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Effect of controlled crystallization on the chemical durability of a lead-containing waste glass

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A favourable microstructure was tailored by controlled crystallization of a quenched glass made of a combination of metal industry slags and a lead bisilicate frit. The frit was used to simulate a lead-containing waste. In the devitrified glass microstructure, lead-rich glassy pockets were contained in an akermanite ($Ca_2MgSi_2O_7$) crystalline matrix. Leaching of lead was reduced by a factor of two as a result of devitrification processing; the low-lead crystalline matrix protected the lead-rich pockets from chemical attack.

1. Introduction

One of the disadvantages of the technological age is the unending production of hazardous substances which were originally not present in nature. Safe disposal of these industrial by-products, and of end-use products when discarded, is a serious problem. For both ecological and economic reasons, it is prudent to recycle wastes into non-hazardous value-added products, or at least into more environment-friendly landfill which will not contaminate ground water.

Hazardous wastes are identified by lists, through test methods for hazardous characteristics, or by declaration. If a waste is not listed, it is generally tested for hazardous characteristics such as ignitability, corrosivity, reactivity, and toxicity by well-established test methods (e.g. ASTM) [1]. Incineration is a means for thermal detoxification of hazardous waste and is generally preferred over other treatments and disposal methods [2]. Incineration works best for organic wastes, wherein most inorganic or metallic components remain in the residue. Because of heavy metals often present in the ash, the residue may still fall under a hazardous waste category. Waste vitrification processes have been developed in an attempt to tie up radioactive heavy metals into a form resistant to chemical corrosion [3–6]. A suitable silicate glass composition for waste vitrification can be formulated either by adding mined raw materials or, preferably, by merging selected waste streams.

Most of the slags from steel industries contain enough silica to form glasses. These slags are produced in voluminous quantities and hence are a significant disposal problem. Slags have already been utilized in several applications such as slag–sitall and slagceram structural ceramic products; fibers (rock wool) for building insulation; abrasives [7]; and raw materials for glasses [8]. Calumite (Calumite Corporation, Boca Raton, Florida, USA) is a tradename for a refined mixture of blast-furnace slags of dependable composition. It is commonly used as a batch additive for the glass industry. The main constituents of calumite are CaO, MgO, Al_2O_3 and SiO_2. Minor constituents, such as the oxides of Na, K, Fe, Mn, Cr and S, are also present. The predominant crystalline phase in as-received calumite is akermanite ($Ca_2MgSi_2O_7$) [9]; other minor crystalline phases as well as a glassy phase are also present. It was found [7] that the minor impurities in slag glass, expected to be in the form of metal sulphides, act as heterogeneous nucleation sites for crystal growth.

Glasses are remarkably accommodating with regard to the solubility of heavy metal ions. Heavy metals may even enhance the properties of glasses and may have a functional role as colorants (e.g. Cr, Ni, Fe, Co, Cd), as well as density, electrical resistivity, and refractive index-enhancing agents (e.g. Pb, Ba). They can also be used as nucleating agents (e.g. Cr, Fe, Zn, Ti) for glass–ceramics. However, a primary and simpler objective of treatment of heavy metal waste by vitrification is to make it non-toxic and non-hazardous. This is a function of the chemical durability of the end-product. Generally, for vitrified products, toxicity is the only consideration and is tested by a toxicity characteristic leaching procedure (TCLP) specified by the US Environmental Protection Agency (EPA) [10]. In this paper, the favourable effects of devitrification heat treatment on the chemical durability of a vitrified heavy metal waste are presented.

2. Experimental procedure

A mixture of 40 wt % lead-bisilicate (Hammond Lead Products) ($PbO \cdot 2SiO_2$) and 60 wt % Calumite was

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melted at 1400 °C in an alumina crucible, and then quenched in air to form a glass. This glass was annealed at the glass transition temperature ($T_g = 688$ °C; see results section) for 2 h. Compositions of the initial batch and the final glass, as determined by wet chemical analysis, are listed in Table I. The slight variation in these two compositions can be largely attributed to the volatilization of the lead oxide during melting.

The dilatometric softening point and coefficient of thermal expansion of the glass were measured using a contact dilatometer (Netzsch Inc., Exton, Pennsylvania, USA; digital interfacing by Innovative Thermal Systems, Atlanta, Georgia, USA) with an alumina casing and pushrod. The crystallization behaviour of this waste glass was studied with differential thermal analysis (DTA) with a chromel/alumel differential thermocouple (Harrop Industries, Columbus, Ohio, USA; digital interfacing by Innovative Thermal Systems). The glass particle size was reduced to less than 212 μm using a clean mortar and pestle, for use as the sample in the DTA. An isothermal DTA experiment was designed to study the soaking time required for complete crystallization. The DTA furnace was preheated to 828 °C, within the crystallization temperature range of the glass. After the temperature of the furnace was stabilized, the furnace was raised, the sample quickly placed over the sample thermocouple, and the furnace was replaced.

Analysis of the crystallized phases was performed using a computer-interfaced X-ray (CuK_α) powder diffractometer (Model VAX-11/730, Digital Equipment Co., Northboro, Massachusetts, USA; Model 12045 X-ray Diffraction unit, Philips Electronic Instruments Co., Mount Vernon, New York, USA) with a 1 s time constant and a 0.02° step size, over a two theta range of 20–80 °. A fine powder of both as-annealed and devitrified samples was dispersed in acetone. A drop of each dispersion was placed on copper grids which were then placed in the sample holder of a transmission electron microscope (Model 2000FX, Japanese Electron Optics Laboratory, Tokyo, Japan). The crystalline and glassy regions were identified by selected area diffraction and further confirmed by dark- and bright-field imaging. Energy dispersive spectroscopy (EDS) was also used to determine the relative elemental composition of various phases (Model TS16-J018, Princeton Gamma Technology, Princeton, New Jersey, USA).

The toxicity characteristic leaching procedure (TCLP) is generally used to determine the mobility of the organic and inorganic species present in liquid, solid and multiphasic waste [11, 12]. A specified test typically consists of the following steps:

1. Determination of percentage solids. This step can be omitted for bubble-free inorganic glasses, as they are 100% solids.
2. Particle size reduction to less than 9.5 mm.
3. Determination of the approximate extraction fluid.
4. Extraction and determination of the concentration of the heavy metal ions.

The EPA-specified particle size range of 0.0–9.5 mm has been argued to be too wide for adequate reproducibility [13]. To demonstrate the sensitivity of chemical durability results to particle size for inorganic glasses, three different size ranges were chosen for the extraction. These sizes were 16 − (US standard mesh, larger than 1.2 mm), 16 + to 70 − (1.2mm–212 μm), and 70 + to 200 − (121–75 μm). An extraction fluid of pH of ∼ 3 was selected; 5.7 ml of glacial acetic acid was added to reagent-grade water to make a total volume of 1 l.

Considering the sensitivity of the EPA-specified TCLP test to particle size, a self-consistent acid extraction procedure was used to emulate the TCLP test, which differed from the EPA specification in some respects. The extraction setup consisted of polyurethane bottles placed vertically in a ball mill jar. The rotation frequency of the ball mill jar chosen in the present work was 80 r.p.m.; the extraction time was 11.5 h. A minimum of 100 g of sample is required by the standard; however in the present study, only 4 g samples were used for extraction. Selection of a larger samplings is important where material properties and compositions are not homogeneous on a macro scale. In the present case, however, the small sample size was chosen as the glasses were homogeneous on the micro scale. This revised procedure was consistent, and served the purpose of measuring relative chemical durability. Extraction was carried out with a 20 times (by weight) quantity of the extraction fluid. Extracts were filtered using a filter paper (Fisher Scientific No. P2), transferred to glass bottles, and immediately tested for lead concentration using atomic absorption spectroscopy.

3. Results and discussion

The mixture of lead bisilicate and Calumite melted to form a fluid liquid at ∼ 1400 °C. Soaking at 1100 °C for ∼ 2 h was required to avoid foaming near the melting temperature. The foaming is expected to be the evolution of sulphate gases.

The resulting model glass had a density of 3.44 g cm^{-3} (Archimedes method) which is not unusual for a high-lead glass. The green colour of the glass can be attributed to the iron content of calumite. A dilatometric study of the resulting glass shows a thermal expansion coefficient of 12 p.p.m °C^{-1}, a glass transition temperature of 688 °C, and a dilatometric softening point of 716 °C.

The DTA trace (Fig. 1) shows an endothermic trend corresponding to the T_g of glass, followed by a crystallization exotherm. The T_g of this glass at 828 °C matches closely with that determined by dilatometry. Comparing XRD results to the JCPDS (Joint Committee on Powder Diffraction Standards)

TABLE I Compositions of glass batch and prepared glass (wt %).

	SiO_2	PbO	CaO	Al_2O_3	MgO	Residual
As-batched	36	26	24.8	6	5.5	1.7
Quenched glass	38	22	25.3	7	6.6	1.1

database showed that this glass crystallized into akermanite ($Ca_2MgSi_2O_7$), starting at ~ 828 °C. This result differs from possible phases predicted by the 10%MgO–CaO–Al_2O_3–SiO_2 phase diagram [14]. Surprisingly, additions of lead bisilicate did not shift the favourable crystalline phase away from the akermanite phase field of as-received calumite.

An isothermal DTA experiment was carried out to determine the time of crystallization at a selected soak temperature (Fig. 2). From the figure, it is apparent that a period of 30 min was required for complete crystallization. All three particle size-range glasses were thus crystallized at 828 °C for 30 min. XRD analysis showed that all samples devitrified to the akermanite phase.

Chemical durability tests for both annealed and crystallized glasses revealed that the amount of lead leaching out decreased with increasing particle size (Fig. 3). This indicates that the particle size range of 0–9.5 mm specified by the EPA standard is too wide for such waste products. With a finer particle size, a larger exposed surface area permits a greater extraction of lead from the glass. Devitrified glasses showed a greater chemical resistance to acid attack than as-annealed glasses. The percentage improvement due to crystallization was greater with a larger average particle size. For the largest particle size range chosen in the study, 16 – (which remains appreciably smaller than the maximum EPA specified size) the durability improvement was ~ 100%.

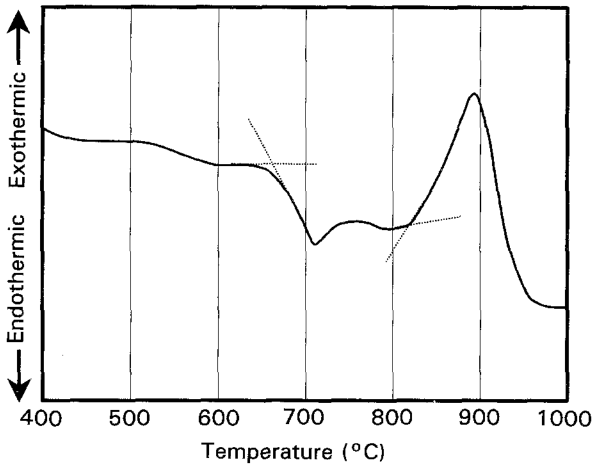

Figure 1 DTA trace of as-quenched glass composition at a heating rate of 10 °C min^{-1}.

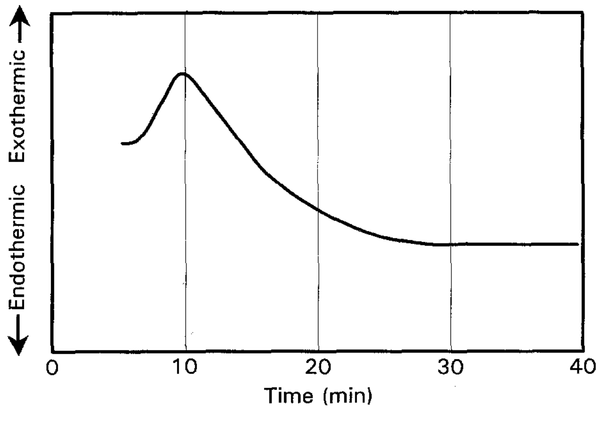

Figure 2 Isothermal DTA trace of glass devitrification at 828 °C. The first ~ 5 min of the trace representing thermal stabilization after sample placement is not shown.

Fig. 4 shows a TEM micrograph of an as-annealed glass. This glass showed no evidence of phase separation. The corresponding electron diffraction pattern showed a diffuse halo, corresponding to an amorphous structure. The TEM micrograph of a specimen which was heated at 10 °C min^{-1} to 828 °C and held for 30 min (Fig. 5), shows a microstructure consisting of two different types of phases: darker islands, ~ 200 nm in diameter, dispersed in a lighter

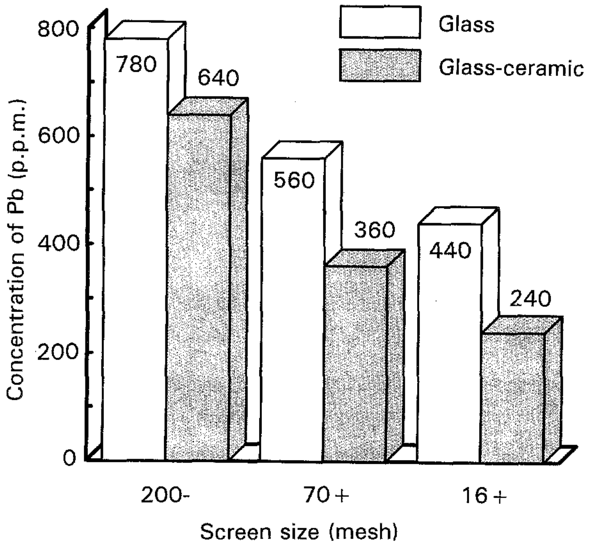

Figure 3 Results from modified toxic constituent leaching procedure of as-quenched and devitrified glasses. □ Glass; ▨ Glass–ceramic.

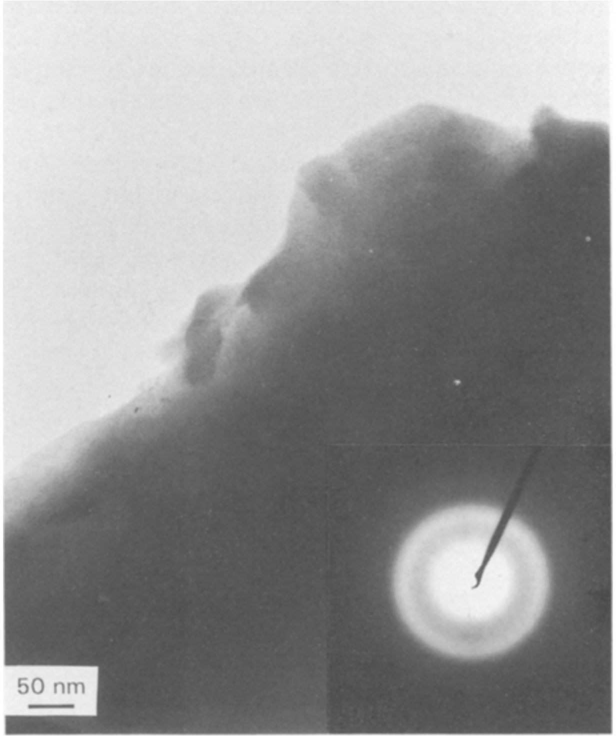

Figure 4 TEM micrograph of as-quenched glass. Inset, selected area diffraction pattern shows that the specimen was amorphous.

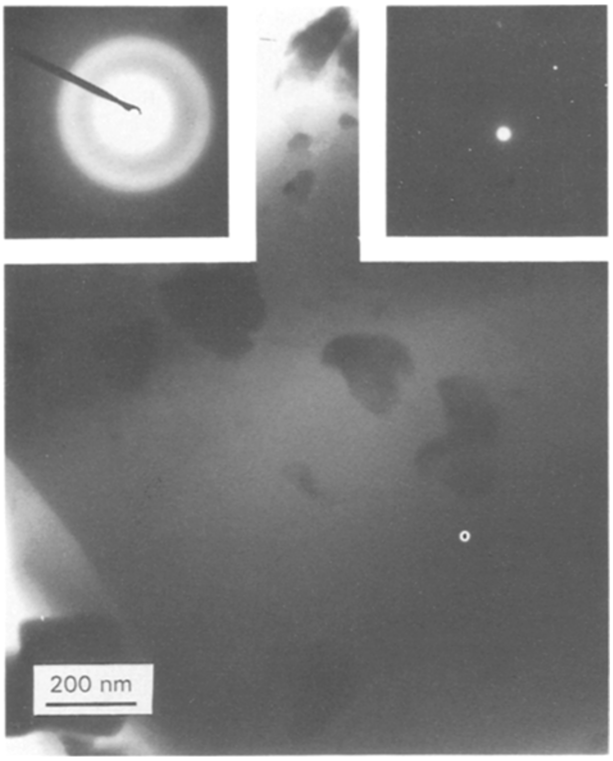

Figure 5 Devitrified glass showing amorphous dark pockets of lead-rich glass surrounded by crystalline matrix. Inset, selected area diffraction patterns of the glassy and crystalline regions are shown in the upper left and the upper right, respectively.

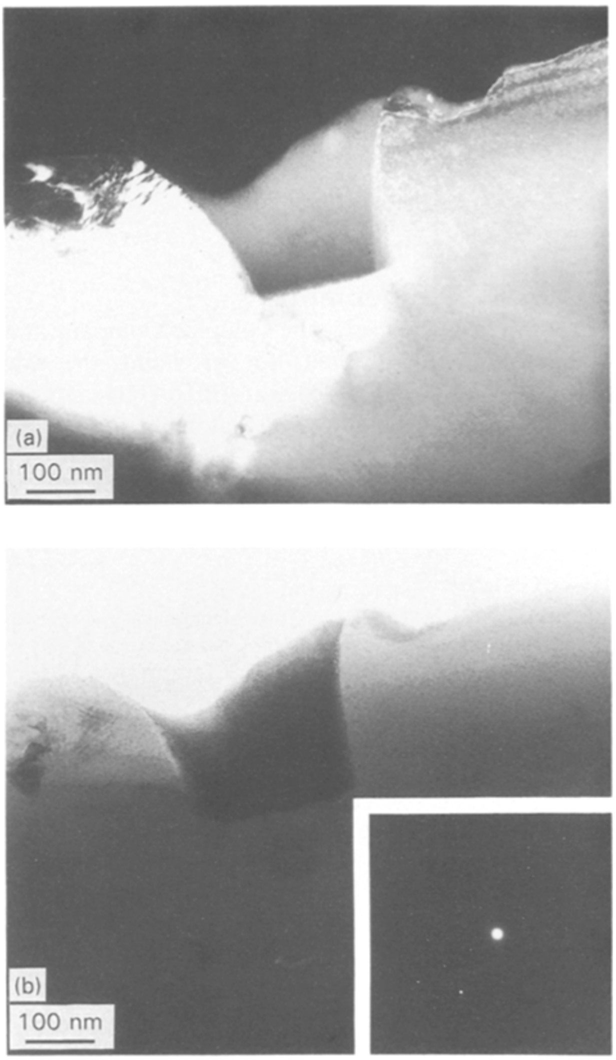

Figure 6 Dark-field (top) and bright-field (bottom) micrographs of devitrified glass. The wedge-shaped region represents an amorphous pocket. Inset, diffraction pattern is from the illuminated region in the dark-field micrograph.

matrix. Selected area electron diffraction of the matrix phase shows a single crystalline pattern, whereas darker pockets show a diffuse halo indicating an amorphous structure. The crystalline nature of the matrix and the glassy nature of pockets is further confirmed by bright- and dark-field imaging shown in Fig. 6. An EDS analysis of annealed glass and a devitrified sample are shown in Fig. 7. The crystalline regions of the devitrified microstructure contain a small amount of lead as compared to the glassy regions. The glassy regions after devitrification were appreciably higher in lead content as compared to the annealed glass.

During devitrification heat treatment, akermanite nucleated and grew, rejecting lead into the surrounding glass until the crystals occupied most of the volume, leaving glassy lead-enriched islands. During extraction, most of the surface exposed to the acidic extraction fluid was a lead-deficient crystalline matrix. The remaining glassy pockets exposed to the surface were thus responsible for most of the lead leached during the extraction process. By contrast, in as-annealed glass, lead was homogeneously distributed in the bulk of glass, and during extraction the whole exposed surface area was prone to leaching, resulting in a higher lead extraction.

The difference in lead extraction between glassy and devitrified samples of coarse particle size was greater, as extraction fluid was less likely to gain access to interior lead-rich amorphous regions. It also follows that for particle sizes greater than those used in this study, improvements in lead extraction resistance in excess of 2 × may be expected.

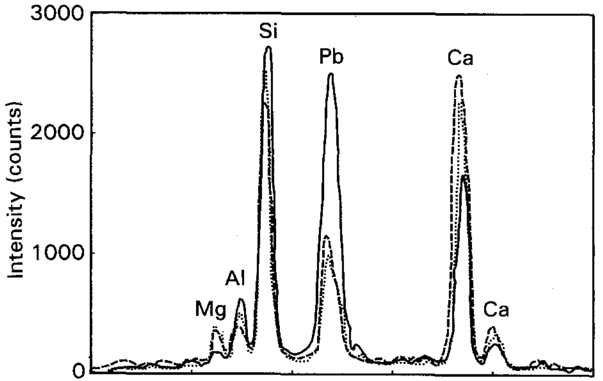

Figure 7 Energy-dispersive spectroscopy of as-annealed glass (- - -); crystalline matrix in the devitrified glass microstructure (· · ·); amorphous pockets in the devitrified glass microstructure (——).

4. Conclusions

The present study demonstrates that an astute formulation of inorganic wastes followed by post-heat treatment will allow for a more environmentally benign waste stream. In the present case, a model waste glass was developed by mixing a refined steel industry slag and a lead-containing compound. The chemical durability of such glass was approximately doubled by controlled crystallization. A favourable microstructure was developed where high-lead glassy islands were shielded from the extraction fluid by a lead-free crystalline matrix.

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