

INERTIZATION OF INDUSTRIAL WASTES BY THE VITRIFICATION TECHNIQUE

Daniela Bortoluzzi^a, Edison Uggioni^a, Adriano Michael Bernardin^{a,b}

amb@unescc.net

^a**Engenharia de Materiais, Universidade do Extremo Sul Catarinense, Criciúma, Santa Catarina, Brazil**

^b**Tecnologia em Cerâmica, Serviço Nacional de Aprendizagem Industrial, Tijucas, Santa Catarina, Brazil**

This paper deals with the study of the vitrification mechanism as an inertization method for industrial wastes contaminated with heavy metals. Ashes from coal (thermoelectric), wastes from mining (fluorite and feldspar) and plating residue were used to compose vitreous systems planned by mixture design. The chemical composition of the wastes was determined by XRF and the formulations were melted at 1450°C for 2h using 10%wt of CaCO₃ (fluxing agent). The glasses were poured into a mold and annealed (600°C). The characteristic temperatures were determined by thermal analysis (DTA, air, 20°C/min) and the mechanical behavior by Vickers microindentation hardness. As a result, the melting temperature is strongly dependent on silica content of each glass, and the fluorite residue, being composed mainly by silica, strongly affects T_m. The microindentation hardness of all glasses is mainly affected by the plating residue due to the high iron and zinc content of this waste.

Keywords: coal ashes, vitreous waste, recycling.

1. Introduction

Over 6.6% of the electricity produced in Brazil is generated from coal. When coal is burned in a power plant, it leaves behind ash, some of which falls to the bottom of the boilers (bottom ash) and some of which is carried upward by the hot flue gases (fly ash). To prevent fly ash from entering the atmosphere, power plants use various collection devices to gather it and keep it from being carried with exhaust gases out the stack. Combustion of coal in Brazil generates over 820 thousand tons of coal combustion products each year. This quantity will continue to increase as more coal is used to generate electricity [1].

Ash produced from coal-fueled power plants is much like volcanic ash. It consists of lime, iron, aluminum, silica sand, and clay, essentially materials from the Earth's crust, melted by the heat of combustion to form glass compounds. In addition, coal ash contains trace quantities (in the parts-per-million range) of the oxidized forms of other naturally occurring elements. These same elements exist in soil, rock and coal, as well as, trace elements that may include arsenic, boron, cadmium, chromium, copper, lead, selenium, and zinc [2,3].

Coal ash composition and mineralogy (including its trace element content and form) vary among power plants and are related primarily to the source of the coal and the combustion conditions. Historically fly and bottom ashes are placed into landfills. The landfills are lined with impermeable clay or plastic liners that prevent leachate from reaching groundwater. The Brazilian ash is landfilled because the supply exceeded commercial demand due markets are not available for "alternative" or recycled materials [1]. Ash from older power plants lacked commercial value caused by high unburned carbon concentrations. Carbon makes ash unusable as a cementing material because it reduces concrete durability under freeze and thaw conditions. The unburned carbon remains in the ash when power plants are unable to convert all of the coal's potential energy to electricity during combustion. Factors that determine the unburned carbon content in ash include the type of coal burned, the design and operating conditions of the coal boilers, and the presence of various emission reduction technologies. Consequently, in 1980 the powerplants landfilled nearly 95 percent of ash [2].

Coal ash has physical and chemical properties that make it useful for construction and industrial materials. The fly ash is used as a raw feed material for Portland cement production, soil stabilization, cold in-place recycling of asphalt pavements, in controlled low-strength materials that are used for backfill or structural fill needs, and as an alloying material for lightweight castings. The bottom ash is used as a replacement for sand, gravel, and crushed stone. Concrete continues to be the leading utilization application, but new and promising technologies continue to be introduced, eliminating the need to construct additional landfills while continually expanding the market for commercially-viable coal combustion products. Today, the U.S. powerplants utilize more than 85 percent (500,000 tons), more than twice the American national average of the coal combustion products generated at U.S. coal-based power plants each year. Through research and development, there are cost-effective processes to recover, reburn and reuse the landfilled ash. In Brazil most of the coal combustion products is landfilled, and only the fly ash is used for Portland cement production [4-8].

Disposal and/or any use of coal ash are becoming a major issue because of its potential to contaminate surface and groundwater with arsenic, boron, heavy metals, etc. Knowledge on the chemistry of fly ash is essential in developing a methodology that can predict release rate(s) and concentration(s) of chemical constituents of environmental concern (pollutants). Safe disposal of fly ash with respect to surface and groundwater protection depends on having the know-how to evaluate the potential of a given fly ash to release toxic pollutants [7-10].

Coal ash is made of three types of solids: 1) chemically water stable solids (SiO_2 , FeO , Al_2O_3), 2) relatively water soluble solids (metal- SO_4 , metal- BO_3), and 3) water reactive metal-oxides (CaO , MgO , K_2O , Na_2O , etc). Ash varies from acidic to alkaline because of the chemical make-up of the source coal. Physical appearance varies depending on coal type and furnace. All fly ash samples are mainly composed of glass-like porous beads that vary in chemical composition with respect to Al/Si/Fe ratio and pH from extremely low (pH near 3) to near pH 12. Alkaline fly ash is often associated with high boron levels and exhibits extremely low pH buffering capacity [2-4].

Because fly ash contains toxic elements, disposal sites should be monitored for excessive buildup of heavy metals, salts and alkalinity. Potential heavy metal problems with power plant wastes are greatly reduced by the pronounced liming effects of the wastes. A problem that some consider an environmental issue is the movement of heavy metals from fly ash in ponds or landfills to drainage waters. Levels of heavy metals or metalloids, e.g., selenium, chromium, boron, and in some instances, mercury and barium, exceeded the regulatory public water supply guidelines. Passage of the leachates through soil columns removed most of the dissolved elements. Thus, passage of pond effluents through soil was found to provide significant protection against ground water contamination. An important consideration is that soils that receive fly ash or ash disposal sites should always have the pH maintained at above 6 in order to keep most heavy metals immobile [2].

At present, hazardous fly ash is stabilized by incorporating it into cement-based materials. However cement-based techniques pose problems inside landfills due to weak chemical and physical stability. Particularly, in cases where fly ash with high concentrations of alkali chlorides, it is difficult to apply the cement-based techniques since the alkali chlorides inhibit hydration of cement so that the cement matrix cannot be fully solidified or stabilized [5-9].

Therefore, it is necessary to search for new techniques for treatment of fly and bottom ashes. Vitrification is one of the most promising solutions among the various available technologies. Furthermore, toxic organic compounds such as dioxins can be destroyed during the vitrification process. There are several reports on the vitrification of solid waste [9-14]. It was demonstrated that the addition of bottom ash and glass wastes into fly ash facilitated the formation of glasses upon melting and quenching.

The aim of this work is to determine the possible use of fly and bottom ashes as raw materials for the glassmaking industry. In this initial study the coal ashes are mixed with other residues obtained from feldspar and fluorite mineral industry and from galvanization process. A mixture design approach was used to determine the best characteristics that could be obtained from each residue.

2. Experimental procedure

Dry bottom ashes from Tractebel Energia S.A. thermoelectrical powerplant (Cativari de Baixo, Brazil) were vitrified with feldspar, fluorite and galvanization residues. All residues were analyzed by X-ray fluorescence spectroscopy (XRF, Philips PW2400, molten sample), table 1. The vitrification of the residues was performed with 10% Na₂CO₃ addition at 1450°C for 2 h, in air, in a chamber furnace using alumina crucibles. The resulting glasses were dark brown.

Table 1. Chemical analysis of the residues

residue	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	MgO	Na ₂ O	CaO	F	Zn	Cl	SO ₃	LOI
coal ash	69.0	24.8	1.9	1.9	1.1	0.3	0.2	0.2	-	-	-	-	0.3
fluorite	80.0	9.7	1.6	3.3	0.4	0.3	0.6	0.9	0.9	-	-	0.2	1.7
galvanic	1.2	0.2	19.9	-	-	-	-	9.3	4.1	9.4	14.0	0.3	41.3
feldspar	73.5	16.3	1.3	2.2	0.1	0.3	3.3	1.0	-	-	-	-	0.9

Five formulations with four factors at two levels were designed. The residues were dried, sieved, mixture according the design and melted at 1450°C during 2h for stabilization. The melts were quenched in a water refrigerated mold and annealed (600°C, 2h). Ash, galvanic mud, fluorite residue and feldspar residue were the factors and their amounts in each glass the levels, table 2. The composition 5C represents the central point of the design and the others (V) represent the vertices.

Table 2. Mixture design for the vitrification process

comp. [%]	ash	feldspar	fluorite	galvanic mud	Tg [°C]	Tm [°C]	HV [kgf/mm ²]
1V	20	30	20	30	602.3	690.0	608.6
2V	20	30	40	10	599.0	681.2	566.6
3V	20	50	20	10	577.1	653.7	578.4
4V	40	30	20	10	552.3	650.9	566.4
5C	25	35	25	15	549.8	670.2	567.4

Thermal analysis was performed by differential thermal analysis (DTA, Netzsch 409). The study was carried out using a 20°C/min heating rate and air atmosphere. The Vickers hardness (HV) was determined for the glasses by a microindentation Vickers tester (Shimadzu HMV 2).

3. Results and discussion

The chemical analysis of the residues is shown in table 1: the ash, feldspar and fluorite residues have similar composition with relatively high contents of SiO₂, Al₂O₃ and alkaline oxides; the galvanic residue has mainly Fe₂O₃, CaO and halogens, with a high loss of ignition.

Table 3 presents the analysis of variance (ANOVA) for the melting temperature (T_m, table 2) for the mixture design. The analysis shows a strong linear dependence of the factors with a high significance (p>95%). The glass transition temperature (T_g, table 2) could not be analyzed because the results were not statistically significant in this study. Figure 1 shows the surface response graph for the melting temperature.

Table 3. ANOVA for the melting temperature of the glass system (°C)

model	SS _{effect}	dF _{effect}	MS _{effect}	SS _{error}	dF _{error}	MS _{error}	F	p	R ²
linear	1151.53	3	383.84	1.25	1	1.25	307.07	0.042	0.999
quadratic	1.25	1	1.25	0	0	0			
total	1152.78	4	288.20						

SS=sum of squares; dF=degree of freedom; MS=mean squares.

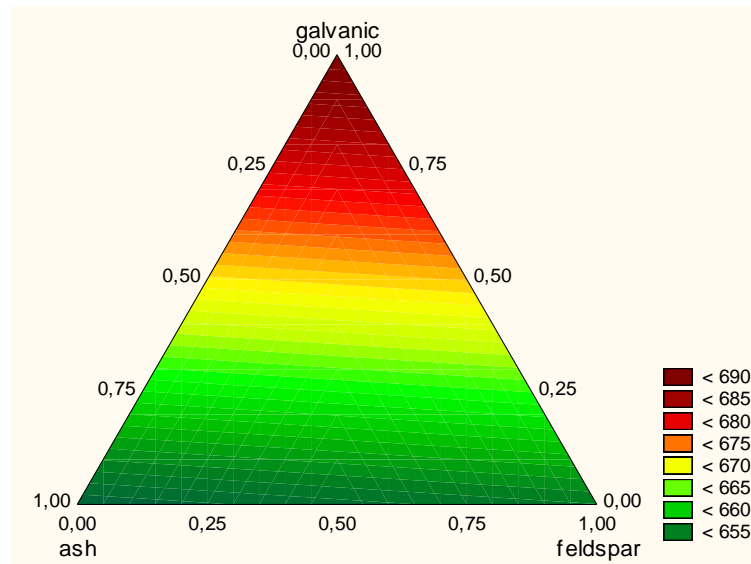


Figure 1. Surface response for the melting temperature of the glass system

The glass melting temperature is strongly affected by the silica content of the system. The fluorite residue tends to raise the melting temperature of the glass system besides its content in melting oxides. Probably the excess of silica related to the fluorite residue causes this effect. On the other hand the coal ash and feldspar contents tend to low the melting temperature besides their alumina content. But the raw material responsible for the highest melting temperatures is the galvanic residue: it is formed mainly by iron and calcium oxides and halogens, but do not contain any silica. Equation 1 shows the relation among melting temperature and the residue content.

$$T_m = +651.15X_{\text{ash}} + 653.95X_{\text{feldspar}} + 681.45X_{\text{fluorite}} + 690.25X_{\text{galvanic}} \quad (1)$$

Table 4 shows the ANOVA of the Vickers microindentation hardness (HV, table 2) for the studied glass system. The analysis shows a linear dependence of the factors with a low significance ($p \sim 70\%$). Figure 2 shows the surface response graph for the glass hardness.

Table 4. ANOVA for the Vickers hardness of the glass system (kgf/mm^2)

model	SS_{effect}	dF_{effect}	MS_{effect}	SS_{error}	dF_{error}	MS_{error}	F	p	R^2
linear	1185	3	395	127	1	127	3.11	0.39	0.90
quadratic	127	1	127	0	0	0			
total	1312	4	328						

SS=sum of squares; dF=degree of freedom; MS=mean squares.

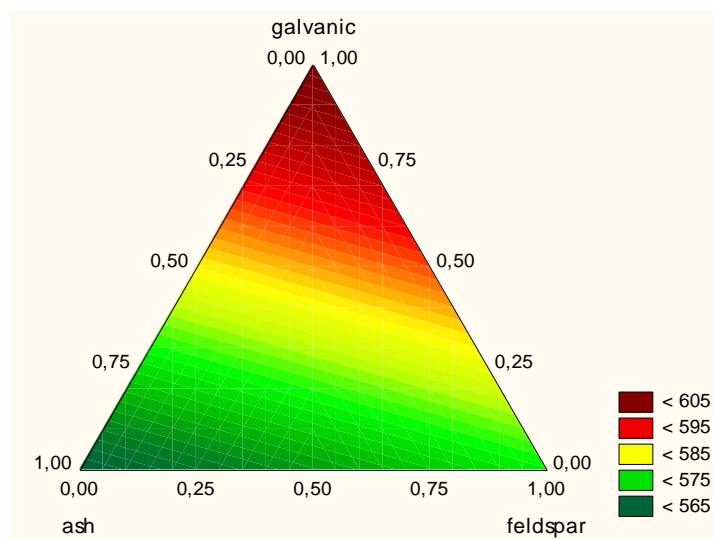


Figure 2. Surface response for the Vickers hardness of the glass system

The glass system hardness is strongly affected by the galvanic residue content. All residues tend to raise the hardness, but the galvanic residue is the most effective in doing this, equation 2.

$$HV = +563.88X_{\text{ash}} + 575.88X_{\text{feldspar}} + 564.08X_{\text{fluorite}} + 606.08X_{\text{galvanic}} \quad (2)$$

The glass structure is usually considered as a random network. The elements are generally classified into three types: (1) network forming atoms: such as Si, B, P, Ge; (2) network modifiers (or glass fluxes): such as Na, K, Li, Ca, Mg; and (3) intermediates: such as Al, Fe, Zn, Ti, Mo. The glass structure is mainly influenced by the glass composition. The components that form the strongest bonds in glasses result in the greatest improvement to glass melting temperature and hardness, whereas those that form the weakest bonds generally prove the greatest detriment to glass melting temperature and hardness [12].

Adding SiO_2 , Al_2O_3 , B_2O_3 , and ZrO_2 may improve these properties; and adding alkali metal oxides may decrease them. If the inorganic oxides from the waste have insufficient glass formers to fall within an accepted glass formulation range, additional glass formers must be added through the process. According to current knowledge, if the coal fly ash does not contain proper ratios of materials for the formation of a glass, additives may be needed. The coal fly ash contains high contents of SiO_2 and Al_2O_3 , but has insufficient glass network modifiers. Although the network modifiers (such as alkali metals) may decrease the glass properties, they are important to control the melted glass viscosity and thermal behavior. The most effective glass modifier is Na_2O . Other than CaO or MgO , adding Na_2O will not increase the crystalline tendency. From the viewpoint of economic, less kinds of additive are also desirable [12].

Therefore, the galvanic residue due its content in Fe and Zn oxides is more suitable to obtain stronger glasses with high melting temperatures because it forms higher bond energies when compared with the alkaline and earth-alkaline residues. Also, it acts as a nucleating agent promoting the devitrification of the glass system, but this feature was not studied in this previous work. Finally, the vitrification of solid wastes is a well-known process used to immobilize hazardous elements, and biological tests were carried out to determine the toxicity of the glass system.

4. CONCLUSION

The mixture design is useful to determine which residue is able to form glasses with high or low melting temperatures and good mechanical properties. The waste vitrification in order to obtain low cost and common glasses is a well-known mechanism to immobilize hazardous elements and to transform them into glass-ceramics containing crystalline phases with high chemical and mechanical properties.

The thermoelectrical bottom ash belongs to the Si-Al-Fe system and so it is easily capable to give glass. In order to decrease the viscosity of the melts (visible as a lowering of the glass transition temperature in DTA) it is necessary to increase the Na_2O content. Also, the presence of Fe_2O_3 and ZnO in the galvanic residue results in higher bond energies in the glass structure and promotes a devitrification process with the transformation of these amorphous materials into the corresponding glass-ceramics product, not explored in this previous work.

5. Acknowledgments

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6. References

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