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Orimulsion fly ash in clay bricks—part 1: composition and thermal behaviour of ash

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Abstract

A bitumen-in-water emulsion (Orimulsion) is currently used as a fuel in several thermal power plants worldwide. Orimulsion combustion produces a fly ash rich in S, Mg, V and Ni, which is processed to recover metals. In order to assess the feasibility of a recycling in clay brick production, a characterization of the physico-chemical and thermal properties of ash was performed by ICP–OES, XRPD, SEM, BET and TGA–DTA techniques. Orimulsion ash resulted in fine-grained (aggregates of submicronic particles), highly hygroscopic, constituted mainly of magnesium sulphate, vanadyl sulphates and magnesium and nickel oxides, and thermally unstable in the usual brick firing conditions. These features can affect the brickmaking process, particularly the plasticity of the clay body and its drying and firing behaviour; furthermore, a mobilization of sulphates could occur, promoting the formation of efflorescence and/or the SO_x release during firing. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Chemical properties; Fly ash; Grain size; Heavy clays; Thermal properties; Waste materials

1. Introduction

An emulsion of natural bitumen (70–73%) in fresh water (27–30%) is currently used as a fuel (Orimulsion® by PDVSA BITOR S.A., Venezuela) in several thermal power plants worldwide.[1] This emulsion is obtained (about 28 million tonnes in 1999) by mechanical mixing of the two constituents with the addition of small amounts of surface-active agents (polyethoxylated nonylphenol).[2]

Combustion produces a fly ash rich in sulphur, magnesium, vanadium and nickel, as a consequence of the composition of the bitumen-in-water emulsion (S 2.4–2.9%, Mg 300–450 ppm, V 270–340 ppm, Ni 60–80 ppm)[1,3,4] and the addition of MgO to neutralize sulphur oxides.[1,5] Fly ash is normally treated to get a dust-free granulate, successively processed to recover metals and magnesium sulphate.[5,6]

This study was undertaken because the growing use of this bitumen–water emulsion led, in the last few years, to a production of ash exceeding the capacity of the metal recovery plants. Therefore, a possible disposal in clay brick production was appraised through the characterization of the chemico-physical properties and the thermal behaviour of the fly ash.

Further investigations, focusing on the advantages and drawbacks connected with the presence of ash in the clay bricks, are presented in the second and third parts of this work. They deal, respectively, with the technological behaviour of clay–ash mixtures in the different phases of the brickmaking process, and with the chemical stability of ash-bearing products.

2. Materials and methods

Two ash samples, collected before the granulation treatment, were taken into consideration, coming from two Italian thermal power plants using Orimulsion as a fuel. They are located in Brindisi, Apulia (ash B) and in Fiume Santo-Porto Torres, Sardinia (ash F) respectively.

The chemical analyses of fly ash were carried out by inductively-coupled plasma emission spectrophotometry (ICP–OES) with a Varian Liberty 200 equipment; the analytical solutions were obtained (a) through microwave-assisted acid digestion, for the bulk composition, and (b) by stirring in distilled water at room temperature for 1 h, centrifugation and separation of the insoluble

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residue, for the water-soluble component. The amount of residual C was measured by means of pyrolysis and absorption of the infrared band with Leco CS-225 equipment (ASTM E-1019). Hygroscopicity was determined following Keeling's method.[7]

The phase composition was determined by X-ray powder diffraction (XRPD) with Ni-filtered CuK_α radiation (Rigaku, Miniflex) on (i) the untreated ash, (ii) the water insoluble residue, and (iii) the ash calcined in static air at 700 and 1000 °C, respectively. The interpretation of the X-ray patterns was done by comparison with data of the powder diffraction file. The measurement of the specific surface of untreated ash was performed by nitrogen adsorption with single point method[8] using a Micromeritics FlowSorb II 2300 apparatus (ASTM C 1069). The particle size distribution of the gold sputtered ash was estimated by image analysis with a scanning electron microscope (Cambridge, Stereoscan 360).

The thermal behaviour was investigated by means of simultaneous thermogravimetric (TGA) and thermodifferential analyses (DTA) in static air, with a thermal gradient of 5 °C/min and maximum firing temperature of 1000 °C on approximately 20 mg of the sample (Netzsch, STA 1500 apparatus).

3. Results and discussion

3.1. Particle size and morphology

The ashes from the combustion of the bitumen-in-water emulsion appear to be formed by aggregates with a prevalently rounded shape resulting by the agglomeration of submicronic particles (Fig. 1). The size distribution of aggregates is different for the two samples taken into consideration: the particles of ash B are for the most part between 5 and 30 μm, with a frequency maximum corresponding to 16–18 μm, while ash F presents a finer distribution, mostly between 2 and 20 μm, with a frequency maximum around 12–14 μm (Fig. 2). These data are consistent with the particle size of the particulate matter from the Orimulsion combustion in several plants.[1]

These differences of size distribution are confirmed by the specific surface data, which are slightly higher for ash F (4.3 ± 0.1 m^2 g^{-1}) with respect to ash B (3.2 ± 0.1 m^2 g^{-1}).

3.2. Chemical and phase composition

The bulk chemical composition of ashes is basically characterized by high amounts of SO_3, MgO and VO_2, which are associated to minor quantities of SiO_2, Al_2O_3, NiO, CaO, Fe_2O_3 and C. The amounts of Na_2O, K_2O, Cr_2O_3 and TiO_2 are below 1% (Table 1). Ash F appears to be richer in V, Mg, Ni and poorer in Si, Al, Fe with respect to ash B. These data are consistent with those reported in literature,[5] though the ashes taken into account contain, in particular, more sulphur and less aluminium and carbon.

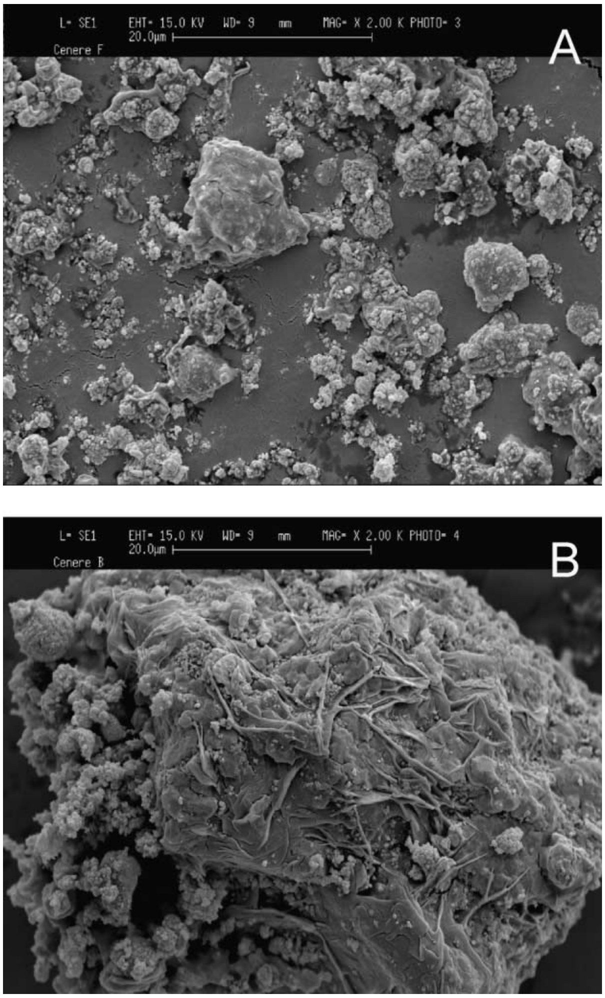

Fig. 1. Photomicrographs of Orimulsion fly ash taken by the scanning electron microscope. (A) Particle aggregates of ash F, (B) particle of an agglomerate of ash B (bar = 20 μm).

Orimulsion fly ashes are easily soluble in water: approximately 73% of ash B and 59% of ash F (Table 1). The water-soluble component accounts for most of SO_3, MgO, CaO and alkalis, as well as a large part of VO_2 and NiO. In particular, no hexavalent chromium was detected.

The phase composition of these ashes is very complex, and the X-ray diffraction patterns exhibit a high number of reflections and several line interferences and overlappings, which make some attributions uncertain (Fig. 3). The interpretation of these patterns highlighted the predominant occurrence of magnesium sulphate monohydrate ($MgSO_4 \cdot H_2O$) and hydrogen vanadyl sulphate [$(VO)_2H_2(SO_4)_3$], accompanied by magnesium monoxide (MgO), anhydrous, monohydrate and pentahydrate vanadyl sulphate (α-$VOSO_4$, $VOSO_4 \cdot H_2O$, $VOSO_4 \cdot 5H_2O$). These phases are associated with minor amounts of calcium sulphate ($CaSO_4$) and nickel monoxide

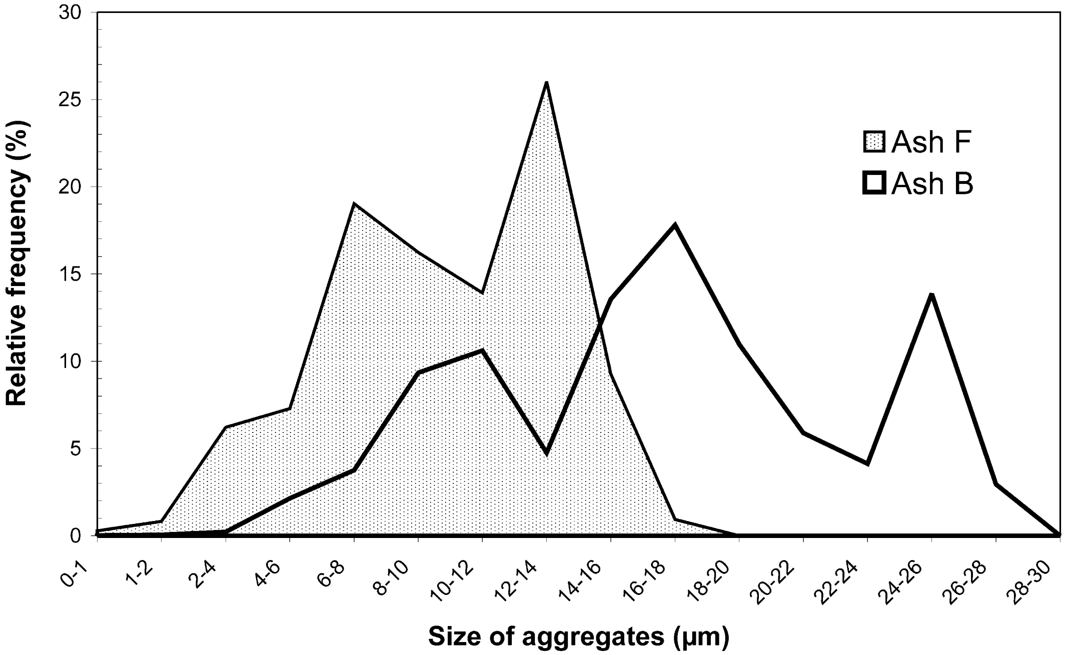

Fig. 2. Particle size distribution of the aggregates of Orimulsion ashes.

Table 1
Chemical composition of fly ashes from the combustion of Orimulsion (average±standard deviation)

Wt.%	Ash B		Ash F	
	Bulk sample	Water-soluble component	Bulk sample	Water-soluble component
SO_3	44.44±0.56	43.27±0.33	45.82±0.94	35.25±0.70
SiO_2	4.15±0.32		0.51±0.11	
TiO_2	0.30±0.02		0.21±0.02	
VO_2	16.57±0.37	11.22±0.16	22.58±0.57	6.98±0.13
Al_2O_3	2.78±0.19		0.38±0.09	
Fe_2O_3	2.32±0.06		1.36±0.03	
Cr_2O_3	0.04±0.01		0.03±0.01	
MgO	20.23±0.41	14.61±0.33	22.51±0.88	13.11±0.27
CaO	2.27±0.14	1.89±0.03	2.28±0.18	2.07±0.04
NiO	2.63±0.06	1.68±0.13	3.60±0.06	1.31±0.05
Na_2O	0.62±0.02	0.47±0.01	0.68±0.05	0.51±0.01
K_2O	0.09±0.01	0.05±0.01	0.06±0.01	0.05±0.01
C	1.70±0.05		1.90±0.05	

(NiO), as well as, presumably, a silicate of aluminium and sodium ($NaAlSi_3O_8$) and traces of magnesium sulphate hexahydrate ($MgSO_4 \cdot 6H_2O$). Moreover, the fair amount of water-soluble Ni, Na and K suggests the presence of sulphates, undetected with the XRPD analysis.

Further analyses on the insoluble residues pointed out—besides magnesium and nickel oxides, and anhydrous vanadyl sulphate found also in untreated ash—small amounts, not detectable on the bulk sample for their low concentration, of other vanadium compounds: i.e. VO_2, β-V_2O_5, VOOH and $VO(OH)_2$. If the identification of these compounds is correct, a complex chemical picture will concern vanadium: the occurrence of small quantities of V^{3+} and V^{5+}, together with the predominat valence V^{4+} characterizing the vanadyl ion, is maybe explainable with variable oxidation conditions in the combustion and/or in the cooling processes.[1,3]

3.3. Thermal behaviour

The thermal behaviour of ashes was studied by means of (DTA) analyses, (TGA) as well as X-ray diffraction of the reaction products formed after thermal treatment at 700 and 1000 °C.

The thermodifferential and thermogravimetric patterns of the two ashes in hand are very similar and will be discussed together (Fig. 4). They show a rather complicated series of exothermic and endothermic reactions,

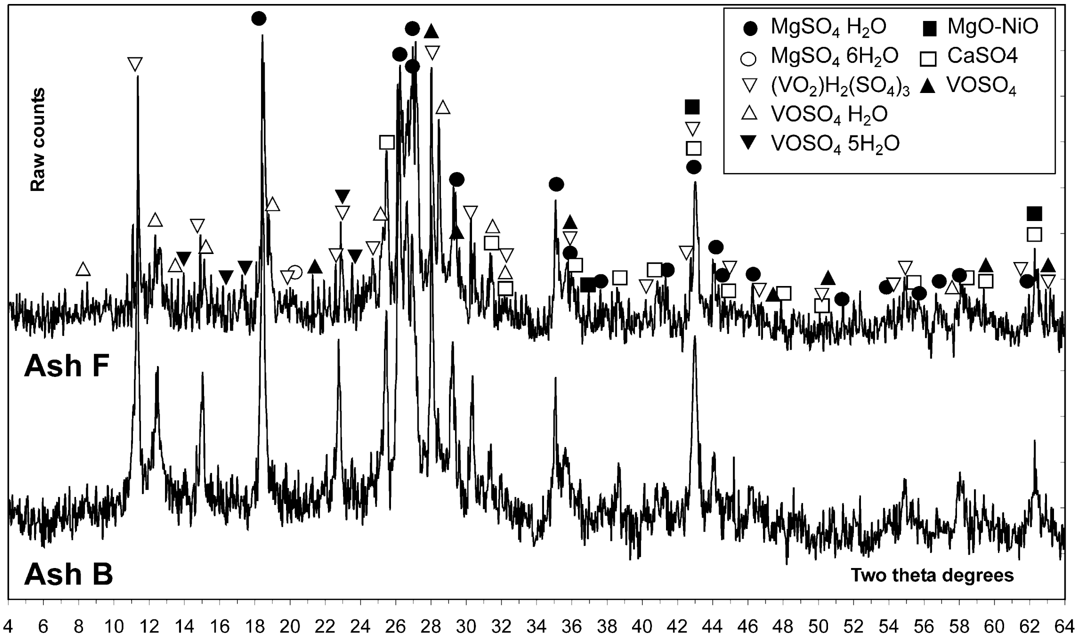

Fig. 3. X-ray patterns of untreated Orimulsion ashes.

which probably exhibit frequent overlappings making the interpretation difficult and to some extent uncertain. The fundamental facts of the thermal behaviour of these ashes are:

(i) conspicuous weight loss at 1000 °C (41.8% ash B, 39.6% ash F);
(ii) wide exothermic trend of the DTA curve up to about 500 °C;
(iii) gradual endothermic shift of the DTA curve between 500 and 1000 °C approximately.

In particular, the following main stages can be distinguished:

Up to ~100 °C: loss of the moisture absorbed for the high hygroscopicity of the material, which is as high as 8.0% in ash B and 5.6% in ash F.

Between ~100 and ~550 °C: remarkable weight loss (approximately 22% for ash B and 18% for ash F) due to a sum of largely overlapping reactions, not clearly distinct from each other. Initially, the process concerns the dehydration of sulphates ($MgSO_4{\cdot}nH_2O$, $VOSO_4{\cdot}$

Table 2
Phase composition of untreated and calcined ashes

Wt.%	Ash B			Ash F		
	Untreated	Calcined 700 °C	Calcined 1000 °C	Untreated	Calcined 700 °C	Calcined 1000 °C
$MgSO_4{\cdot}H_2O$	~50			~45		
$(VO_2)_2H_2(SO_4)_3$	~15			~10		
$VOSO_4{\cdot}nH_2O$	~5			~20		
$CaSO_4$	~5			~5		
$NiSO_4{\cdot}nH_2O$	~5			Traces		
$(Na,K)_2SO_4$	Traces			Traces		
Silicates	~10	~10	~15	Traces	Traces	Traces
C residue	Traces			Traces		
VO_2	Traces			Traces		
VOOH–$VO(OH)_2$	Traces			Traces		
V_2O_5	Traces	~20		Traces	~25	
MgO–NiO	~5	~10	~15	~10	~15	~25
β-$MgSO_4$		~60	~5		~60	~20
$Mg_3(VO_4)_2$			~60			~50
$NaCaVO_4$		Traces	~5		Traces	~5

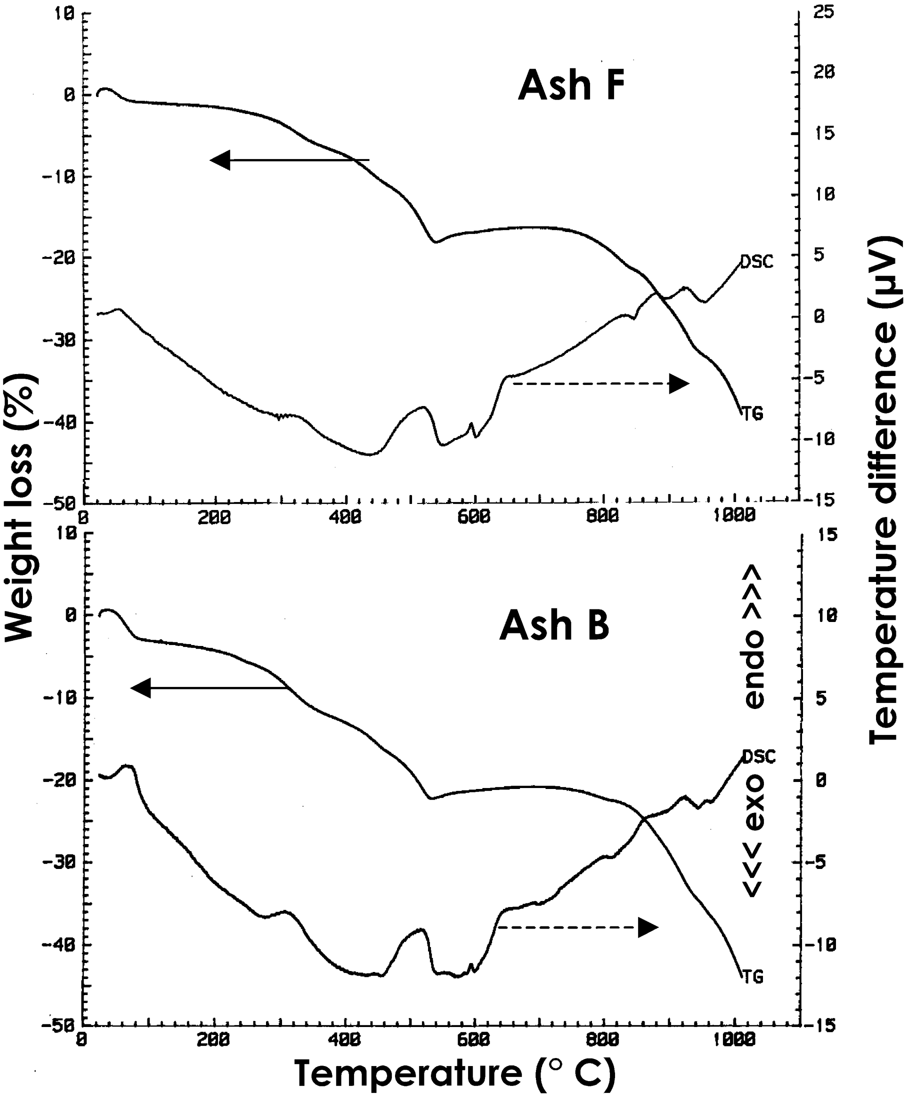

Fig. 4. Thermogravimetric (TG) and thermodifferential (DSC) curves of Orimulsion ash.

nH_2O); then, from about 400 °C, both combustion of the carbonaceous component and decomposition of vanadyl sulphates occurred.[9]

Between ~550 and ~800 °C: slight weight increase, at first rather fast then very gradual, corresponding to a sharp endothermic band of the DTA curve. This trend is presumably connected to a large extent with a progressive oxidation of the vanadyl ion.[9] As a matter of fact, the oxidation of vanadium ($VO_2 \rightarrow V_2O_5$) leads to a weight increase of about 10%, which would translate, in the ashes in hand, in a weight growth of about 2%; this increment corresponds well to the weight change actually occurring in the thermogravimetric curves.

Between ~800 and 1000 °C: considerable weight loss (approximately 20%) occurring with a series of apparently endothermic reactions, probably attributable to the thermal decomposition, with SO_x release, of magnesium sulphates and the small amounts of alkaline and nickel sulphates.

3.4. Phase transformations during thermal treatment

The complex series of phase modifications occurring during the thermal treatment of Orimulsion ashes is summarized in Table 2.

The phase analysis of ashes burned at 700 °C pointed out the occurrence of anhydrous magnesium sulphate (β-$MgSO_4$) prevalent on the magnesium, nickel and vanadium oxides and probably a sodium and calcium vanadate (Fig. 5). This phase composition confirms the hypothesis made interpreting the TGA–DTA data, about the slight weight increase between 500 and 700 °C, which has been attributed to the vanadium oxidation consequent to the decomposition of vanadyl sulphates.

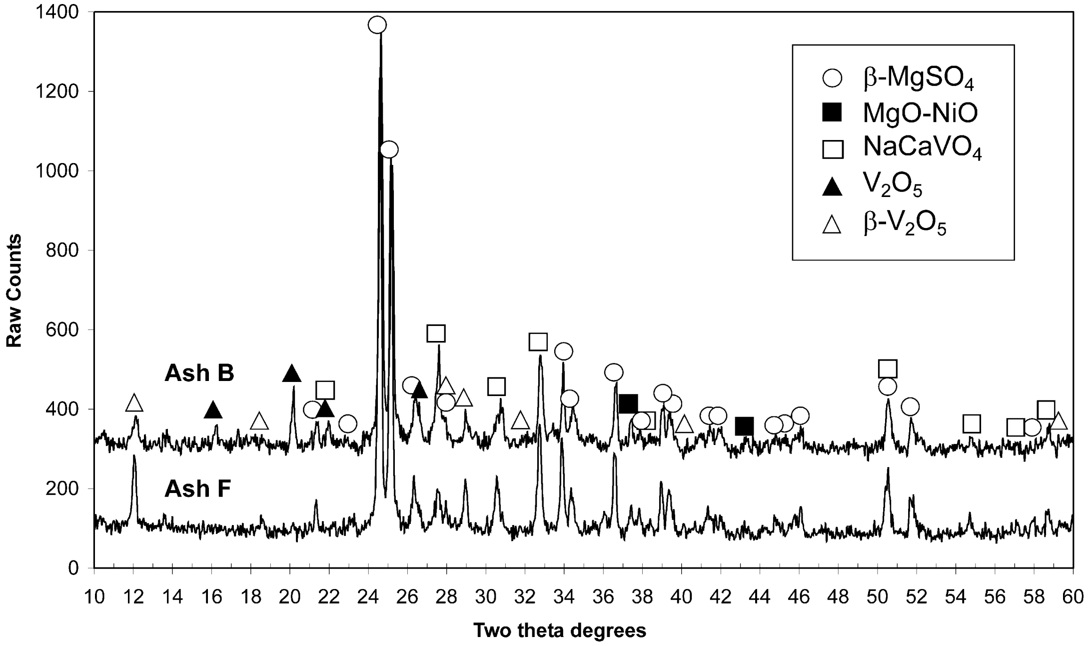

Fig. 5. X-ray patterns of Orimulsion ashes calcined at 700 °C.

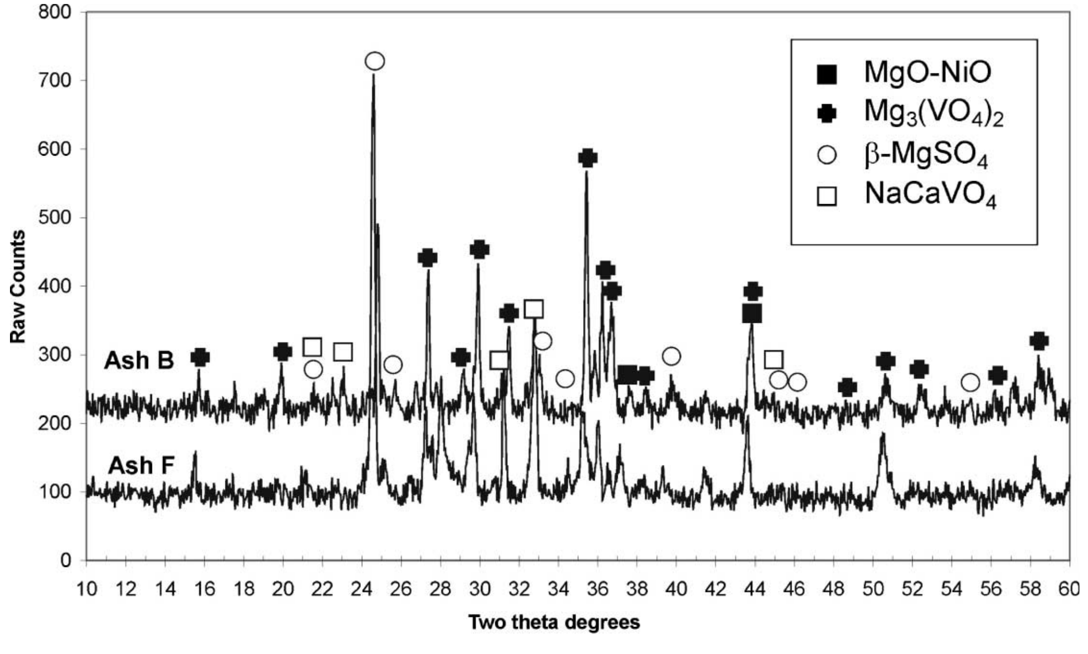

Fig. 6. X-ray patterns of Orimulsion ashes calcined at 1000 °C.

As a matter of fact, at 700 °C there are no longer vanadyl (V^{4+}) compounds, but just pentavalent vanadium (V^{5+}) oxides. In respect of untreated ash, there is also the absence of calcium sulphate, which in all events was expected to be stable at least up to 900 °C.[10]

In the ashes burned at 1000 °C, only a modest quantity of residual β-$MgSO_4$ remained and the main crystalline phase became magnesium vanadate, accompanied by sodium and calcium vanadate and by magnesium and nickel oxides (Fig. 6). This phase composition explains the strong weight loss exhibited by the ashes approximately between 800 and 1000 °C, which is, therefore, due to a large extent to the thermal dissociation of magnesium sulphate, with volatilization of SO_3 and solid state reaction between the magnesium and vanadium oxides: $3\ MgSO_4 + V_2O_5 \rightarrow Mg_3(VO_4)_2 + 3\ SO_3$.

4. Conclusions

The fly ashes produced by the combustion of a bitumen-in-water emulsion (Orimulsion) exhibit some peculiar features. In particular, they are:

- fine grained and constituted mainly by agglomerated submicronic particles;
- highly hygroscopic and to a large extent easily soluble in water;
- rich especially in sulphur, vanadium, magnesium and nickel;
- composed mainly of magnesium and vanadyl sulphates, associated with minor magnesium and nickel oxides, and calcium sulphate;
- thermally unstable in oxidizing conditions with: decomposition of vanadyl sulphates (300–450 °C), combustion of carbonaceous matter and oxidation of V^{4+} to V^{5+} (450–700 °C), decomposition of magnesium sulphate (800–1000 °C).

These chemico-physical characteristics of Orimulsion fly ash may cause some drawbacks in brickmaking. For instance, high hygroscopicity, fine particle size and water solubility could interfere with body preparation, shaping or drying. On the other hand, soluble vanadium and magnesium sulphates may be mobilized during firing and produce efflorescence and/or SO_x release. At any rate, a precise and reliable prediction of these effects on clay bricks is not possible on the basis of chemico–physical properties of Orimulsion fly ash. Thus, technological behaviour and chemical stability of clay–ash mixtures will be assessed in the following parts 2 and 3 respectively.

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References

1. Miller, C. A. and Srivastava, R. K., The combustion of Orimulsion and its generation of air pollutant. *Progress Energy Combustion Sci.*, 2000, **26**, 131–160.
2. Wang, Z. and Fingas, M., Separation and characterization of petroleum hydrocarbons and surfactant in Orimulsion dispersion samples. *Environ. Sci. Technol.*, 1996, **30**, 3351–3361.
3. Irons, R. M. A. and Jones, A. R., The effectiveness of Orimulsion as a reburn fuel for reduction of NO_x in a pilot-scale pulverised-fuel flame. *J. Institute of Energy*, 1996, **69**, 163–166.
4. Sommerville, M., Orimulsion containment and recovery. *Pure Appl. Chem.*, 1999, **71**, 193–201.
5. Vitolo, S., Seggiani, M., Filippi, S. and Brocchini, C., Recovery of vanadium from heavy oil and Orimulsion fly ash. *Hydrometallurgy*, 2000, **57**, 141–149.
6. Rodrigues, F., Sunderland, G., Krummen, N. and Gibson, J. R., The recovery of vanadium and nickel products from Orimulsion combustion ashes. *Environ. Res. Forum*, 1996, **1–2**, 19–25.
7. Keeling, P. S., A simple aid to clay mineral identification. *Clay Minerals Bull.*, 1958, **20**, 271–275.
8. Brunauer, S., Emmett, P. H. and Teller, E., Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.*, 1938, **60**, 309–319.
9. Lawton, S. A. and Theby, E. A., Synthesis of vanadium oxide powders by evaporative decomposition of solutions. *J. Am. Ceram. Soc.*, 1995, **78**, 104–108.
10. Brosnan, D. A., SO_x emissions in firing ceramics. *Am. Ceram. Soc. Bull.*, 1997, **76**, 53–55.