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Glass-Ceramics Manufacturing from Sludge and Anodized Waste

Feasibility of manufacturing ceramic-tile from sludge ash from a city water-treatment plant and from anodized aluminum process water from local industries has been studied to reuse both residues and prevent their disposal.

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A great problem faced by constantly developing cities, such as Tijuana (the most populated municipality in the state of Baja California, Mexico, with more than one million inhabitants), is the high amount of wastewater generated. This generates increasing amounts of activated sludge produced by the wastewater-treatment plant. The sludge is disposed of in an outdoor confinement area in the Punta Bandera area. This sludge contains a high amount of organic material and humidity (70%), which generates bad odors and leaching. The city's climatic conditions make this confinement area a potential source of infectious disease. Also, in the industrial sector, anodizing processes generate a significant amount of aluminum-rich waste.

It is important to introduce the possibility of applying ceramic processes as a new alternative to disposal of corporate inorganic industrial waste, because its metal content might be highly toxic in otherwise inert materials. Currently, many countries have prioritized research on (cement, ceramic, glass and glass-ceramic) matrix development that can guarantee the removal of inorganic industrial waste. The matrix must present chemical and thermodynamic stability and must be easily produced and manipulated.[1–3]

In some countries—such as Japan—recent legislation limits transportation and dumping of heavy-metal-containing ash (such as those generated by incinerators). As a result, a technology called "sludge fusion or vitrification" has developed. This process also is used in the United States to permanently encapsulate harmful chemicals in a solid block of a material similar to glass, which prevents their release into the environment. This process can be conducted underground or over a surface.

The activated sludge process is the most frequently used worldwide. It is estimated that the amount of sludge produced in the European Union was between 15 and 20 metric tons in 2005.

The major means of eliminating generated sludge has been its transport to dumps, its dispersion on the ground, its use as compost, its dumping into the sea or its incineration.[4] The most attractive option is to spread the sludge on agricultural lands to recycle the nutrients. This is useful from an agronomic point of view. However, this application is limited to treated water. Untreated water can contain traces of heavy metals and organic compounds that are barely biodegradable. This may cause concern because of the possibility of environmental risks, which intensifies the sludge elimination issue.

An important factor to take under consideration is that the chemistry of sludge is not constant. It varies according to the characteristics of plant design and type of sewage water to be treated.

Dumping toxic influents into sewage municipal water treatment plants inhibits the biological activity of the activated sludge, which generally contains protozoan, rotiferous and bacteria. If the sludge activity decreases, the volume of generated sludge increases, because the organic matter does not degrade.

Because of the problem caused by the great amount of sludge, studies have been made to create incinerators that allow easy handling of this residue by considerably decreasing its volume, which decreases disposal and treatment costs.

Table 1 Composition of Glass-Ceramic Materials

Material	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	Li_2O (%)	Feldspar (%)	Sludge ash (%)	Anodized residue	T (°C)
1	40	12.5			5	12.5	30		1000
2	30	18	9.5			12.5	30		1100
3	33	17.5		7		12.5	30		1100
4	40				5	12.5	30	12.5	1000
5	30		9.5			12.5	30	18	1100
6	33			7		12.5	30	17.5	1100

These ashes can be used as raw material for the manufacture of various products, such as construction materials,[5–7] concrete,[4] ceramics[8,9] and glass-ceramics.[10]

Materials and Methods

Three systems were selected for study: SiO_2–Al_2O_3–CaO, SiO_2–Al_2O_3–MgO and SiO_2–Al_2O_3–Li_2O. Sludge (bio-solid) was dried at 105°C for 5 h and burned at 700°C for 3 h. Six glass-ceramic materials was prepared (Table 1), where sludge ash and aluminum-containing residue were incorporated in the form of salts as a replacement for Al_2O_3 in each system. Two series of tiles were prepared: the first used industrial grade Al_2O_3; the second used aluminum-salt residues. Both series contained 30% sludge ash.

Pieces of tile (5 × 5 × 1 cm) were obtained by applying a biaxial pressure of 5000 lb/in.^{2}. Subsequently, the tile was sintered and crystallized: the SiO_2–Al_2O_3–CaO and SiO_2–Al_2O_3–MgO at 1100°C for 5 h and at 900°C for 4 h; and the SiO_2–Al_2O_3–Li_2O at 1000°C for 5 h and at 900°C 4 h.

Material Characteristics

The glass-ceramic materials obtained possess diverse textures, aspects and colors because of the variety of properties offered by the oxides used in their preparation. Nevertheless, they share particle-size homogeneity. However, weight loss and compression increase when aluminum-salt residues are added. Because of the nature of the waste, the mixture of aluminum salts (predominantly sulfates and hydroxides) permits a better interaction with the raw material, which contributes to diminished porosity. Therefore, the weight loss is increased (Table 2).

A similar effect occurs for density and water absorption. The materials obtained using aluminum-salt residues present greater density, which is attributed to the greater compression of the material. This also presents better thermal reaction and decreases porosity because of decreased presence of pores and/or micropores. It might be that, in the materials that contain anodizing waste, the water absorption capacity decreases while the density increases. An exception is the material that contains lithium, as evident when material 4 (which contains Li_2O) is compared with material 6 (which contains MgO). In the latter material, water absorption occurs within the range determined by the norm (10–18%).

The predominant crystalline phases in each system have been identified using X-ray diffractometry (XRD). The SiO_2–Al_2O_3–CaO material contains predominantly anorthite ($Ca(Al_2Si_2O_8)$) as well as quartz (SiO_2). The SiO_2–Al_2O_3–MgO material contains cordierite ($Mg_2(Al_4Si_5O_{18})$), enstatite ($MgSiO_3$), anorthite ($Ca(Al_2Si_2O_8)$) and quartz (SiO_2). The SiO_2–Al_2O_3–Li_2O material contains spodumene ($Li(AlSi_2O_6)$) and quartz (SiO_2).

In all cases (Fig. 1), an increment in the vitreous phase is observed when aluminum-salt residues are added This is attributed to the greater melting effect of the residue that originates in solubility of SiO_2. A different effect is observed for the SiO_2–Al_2O_3–MgO material. The presence of aluminum-salt residue permits the solubility of cordierite and the presence of calcium, which favors the formation of an anorthite phase.

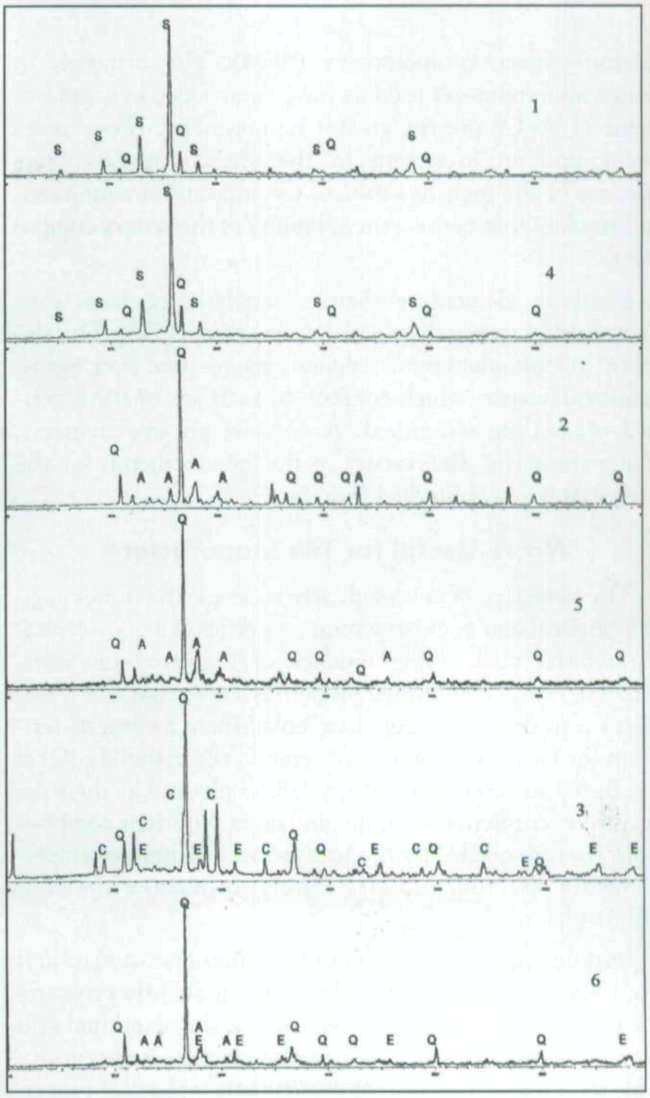

Fig. 1 XRD patterns of glass-ceramic materials (Q is quartz, S is spodumene, A is anorthite, C is cordierite and E is enstatite).

Table 2 Physical Properties of Glass-Ceramic Materials

Material	Compression (%)	Weight loss (%)	Water absorption (%)	Density (g/cm^3)
1	2.20	7.06	27.01	2.5212
2	2.65	7.25	26.22	2.6147
3	5.08	4.0	15.3	2.5884
4	10.67	10.49	2.54	1.8184
5	7.37	11.86	19.75	2.6295
6	9.28	8.98	13.3	2.6454

The morphology of the materials has been studied using scanning electron microscopy (SEM). The materials to which aluminum-salt residues have been added as a replacement of Al_2O_3 present greater homogeneity. Fewer pores occur, and an increment in the vitreous phase occurs because of the melting effect of the mixture of aluminum-salt residues that permits the solubility of the system components.

Similarly, elementary chemical analysis has been conducted using energy-dispersive spectroscopy (EDS). The elements silicon, aluminum, calcium, magnesium, iron, potassium and oxygen, which conform to each one of the identified phases, are recognized. A series of photomicrographs that permit the observation of the microstructure of the materials has been studied (Fig. 2).

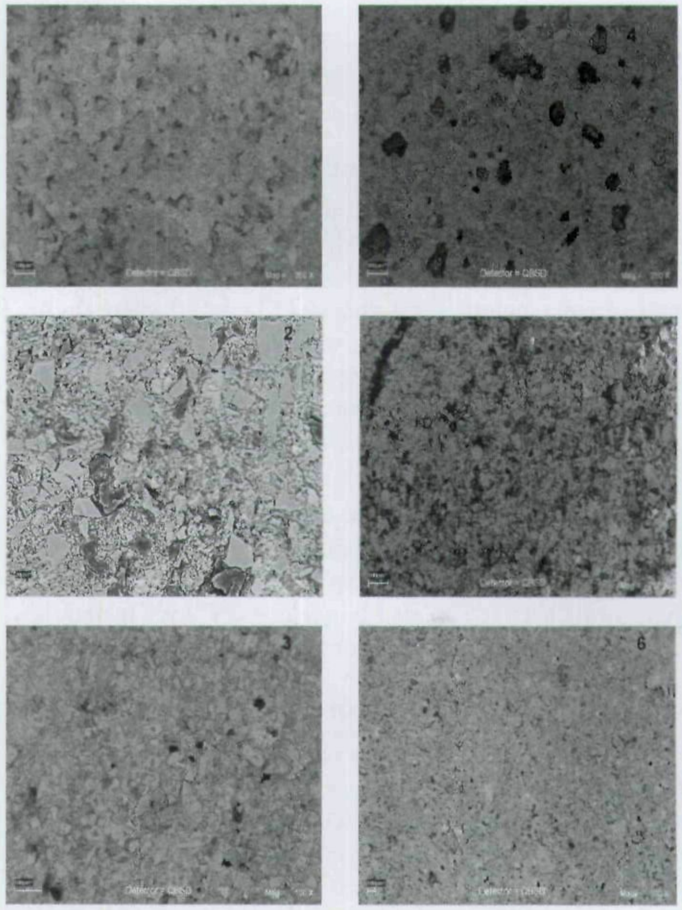

Fig. 2 SEM microphotographs of glass-ceramic materials.

Waste Useful for Tile Manufacture

The objective of this study was to assess the mineralogical, physical and microstructural properties of a glass-ceramic material made using residues of industrial processes. Analysis of the determined properties shows that it is possible to consider the residues as a replacement for raw materials in the fabrication process of ceramic-tile materials. All of the tested materials present crystalline phases (spodumene, anorthite, cordierite, enstatite and quartz) in their compositions that are needed for the specific heat treatment temperatures for sintering and crystallizing to promote the crystalline phase.

Introduction of aluminum-salt residues does not inhibit the formation of the phases. However, it slightly promotes the presence of a vitreous phase, because the aluminum salts act as melting agents, which promotes decreased porosity. This results in materials that present better physical properties. The SiO_2–Al_2O_3–Li_2O material presents a greater proportion of vitreous phase because of the double presence of flux, lithium and hydroxides. The SiO_2–Al_2O_3–MgO system contains the phases enstatite, cordierite and quartz. Introduction of residue during the melting action tends to make the cordierite phase soluble. ■

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References

[1]D. Dermatas and X. Meng, *Eng. Geol.*, **70**, 377–94 (2003).

[2]M.J. Ribeiro, et al., *Ceram. Int.*, **28**, 319–26 (2002).

[3]J.M. Magalhães, et al., *J. Hazard. Mater.*, **106B**, 139–47 (2004).

[4]J.H. Tay, *Resources, Conservation and Recycling*, **2** [3] 211–27 (1989).

[5]N. Okuno and S. Takahashi, *Water Sci. Technol.*, **36** [11] 243–50 (1997).

[6]B. Wiebusch and C.F. Seyfrie, *Water Sci. Technol.*, **36** [11] 251–58 (1997).

[7]J.H. Tay and K.Y. Show, *Water Sci. Technol.*, **36** [11] 259–66 (1997).

[8]C.R. Cheeseman, et al., *Resources, Conservation and Recycling*, **40**, 13–25 (2003).

[9]C. Favoni, et al., *Ceram. Int.*, **31**, 697–702 (2005).

[10]H. Endo, et al., *Water Sci. Technol.*, **36** [11] 235–41 (1997).