

Effect of heat treatment on glass-ceramics covering of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ system using industrial waste as raw material

B.C. Alcántar, J.A. Chávez, G.C. Díaz

Abstract— On a day to day basis, the demand for goods and services cause environmental damage due to the overuse of natural resources and the increase in residues related to these activities. The biological treatment of wastewater has become an important source of solid residues. At the same time, industrial development and technological advances have generated processes that produce a great variety of residues as byproducts. Some of these residues, because of their inorganic composition and innocuousness, can be incorporated into the production of ceramic materials to substitute traditional or natural raw materials. The biosolid ashes resulting from the biological treatment of wastewater are rich in CaO, SiO_2 , Fe_2O_3 and P_2O_5 , while the residues from the anodization process mainly contain $\text{Al}_2(\text{SO}_4)_3$ and $\text{Al}(\text{OH})_3$ salts; under this premise, a ceramic system is designed, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$, where biosolid ashes are incorporated as supplementary sources of SiO_2 and the aluminum salts as substitute for Al_2O_3 . The type of thermal treatment applied was a continuous and intermittent system. Upon examination of the results in the mineral composition and the morphology of the materials obtained through DRX (X-ray Diffraction) and SEM (Scanning Electron Microscopy), it can be observed that the material submitted to both types of thermal treatments show phases of elevated hardness and of highly ordered crystal structures, such as corundum. Nevertheless the materials that are more homogeneous and have more defined crystals are identified in those samples submitted to a continuous system thermal treatment.

Index Terms— waste water Sludge, Glass-Ceramic, Coating, Anodizing residue.

I. INTRODUCTION

The increase in population generates a growing demand for consumer goods and services, thus augmenting the number of companies necessary to satisfy this demand. This in turn results in an increment in domestic and industrial residues that must be confined in order to minimize environmental pollution. These residues must be classified into those that by their characteristics, and in any of their forms, represent a health hazard and must be disposed of in authorized locations, therefore resulting in further costs for their handling and disposal.

Brenda Cecilia Alcantar Vazquez, Postdoctoral in the Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México (Mexico) in Metallic and Ceramic Materials Department.

Jose Alvaro Chavez Carvayar, Professor at the Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México (Mexico) in Metallic and Ceramic Materials Department.

Gerardo Cesar Diaz Trujillo, Professor at the Facultad de Ciencias Químicas e Ingeniería, Universidad Autónoma de Baja California (Mexico).

On the other hand, some residues do not represent any danger, such as solid city residues and some industrial and agricultural residues which can be disposed of in landfills. Depending on their composition, these residues can be used as soil enrichers, raw material in the production of materials (ceramics, glass-ceramics, cement, concrete, etc.), and conditioners for the filtration of sludge in water treatment [1], modifying the characteristics of the final product, resulting in low-cost materials, with technological applications and environmental and energy saving advantages [2].

In Mexico sludges from the biological treatment of wastewater require special handling. 3,201 tons of this residue are generated daily [3]; they have become a problem for most highly urbanized cities because their disposal in open air locations is a pollution focal point for nearby cities as well as an environmental risk. Some ways of reusing these residues is to use them as fertilizers in agriculture; calcinate them and incorporate the ashes into ceramic based compound materials, including glasses and glass-ceramics with applications in construction materials (tiles, cement, etc.); esthetics (coatings or pigments); and in refractory materials, among others [4].

At the same time, the industrial processes of metallic coating (anodizing, galvanizing, powder coating, etc.) consume elevated amounts of water, generating an enormous flow of residual water, which when treated results in the formation of high quantities of sludge. The presence of impurities in the materials formed from the residues produces changes in the functional properties of the materials (for example: refractivity) [5]. The ashes from such residues have been used in the making of construction materials without finding significant changes in the materials properties, compared to the materials made with industrial grade Al_2O_3 [6]. It is also reported that the simultaneous incorporation of anodized residues (without any previous treatment) and biosolid ashes (as substitute for clay) in glass-ceramic materials yields better physical properties in the finished product [7, 12]. Some studies also suggest, as a good environmental option, the recycling of anodized sludge rich in aluminum in refractory bodies of mullite ($3\text{Al}_2\text{O}_3\text{-2SiO}_2$) and cordierite ($2\text{Al}_2\text{O}_3\text{-5SiO}_2\text{-2MgO}$) [8].

In the field of research on use and reutilization of industrial residues, this work poses the incorporation of the biosolid ashes from the biological treatment of wastewater and the residues from the anodizing process as raw material in the production of glass-ceramic coatings based on the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ with the purpose of diminishing the use of natural raw materials, lowering the cost for treatment and disposal of the residues generated from the goods and services rendered to the community.

II. MATERIAL AND METHOD

precursor	Flux				
	B ₂ O ₃	ZnO	P ₂ O ₅	Na ₂ O	K ₂ O
70	7	7	8	4	4

2.1. *Precursor*; The biosolids resulting from the biological treatment of wastewater (R₁) were submitted to a previous dehydration treatment at 105 °C, then to calcinations at 700 °C for 3h, to eliminate the organic matter present, and lastly were milled to obtain a homogeneous size grain. The composition of the biosolid ashes obtained through XRF (X-ray Fluorescence) is shown in Table I [9].

Table 1. Quantitative composition of biosolid by X-ray fluorescence (%w/w)

Oxide	% w/w	Oxide	% w/w
SiO ₂	18,10	K ₂ O	1,03
Al ₂ O ₃	4,17	Na ₂ O	0,39
TiO ₂	0,712	MnO	0,18
Fe ₂ O ₃	14,30	BaO	0,16
P ₂ O ₅	12,20	ZnO	0,52
Cr ₂ O ₃	ND	SO ₃	6,01
CaO	34,30	Loss lg.	4,75
MgO	2,89		

In Table II the composition of the precursor vitreous material is presented, where R₁ is used as a complementary source of SiO₂ as well as the residues of the anodizing process (R₂) rich in Al(OH)₃ with gibbsite crystal phases and synthetic bayerite as substitute for de Al₂O₃ [10-12].

Table 2. Glass-ceramic precursor composition (% w/w)

R ₁	R ₂	SiO ₂	TiO ₂
62.5	8.5	22.0	6.9

A high temperature Thermolyne furnace (1700 °C) and alumina containers were used to carry out the thermal treatment, with heating and cooling rate of 5 °C min⁻¹. The thermal treatment of the precursor glass was 900 °C for 30 min. with the purpose of eliminating the organic compounds and carbonates present in the mixture. It is later fused at 1450 °C for 2 h, followed by a period of thermal stability at 900 °C for 1h to initiate nucleation; finally it is raised to 1000 °C for 4 h in order to accomplish crystal growth.

2.2. *Coatings*; The starting mixture in a weight proportion of 70:30, GC precursor: flux (Table III), is used for the preparation of a paste, using a solution of carboxyl methyl cellulose, with the purpose of increasing the adherence between the coating molecules and the ceramic substratum to be used as a base. A layer of this paste is applied over the ceramic substratum and two thermal treatments are carried out in different samples at the same heating rate of 5 °C min⁻¹ with the purpose of evaluating its effect in the formation of crystal phases; first in a continuous manner; 2 h at 800 °C + 1200 °C for 4 h + 1000 °C for 4 h, and on a second sample an

intermittent treatment is applied in two stages, at 800 °C for 2 h + 1200 °C 4 h, and later at 800 °C for 2 h + 1000 °C 4 h.

Table 3. Glass-ceramic coating composition (%w/w)

The mineral composition of the materials produced was determined by X-ray diffraction in dusts (DRX) using a Bruker diffractometer model Advance D-8, the microstructural analysis was carried out by SEM using a STEREOSCAN 440 microscope and the EDS semiquantitative analysis. MATH

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern from the GC-Ca precursor material, where we can identify the presence of phases with crystal structures such as calcium phosphate and magnesium, as whitlockite [Ca_{2,86}Mg_{0,14}(PO₄)₂] (trigonal), Anorthite [CaAl₂Si₂O₈] (triclinic), Calcium Aluminum Silicate [Ca(Al₂Si₂O₈)] and pseudobrookite [Fe₂TiO₅] (orthorhombic), over a vitreous zone (identified by the band-wide depth between 10° and 35°).

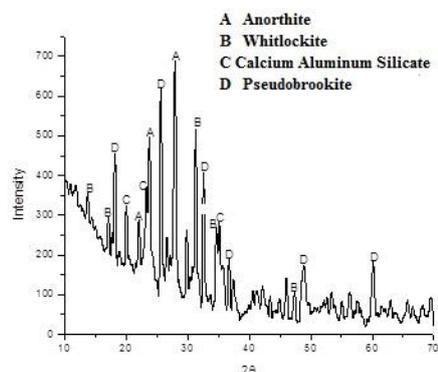


Figure 1. XRD patterns of glass-ceramic precursor

According to the diffractogram shown in Figure 2, the ceramic coatings under a continuous treatment present crystal phases of Anorthite, Nepheline and Corundum, while as under an intermittent treatment, the phases of Anorthite and Corundum remain, the Nepheline is dissolved and the vitreous phase diminishes and a new gibbsite phase is generated.

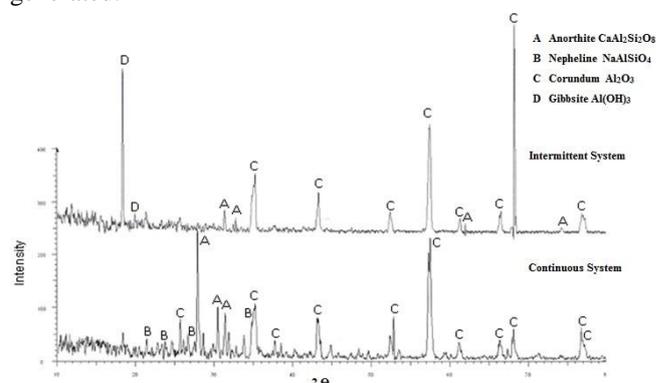


Figure 2. XRD patterns of glass-ceramic coatings.

SEM analysis showed that the coating under continuous thermal treatment presents homogeneity in the sample, with the outstanding presence of hexagonal crystal with an approximate diameter of 13 μm parallelly oriented by the

plane surfaces, with the presence of crystallization nuclei and dendritic growth of less than 1 μm (Figure 3).

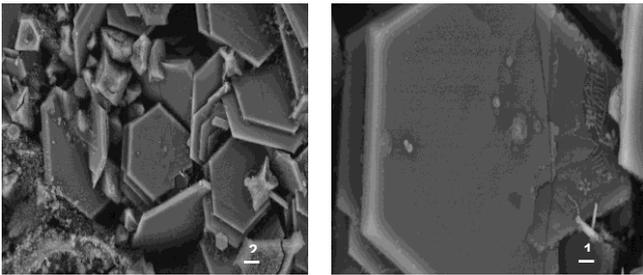


Figure 3. SEM micrograph of glass-ceramic coatings; Continuous System.

The coating with intermittent thermal treatment shows less proportion of hexagonal crystals (Figure 4); it can be considered that a partial solubility of Anorthite crystals is present as consequence of a major exposure to temperature, generating predominance of corundum due to its more refractory character.

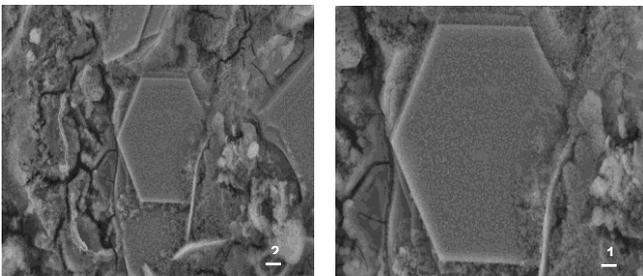


Figure 4. SEM micrograph of glass-ceramic coatings; intermittent System

In Table IV the composition of the materials obtained by EDS is shown, emphasizing the high content of aluminum and calcium, the main elements in corundum and anorthite, it is possible to observe a major proportion of aluminum in the intermittent treatment, and the contrary is observed with calcium in relation to the continuous treatment, asserting the presence of these phases in both thermal cycles.

Table 4. Coating EDS analysis under continuous and intermittent system (%w/w).

Element	Continuous System	Intermittent System
O	43.28	58.30
Al	12.56	20.65
Ca	17.56	8.95
Fe	4.73	4.92
P	7.16	1.64
Zn	5.90	2.78
Ti	0.49	2.76
Mg	5.96	--
Si	2.35	--

IV. CONCLUSION

The characterization of the materials developed shows it is possible to incorporate the biosolid ashes obtained from the biological treatment of wastewater as complementary source

for SiO_2 , and residues from the anodizing process as substitute for Al_2O_3 in glass-ceramic materials for coating purposes. Ordered system crystal structures are predominant in the continuous system, thus diminishing the vitreous phase. In the intermittent treatment a major crystal definition is present, while undergoing a rearrangement, giving as a result a heterogeneous material. The thermal treatment in a continuous system at a rate of 5 $^\circ\text{C}$ per minute is emerging as a convenient option for producing glass-ceramic coatings based on the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ because it reduces production time and energy cost.

ACKNOWLEDGMENT

The authors thank to MC. Adriana Tjeda and Omar Novelo of the Instituto de Investigaciones en Materiales, UNAM for XRD and SEM measurements assistances. This work is the product of a study supported by Universidad Autónoma de Baja California (UABC) in Internal Program Research with registration number: 300/1090 and collaboration of the Applied Chemical Group.

REFERENCES

- [1] C. Ferreira, A. Ribeiro, L. Ottosen, Possible applications for municipal solid waste fly ash, *J. Hazard. Mater. B96* (2003) 201-216.
- [2] J. H. Tay, Reclamation of wastewater and sludge for concrete making, *Resour. Conservat & Recycl*, 2 (1998) 211-227.
- [3] Programa Nacional para la Prevención y Gestión Integral de los Residuos 2009-2012, SEMARNAT, (2008) 9-15.
- [4] K. Halada, Progress of ecomaterials toward a sustainable society, *Curr Opin Solid State Mater Sci*, 7 (2003) 209-216.
- [5] F. Raupp-Pereira, D. Hotza, A. M. Segadães, J. A. Labrincha, Ceramic formulations prepared with industrial wastes and natural sub-products, *Ceram. Int.* 32 (2006) 173-179.
- [6] L. Deng-Fong, L. Huan-Lin, S. Yeong-Nain, Glazed tiles manufactured from incinerated sewage sludge ash and clay, *A&WMA*, 55 (2005) 163-172.
- [7] Z. Stmad, *Glass-Ceramic Materials*, (1986) 167-174.
- [8] M.J. Ribeiro, S. Blackburn, J.A. Labrincha., Single screw extrusion of mullite-based tubes containing Al-rich anodising sludge, *Ceram. Int.* 35 (2009) 1095-1101.
- [9] B. Alcántar, Aplicación y caracterización de recubrimientos cerámicos elaborados con residuos industriales, UABC, Tesis de maestría, (2008) 31.
- [10] J. Vargas, O. Hernández, Obtención de subproductos de aluminio a partir de lodos del proceso de anodizado, UABC, Tesis de licenciatura, (2007) 75.
- [11] M. Haro, Materiales cerámicos elaborados con biosólidos y residuos industriales inorgánicos, UABC, Tesis doctoral, (2008) 121.
- [12] M. Haro, B. Alcántar, E. Carrillo, M. Villafuerte, G. Diaz, Glass-ceramics manufacturing from sludge and anodized waste, *Am. Ceram. Soc. Bull.* 87 (2008) 50-52.

Brenda Cecilia Alcantar Vazquez, Postdoctoral in the Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México (Mexico) in Metallic and Ceramic Materials Department. Its research are based in CO_2 capture and confinement in various multicomponent materials and study of the sustainable transformation of CO_2 into value-added products.

Jose Alvaro Chavez Carvayar, Professor at the Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México (Mexico) in Metallic and Ceramic Materials Department.

Gerardo Cesar Diaz Trujillo, Professor at the Facultad de Ciencias Químicas e Ingeniería, Universidad Autónoma de Baja California (Mexico), since 1983 performing their tasks in the area of Analytical Chemistry and Materials Development Research.