



A REVIEW ON ECO-TECHNOLOGICAL PROCESS OF GLASS -CERAMIC PRODUCTION FROM ALUMINIUM SLAG

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ABSTRACT

Methods of purification of waste water by chemical oxidation and reduction, neutralization, sedimentation, coagulation and flocculation. Consequently, these methods generate waste sludge which unless adequately stabilized represents hazardous material. Untreated aluminium slag is contaminating environment by emission of liquid and gaseous phases of dangerous matter. This paper representing new technology of aluminium slag by converting it into the useful products, eliminating generation of dangerous and harmful matters and transformation of these waste materials into glass ceramic structure through sintering. The obtained product was analyzed with Fourier transform infra-red spectroscopy (FT-IR) and X-ray diffraction (XRD). Glass ceramic is characterized by large contents of alumino-silicates and the structure of it is approved. Such a new eco- technological procedure of the process of treatment of aluminium slag is enabling complete protection of environment together with using slag as secondary raw material. This is in accordance with the recent trends in recycling and regeneration of waste.

Keywords: Aluminium Slag, Glass Ceramics, Eco-Technological Procedure

I. INTRODUCTION

Aluminium salt slag is also known as cake aluminium salt which is produced by the secondary aluminium industry, is formed during aluminium dross melting and contains 15-29% aluminium oxide, 30-54% sodium chloride, 15-29% potassium chloride, 5-6% metallic aluminium and impurities (carbides, nitrides, sulphides and phosphides). Depending on the raw material mix the amount of salt slag produced per tonne of secondary aluminium ranges from 200 to 450 kg. As salt slag has been classified as toxic and hazardous waste, Its landfill disposal is forbidden in most of the European countries and it should be recycled and processed in a proper way by taking the environmental impact into consideration. This paper presents a review of the aluminium salt slag chemical and mineralogical characteristics, as well as various processes for metal recovery, recycling of sodium and potassium chlorides content back to the smelting process and preparation of value added products.



Figure 1 aluminium slag picture

Lithia–alumina–silica ternary phase diagram (Eppler 1963) provides important information regarding phases useful for glass–ceramic material. Glass–ceramics are the ceramic material formed through the controlled nucleation and crystallization of the parent glass. This is one of the most important glass–ceramic system which has been extensively investigated and commercialized because of its low, zero or negative thermal expansion coefficients as well as excellent thermal and chemical durability. Several researchers reported their crystallization behaviour with different types of nucleating agents (Locsei 1962; Freimann and Hench 1971; Macmillan 1980; Hlavac 1983). Various types of glass–ceramic materials are produced from conventional raw materials and there is a growing interest to produce glass–ceramic material from the industrial waste due to their great technological advantage and scientific importance with proper correction of the chemical composition (Wang and Hon 1990; Suzuki and Taraka 1997; Boccacini and Rawlings 2002; Khater 2002; Kneiss *et al* 2002; Rozenstrauha *et al* 2002; Park *et al* 2003). The transformation of wastes into glass or glass–ceramic provided the opportunity for making useful marketable products out of hazardous waste like fly ash, iron and steel slag and other silicate and municipal wastes. Kneiss *et al* (2002) studied the development of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass ceramic system from coal bottom ash. Lithium carbonate was used to promote glass melting and rutile as nucleating agent. Controlled heat treatment of this glass resulted in the formation of lithium alumino-silicate glass and *b*-eucryptite as crystalline phase with negative coefficients of thermal expansion. Lithium alumino–silicate phases are well known for their low linear thermal expansion coefficient over a wide range of temperature which permits the development of glass–ceramic material with a large range of interval of thermal expansion, (–) to $43 \times 10^{-7}/^\circ\text{C}$. Almost similar large range interval of thermal expansion values have been reported by other workers also (Strand 1986; Kneiss 2002) for other $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ based glass–ceramic materials. Suzuki and Taraka (1997) and Park *et al* (2003) reported the characteristics of glass–ceramics made of sewage sludge ashes from the municipal solid waste incinerator. Although glass–ceramics prepared from sewage sludge ash consisted of anorthite as main crystalline phase, control of crystalline phase formation was not possible due to complex composition of the waste. Khater (2002) reported that different types of slag viz. silicon manganese slag and steel slag, can be used successfully for the production of crystalline glass material of different microstructures and mineralogical constituents that have many valuable technological properties. He observed an increase in bulk crystallinity with the increasing content of bustamite phase in the glass. Preparation of glass–ceramics from blast furnace slag has been described by many workers (Yoshimi *et al* 1977; Strand 1986; Chang *Author for correspondence (swapan@cgcri.res.in) and Jung 1980) and the main crystalline phases identified 438 S Mandal *et al* by them were disopside, spinel, wallostanite and anorthite. Wang and Hon (1990) produced $\text{Li}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ based glass–ceramic from blast furnace slag with addition of silica, alumina, lithium carbonate and rutile as nucleating agents. The major crystalline phase identified in this case was *b*-



spodumene. Boccacini and Rawlings (2002) produced new glass–ceramic material in their recent work with interesting magnetic and constructive properties utilizing slag, fly ash and combustion dust waste materials. The heavy iron content of coal fly ash contributed towards the development of magnetic phases with well developed dendrite structure ascribed to magnetite, which offered soft magnetic properties to the materials. In another work (Mandal *et al* 2000), glass produced from a mixture of blast furnace slag and clay were studied for their crystallization behaviour with rutile and zirconia as nucleating agents. Formation of crystalline phases like *b*-spodumene and *b*-quartz solid solution was observed. However, controlling of the glass composition was found to be a major problem in this system. The aim of this paper is to use waste material like quenched and granulated blast furnace slag with pyrophyllite, a hydrous alumino–silicate mineral ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$) for the development of ultra low thermal expansion material. Judicious selection of other additives were made in controlling the composition of the glass. Titania (TiO_2) was used as the nucleating agent. The crystallization behaviour was studied at different time temperature schedules after DTA analysis of the parent glass powder. The resulting material was subjected to thermal expansion and flexural strength measurements. The phase assemblages were characterized by XRD studies. This is the another method of preparation of glass-ceramic material from blast furnace slag. Mainly we concentrated only preparation of glass-ceramic material by aluminium slag.

II. EXPERIMENTAL

Ecological risk of waste sludge and aluminium slag is determined on the basis of defining high-flow and low-flow fractions of a series of metals by a standard procedure U.S.EPA 1997/222. The primary ecological risk of waste sludge was determined on the basis of rinsing representative samples in distilled water and analyzing metal with atomic absorption spectrophotometry (*Perkin Elmer AAM1100 and Varian AA-20*). In the results the term water eluate has been adopted for this movable fraction. For the sake of a more detailed insight into the pollution potential, and at the same time bearing in mind the chemical origin of waste sludge and aluminium slag, a low-flow fraction was also determined, which is more strongly bonded and thus represents a pollutant reservoir. A low-flow metal fraction was also isolated by a standardized procedure of rinsing with diluted nitric acid. This fraction is marked as HNO_3 -eluate. The criteria based on which the comparison of concentration of metals in water after rinsing the representative samples of waste sludge was carried out are taken from the Holland list 8935/1998. The results are shown in (**Tables 1 and 2**) where A is the referential value for standard groundwater and B is the concentration at which detailed testing and safety measures are recommended (EEC regulation) [7].

Table 1 Comparison of concentrations of high-flow (H_2O -eluate) and low-flow (HNO_3 -eluate) metal fractions in representative samples of waste sludge

Pollutant	H_2O -eluate (mg/l)	HNO_3 - eluate (mg/l)	A (mg/l)	B (mg/l)	Failure to meet criteria
Cu	0.137	106.1	0.015	0.050	A, B
Zn	0.269	1222	0.150	0.200	A, B
Cr	9.56	977	0.001	0.050	A, B
Ni	1.935	1210	0.015	0.050	A, B



Cd	2.839	1203	0.005	0.050	A, B
Pb	0.000	9.585	0.005	0.050	A, B

Table 2 Comparison of concentrations of high-flow (H₂O-eluate) and low-flow (HNO₃-eluate) metal fractions in representative samples of aluminium slag

Pollutant	H ₂ O-eluate	HNO ₃ - eluate (mg/l)	A (mg/l)	B (mg/l)	ure to meet criteria
Cu	3.972	8.261	0.015	0.050	A, B
Zn	0.536	2.315	0.150	0.200	A, B
Cr	1.216	15.441	0.001	0.050	A, B
Mn	0.326	0.650	0.050	0.100	A, B
Be	0.7815	0.8069	0.0002	0.0005	A, B
Ti	0.533	2.287	0.100	0.150	A, B
Al	88.816	109.359	*	*	A, B

* The values for aluminium were not standardized under the A and B criteria.

The presented data indicate that the concentration of toxic metal after rinsing of composite samples of galvanic sludge and aluminium slag is higher than that in standard groundwater (criterion A). The Holland list 8935/1998 also recommends safety measures – purification of seepage water in case waste is disposed of unprocessed.

III. ECO-TECHNOLOGICAL PROCEDURE OF WASTE SLUDGE TREATMENT

The primary material is waste aluminium slag, which contains certain amounts of aluminium, metal oxides (Al₂O₃, BeO, TiO₂, CuO, Cr₂O₃, and others), and predominantly Al₂O₃ and solidified refinement salts, which mostly contain KCl, NaCl, Na₃AlF₆, MgCl₂, CaF₂, MgF₂, etc. Waste glass was used as an auxiliary material. Average composition of waste glass in mass percentage is 76% SiO₂, 11% PbO, 8% ZnO, 2% B₂O₃, 2% BaO, and 1% ZrO₂. Apart from the basic waste materials, boron trioxide (B₂O₃) was also used as a liquefier for glass-ceramics synthesis. Since aluminium slag contains high-flow fluorides which could destroy glass-ceramics phase, it is rinsed with water in order to remove the fluorides. The slag is sunk in the water and left like that for 24 hours, during which the fluorides dissolve. The insoluble part of the slag is separated by filtration and fluorides are regenerated by evaporation and crystallization. The residue thus obtained is then processed further. To obtain dehydration, it is necessary to dry the galvanic sludge. A low-temperature dry kiln can be used for this purpose.

After these operations all the elements (sludge, slag, glass, and borax) are ground in a colloid mill to facilitate melting. When the ingredients are ground, they are mixed until the mixture is homogenized and then the same mixture is poured into the melting mould. The mould with the mixture is put into a blast furnace where it is heated at 1200-1400⁰C. The melting temperature of the mixture depends on the quantity of several components included in the mixture. An increased quantity of glass will lower the melting temperature and reduce the solidity of the obtained ceramics. With the increase in the quantity of aluminium slag the solidity of

the ceramic structure will also increase, but this requires a higher melting temperature, which sometimes presents a difficulty. In order to get to phase transformations, the mixture has to be absolutely liquid, which is why the mould is kept in the blast furnace for about 40 minutes. After melting, the melted content is poured into a preheated graphite mould. The preheated graphite mould is preheated at 250-300^oC so that glass-ceramics would not crack due to sudden cooling in a cold mould. The analyses of determining the concentration of metals in the obtained glass- ceramics show absence of metals in the water in which the sample is rinsed, which proves the efficiency of the method of stabilization of this waste.

IV. RESULTS AND DISCUSSION

The efficiency of the eco-technological procedure of transforming aluminium slag into a glass-ceramic structure was confirmed with Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray diffraction (XRD). Infrared spectra of glass-ceramics were obtained with a BOMEM (Hartman & Braun) FT-IR

spectrophotometer, model MB-Series, in a spectral range 4000 to 400 cm⁻¹, with a resolution of 2 cm⁻¹, by method of pressed pellets. The Potassium Bromide (KBr) Technique for sample preparation was used to record spectra. A quantity of 1-2 mg of tested sample is mixed with 150 mg of spectroscopically pure KBr. The mixture is then vacuumed and pressed at 200 Mpa, which forms thin permeable pellets. A reference pellet for BACKGROUND recording was prepared from pure KBr (**Figure- 2**

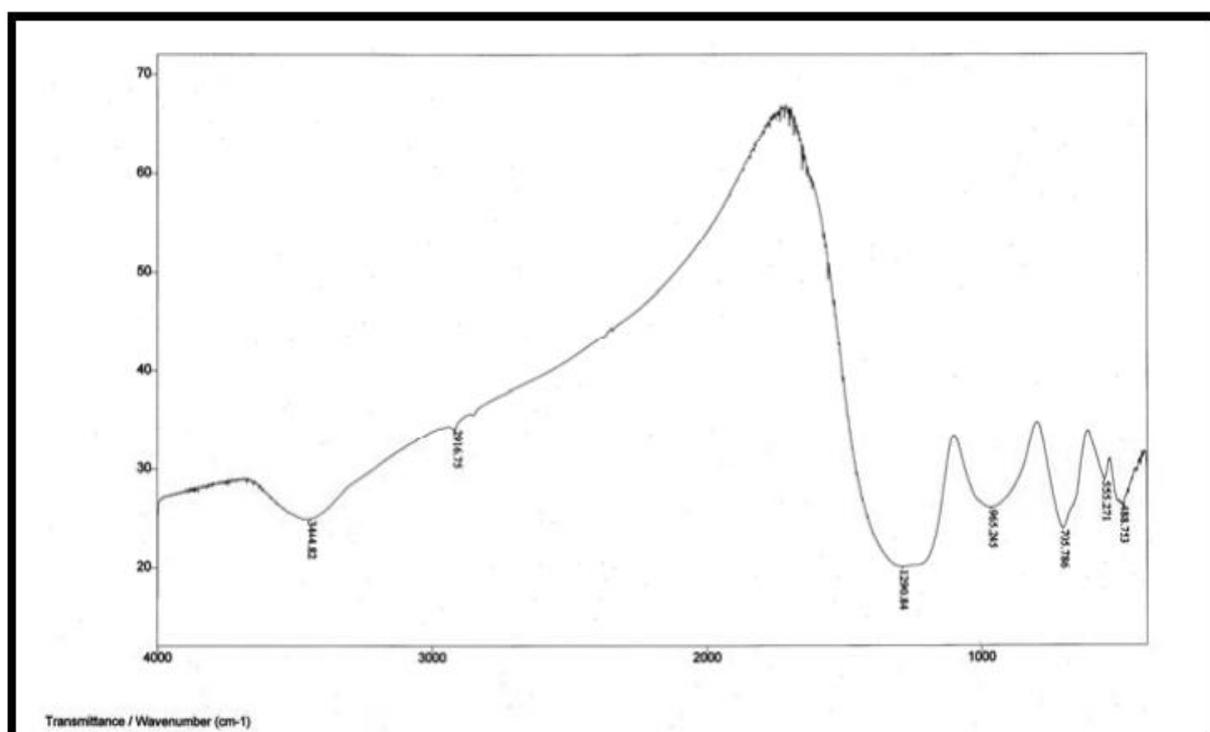
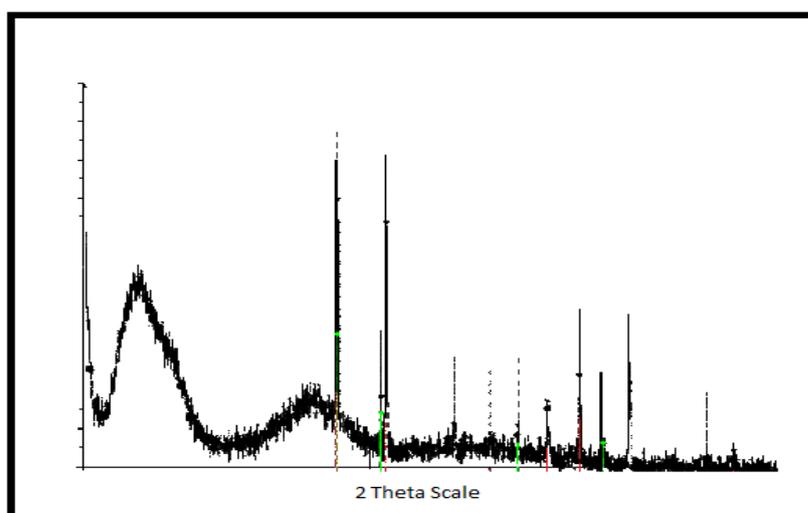


Figure 2 FT-IR Spectrum of Glass Ceramics

On the basis of the FT-IR spectrum we observe lines at 560 and at 660 cm^{-1} as well as at 1350 cm^{-1} , which indicate the presence of Cr_2O_3 . It is these lines that reveal that highly toxic chromium is bonded as an oxide with a silicate phase and that it is chemically completely inert. Apart from detoxication of chromium, glass-ceramics gets an aesthetic value because Cr_2O_3 is a very well-known pigment and it gives a very beautiful green colour. Stronger in intensity and its form, the line in the range from 600 to 800 cm^{-1} confirms the presence of silicate phase with the dominant content of aluminosilicates in the form of $\text{Al}_2\text{O}_3 \times \text{SiO}_2 \times 2\text{H}_2\text{O}$. Likewise, during melting at high temperature the elimination of crystal water in the structure due to no lines at 1630 cm^{-1} and the dominant presence of copper (II)- titanate (IV) (CuTiO_3) are obvious, based on the form and intensity of the lines in the range from 400 to 800 cm^{-1} . These lines (from 400 - 800 cm^{-1}) reveal the transformation of highly toxic copper and titanium, which are bonded in the form of oxides as solid solutions and are completely chemically inert, which is very important from the environmental perspective [8].

The presence of aluminosilicates in the form of $\text{Al}_2\text{O}_3 \times 2\text{SiO}_2 \times 2\text{H}_2\text{O}$ confirms the obtained glass-ceramic structure with the bonding of hazardous and harmful substances (CuTiO_3 , Cr_2O_3), which qualifies them as chemically inert. The XRD analysis of samples prepared from a compact piece or powder was conducted with a SIEMENS D500 powder diffractometer. Recording was done with $\text{CuK}\alpha$ radiation ($\lambda = 1,54184\text{ \AA}$) in angle ranges 5 - $90^\circ 2\theta$ at the speed of $0,02^\circ 2\theta/s$. Identification of crystal phases in samples was conducted by means of *Diffraction^{plus}* software and PDF (Powder Diffraction File, PDF 2) database [9]. Sample diffractogram (**Figure 3**) indicates a presence of a significant quantity of amorphous phase, which causes a wide diffraction profile at about $28^\circ 2\theta$. The $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ crystal phase and substantial quantities of elemental lead were identified in the samples.



2.  iz tigla - File: I K_2 iz tigla. raw - Type: 2Th/Th locked - Start: 2.000° - End: 90.000° - Step: 0.020° - Step time: 1. s - Anode: Cu



04-0686 (*) - Lead syn - Pb

05-0669 (*) - G ahnit e syn - ZnO.A l2O 3

Figure 3 XRD Spectrum of Glass-Ceramics**V. CONCLUSION**

Waste management and recycling is an important aspect of environmental sanitation. It also reduces the exploitation of run-materials for the purpose of production. Glass - ceramics raw - material is obtained by digging landfills which leads to the distortion of the environment. The utilization of aluminium-wastes for the purpose of this production is a welcome development that checks the environmental distortion. Economically, it is viable, but the process of productions that involves incinerations may lead to the production of toxic gases that pollute the environment. Proper control of this will enhance the environmental sanitation and reduce production cost in glass-ceramics industries

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