

## RECYCLED WASTE AS CERAMIC

*Marilena Lefter de Gamarra, Nicolas G Moreno*

Universidad Nacional de Salta, Consejo de Investigacion-Facultad de Ingenieria, Buenos Aires 177, 4400 Salta, Argentina. Email: [lefterm@ciunsa.unsa.edu.ar](mailto:lefterm@ciunsa.unsa.edu.ar)

### ABSTRACT

The mud of industrial plants which produce boric acid  $H_3BO_3$  or borax  $Na_2B_4O_7 \cdot nH_2O$  with a great amount of boron B can be an interesting source of raw material for solid-state sinterized ceramics.

The proposed aim of this work was the recycling of the residue through the boron as the fluxing agent.

Three compact mixtures were submitted at 900°C and 1100°C. The ceramic material obtained indicate after microscopic and X-Ray diffraction analysis, a vitreous phase with quartz and feldspar crystals.

The extracted boron in the leaching process with HCl,  $HNO_3$ ,  $H_2SO_4$  and NaOH 1 M and 0,1 M, more aggressive concentrations than a natural agent, are less than 0,5 ppm. The lost weight is less than 0,1 mg.

The work shows the feasibility of the use of this contaminant residue as a base raw material for the production of a vitro-ceramic material with mechanical properties, fit for construction.

### INTRODUCTION

Man's impact on the environment (I) has often been characterized by the identity,  $I = PAT$ , where P is the population, A stands for affluence – a surrogate for production or consumption per capita – and T, denoting technology, is a measure of the impact per unit of production and consumption (Goklany, 1986).

The environmental fate of chemicals in soils is an issue of great concern today, due to the problems that result from the use of mobile and persistent molecules, such as deterioration in surface and groundwater quality (Bergström and Stenström, 1998).

The term S/S, Solidification and Stabilization, is used to designate techniques that consist in using different agents to immobilize those contaminant compound from the residue. Solidification refers to the treatment of aqueous and sludge residues to obtain a solid which

suppose a certain physical immobilization of the contaminant. Estabilization is a more ambitious treatment and it pursue to fix the dangerous compounds in a stable matrix which hinder its liberation to the environment (Vale et al., 1996).

The vitrification process – densification with the aid of a viscous liquid phase – is the major firing process for the great majority of silicate systems. A viscous liquid silicate is formed at the firing temperature and serves as a bond for the body. For satisfactory firing the amount and the viscosity of the liquid phase must be such that densification occurs in a reasonable time without the ware slumping or warping under the force of gravity. The relative and absolute rates of this two processes – shrinkage and deformation – determine to a large extent the temperature and composition suitable for a satisfactory firing.

The importance of the vitrification process lies in the fact that most silicates system form a viscous glass at the firing temperature and that the major part of densification results from viscous flow under pressure caused by fine pores. Questions that naturally arise are how much liquid is present and what are its properties. The liquid is siliceous and has a high viscosity; the major effect of compositional changes is to alter the relative amount of mullite and the liquid phase present (Kingery et al., 1976) (Mari, 1998).

In this work the role of Boron is to increase the vitreous phase acting as a fluxing agent.

The principal advantages of glass ceramic materials over conventional ceramics are associated with the absence of porosity in the materials.

The creep rate of ceramic materials is affected by temperature, microstructure (grain size, porosity), composition (Richerson, 1992).

The chemical durability of glasses is determined by a number of factors such as sample states and corrosion conditions. Samples states include: glass composition, mole fraction of the cristal phase, internal or applied stresses, surface roughness and homogeneity. Corrosion conditions include: relative humidity, gas surface reactants, pH of the coroding solution, initial and final

composition of the coroding medium. Even when a detailed knowledge of the different variables is available, however, it remains difficult to derive generalizations from the literature. The conventional techniques include weight loss measurement and Boron concentration in solution.

Certain borosilicate glasses show higher durability in aqueous solution than soda-lime- silicates. The durability of borate glasses as a function of composition has been correlated with the structural connectivity of the glasses. That is, the dissolution rate decreases with the number of four-coordinate borons and increases with the number of single-bonded oxygens.

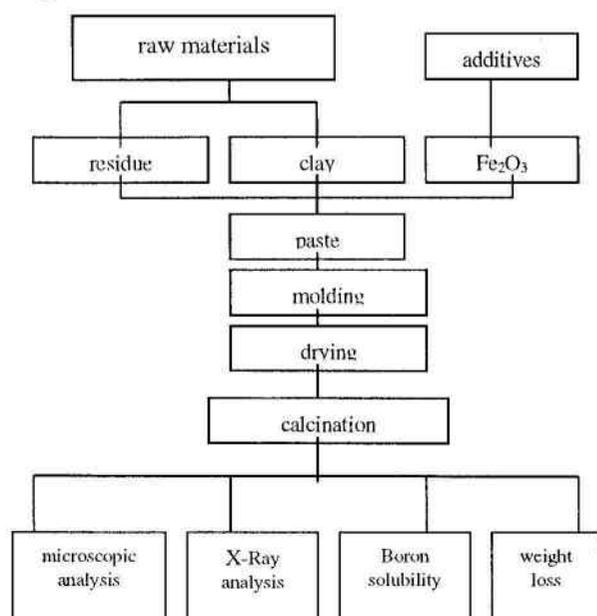
### EXPERIMENTAL

The samples were prepared from comercially available clay, kaolin type, borate residue and Fe<sub>2</sub>O<sub>3</sub> as additive (sample 2 and 3). The experimental composition of the crude material and the termic treatment are shown in table N° 1.

Table N° 1: Samples composition en % oxides

| Sample      | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | B <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | CaO | MgO |
|-------------|------------------|--------------------------------|-------------------------------|--------------------------------|-------------------|-----|-----|
| 1<br>900°C  | 54,5             | 22,0                           | 8,0                           | 1,6                            | 5,4               | 2,5 | 1,8 |
| 2<br>900°C  | 53,4             | 19,8                           | 8,5                           | 10,5                           | 3,2               | 2,0 | 1,5 |
| 3<br>1100°C | 53,4             | 19,8                           | 8,5                           | 10,5                           | 3,2               | 2,0 | 1,5 |

The flow sheet for obtaining and characterization of the glass ceramic material is:



Borate residue is the base raw material for this work. Due to the high content of Boron it is important for a system to vitrify at the temperature of 900°C and 1100°C.

As inorganic binder, clay minerals as kaolinite was used. Kaolinite has a layered structure and interact with water to yield a flexible, plastic mixture. The clay minerals do not burn during densification, but instead become part of the ceramic. Use of suitable binders can reduce density variation.

As additive Fe<sub>2</sub>O<sub>3</sub> decrease the linear shrinkage during firing due to Al<sub>2</sub>O<sub>3</sub> anisotropy.

The starting material were mixed in a planetary model mixer, then molded in 9.7.1 pieces and dry for three days at room temperature, for 48 hours at 60°C and 48 hours at 120°C in a temperature controled oven. After drying the pieces were heated from 100°C up to 900°C, sample 1 – 2 and up to 1100°C, sample 3 by increasing steps of 100°C, maintaining the sample at the final temperature 2 hours.

Structural characteristics were studied by means of X-Ray diffraction in a RIGAKU DENKI D/Max II-C using Cu K<sub>α</sub> radiation, Ni filter, 1° receiving and divergence slits and 0,15 mm dispersion slit. The scanning rate was 2θ/min and the sample path 0.02° ( Reynolds et.al., 1989).

Microstructure was determined by microscopic analysis using a ORTHOMAT-POL-LEITZ microscope by transmission with CB 12 filter, 100% light and parallel nicols on 30μ width preparates (Gamarra et.al., 1999)

Chemical analysis on free organic matter samples used: gravimetric methods for Si; atomic absorption spectrophotometry in a SHIMADZU-AA-6500F for Al, Fe, Ca, Mg, Na, K; UV-Visible spectrophotometry in a SPECTRONIC 401 for B with azomethine H method (Kolthoff et.al., 1985).

The experimental leaching process of the ceramic pieces in order to estimate the Boron immobilization was carried out with solutions of: HCl 0,1 M and 1M; HNO<sub>3</sub> 0,1 M and 1 M; H<sub>2</sub>SO<sub>4</sub> 0,1 M and 1 M; NaOH 0,1 M and 1 M at ambient temperature. The extracted quantities of B in all the solutions were used to determine the immobilizatin of this contaminant element in the glass ceramic material.

The weight loss was calculated as the weight diference of the samples before and after the leaching process.

## RESULTS AND DISCUSION

### Microstructure

The different composition and termic treatment determine the diferencies in the microstructure of the ceramic material obtained.

Sample 1, residue-clay-900°C shows a heterogeneous vitreous phase with isothrope and anisothrope birefringence a heterogeneous cristaline phase and a high density of wide pores. The fusion is parcial without borate cristals. Fig. 1

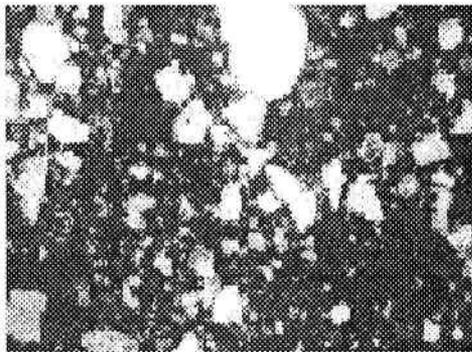


Figure N° 1: Sample 1, micrography.

Sample 2, residue-clay-Fe<sub>2</sub>O<sub>3</sub>-900°C shows a vitreous phase with small fragments of lithoclast quartz in fusion process. The vitreous phase sorrounds the cristals. The pores are smaller and the density of the pores is lower. Fig. 2.

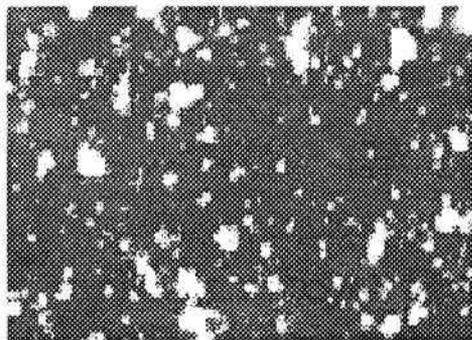


Figure 2: Sample 2, micrography

Sample 3, residue-clay-Fe<sub>2</sub>O<sub>3</sub>-1100°C shows a vitreous phase with a lower density of very small pores and small fragments of cristals. Fig. 3

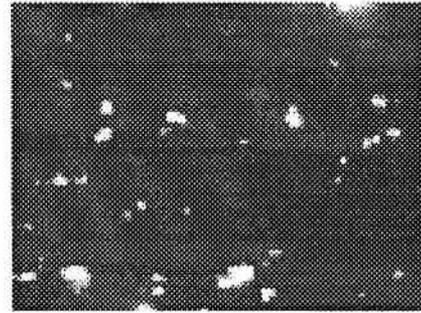


Figure 3: Sample 3, micrography

### X-Ray diffraction analysis

For samples 2 and 3 the addition of Fe<sub>2</sub>O<sub>3</sub> as additive and the calcinating temperature increase from 900°C to 1100°C the presence of broad diffraction lines shows that exists an amorphous vitreous phase. The presence of quartz as very small cristal fragments and clays as illite, mullite and non borate minerals were detected.

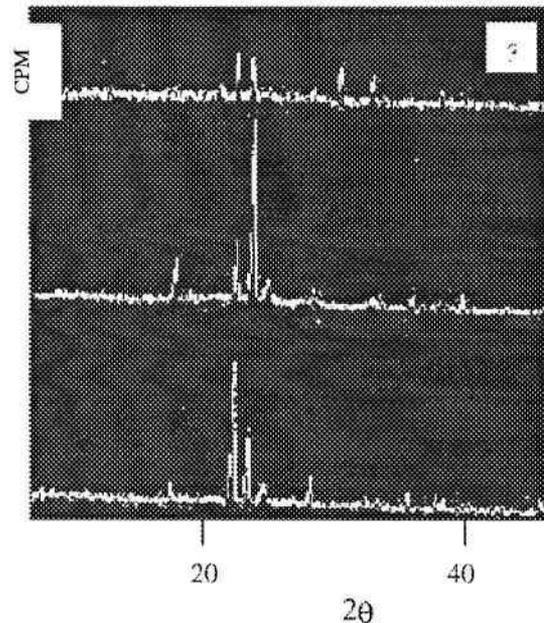


Figure 4: Diffractogram, sample 1, 2, 3

### Chemical durability

The leaching process with HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, NaOH solutions followed by Boron concentration measurements, Table 2 and weight loss, Table 3 for the ceramic samples shows a lower weight loss and Boron concentration in order 3-2-1.

Table 2: Boron concentration ppm

|   | HCl 0,1 M | HCl 1 M | HNO <sub>3</sub> 0,1 M | HNO <sub>3</sub> 1 M | H <sub>2</sub> SO <sub>4</sub> 0,1 M | H <sub>2</sub> SO <sub>4</sub> 1M | NaOH 0,1 M | NaOH 1 M |
|---|-----------|---------|------------------------|----------------------|--------------------------------------|-----------------------------------|------------|----------|
| 1 | 0.01      | 0.01    | 0.02                   | 0.02                 | 0.00                                 | 0.00                              | 0.03       | 0.05     |
| 2 | 0.01      | 0.00    | 0.01                   | 0.01                 | 0.00                                 | 0.00                              | 0.01       | 0.02     |
| 3 | 0.00      | 0.00    | 0.00                   | 0.00                 | 0.00                                 | 0.00                              | 0.00       | 0.00     |

Table N° 3: Weight loss mg/100 g

|   | HCl 0,1M | HCl 1M | HNO <sub>3</sub> 0,1M | HNO <sub>3</sub> 1M | H <sub>2</sub> SO <sub>4</sub> 0,1 M | H <sub>2</sub> SO <sub>4</sub> 1M | NaOH0,1 M | NaOH 1M |
|---|----------|--------|-----------------------|---------------------|--------------------------------------|-----------------------------------|-----------|---------|
| 1 | 0.00     | 0.001  | 0.001                 | 0.003               | 0.001                                | 0.00                              | 0.01      | 0.01    |
| 2 | 0.00     | 0.00   | 0.001                 | 0.001               | 0.001                                | 0.00                              | 0.00      | 0.01    |
| 3 | 0.00     | 0.00   | 0.00                  | 0.00                | 0.00                                 | 0.00                              | 0.00      | 0.00    |

The Fe<sub>2</sub>O<sub>3</sub> as additive and the termic treatment at 1100°C increase the chemical durability of the ceramic material obtained in these conditions.

The vitreous phase increases due to Boron presence in the system with the consequent effect on pores density and pores size.

### CONCLUSIONS

This work show a clear correlation between composition-treatment conditions and microstructure, chemical durability of the ceramic material obtained.

The ceramic material obtained in this way shows similar o superior properties to a comercial ceramic. Its small pore size make it a material fit for construction.

The inclusion of Boron in the vitreous phase indicate that it is a possible way to immobilize this toxic element as an insoluble in a ceramic material avoiding its contaminant effect.

The borate residue is a good alternative as a low cost raw material to replace another fluxing agents in the base paste in the process of obtaining ceramic materials with special physic mecanical and chemical properties resistant to ambiental agents.

### ACKNOWLEDGEMENTS

The authors are grateful to Consejo de Investigacion and to Facultad de Ingenieria of Universidad Nacional Salta, Argentina for the economical support.

### REFERENCES

- Bergström, L. and Stenström, J. Environmental Fate of Chemicals in Soil. *AMBIO* Vol. 27 N° 1, Royal Swedish Academy of Sciencies, Feb. 1998
- Gamarra, M. Moreno, N. Maidana, M. Microestructura de Material Ceramico Obtenido por Reciclado de Residuo Contaminante, CIT La Serena Chile en prensa.
- Goklany, I.M. Factors Affecting Environmental Impacts: The Effect of Technology on Long-term Trends in Cropland, Air Pollution and Water-related Diseases. *AMBIO* Vol. 25 N° 8 Royal Swedish Academy of Sciences, Dic. 1996.
- Hamerly, J.A. Marracino, J.M. Piagentini, R.O. Curso de Quimica Analitica El Ateneo 1984.
- Kingery, W.D. Bowen, H.K. Uhlman, D.R. Introduction to Ceramics, John Wiley and Sons, New York 1976.
- Mari, E. Los Materiales Ceramicos, Libreria y Editorial Alsina, 1998.
- Reynolds, R.C.J. Principles of Powder Diffraction in Modern Powder Diffraction D.L. Bish and J.E. Post editors, 1989
- Richerson D.W. Modern Ceramic Engineering Ed. Marcel Dekker 1992.
- Vale, J. Pereira, C.F. Rodriguez-Piñeiro, M. Ruiz de Elvira, C. Olovaes, J. Troyano, D. Salvador, L. Tratamiento E/S de un Residuo Siderurgico con Cenizas Volantes, Ingenieria Quimica, Año XXVIII N° 320, Enero 1996, Madrid, España.