VALORIZATION OF CFB-COMBUSTION FLY ASHES AS THE RAW MATERIALS IN THE DEVELOPMENT OF VALUE-ADDED CERAMICS

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ABSTRACT

The amounts of ashes from circulating fluidized bed (CFB)-combustion steadily increase with the increasing rate of implementation of this environmentally-friendlier technology for firing solid fuels in power generation units. Therefore, beneficial uses of these powdery by-products, which possess particular characteristics, should be identified instead of landfilling them at significant environmental and economic impact. Their valorization in the manufacturing of value-added ceramics is a challenging research area. In the present study, CFB-coal combustion fly ashes, mainly bearing Si-Al phases, were utilized as 100% raw materials for the synthesis of ceramics by powder metallurgy (PM) techniques. Test specimens were fabricated by powder cold pressing followed by sintering at 900, 1000 or 1100 °C. The produced materials were characterized by means of XRD and SEM-EDAX. Shrinkage upon sintering, apparent density, water absorption capability and Vickers microhardness were determined. The experimental results show that the recycling of CFB-fly ashes towards PM ceramics development is feasible. In fact, integral lightweight materials are obtained, exhibiting successfully-densified ceramic microstructures where quartz phases prevail. The physico-mechanical properties are proved to be influenced by the starting ash composition and the sintering temperature. The so-produced ceramics possess the potential to be tailored appropriately to meet requirements for specific applications of possible commercial interest.

KEYWORDS: Circulating Fluidized Bed (CFB)-combustion; fly ash; ceramics; powder metallurgy; microstructure; physico-mechanical properties.

1. INTRODUCTION

The management and valorization of waste by-products derived from the combustion of solid fuels has been a major subject of research and represents an increasingly urgent priority nowadays, both from the environmental and economic perspective [1-3]. Actually, only limited quantities of by-products generated in coal-fired power stations are used as raw materials for cement and concrete manufacture [3-6], while the remainder is discharged into fly ash ponds or landfills. In the last years, various alternative applications of fly ash have come into the limelight, including its use in agriculture as soil additive to decrease soil acidity and as a sulphur fertilizer, its utilization as an additive for sewage sludge stabilization or as a reinforcement in metal-based composites etc. [7-9]. Nevertheless, other applications should also be investigated in order to more effectively recycle and upgrade the large ash output. Recently, noticeable research has been devoted to find beneficial uses for these by-products in the construction field. Since fly ash has a similar chemical composition to that of clay, it may be used as a replacement or partial substitute for the clay fraction in unburned or fired bricks manufacturing [10,11]. The production of ceramics has, indeed, the potential to be an important application of fly ash, taking into consideration the large quantities of raw materials needed for ceramic production.

In particular, the amounts of fly ash produced from circulating fluidized bed (CFB)-coal combustion in power stations are steadily growing, as this technology continuously gains ground for environmentally-friendlier power generation. This is mainly due to the possibility of reducing SO2 and NOX contents in flue gases to meet strict emission control regulation. Moreover, the character of this technology, with its fairly high efficiency along with its fuel and operational flexibility as well as multifuel capability, can provide economical and environmental advantage in utility scale thus improving operators competitiveness at deregulated energy markets.
Due to the intrinsic characteristics of CFB technology, the ash by-products formed can be different from those generated in the conventional processes [12-16]. With larger CFB boilers in operation in the last years, a greater emphasis is being placed on enhanced beneficial use of ash than in the past. Studies have shown that the environmental impact from CFB ashes is inferior than that from ashes derived from conventional burners and should not limit their utilization as marketable by-products, in an effort to increase economical effectiveness [17].

Recently, ashes of this type have been used in the development of zeolitic materials for the removal of heavy metals from wastewater [16], in the synthesis of geopolymer composites [18], as a filler material in polymer composite materials [19] and in asphalt concrete [20], and as a stabilizer for local sandy soils and pavement base course material [21]. So far, only few studies have tested the recycling of CFB-ashes, which normally contain significant percentages of sulphur trioxide, into ceramic applications of potential commercial interest such as extruded clay bricks, in limited however percentages [22, 23]. Therefore, ceramic bodies could be designed to maximize the amount of ash in the initial mixture, i.e. for ceramic roof tile applications, because the production could, otherwise, be economically unjustified.

The current study focuses on the innovative valorization of CFB-combustion fly ashes as 100% raw materials in the development of value-added ceramics by employing established powder metallurgy (PM) procedures including cold pressing followed by sintering. The microstructure and physico-mechanical properties of the materials produced are examined to assess the technical feasibility of CFB-ash use in construction applications of this category.

### 2. MATERIALS AND METHODS

#### 2.1 CFB-combustion fly ashes

Two different fine-grained coal fly ash samples, derived from pilot-scale CFB-coal combustion facilities [12,16] and codified as CFB1 (obtained from Polish bituminous coal) and CFB10 (obtained from South African bituminous coal), were utilized as secondary raw materials in the development of ceramics.

The chemical composition of these materials via X-ray fluorescence (XRF) analysis (Spectro X-Lab 2000 spectrometer) is presented in Table 1. According to the chemical data (Table 1) these fly ashes are clearly siliceous. As other CFB-ashes, they also contain significant amounts of sulphur. Furthermore, the total % CaO content should be taken into consideration, as it could lead to salt scum deposition on the surface of fired ceramics [24].

Fly ash particles generally assume a characteristic spherical microscopic scheme, which was obtained as the molten droplets of inorganic coal combustion residues cooled down and the fly ash particles solidified around trapped hollow gas bubbles and separated out as cenospheres (hollow spheres) [25]. Specific gravity amounts to 2.35 g cm⁻³ and 2.60 g cm⁻³ for the CFB1 and CFB10 samples, respectively.

#### Table 1 - Major chemical compounds of the CFB-coal fly ashes (wt. %)

<table>
<thead>
<tr>
<th>Compound</th>
<th>CFB1</th>
<th>CFB10</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>38.99</td>
<td>48.94</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>25.39</td>
<td>34.71</td>
</tr>
<tr>
<td>CaO</td>
<td>17.54</td>
<td>10.12</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.70</td>
<td>0.35</td>
</tr>
<tr>
<td>SO₃</td>
<td>8.82</td>
<td>5.59</td>
</tr>
</tbody>
</table>

#### 2.2 Preparation and characterization of specimens

Established and economical powder metallurgy (PM) fabrication techniques were applied for preparation of compacted specimens: CFB1 and CFB10 fly ash samples, as well as 50-50 wt. % mixtures of them, were uniaxially cold pressed in a stainless steel die using a hydraulic press (Specac, 15011) to form 13 mm diameter disc-shaped green specimens. The compression pressure was optimized at 500 MPa after preliminary trials, since microstructure of a sintered compact is strongly influenced by the quality of the green compact, thus by pressure. All compositions were subjected to three different heating programmes for sintering in a laboratory chamber programmable furnace (Thermoconcept, KL06/13): the specimens were, first, heated from room temperature up to 900, 1000 or 1100 °C, at the relatively slow heating rate of 10 °C/min in order to reduce abrupt thermal gradients that could possibly lead to process-induced stresses. Then, they were held at the respective maximum sintering temperature for 6 h, a sintering time commonly employed to accomplish consolidation of ceramics. Finally, they were gradually cooled to ambient temperature.

The mineralogical composition of the sintered specimens was identified by X-ray diffraction (XRD) (Siemens, Diffractometer D-500). The surface morphology was examined via scanning electron microscopy (SEM) (JEOL JSM-5600) coupled with energy dispersive X-ray spectroscopy (EDX). The following physico-mechanical properties were determined on the produced specimens and studied as a function of the particular fly ash composition and the sintering temperature: shrinkage upon sintering by the changes in specimen dimensions; apparent density by means of a specific apparatus (Shimadzu, SMK401-AUW220V) according to the Arimedes principle, water absorption as the weight change (%) after immersion in distilled water for 24 hours, and mean microhardness over five valid indentations per specimen using a Vickers indentor (Shimadzu, HMV-2T) with a load of 200 g and a dwell time of 15 s.
3. RESULTS AND DISCUSSION

Representative photographs of sintered specimens of all compositions used are presented in Figure 1.

The specimens present a fairly smooth surface. Surface visual inspection (Figure 1) shows uniform microstructures and absence of crack formation for all sintered specimens. Despite the relatively high percentages of CaO in the fly ashes used as the raw materials, there is no indication of random “chalky” deposits on the materials produced.

The effect of the sintering temperature on the mineralogical composition of CFB1-ash specimens, as determined by means of XRD analysis, is illustrated in Figure 2.

First, background levels are shown in the XRD patterns of Figure 2, indicating that the sintered products should contain some amorphous aluminosilicate glass, which is known to also exist in the ash raw materials [16]. Among several ceramic phases present, silica phases (mainly quartz) are clearly dominant due to the strongly siliceous character of the starting raw material (CFB-ash). When increasing the sintering temperature from 900 to 1000 °C, mullite also appears, a desirable mineral, because it is generally known to markedly improve the performance of ceramic bodies [26], given its interesting properties (low thermal expansion, excellent creep resistance up to high temperatures and low thermal conductivity). A more complex crystalline microstructure is depicted in the 1100 °C sintering diffractogram, in which the presence of cristobalite, a high-temperature polymorph of silica, should be pointed out. Cristobalite is stable only above 1470 °C, but can crystallize and persist metastably even at lower temperatures. Formation of cristobalite at these relatively moderate temperatures suggests that it probably forms by amorphous to crystalline transformations, preferentially on the outer surface of fly ash particles from their outer glassy phases [27]. The persistence of cristobalite outside of its thermodynamic stability range should be attributed to the considerable activation energy that would be required for its transition to the thermodynamically more stable quartz or tridymite phases involving the breaking of bonds and the rearrangement of atoms. Metastable phases such as cristobalite are considered closer to glass phase than the more stable ones and therefore are expected to exhibit higher chemical and thermal reactivity into ceramics.

The effectiveness of the densification process can be evaluated upon microstructural observation of the sintered specimens via SEM analyses (Figure 3).

At 900 °C firing, a connection of macropores leads to formation of pronounced open pores in specimens prepared from CFB1-ash (Figure 3a). A slightly better solidification degree appears in the ceramic microstructures made of CFB10 (Figure 3b) where quartz crystals can be identified due to the high SiO$_2$ content (almost 50 wt. %) of the raw material used. In the sintered mixture, the residual porosity rather assumes the form of closed pores (Figure 3c).

![FIGURE 1 - Photographs of specimens (diameter: 13 mm) made of CFB1 (a,b,c), CFB10 (d,e,f) and 50-50 wt.% mixture (g,h,i), sintered at 900, 1000, 1100 °C, respectively (from left to right).](image-url)
When the sintering temperature is increased from 900 to 1100 °C, densification improvements are generally attained (Figure 3d compared to 3a as well as 3f compared to 3c). Actually, it is the alkali metal components that have a strong effect on the sintering of ash at temperatures of 900-1000 °C [28]. Sintering necks can be seen in the ceramic microstructures, especially throughout the specimens obtained from CFB1-CFB10 mixture sintered at 1100 °C (Figure 3f). Indication of surface viscous flow also appears, particularly for CFB1-specimens sintered at 1100 °C (Figure 3d). This can be attributed to the sodium and potassium content of this specific ash sample. In fact, when sodium and potassium are present in ash, they are usually found in the form of sulfates [28], with melting points of 884 °C and 1076°C for sodium sulfate and potassium sulfate respectively (lower than the 1100 °C thermal processing applied for sintering in this case). Moreover, low melting-point eutectics, with a melting point even below 900°C, can also be formed in the surface layer between the sulfates of sodium, potassium, calcium, and other metals contained in ash [29].

FIGURE 2 - Typical XRD spectra of CFB1-samples sintered at 900, 1000, 1100 °C (from left to right).

FIGURE 3 - Micrographs of specimens made of CFB1 (a,d), CFB10 (b,e) and 50-50 wt.% mixture of them (c,f), sintered at 900 or 1100 °C, respectively (from top to bottom).
The experimental results for shrinkage (% volume change), apparent density, water absorption capacity (wt. %) and Vickers microhardness of the fired CFB-ash specimens are presented in Figure 4 as a function of sintering temperature.

Water absorption is an important factor affecting the durability of ceramic pieces. It also gives an indirect measure of open porosity that would be of importance in terms of heat insulating behavior, while Vickers microhardness data provide a measure for consolidation. Volume change (shrinkage) accompanies the reduction in surface area of ash particles during sintering. The experimental results are, generally, in accordance with the aforementioned microstructural observation findings as well as with the other properties results. In fact, the strong increase in mean microhardness recorded for the specimens made of CFB1 and of the CFB-ash mixture and sintered at 1100 °C (Figure 4), obviously reveals an improved densification process leading to intense volume shrinkage, a clear reduction in open porosity and thereby in water absorptivity, along with a higher apparent density. The most significant hardening is obtained for the CFB-ash mixture when sintered at 1100 °C, indicating a synergistic effect between the CFB1 and the CFB10 ashes in the mixture.

On the other hand, CFB10 ash appears less sensitive to sintering temperature variations according to the experimental results, thus verifying the microstructural examination findings. Its higher % content in SiO₂ (almost 50 wt. % of this particular ash), a hard compound, in combination with its lower CaO percentage, should be taken into consideration for understanding this sintering behaviour. Moreover, a volume swelling (overpassing 20%) occurs for CFB10-specimens upon sintering, independent of the sintering temperature employed.

Furthermore, a variation in volume change upon sintering at a given maximum temperature is also recorded between the CFB-ash samples examined, reflecting the differences in the chemical composition of the ashes. In fact, the elemental oxide composition strongly affects the sintering behavior of the ashes, particularly the viscosity at higher firing temperatures, and thereby also the final microstructure of sintered bodies [30].

4. CONCLUSIONS

The main conclusions of the study can be summarized as follows:

- The recycling of CFB-combustion fly ashes as 100% raw materials in ceramics fabrication by established powder metallurgy techniques is feasible.
- Generally, successfully-densified ceramic microstructures are produced, where quartz phases prevail.
- The physico-mechanical properties of the lightweight sintered materials obtained are influenced by the start-
ing material and the sintering temperature, especially for thermal processing at 1100 °C.

- Intrinsic characteristics of CFB-fly ash, such as their chemical composition, are of importance in the perspective of their beneficial utilization into ceramic applications.

Although the results are encouraging, continuing research on the long-term performance of the produced materials will ultimately assess the potential for upgrading the CFB-ashes by their valorization in the development of value-added ceramics.

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