-chemical characteristics of the ashes in result of their exposition to atmospheric air. The pH of the distinct ash samples was alkaline, with values in range 10.3 to 12.7. The conductivity of the ashes varied in the range 0.9 to 19.3 mS/cm, with the fresh fly ashes from the electrostatic precipitator showing the higher value. During the atmospheric air exposition, a decrease in pH and conductivity of the ash leaching solutions was observed. Calcium was the water soluble element with higher concentration in the leaching solution. Due to ash exposition to atmospheric air, a decrease on the leaching of Ca and an increase on the Cl and Al from the fly ashes from the electrostatic precipitator was observed. The process of ash-atmospheric air interaction is of major importance considering the characterization of the ashes and their environmental management.

Keywords: Biomass, Combustion, Fluidized bed, Ashes.

1 INTRODUCTION

Energy resources are essential in the economy, sustainable development and in generation of prosperity for all countries [1, 2]. In the European Union, the utilization of renewable sources has been increased, with the main goals of: diversify the energy supply, reducing the dependence on fossil fuel markets and reducing greenhouse gas emissions [3]. For that, it was created some directives, which require national targets and strategies for the development of renewable energy sources and establish sustainable criteria for biomass sources [4].

Biomass is a resource always associated with environmental sustainability and climate stabilization, with large potential, economic viability and social and environmental benefits [2, 5, 6]. So, its use has being increasing during the last years and makes part of the energy strategies for several countries [5]. There are various sources of biomass that can be use as a fuel, some of them can be taken directly from the forest, which include residues from plantations, logging residues from forest management activities and extraction of wood, several agricultural residues, animal wastes, and other fuels derived from biological sources (e.g. sludge) [2, 5, 6].

Biomass is also an important source of energy for many industries in many countries [2]. Combustion is the main technology for thermochemical conversion of biomass to power or/and heat at industrial level. The selection and design of combustion systems is determined by the environmental legislation, the characteristics of the fuel, the operational costs, performance of the system and the energy needs [7]. Nowadays, fluidized bed (FB) technology is recognize as the most appropriate for biomass combustion, due to the inherent advantages such as: low process temperatures, isothermal operating conditions and fuel flexibility. Two types of FB exist at industrial scale, the bubbling fluidized bed combustors and the circulating fluidized bed combustors. These technologies differ in the size of the bed particles, in the pattern of gas-solid hydrodynamics in the reactor, the heat and mass transfer rates in the reactor and the temperature and flue gas composition profile along the reactor [7-9].

In Portugal, several industrial sectors are intensive consumers of forest biomass, and in some of them heat or/and power are produced using this resources in combustion process. Some of these biomass resources are residues/sub-products from industrial related activities as the preparation of feedstock and operations of forest maintenance. On the other hand, Portuguese government established the renewable energy resources as priorities for energy strategy, and biomass is among these resources.

Several operating and environmental problems are recognized during biomass combustion in fluidized beds. The operating problems are mainly related to bed agglomeration and defluidization, which can lead to costly and unscheduled shutdown of the combustors [10-12]. Among the environmental problems, those related to the ashes produced and its environmental management are of major concern [13, 14]. In this context, it is important to know in detail the physical-chemical characteristics of the ashes and how their physical-chemical properties change with time when exposed to environment conditions.

Important physical-chemical properties of the ash include particle size distribution, density and porosity, specific surface area, pH, leaching, chemical composition, and mineralogy [8]. During fluidized bed combustion two main flows of ashes can be identified and classified [7, 15]: bottom ashes and fly ashes. The fly ashes can be collected in super-heaters, economizers and air pollution control devices (cyclones, bag filters and electrostatic precipitators). Often, in thermal plants the distinct fly ash flows are mixed and managed together, although it is recognized that each ash flow has distinct characteristics [7, 8, 17, 16-28].

The ashes from biomass combustion are very alkaline [8, 9, 23, 25, 29] and reactive, and some modifications in their physical-chemical characteristics can occur, as for example carbonation [14, 30], when they are exposed to environmental conditions. This behavior has to be taken in consideration when studying ash management options, and it is also important in the context of developing appropriate characterization methodologies for the ashes; for example, the storage conditions applied to the ash samples prior to physical-chemical analysis can influence the results.

Ash disposal in landfill has been used worldwide. However, the increasing costs and unsustainability of this management practice has been driving efforts in order to develop appropriate management practices for the ashes, e.g. the recycling of ashes to forest soil [28, 29, 31-33], and the incorporation in construction materials [34, 35], thus saving other natural resources often used in those applications.

In this work it was made the characterization of distinct ash flows (bottom ashes and fly ashes (superheater, economizer and electrostatic precipitator)) from a biomass thermal power plant using a bubbling fluidised bed combustor (BFBC). The ash samples were exposed to atmospheric conditions inside a laboratory during six months, aiming to study the modification on the ash properties with time of atmospheric air exposure. This study is part of an integrated research project [36] in which characteristics of ashes from Portuguese thermal plants have been studied together with some alternatives of material valorization, in order to establish guidelines to a proper ash management.

2 EXPERIMENTAL WORK

The ashes analyzed in this study were collected in a Portuguese thermal power plant with BFBC (50 MW_{th}). The thermal plant use forest biomass residues (FBR) as fuel, mostly resulting from activities related to eucalyptus and pinus stands exploitation for wood to several other industrial sectors. The ashes were sample from the bottom bed (BA), superheater (FA_SH), economizer (FA_EC) and electrostatic precipitator (stage 1 (FA_ESP1) and stage 2 (FA_ESP2)).

The layout of the industrial thermal power plant is shown in Fig. 1, together with the respective indication of location of ash samples collection point.

The ash samples collected were exposed to atmospheric air conditions inside a laboratory during six months. The laboratory conditions of temperature and moisture were monitored (Fig. 2). Physical-chemical characterization of the ashes was done at distinct time periods: (i) fresh samples, (ii) after 1 week, (iii) after 1 month, (iv) after 3 months (only for bottom bed ashes) and (v) after 6 months.

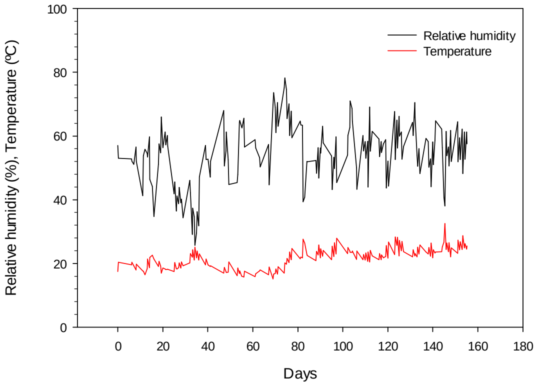


Figure 2: Air temperature and relative humidity inside the laboratory during the period of the study.

2.1 Methodology of ash analysis

The ashes were characterized for some physical-chemical parameters: particle size distribution, chemical composition, mineralogy, and leaching characteristics (pH, conductivity and water soluble elements).

The particle size distribution was analyzed using two methodologies: i) sieving analysis, using ASTM sieves and ii) Coulter analysis – LS230 (for size particles below 2 mm).

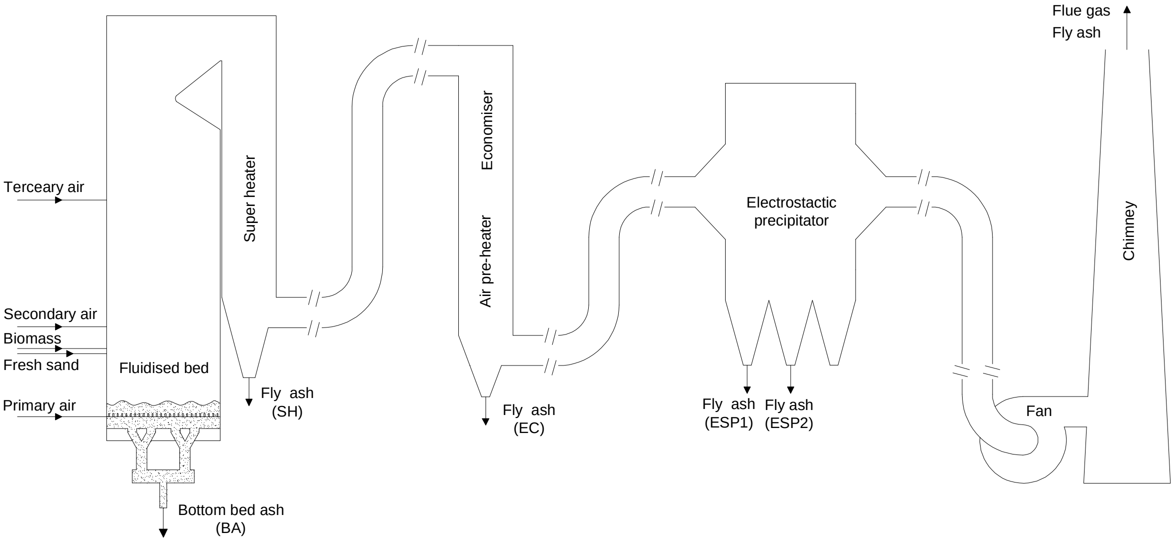


Figure 1: Schematic representation of the industrial thermal power plant with BFBC.

The chemical composition of the ashes was determined by X-Ray Fluorescence (XRF) using a Panalytical Axios spectrometer. Prior to analysis, the ash samples were subjected to a grinding process in an Agatha mill. The analysis was performed considering: i) Loss on ignition (LOI) and ii) XRF analysis on a pressed pellet previously prepared. For LOI determination, approximately 1.5 grams of the sample milled were dried, and heated to 1100ºC for 3 hours in a Carbolite furnace. The LOI was obtained based on the loss of weight after the heating at 1100ºC. A pressed pellet for XRF analysis was prepared with proximately 10 grams of milled and dried ash sample. The ash sample was mixed with 4 or 5 drops of polyvinyl alcohol and homogenized in a plastic recipient, and further pressed in a standardized form. After drying, the pressed pellet was analyzed by XRF.

The mineralogy composition of the ashes was determined by X-Ray diffraction (XRD) using a Rigaku Geigerflex diffractometer D/max-Series, power 40kV/30mA, scan mode continuous/speed – 3º/min).

The water leaching was performed according the European Norm EN 12457-2 [37]. The pH and the conductivity of solutions were measured after 24h leaching. The chemical analysis of the leaching solutions was performed using Flame Atomic Absorption Spectroscopy (FAAS) (for Ca, Mg, Na, K, Fe), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) (for As, Cd, Mn, Pb, Mo, Ni), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (for Al, Zn, Ba, B, Cr, Sr, Cu, P), and Chloride-selective Ion Electrode method for Cl (analyzed as chloride (Cl^-)).

3 RESULTS AND DISCUSSION

The particle size distribution (mass distribution) of the bottom bed ashes and fly ashes determined by sieving is shown in Fig. 3. It is observed that the bottom bed ash shows a particle size distribution enriched in coarse particles when compared to the fly ashes. A decreased in the particle size from bottom bed ash to the electrostatic precipitator ashes (FA_ESP1 and FA_ESP2) it is observed.

The average particle size (volume basis), determined by Coulter analysis (Figure 4) shows the same pattern as that observed by sieving. It is important to state that for this analysis only the bottom ash particles below 2m were considered. The FBR used as fuel in Portugal in thermal plants has considerable amounts of inert material, such as soil particles and small stones [25], and that influences the physical-characteristics of the ashes produced in the thermal plant. The chemical composition of ashes is shown in Fig. 5 and Fig. 6, for LOI, and major and minor chemical elements. It is observed a clear difference between the composition of BA, FA_SH, FA_EC, and the FA_ESP1 and FA_ESP2. The LOI is below 0.5%wt (dry basis) for the BA, and for fly ashes the LOI increases from FA_SH and FA-EC (below 1%wt, dry basis) to FA_ESP1 and FA_ESP2.

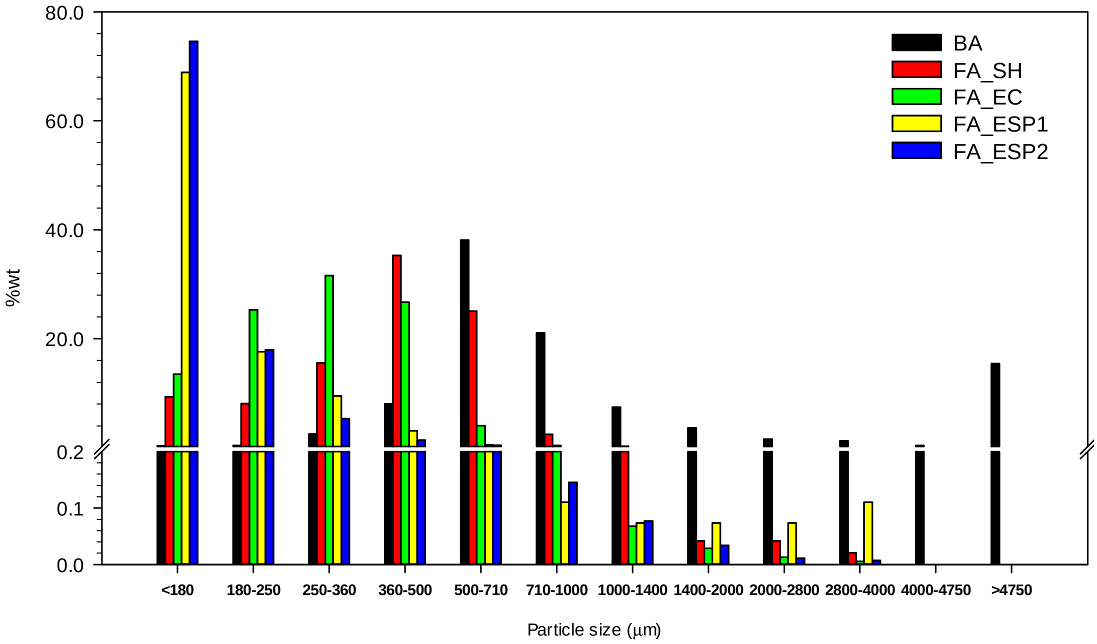


Figure 3: Particle size distribution (mass basis), determined by sieving for the bottom and fly ashes. Legend according locations in the plant (in Fig. 1).

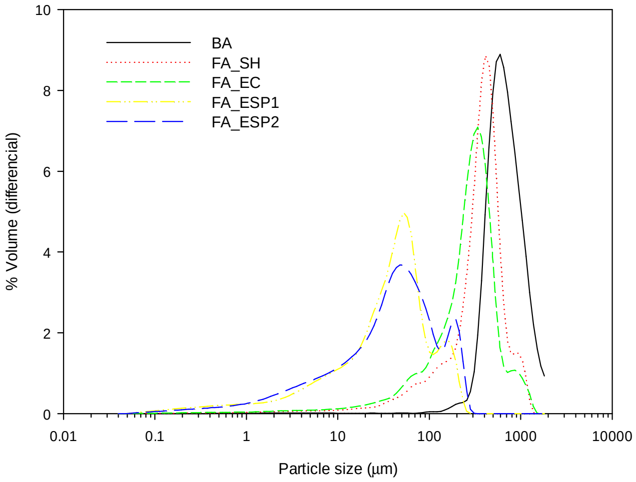


Figure 4: Particle size distribution (volume basis), determined by Coulter analysis, for the ash samples. Legend according locations in the plant as shown in Fig. 1. For the BA sample it was selected the fraction with particle size below 2000µm.

The unburned content of ashes (determined at 550ºC, procedure adpated from standard CEN/TS 14775:2004 [39]) revealed a loss on weight lower than 0.1%wt for BA, below 0.5%wt for FA_SH and FA_EC and below 1.5%wt for FA_ESP1 and FA_ESP2. These show that the amount of organic content present in the ashes is relatively low, which confirm a high efficiency of fuel conversion in the furnace. The increase in unburned material content from BA to FA_ESP2 is explained in result of the fact that the high temperature of bottom bed allows a high conversion of the fuel, and the low particle size and density of some fuel particles under combustion are transported with the fuel gases through the furnace and collected at the air pollution control equipment (electrostatic precipitator). The higher values of LOI determined at 1100ºC compared with the unburned material content determined at 550ºC show the contribution of thermal decomposition and volatilization of other components than unburned fuel (organic material) in the ashes.

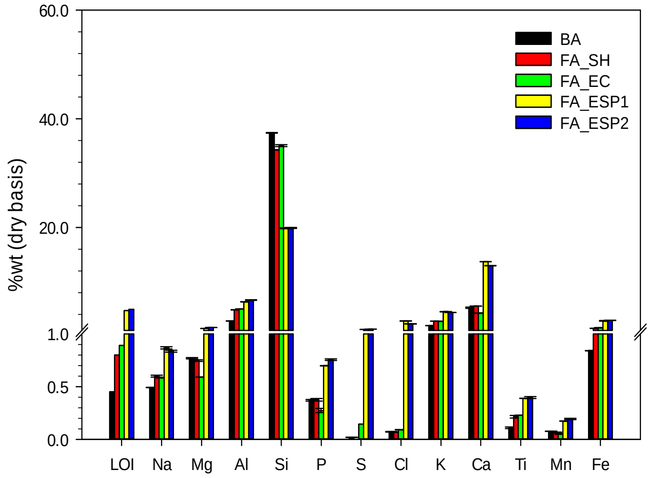


Figure 5: Major chemical elements in the ash samples collected at distinct locations along the thermal plant, values expressed in %wt (dry basis (db)). Legend according to locations in the plant as shown in Fig. 1.

Bottom ash and fly ashes from superheater and economizer are enriched in Si when compared to fly ashes from electrostatic precipitator (Fig. 5); this result is also verified by mineralogy analysis (Fig. 7). The mineralogy analysis shows a higher intensity of Si in these ashes, present mainly as quartz (SiO_2). The high content of Si in the bottom ash is explained by the original bed material used (sand with more than 98.5%wt, dry basis of SiO_2) and the inert material (forest soil an stones) fed mixed with the FBR used as fuel.

Fly ashes from electrostatic precipitator also show Si as the chemical element with higher concentration. However, it is observed enrichment in other chemical elements typical of the inorganic content of the biomass, such as: Na, Mg, Al, P, S, Cl, K, Ca, Ti and Fe when compared with the other ash flows. The contribution of fine particles carried out with the combustion flue gases, which include the chemical elements typical of the inorganic content of biomass [40, 41] can explained this result. The second more abundant chemical element present in the FA_ESP1 and FA_ESP2 ashes is Ca. Cl and S are present in higher concentrations in the FA_ESP1 and FA_ESP2 when compared to bottom ashes, and this result can be explained by the higher contribution from the inorganic content of the biomass to the fly ashes. Also, the physical-chemical characteristics of FA_ESP1 and FA_ESP2, manly the high calcium content (Fig. 5), allows the adsorption of some gas phase chlorine and sulfur released (HCL and SO_2) during the combustion of biomass.

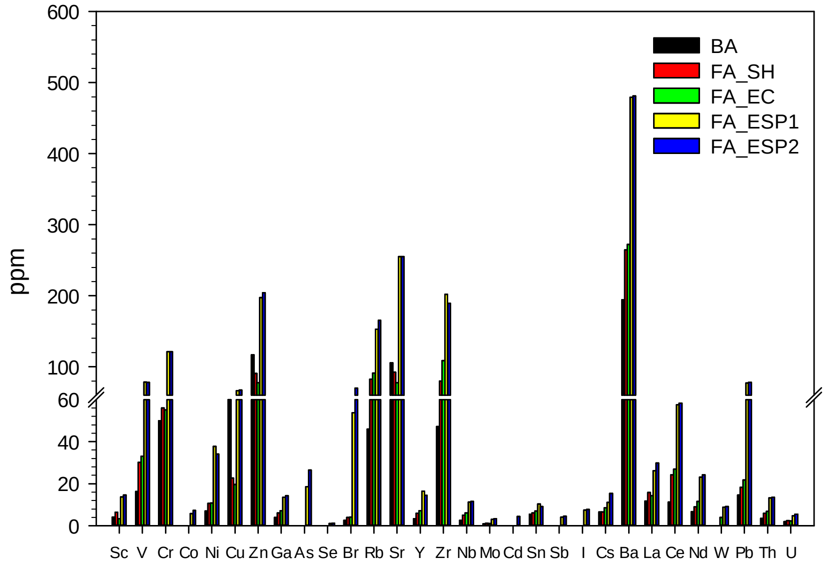


Figure 6: Minor chemical elements in the ash samples collected at distinct locations along the thermal plant, values expressed in ppm (weight (wt), dry basis (db)). Legend according locations in the plant as shown in Figure 1. Other elements were below the detection limit: Ge < 1.04 mg/kg, Ag < 4.98 mg/kg, Te<6.28 mg/kg, Sm<6.42 mg/kg, Yb<5.54 mg/kg, Hf<4.06 mg/kg, Ta<3.86 mg/kg, Tl<2.14 mg/kg, Bi<1.54 mg/kg).

In general, the concentration of minor chemical elements analyzed increases from BA to FA_ESP1 and FA_ESP2 (Fig. 6). Barium is the minor chemical element presents in higher concentration in the ashes, followed by Sr, Zn, Zr and Rb. Some elements, such Co (5.8-7.3 ppm), As (18.5-26.5 ppm), Cd (4.4 ppm), I (7.4-7.8 ppm), Se (1.0-1.2 ppm), Sb (4.1-4.5 ppm) were only found in the electrostatic precipitator fly ashes (Fig. 6).
The presence of these elements only in fly ashes can be explained in result of the contribution of inorganic content of the biomass; it is known that distinct amounts of these minor chemical elements can be found in biomass fuels [40, 41].

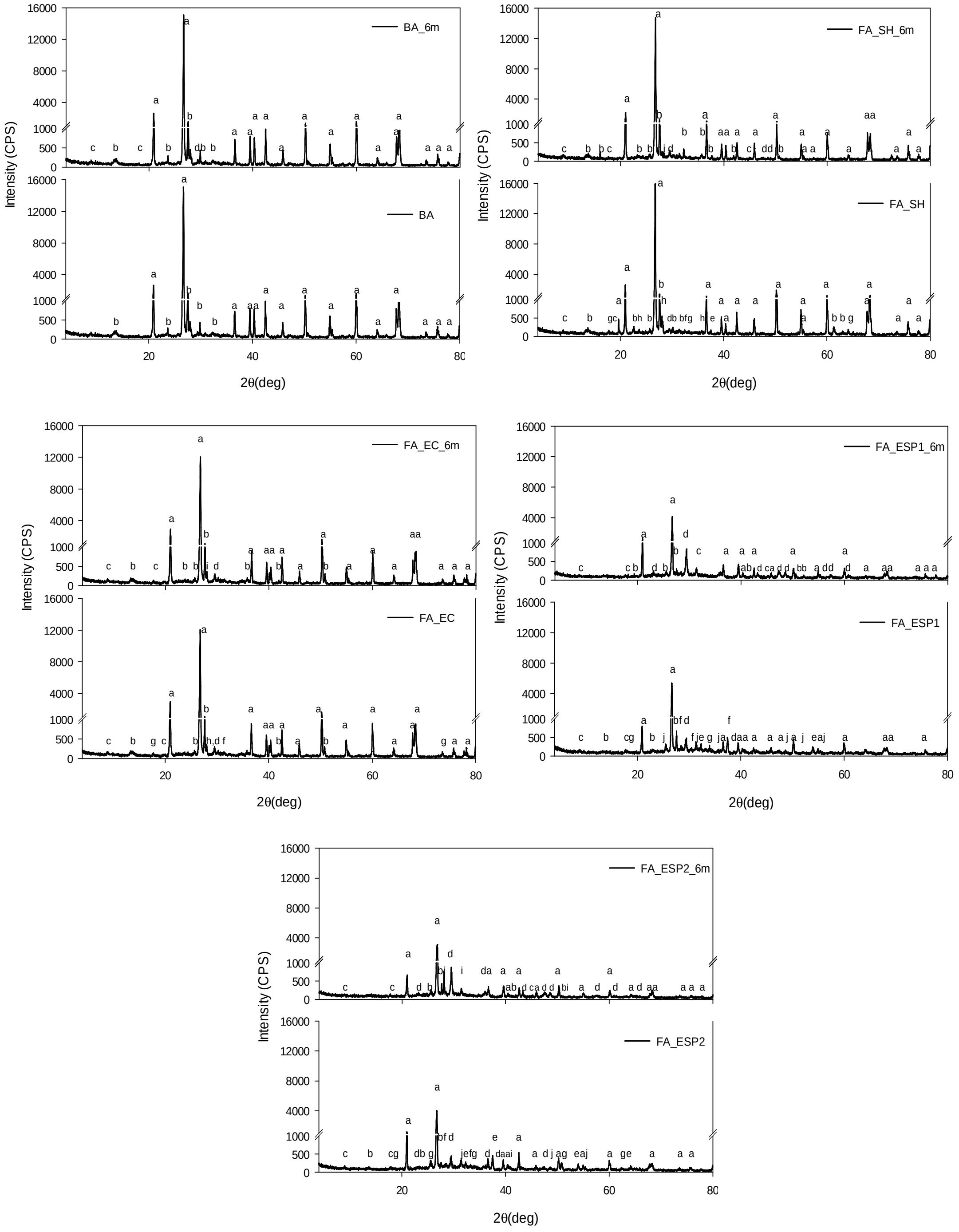


Figure 7: Ash mineralogy determined by X-Ray Diffraction (XRD) analysis, for the fresh ashes collected at distinct locations along the thermal plant and ashes after 6 months (6m) of exposition to atmospheric air conditions: a - quartz, b - microcline, c - lime, d - calcite, e - enstatite, f – muscovite 3T, g – portlandite, h – albite, i – calcium sulphate. Legend according locations in the plant as shown in Fig. 1: BA – bottom ashes, FA_SH – superheater ashes, FA_EC – Economizer ashes, FA_ESP1 – Electrostatic precipitator first stage ashes, FA_ESP2 – Electrostatic precipitator second stage ashes.

X-Ray Diffraction of fresh ash samples show four main phases: quartz, calcite, portlandite and anorthoclase (Fig. 7); these compounds are usual in ashes from biomass combustion. In bottom ash (BA), the main component is quartz, which is in agreement with the X-Ray Fluorescence results and with the characteristics of the original sand bed [25], and small amounts of potassium feldspars (microcline) are present, and this can be explained as resulting from the inert material (forest soil) fed with biomass and with the existence of those crystalline phases in the biomass ash [40, 42]. In the distinct fresh fly ashes, quartz is the most abundant crystalline phase; however, its abundance decreases from FA_SH to the FA_ESP2. Fly ashes from electrostatic precipitator present other crystalline phases (Fig. 7) typical from the biomass ash [40, 42], with different abundance.

An important characteristic of ashes from biomass combustion biomass is their high concentration in plant nutrients [24]. The water leaching of ash works as an indicator of the soluble chemical elements that can be released from ash to the soil.

Water leaching depends on the characteristics of ashes, and also on the reactions that can occur during the process. In this context, the fresh ashes and air exposed ashes can behave in a distinct way. Some ashes have cementious characteristics in presence of moderate amounts of water; some hydrated minerals (ettringite, portlandite and calcite) and calcium silicates, aluminate-hydrates and gypsum could be formed during the process [14]. The formation of these new phases in the ashes affects the solubility and leaching of chemical elements present in the ashes.

The XRD results show that some modifications occur in the ash material in result of air exposition. Those modifications are mainly observed in the fly ashes (Fig. 7); the increase in the amount of calcite observed in the fly ashes after 6-moths air exposition (6m) is an evident modification. Portlandite ($Ca(OH)_2$) is formed by hydration of CaO present in fresh ashes, as a result of interaction o air moisture with the CaO, and then reacts with the CO_2 presents in the atmospheric air and produces calcite [14, 30] according to reaction 1:

$$Ca(OH)_2(cr) \rightarrow Ca(OH)_2(aq) + CO_2(aq) \rightarrow CaCO_3(cr) + H_2O \qquad (1$$

The formation of calcium carbonate (calcite) is one of most important phenomena related to the self-hardening process of biomass ash [14, 43].

The pH, conductivity and release of chemical elements upon water leaching are given in Fig. 8 and Fig. 9. These characteristics were evaluated along distinct time periods of exposition of the ashes to atmospheric air.

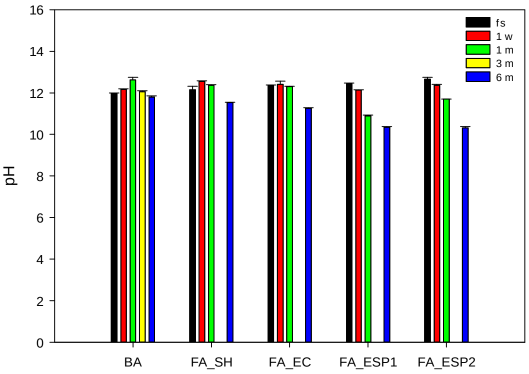


Figure 8: pH of the leaching solution; leaching according standard EN 12457-2 [37]. The pH of the leaching solutions was measured at a temperature of 23.0±2.2ºC. X-axis titles according to ash sampling locations in the thermal plant as shown in Fig. 1. Legend: fs-fresh sample, 1w-one week of air exposition, 1m- one month of air exposition, 3m- three months of air exposition (only for bottom ash), 6m-six month of air exposition.

The water leaching (standard EN 12457-2 [37]) of fresh ash samples originates alkaline solutions, with pH in the range 12 a 12.7. The pH increases from the bottom ash to the fly ash from electrostatic precipitator (Fig. 8), and this can be explained as related with the chemical composition of the ashes, namely the higher alkali content of the ashes from electrostatic precipitator (Fig. 5).

The conductivity of fresh ash samples varies in the range 5 to 19 mS/cm (Fig. 9), and increases from the BA to the FA_ESP2 ashes. The conductivity is related with the concentration of dissolved ions, among those, the ions derived from alkali elements like Na, K, Ca, and also ions derived from Cl and S. Higher conductivity reveals higher ionic strength of the solution and this is associated with higher concentration of ions, thus reflecting a higher solubility of alkali elements, chlorine and sulphur from the fly ashes, when compared to the observed for FA_BA, FA_SH and FA_EC.

In general, it was observed that pH and conductivity of the ash leaching solutions decreased with the time of air exposition of ashes; that decrease is higher in the case of FA_ESP1 and FA_ESP2, and this result could be related with the formation of new crystalline phases (Fig. 7), e.g. as calcium carbonate, which reduces the solubility of some chemical elements present in the ashes [14].

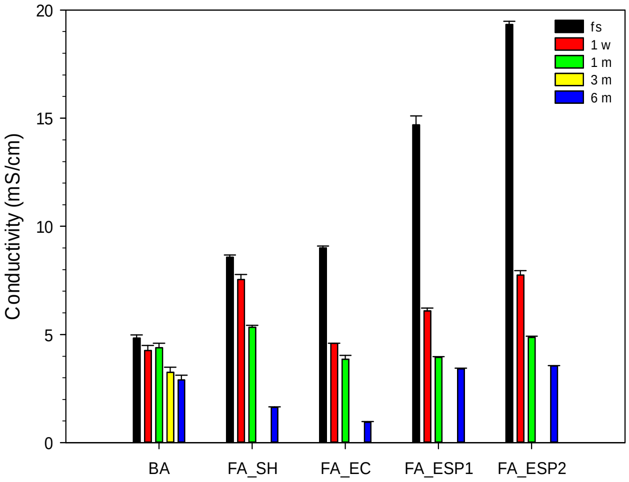


Figure 8: Conductivity of the leaching solution; leaching according standard EN 12457-2 [37]. The conductivity of the leaching solutions was measured at a temperature of 23.0±2.2ºC. X-axis titles according to ash sampling locations in the thermal plant as shown in Fig. 1. Legend: fs-fresh sample, 1w-one week of air exposition, 1m-one month of air exposition, 3m- three months of air exposition (only for bottom ash), 6m-six month of air exposition.

The major chemical elements present in the ash leaching solutions are shown in Fig. 9. Calcium is the element present in higher concentration in the leaching solution of fresh ash samples. Leaching solutions of FA_ESP1 and FA_ESP2 show the higher concentration of calcium and potassium, and this can be explained by the fact that these two ashes present a higher concentration of calcium and potassium (Fig. 5).

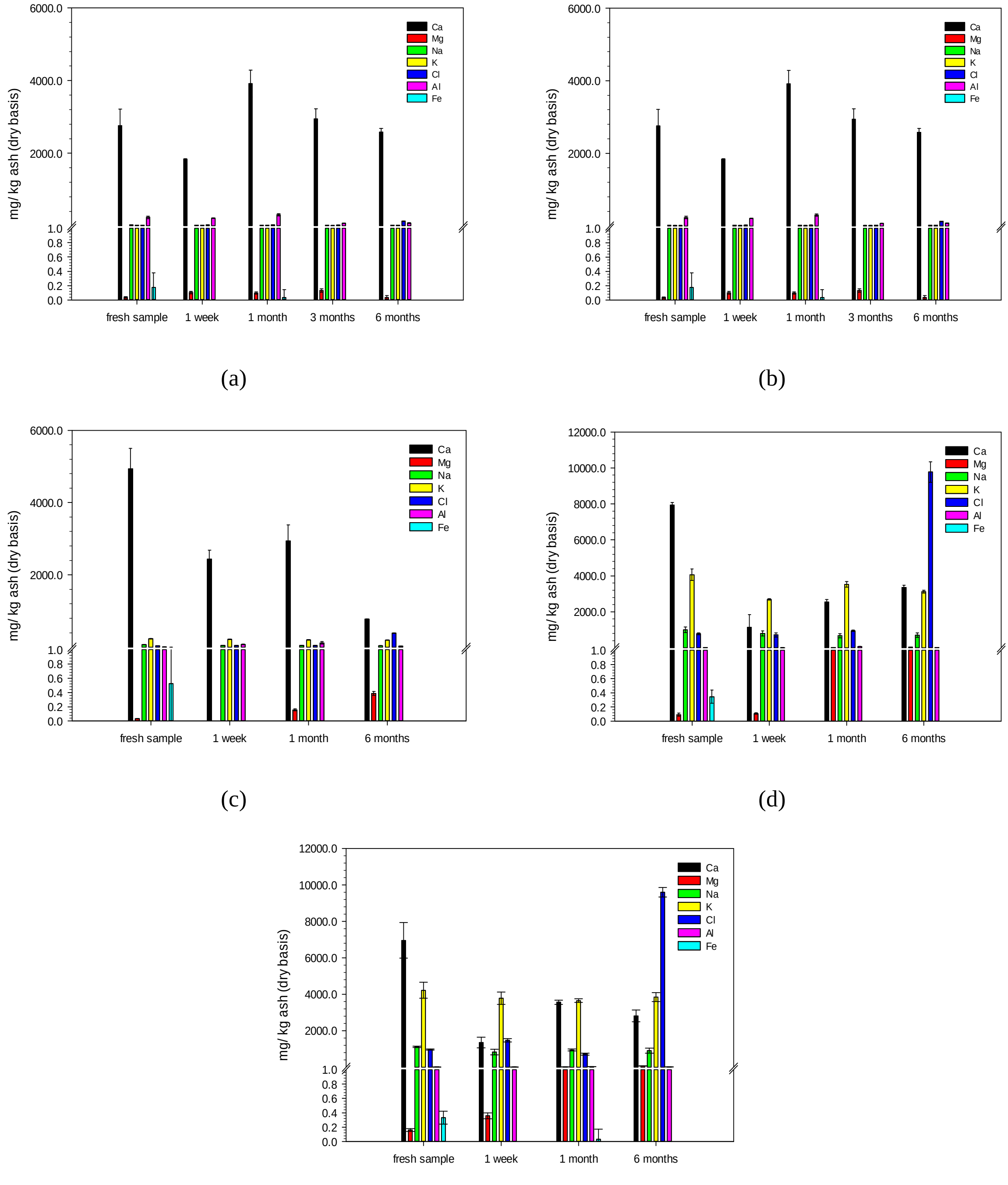
In general, in result of exposition of the ashes to atmospheric air it is observed a decreased in the concentration of calcium in all leaching solutions. This can be caused by the decrease of solubility of calcium compounds, due to the formation of compounds as calcite, which are less soluble than other Ca-based compounds as CaO. On the other hand, it is observed a significant increase in concentration of chlorine (determined as Cl^-) in the leaching solution of FA_ESP1 and FA_ESP2 exposed to air during a period of six months; although observed also for the other ash fractions after six month of exposition, the effect is less pronounced that that observed for FA_ESP1 and FA_ESP2. This can only be explained in result of modifications on the forms according which chlorine is bounded in the ashes, thus becoming more soluble with time.

The concentration of aluminum in the leaching solution of fresh ash sample of bottom ash is significant higher than in the leaching solutions of fly ashes, although this chemical element is present in higher concentration in the fly ashes (Fig. 5); the reasons behind this behavior can be the more or less soluble forms according which this element is bound in the ashes.

The minor chemical elements present in the leaching solutions are shown in Fig. 9. Among those, Ba and Sr are the elements present in higher concentration in the leaching solution of fresh ash samples. Barium varied between 1.8 mg/kg of ash in the FA_ESP2 and 6 mg/kg of ash in the FA_EC leaching solution. The concentration of Sr in the leaching solutions varied in a range of 3.4 to 41.8 mg/kg of ash, being the FA_ESP2 leaching solution which presented the highest concentration.

During air exposition of ashes the concentration of Zn, Ba and Sr decreased, mainly for the case of FA_ESP1 and FA_ESP2. On the other hand, the concentration of B in the leaching solutions of BA, FA_ESP1 and FA_ESP2 increase during the air exposition (Fig.9).

Some elements, such as As (0.02-0.03 mg/kg of ash) and Cd (3.4×10^{-4}-1.8×10^{-3} mg/kg of ash) only were measured in leaching solution of fly ashes from electrostatic precipitator, and their concentration did not change during air exposition. The presence of those elements only in these ashes can be explained by the fact that the FA_ESP1 and FA_ESP2 present a higher concentration (6) of minor chemical elements than BA, FA_SH and FA_EC.



(a)

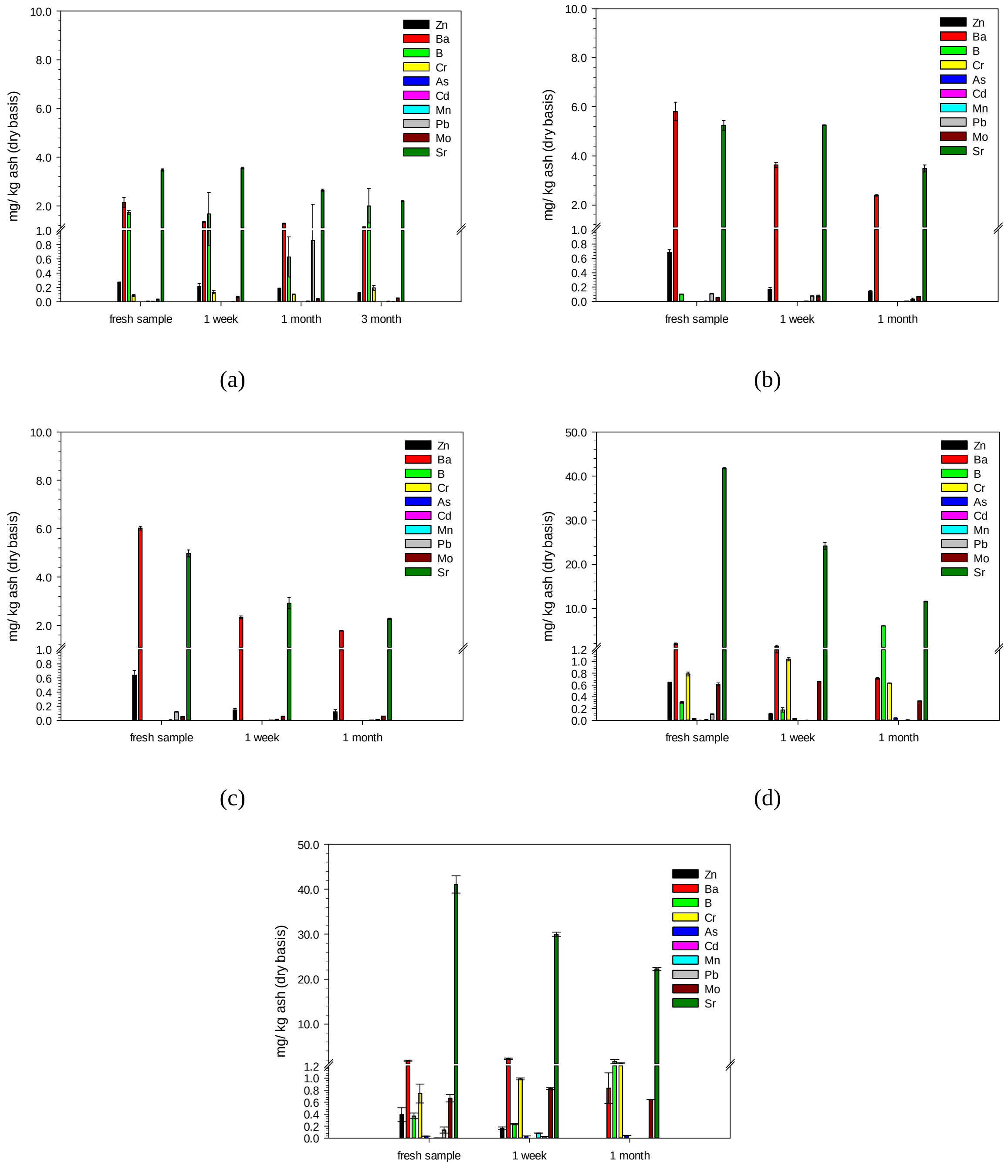
(b)

(c)

(d)

(e)

Figure 9: Major chemical elements present in the leaching solutions from ash samples collected at distinct locations along the thermal plant ((a) Bottom ash (BA), (b) Fly ash from superheater (FA_SH), (c) Fly ash from economizer (FA_EC), Fly ash from electrostatic precipitator stage one (d) and stage two (e) (FA_ESP1 and FA_ESP2)), for fresh ash samples and ash samples after distinct time periods of exposition to atmospheric air.



(a) (b)

(c) (d)

(e)

Figure 9: Minor chemical elements present in the leaching solution from ash samples collected at distinct locations along the thermal plant ((a) Bottom ash (BA), (b) Fly ash from superheater (FA_SH), (c) Fly ash from economizer (FA_EC), (d) Fly ash from electrostatic precipitator stage one (FA_ESP1), and (e) Fly ash from electrostatic precipitator stage two (FA_ESP2)), for fresh ash samples and ash samples after distinct time periods of exposition to atmospheric air.

4 CONCLUSIONS

Different ash flows from a biomass thermal power plant were collected and exposed to atmospheric conditions under laboratory conditions during six months. Some physical and chemical characteristics of the ash flows were analyzed. Bottom ash shows particle size distribution enriched in coarse particles when compared with fly ashes. This result is mainly due to the biomass used as fuel, because this it has considerable amounts of inert material, such as soil particles and small stones. An important difference between the chemical composition of distinct ash flows was observed. The LOI increases from bottom bed ashes to fly ashes from electrostatic precipitator. The higher values of LOI for FA_ESP1 and FA_ESP2 were related not only with the unburned material content but also with the thermal decomposition and volatilization of components, such as alkaline elements present in those ashes. Enrichment in compounds of silicon was observed for bottom ash, fly ash from superheater and economizer. The high content of silicon in the ashes is explained by the original material used as bed and by the inert material feed with the biomass that is dragged with the combustion flue gases.

Fly ashes from electrostatic precipitator show the silicon as the chemical element with the higher concentration, followed by calcium. However, enrichment in elements such as sodium, magnesium, calcium and potassium was observed. This result is related to the contribution of fine particles constituted by chemical elements of the inorganic content of biomass, which were carried out with the combustion flue gases. The concentration of minor chemical elements increased from bottom ash to fly ash from electrostatic precipitator. Barium was the minor chemical element with higher concentration in ashes. The abundance of these elements in the fly ash from electrostatic precipitator is due to the contribution of inorganic content of biomass released during the combustion. As a result of the atmospheric air exposition, a modification in the mineralogy of ashes was observed, mainly for the fly ashes, with the appearance of compounds such as calcite. The formation of those compounds is a result of self-hardening and carbonation of the ashes due to the atmospheric carbon dioxide. These changes in the mineralogy, promote a decrease on the solubility of the chemical elements, and a decrease on pH and conductivity during the air exposition. Calcium was the major water soluble element with higher concentration in the leaching solution, followed by potassium, sodium and chloride. A decrease on the leaching of calcium from the ash samples exposed to air conditions was noted. A possible explanation can be the decrease of solubility of calcium compounds, due to the formation of compounds as calcite which are less soluble than other Ca-base (such as CaO).

A significant increase in the concentration of chloride in the leaching solution of fly ashes from the electrostatic precipitator exposed to air during a period of six months was observed. This can be explained by modifications in which Cl is bounded in the ashes, which becoming more soluble with time.

Ba and Sr were the minor water soluble elements with higher concentration in the leaching solutions of ashes. During air exposition their concentrations decrease. This can be due to the forms in which those elements are bounded in the ashes, which becoming more insoluble with time.

The results observed in this study, show that the process of ash - atmospheric air interaction is of major importance considering the characterization of the ashes and their environmental management. The relevance of this process appears to be dependent on the ash characteristics, and a deep understanding of this phenomenon is needed in the perspective of material valorization of ashes.

5 REFERENCES

[1] A. Demirbas, Potential applications of renewable energy sources, biomass combustion in boiler power systems and combustion related environmental issues, Progress in energy and combustion science, 31, (2005), pag. 171.

[2] S. Bilgen, K. Kaygusuz, A. Sari, Renewable Energy for a clean and sustainable future, Energy Sources, 26, (2004), pag. 1119.

[3] A. Moiseyev, B. Solberg, A.M.I. Kallio, M. Lindner, An economic analysis of the potential contribution of forest biomass to the EU RES target and its implications for the EU forest industries, Journal of Forest Economics, 17, (2011), pag. 197.

[4] S. Bringezu, M. O'Brien, H. Schutz, Beyond biofuels: Assessing global land use for domestic consumption of biomass: A conceptual and empirical contribution to sustainable management of global resources, Land Use Policy, 29, (2012), pag. 224.

[5] D.O. Hall, Biomass energy in industrialized countries – a view of the future, Forest Ecology and Management, 91, (1997), pag. 17.

[6] D. Roser, K. Pasanen, A. Asikainen, Decision-support program "EnerTree" for analyzing forest residue recovery options, Biomass and Bioenergy, 30, (2006), pag. 326.

[7] Handbook of biomass combustion and co-firing. van Loo S, Koppejan J. (Eds), 2nd ed. Earthscan, London, UK. (2008).

[8] L.A.C. Tarelho, E.R. Teixeira, D.F.R. Silva, R.C.E. Modolo, J.J.F. Silva, Characteristics, management and applications of ashes from thermochemical conversion of biomass to energy, Proceedings of the World Bioenergy 2012: Conference & Exhibition on Biomass for Energy, May 29-31, (2012) Jonkoping, Sweden.

[9] L.A.C. Tarelho, E.R. Teixeira, D.F.R. Silva, R.C.E. Modolo, Treatment by leaching of bottom bed ash from biomass combustion in bubbling fluidized bed, Proceedings of the Ash Utilisation 2012: Ashes in a Sustainable Society, January 25-27, (2012) Stockholm, Sweden.

[10] E.R. Teixeira, L.A.C. Tarelho, M.C.E. Sequeira, C.E.C. Santos, M.A.A. Matos, Characteristics of co-combustion of sewage sludge with forest biomass in bubbling fluidized bed, Proceedings of the Ash Utilisation 2012: Ashes in a Sustainable Society, January 25-27, (2012) Stockholm, Sweden.

[11] G. Olofsson, Z. Ye, I. Bjerle, A. Andersson, Bed agglomeration problem in fluidized-bed biomass

combustion, Ind. Eng. Chem. Res., 41, (2002), pag. 2888.
[12] M. Ohman, A. Nordin, Bed agglomeration characteristics during fluidized bed combustion of biomass fuels, Energy and Fuels, 14, (2000), pag. 169.
[13] J. Osan, B. Alfoldy, S. Torok, R. van Grieken, Characterisation of wood combustion particles using electron probe microanalysis, Atmospheric Environment, 36, (2002), pag. 2207.
[14] B-M. Steenari, S. Schelander, O. Lindqvist, Chemical and leaching characteristics of ash from combustion of coal, peat and wood in a 12 MW CFB – a comparative study, Fuel, 78, (1999), pag. 249.
[15] Guideline for classification of ash from solid biofuels and peat utilized for recycling and fertilizing in forestry and agriculture, NT Technical Report 613, Nordic Innovation Centre, Oslo, Norway, (2008).
[16] I. Obernberger, F. Biedermann, W. Widmann, R. Riedl, Concentration of inorganic elements in biomass fuels and recovery in the different ash fractions, Biomass and Bioenergy, 12, (1997), pag. 224.
[17] C. Liao, C. Wu, Y. Yan, The characteristics of inorganic elements in ashes from a 1 MW CFB biomass gasification power generation plant, Fuel Processing Technology, 88, (2007), pag. 149.
[18] J. Capablo, P.A. Jensen, K.H. Pedersen, K. Hjuler, L. Nikolaisen, R. Backman, F. Frandsen, Ash properties of alternative biomass, Energy and Fuels, 23, (2009), pag. 1965.
[19] I. Obernberger, K. Supancic, Possibilities of ash utilisation from biomass combustion plants, Proceedings of the 17th European Biomass Conference & Exhibition, 29 June – 03 July (2009), Hamburg, Germany.
[20] J. Latva-Somppi, M. Moisio, E.I. Kauppinen, T. Valmari, P. Ahonen, U. Tapper, J. Keskinen, Ash formation during fluidized-bed incineration of paper mill waste sludge, Journal Aerosol Science, 4, (1998), pag. 461.
[21] J. Latva-Somppi, E.I. Kauppinen, T. Valmari, P. Ahonen, A.S. Gurav, T.T. Kodas, B. Johanson, The ash formation during co-combustion of wood and sludge in industrial fluidized bed boilers, Fuel Processing Technology, 54, (1998), pag. 79.
[22] M.J.F. Llorente, R.E. Cuadrado, J.M.M. Laplaza, J.E.C. Garcia, Combustion in bubbling fluidised bed with bed material of limestone to reduce the biomass ash agglomeration and sintering, Fuel, 85, (2006), pag. 2081.
[23] O. Dahl, H. Nurmesniemi, R. Poykio, G. Watkins, Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler, Fuel Processing Technology, 90, (2009), pag. 871.
[24] O. Dahl, H. Nurmesniemi, R. Poykio, G. Watkins, Heavy metals concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized-bed boiler with respect to their Finnish forest fertilizer limit values, Fuel Processing Technology, 91, (2010), pag. 1634.
[25] L.A.C. Tarelho, A.M.S.L. Coelho, E.R. Teixeira, R. Rajamma, V.M. Ferreira, Characteristics, of ashes from two Portuguese biomass co-generation plants, Proceedings of the 19th European Biomass Conference & Exhibition, June 6-10, (2011) Berlin, Germany.
[26] G. Wang, L. Shen, C. Sheng, Characterization of biomass ashes from power plants firing agricultural residues, Energy and Fuels, 26, (2012), pag. 102.
[27] P. Teixeira, H. Lopes, I. Gulyurtlu, N. Lapa, Use of chemical fractionation to understand partitioning of biomass ash constituents during co-firing in fluidized bed combustion, Fuel, 101, (2012), pag. 215.
[28] M. Ingerslev, S. Skov, L. Sevel, L.B. Pedersen, Elements budgets of forest biomass combustion and ash fertilization – A Danish case-study, Biomass and Bioenergy, 35, (2011), pag. 2697.
[29] A. Demeyer, J.C.V. Nkana, M.G. Verloo, Characteristics of wood ash and influence on soil properties and nutrient uptake: An overview, Bioresource Technology, 77, (2001), pag. 287.
[30] B-M. Steenari, L.G. Karlsson, O. Lindqvist, Evaluation of the leaching characteristics of wood ash and the influence of ash agglomeration, Biomass and Bioenergy, 16, (1999), pag. 119.
[31] From extraction of forest fuels to ash recycling, International Handbook, Swedish Forest Agency, (2006).
[32] M. Mahmoudkhani, T. Richards, H. theliander, Sustainable use of biofuel by recycling ash to forests: Treatment of biofuel ash, Environmental Science and Technology, 41, (2007), pag. 4118.
[33] R.M. Pitman, Wood ash use in forestry – a review of the environmental impacts, Forestry, 79, (2006), pag. 563.
[34] S.P. Pandey, R.L. Sharma, The influence of mineral additives on the strength and porosity of OPC mortar, Cement and Concrete Research, 30, (2000), pag. 19.
[35] D. Ravina, Properties of fresh concrete incorporating a high volume of fly ash as partial fine sand replacement, Materials and Structures/ Matèriaux et Constructions, 30, (1997), pag. 473.
[36] PTDC/AAC-AMB/098112/2008, Biomass ash: Characteristics in relation to its origin, treatment and application to soil, Project financed by Fundação para a Ciência e a Tecnologia, Portugal.
[37] EN 12457-2 (2002) – Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludge – Part 2.
[38] M. Fan, R.C. Brown, Comparison of the loss-on-ignition and Thermogravimetric analysis techniques in measuring unburned carbon in coal fly ash, Energy and Fuels, 15, (2001), pag. 1414.
[39] CEN/TS 14775 (2004) – Solid biofuels – Method for the determination of ash content.
[40] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the chemical composition of

biomass, Fuel, 89, (2010), pag. 913.

[41] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the chemical composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification, Fuel, 105, (2013), pag. 40.

[42] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, T.J. Morgan, An overview of the organic and inorganic phase composition of biomass, Fuel, 94, (2012), pag. 1.

[43] B-M. Steenari, O. Lindqvist, Stabilisation of biofuel ashes for recycling to forest soil, Biomass and Bioenergy, 13, (1997), pag. 39.

6 ACKNOWLEDGEMENTS

This work was financially supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal, through the project Bias-to-soil - Biomass ash: Characteristics in relation to its origin, treatment and application to soil (PTDC/AAC-AMB/098112/2008 - FCOMP-01-0124-FEDER-008487).