

INCORPORATION OF CHROMIUM (III & VI) OXIDES IN A SIMULATED BASALTIC, INDUSTRIAL WASTE GLASS-CERAMIC

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ABSTRACT

Chromium, an EPA listed toxic element concentrated in many industrial wastes, was stabilized utilizing waste vitrification. Cr_2O_3 and CrO_3 were loaded into a simulated basaltic base composition, vitrified, and cooled at various rates. Chromium incorporation mechanisms, vitrification processability, effect of initial Cr oxidation state, and product performance were investigated. At 1500°C , Cr_2O_3 has a low solubility limit (0.54wt%) in the base composition, and crystallized as Cr-rich primary spinel $(\text{Mg, Fe})(\text{Fe, Al, Cr})_2\text{O}_4$. Upon cooling, Cr-depleted secondary spinel and augite $(\text{Na, Ca})(\text{Mg, Fe}^{2+}, \text{Al})(\text{Si, Al})_2\text{O}_6$ crystallized. Cr(VI) was converted into Cr(III) upon vitrification. The apparent viscosity of the melts was estimated using the Bottinga-Weill model as corrected by Roscoe's equation. The end products showed Cr_2O_3 loading capacities as high as 16.7wt% without exceeding the toxicity-leaching limit defined by EPA. The annealed products had Vicker's hardness of about 800 KgF/mm^2 and can be classified as medium-grade abrasives.

Key words: waste, vitrification, chromium, basaltic.

INTRODUCTION

Waste vitrification can immobilize toxic elements into glasses or glass-ceramics, producing harmless, sometimes recyclable products. Recently, this method has become a useful and affordable technology for producing chemically durable materials from hazardous industrial wastes [1-2].

In 1988, Seiler Pollution Control Systems Inc. developed a successfully commercialized high-temperature vitrification (HTV) technique, using a preheater (800°C), a high temperature vitrification converter ($1700 \sim 2000^\circ\text{C}$), a homogenization reservoir (1500°C), and a pollution control system. Typical waste residence times in the converter were 10-15 minutes and the throughput rate for a commercial system was 500kg/hour.

In support of the Seiler HTV system, bench-scale studies have been conducted. Medium-grade abrasive and roofing granule products were developed from the industrial wastes such as electric arc furnace dust and foundry sand [3]. The product chemical compositions were similar to naturally occurring geological basaltic glasses, which have exceptional resistance against environmental corrosion. The glass-ceramic materials contained, in addition to a glassy phase, spinel and augite crystalline phases, which impart increased hardness and fracture toughness, respectively. Previous research has also investigated the effect of oxygen partial pressure and thermal history on this glass-ceramic system, as well as the chemical durability of the products [4].

Chromium is one of the eight toxic metal elements listed by the Resource Conservation and Recovery Act (RCRA). In particular, the hexavalent chromium is a human carcinogen. Unfortunately, chromium compounds are contained in many common industrial wastes. For example, spent chromium refractory contains up to 60wt% of Cr_2O_3 . Carcinogenic forms of chromium have been found in the $\text{CaO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ refractory systems [5]. Electric arc furnace dusts and electric plating sludge can also contain high levels of hazardous chromium.

The Occupational Safety and Health Act (OSHA), RCRA and the Environmental Protection Agency (EPA) each established certain regulations regarding the toxicity of chromium. But the standard toxicity test required by EPA is the Toxicity Characteristic Leaching Procedures (TCLP) [6]. TCLP utilizes an extraction procedure to simulate the leaching of a solid waste, followed by a determination of the concentrations of hazardous contaminants in the solvent. A chromium leaching greater than 5.0mg/L is considered hazardous.

There are currently some methods available for the treatment of hazardous chrome-bearing wastes, such as chemical reduction process, cementation, and the high-temperature chromium extraction process, but on a nationwide basis, a sufficient treatment capacity is not available [7]. Based on the previous studies, the authors' approach was to stabilize chromium in a simulated basaltic, industrial waste glass-ceramic. The focuses of this research include the chromium incorporation mechanisms, the effects of the initial Cr oxidation state, as well as chemical durability and hardness of the end products.

In addition, the melt viscosity and solid content were investigated because these factors are critical for the processability of a vitrification system. A low viscosity is usually desired because it facilitates mixing and reaction and hence improves the throughput rate. Furthermore, stable long-term operation of the reservoir can be jeopardized by accumulation of solids on the surface or bottom of the melt [2].

EXPERIMENTAL

Chemical compositions

The base composition of the waste glass-ceramic was developed in previous studies in the authors' group [4], utilizing electric arc furnace dust, foundry sand, bauxite waste, and MgO dust as the primary constituents. The vitrified waste products had excellent chemical durability and high hardness, and could be recycled as a medium to high-grade abrasive. The base composition (Table 1) is similar to naturally occurring geological basalt (Table 2) [8], and the components are available in common industrial wastes. In this research, however, industrial wastes were not used in order to minimize compositional variations. Instead, all raw materials were reagent-grade oxides (Na₂CO₃ was used for Na₂O).

Table 1 Formulation of the base composition

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	Total
wt%	40.5	11.5	23.0	11.5	10.0	3.5	100

Table 2 Composition range of natural basalt [8]

	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂
wt%	12.7 ~	5.8 ~	5.5 ~	0.4 ~	3.2 ~	0.1 ~	2.0 ~	0.2 ~	47.1 ~	0.7 ~
range	15.8	10.7	14.1	1.9	10.3	0.2	4.7	1.1	61.3	3.1

Because Cr (III) is usually the most stable oxidation state of chromium in glass [9], in the initial experiments Cr₂O₃ was added into the base composition as the hazardous waste. It is also known that chromium has a low solubility in silicate glasses (<2.0wt% for Cr₂O₃ and even lower for CrO₃[10]). Thus, low Cr₂O₃ (1.0 ~ 2.0wt%) loadings were first explored. Based on the finding that Cr can be incorporated in chemically durable spinel phases, higher Cr₂O₃ loadings (4.8 ~28.6wt%) were investigated. Furthermore, the influence of initial Cr oxidation state was investigated by substituting CrO₃ for Cr₂O₃ in the formulations.

Sample preparation

The sample size of each melt was 10 grams. The oxides were mixed and ground using a mortar and pestle to break down the agglomerates before melting in Al₂O₃ crucibles.

Previous studies [11] indicated that melting at 1500°C for 2 hours resulted in a homogeneous melt with minimal volatilization loss. These processing conditions were also used in this study. The heating rate was 10°C/min.

Different cooling methods were used in this study. Water-quenched samples were removed from the furnace and immediately quenched into water; air-quenched samples were cooled in still air; and furnace-annealed samples were cooled in the furnace. It was difficult to measure the temperature history of the water and air-quench samples. But based on the time required for cooling, the cooling rates of water

and air-quench samples were estimated to be on the order of 10^3 and $10^\circ\text{C}/\text{sec}$, respectively, during the initial several hundred degrees of cooling. The cooling rate of furnace-annealed samples was determined to be approximately $0.4^\circ\text{C}/\text{sec}$ from melt temperature to 800°C . Variation in cooling rate within the samples was observed.

Sample characterization

Crystalline phases were identified using a Scintag PAD-V X-ray powder diffractometer. A Scanning Electron Microscopy (SEM) (Philips XL-30 CP) was used to investigate the material microstructure. Image analysis software Buehler Omnimet 4 (Version 1.5) was used to analyze and calculate the morphological parameters, such as particle average size and phase volume fractions. Energy Dispersive Spectroscopy (EDS) and Wavelength Dispersive Spectroscopy (WDS) were used to determine the chemical compositions of the phases. A Perkin-Elmer Differential Temperature Analysis (DTA) system was utilized to investigate the crystallization temperatures. A Buehler Micromet II Digital Micro Hardness Tester was used to measure the Vicker's hardness of the products, based on 10 random measurements on each sample.

Product chemical durability was measured by the Belmonte Park Environmental Laboratories, Trotwood, OH using TCLP.

RESULTS AND DISCUSSION

Cr(III) solubility in the glass

When the melt viscosity is sufficiently high and the crystallization rate is relatively low, the melt structure can be "frozen in" by rapid cooling. By studying the morphology of the water-quenched samples, information about the molten state was obtained.

Without Cr_2O_3 , the water-quenched sample was completely amorphous. With 1.0 ~ 2.0wt% Cr_2O_3 loadings, equiaxial spinel $(\text{Mg, Fe})(\text{Fe, Al, Cr})_2\text{O}_4$ was found in the water-quenched samples, as shown in Fig. 1. It was found that Cr_2O_3 had a low concentration in the glass phase and a high concentration in the spinel phase (Table 3). The Cr concentration level in the glass phase was consistently 0.54wt% when Cr_2O_3 loading was increased from 1.0wt% to 2.0wt%. In addition, crystal sizes of spinel in the water-quenched samples increased with the melt time, which is most likely the result of coarsening or growth [11]. Thus, it is believed that Cr-rich spinel phase forms in the molten state when the solubility limit (0.54wt%) is exceeded. This spinel is denoted as primary spinel.

It was also found that an increased Cr_2O_3 loading resulted in a higher volume fraction of the primary spinel. As shown in Figure 2, this relationship is nearly linear, with 28vol% spinel at a 16.7wt% Cr_2O_3 loading. In a previous study on the chemical durability of vitrified products with similar compositions, the spinel phase demonstrated superior chemical durability to glass and other crystalline phases [13]. Thus, the formation of a Cr-rich spinel phase is believed to be beneficial for the stabilization of chromium. However, high volume fractions of spinel will alter the compositions of the remaining liquid, which can consequently affect the viscosity of the melt. This will be discussed in later sections.

Table 3 Phase compositions of the 2.0wt% Cr_2O_3 , water-quenched samples

(Weight percentage determined by WDS)

	Na_2O	MgO	Al_2O_3	SiO_2	CaO	Fe_3O_4	Cr_2O_3
Glass	3.34	9.40	13.91	40.42	11.34	21.05	0.53
Spinel	0.01	16.07	9.66	0.52	0.24	47.20	26.30

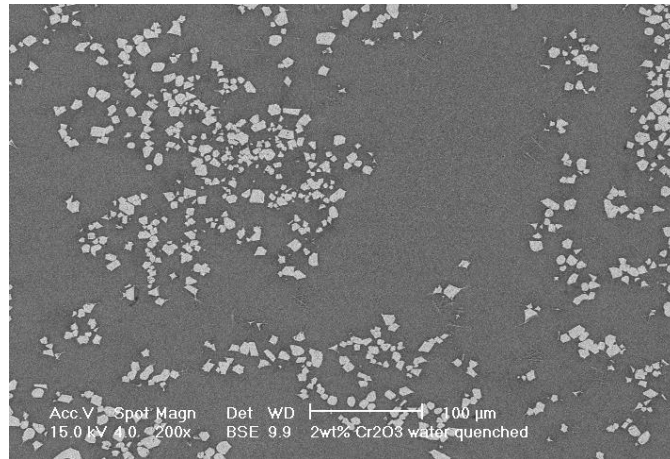


Fig. 1 2.0wt% Cr₂O₃ waste glass-ceramic, water-quenched, SEM, 200X

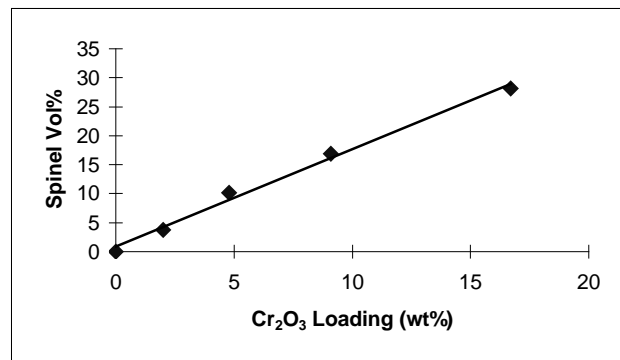


Fig. 2 Primary spinel volume fraction as a function of Cr₂O₃ loading

Crystallization of the glass-ceramic

In air-quenched and furnace-annealed samples, in addition to the primary spinel, another form of spinel (denoted as secondary spinel) and augite (Na,Ca)(Mg,Fe²⁺,Al)(Si,Al)₂O₆ were found, as shown in Figure 3. The secondary spinel and augite were believed to have formed during cooling, since they were absent in the water-quench samples. The primary and secondary spinel differed in chemical composition and morphologies: the former was Cr-rich and equiaxial while the later was Cr-depleted and often dendritic.

Compositions of the primary and secondary spinel are listed in Table 4. The secondary spinel was Fe-rich and Cr-depleted as it crystallized from the Cr-depleted melt. Furthermore, in low-Cr₂O₃ samples, the secondary spinel was usually dendritic (Figure 3). A variety of the dendritic shapes were observed in different areas of the samples due to variations in cooling rate. It was observed that a decreased cooling rate usually resulted in a larger dendrite size with increased arm spacing.

Dendritic secondary spinel was less frequently observed in higher-Cr₂O₃ samples (Figure 4). This was probably due to the greater primary spinel density in these samples. In this case, the secondary spinel tends to grow on the surface of preexisting primary spinel instead of forming dendrites. In fact, equiaxial spinel in Figure 4 often has a Cr-rich core and Cr-depleted exterior, which supports this hypothesis.

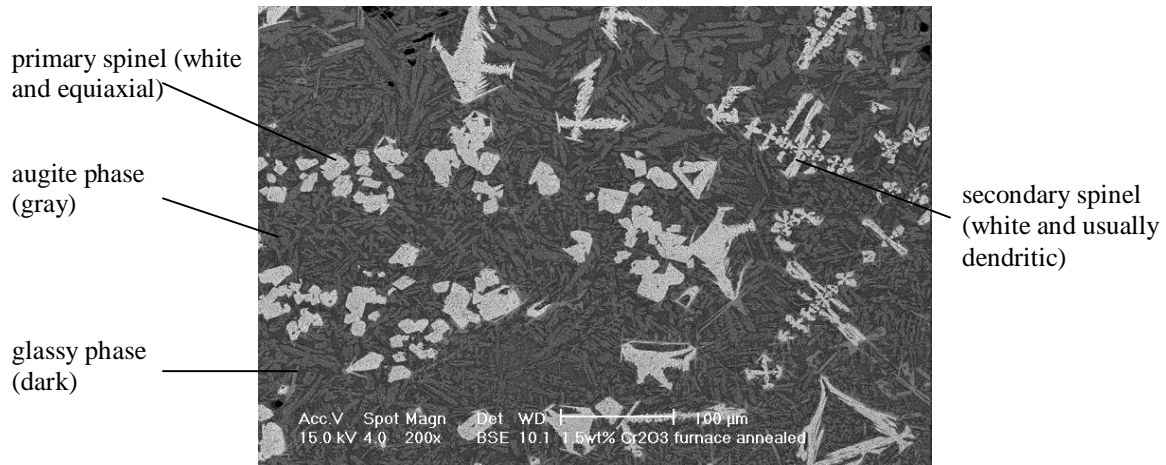


Fig. 3 1.5wt% Cr₂O₃ waste glass-ceramic, furnace-annealed, SEM 200X

Table 4 Phase compositions of 1.5wt% Cr₂O₃, furnace-annealed samples

(Weight percentage determined by EDS)

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	Fe ₃ O ₄	Cr ₂ O ₃
primary spinel	0	15.8	12.7	0	0	44.2	27.4
secondary spinel	0	13.0	11.4	0	0	73.0	2.6
augite	1.3	12.7	11.8	45.1	18.1	11.1	0
glass	7.3	3.4	21.9	53.7	4.8	8.9	0

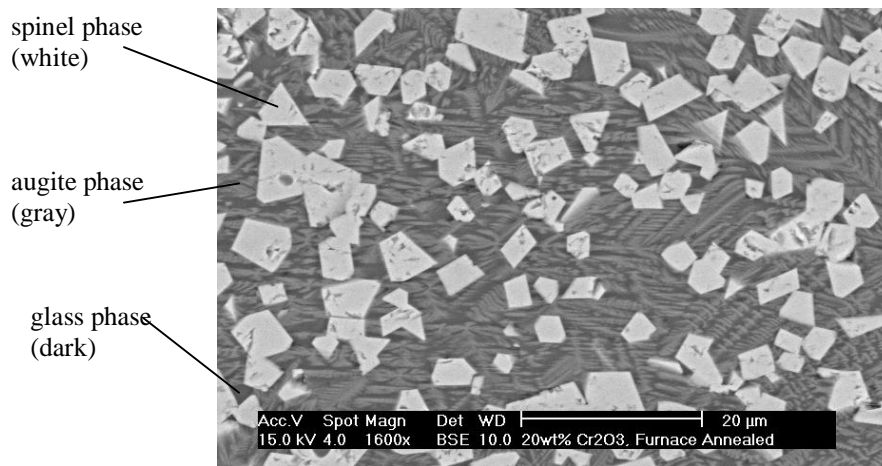


Fig. 4 16.7wt% Cr₂O₃ waste glass-ceramic, furnace-annealed, SEM 1600X

It was somewhat surprising that such high Cr₂O₃ loadings (up to 28.6wt%) were incorporated in the base composition without phase separation or crystallization of Cr₂O₃. X-ray analysis was used to confirm this observation. As shown in Fig. 5, no Cr₂O₃ (corundum structure) peaks were detected. This high volume fraction of spinel was partially attributed to sufficient divalent spinel-forming cations (Mg²⁺ and Fe²⁺) in the melt. It is expected that if the MgO and Fe₂O₃ were removed from the base composition,

Cr₂O₃ rather than Cr-rich spinel would crystallize in the melt. This expectation has been confirmed experimentally by Wang [14].

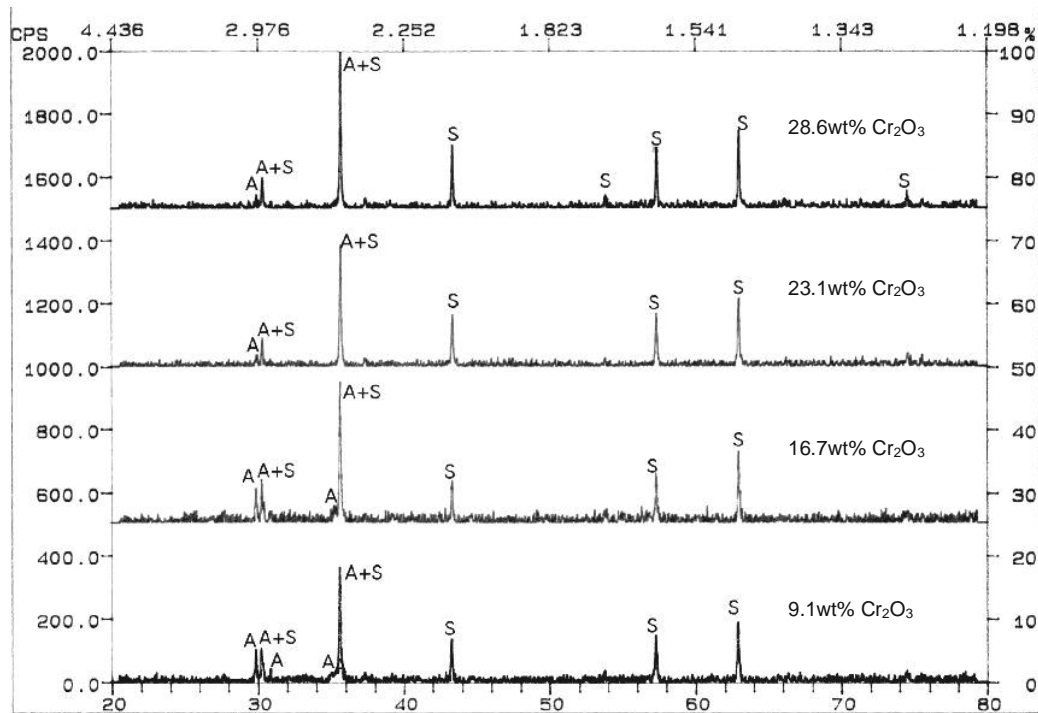


Fig. 5 X-ray diffraction of 9.1 – 28.6wt% Cr₂O₃, furnace-annealed Samples (S: spinel, A: augite)

Melt viscosity

The viscosity of silicate liquids at high temperatures such as 1500°C is difficult to measure. Fortunately, the basaltic magma systems have been well studied by geologists. A viscosity model for magmatic silicate liquid established by Bottinga and Weill (B-W model) [15] was utilized to estimate the melt viscosity of this waste basaltic system:

$$\ln \eta = \sum_i X_i D_i$$

where η is the Newtonian viscosity (in P), X_i is the mole fraction of oxide component i , and D_i is an empirical constant associated with component i over a restricted range of SiO₂ concentrations and temperatures. The D_i constants at 1500°C with SiO₂ molar fraction within 0.35 - 0.65 are listed in Table 5. Due to the dual role of Al₂O₃ in silicate liquid structure, Al₂O₃ was combined with other metal oxides in the order of K₂O, Na₂O, CaO, and MgO until all Al₂O₃ was depleted.

Table 5 The D_i constants for viscosity calculation [14]

Component	SiO ₂ molar fraction 0.35-0.45	SiO ₂ molar fraction 0.45-0.55	SiO ₂ molar fraction 0.55-0.65
SiO ₂	3.67	6.00	7.97
FeO or ½ Fe ₂ O ₃	-4.02	-5.39	-4.58
MgO	-1.23	-2.32	-3.93
CaO	-1.17	-2.88	-5.52
Na ₂ O	-5.11	-6.11	-7.79
NaAlO ₂	/	7.58	6.54
CaAlO ₂	4.01	0.73	-1.64
MgAl ₂ O ₄	/	2.41	-3.83

This model gave reasonable estimates of the viscosity of a number of natural magmatic and molten rock compositions, including the basaltic system with Si₂O content 45-65wt% at 1300~1500°C. Comparisons of calculated viscosities with the published data over a viscosity range from 1 to 10⁶ P exhibited errors in 77% of the total comparisons between $-0.25 < \Delta \ln \eta < 0.25$, and 99% between $-0.75 < \Delta \ln \eta < 0.75$.

If solid particles are contained in the melt, the melt becomes non-Newtonian and the apparent viscosity increases appreciably. Roscoe's equation [15] was used to estimate the apparent viscosity of the solid-liquid suspension:

$$\eta_e = \eta (1 - 1.35 \phi)^{-2.5} \quad (\phi < 30\text{vol}\%)$$

(η_e : effective viscosity; η : liquid viscosity; ϕ : solid volume fraction)

The apparent viscosity of the melt shown in Figure 6 was calculated using the B-W model as corrected by Roscoe's equation. The dramatic increase in apparent viscosity with increased Cr₂O₃ loading was the result of an increased volume fraction of primary spinel accompanied with the depletion in the liquid phase of trivalent and divalent cations (Table 5). For example, a 4.8wt% Cr₂O₃ loading increased the apparent melt viscosity by 0.29P, which consists of a 0.08P due to chemical compositional change in the liquid phase with an additional 0.21P the result of increased solid content. Because of this rapid increase in melt viscosity, the processability of such melts will be sensitive to Cr₂O₃ loading.

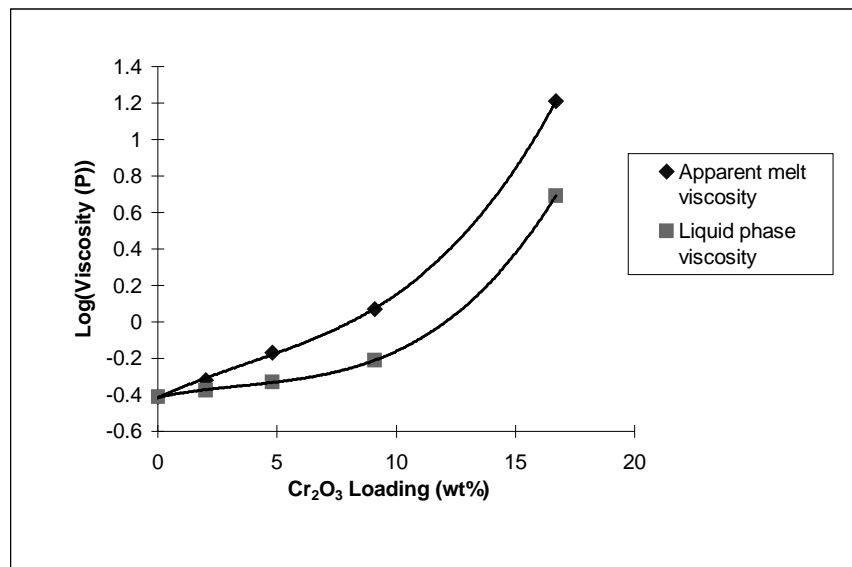


Fig. 6 Viscosity estimated using Bottinga-Weill model and Roscoe's equation (1500°C)

Table 5. Glass phase compositions of the water-quenched samples

(Mole percentage determined by EDS)

Cr ₂ O ₃ loading (wt%)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	Fe ₃ O ₄
0.0	4.0	17.8	8.0	48.3	14.7	7.1
2.0	4.1	17.4	6.6	50.0	15.2	6.8
4.8	4.3	17.3	5.2	51.1	15.9	6.1
9.1	4.7	15.1	5.2	52.8	16.9	5.4
16.7	5.4	5.7	9.5	59.0	17.6	2.8

The estimated melt viscosity was used in Stoke's equation to calculate the settling velocity of the solid particles:

$$u = [(\rho_p - \rho_l) g D]^2 / (18 \eta)$$

(u : settling velocity of the particles; ρ_p : density of the particle; ρ_l : density of the liquid phase; g : gravity constant; D : diameter of the particles; η : viscosity of the liquid.)

The calculation predicted a settling velocity of a 10 μm diameter primary spinel particle on the order of 1mm/h. This result was consistent with experimental observations, where the upper portion of the crucible usually contained little or no spinel, but the lower portion contained a significantly higher concentration of spinel [11]. This settling velocity may not cause serious problem if the resident time in the reservoir is short; however, agglomerates of solid particles would have greater settling velocities, which may be problematic.

Influence of Cr initial oxidation state

For samples formulated with CrO₃, no Cr(VI) but Cr(III) was found in the resultant glass-ceramic upon vitrification. This result is consistent with other observations [8] that Cr(VI) was generally unstable in silicate melts, and could be retained only in rather basic glass. Furthermore, higher melting temperatures and longer melting times both promote the reduction of Cr(VI).

However the microstructure of Cr(VI)-loaded and Cr(III)-loaded samples were somewhat different. Micrographs (Fig. 7) showed that Cr(VI) loading inhibits the formation of augite. Moreover, X-ray analysis revealed higher volume fractions of spinel in Cr(VI)-loaded samples than in corresponding Cr(III)-loaded samples. This was attributed to the oxidative effect of Cr(VI) oxidizing some Fe(II) to Fe(III). With increasing Fe(III) content, additional spinel formed since there were sufficient divalent spinel-forming cations in the melt. This reaction might also result in a residual liquid phase that inhibited the formation of augite. This observation is consistent with a previous study in a similar system [17], and the observations on geological magma [8].

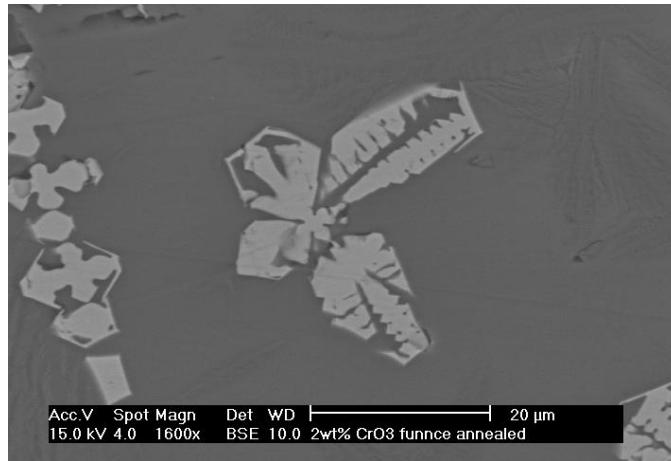


Fig. 7 2.0wt% CrO₃ waste glass-ceramic, furnace-annealed, SEM 1600X

The estimated apparent viscosity of CrO₃-loaded melt was slightly greater than the Cr₂O₃-loaded melts with the same Cr mole fraction, as a result of a larger volume fraction of spinel and greater glass viscosity.

Product performance

1. Chemical durability

The resultant glass-ceramic exhibited excellent Cr leaching resistance in the TCLP tests, as listed in Table 4. The overall Cr extractions of the products were all far below the EPA total Cr leaching regulatory limit of 5mg/L. Table 4 also shows that the Cr leaching increased almost linearly with Cr₂O₃ loading, which implies that the Cr leaching mode did not change as Cr₂O₃ loading increased. Furthermore, the initial Cr oxidation state did not show significant influence on the overall chemical durability of the products.

Table 4 End product TCLP Cr extraction

Loading	TCLP Total Cr extraction (mg/L)
2.0wt% Cr ₂ O ₃	<0.01
4.8wt% Cr ₂ O ₃	0.01
9.1wt% Cr ₂ O ₃	0.03
16.7wt% Cr ₂ O ₃	0.05
6.2wt% CrO ₃ (Equivalent Cr content as 4.8wt% Cr ₂ O ₃)	<0.01

2. Hardness

The Vicker's hardness varied throughout the tested area as a function of the phase indented. Thus, an average of 10 random measurements were used to determine the hardness of a sample. The hardness increased with Cr₂O₃ loading (Figure 8), due to increased content of spinel with greater hardness. The furnace-annealed samples were 200 kgF/mm² harder than the corresponding water-quenched samples due to the crystallization of augite and secondary spinel. The furnace-annealed samples (~800 kgF/mm²) have hardness comparable to medium-grade abrasives.

Thermal analysis of the water-quenched samples revealed an exothermic peak at 826°C, which was associated with augite crystallization. Heat treatment at 826°C was conducted on the water-quenched

samples. The hardness as a function of heat treatment time was then determined (Figure 9). The maximum hardness was obtained at 0.5 h of heat treatment.

The Cr initial oxidation state had little influence on the hardness of water-quenched samples. But for furnace-annealed samples, the CrO_3 samples had hardness value 70 KgF/mm^2 lower than the Cr_2O_3 samples, which was probably due to the absence of augite.

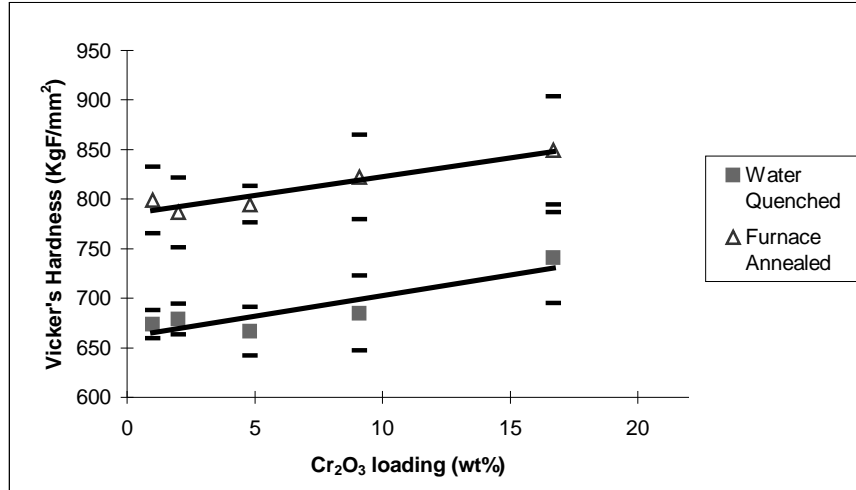


Fig. 8 Hardness of water-quenched and furnace-annealed samples with various Cr_2O_3 loading

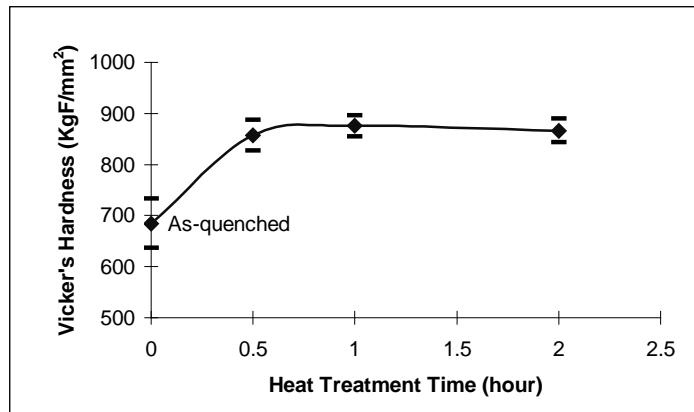


Fig. 9 Hardness as a function of heat treatment time at 825°C ($9.1\text{wt}\%$ Cr_2O_3 loading)

CONCLUSIONS

A simulated basaltic formulation was used to stabilize chromium wastes. Up to $16.7\text{wt}\%$ Cr_2O_3 was incorporated in the base composition obtaining acceptable chemical durability and hardness to be used as a medium-grade abrasive.

In the melt at 1500°C , Cr_2O_3 exceeded a low solubility limit ($\sim 0.54\text{wt}\%$) and crystallized as Cr-rich spinel $(\text{Mg, Fe})(\text{Fe, Al, Cr})_2\text{O}_4$ (primary spinel), whose volume fraction increased with Cr_2O_3 loading. A Bottinga-Weill model estimated that the melt viscosity increased ($0.5 - 16 \text{ Pa}\cdot\text{s}$) with Cr_2O_3 loading (2.0

– 16.7wt%). Upon cooling, Cr-depleted secondary spinel and augite (Na,Ca)(Mg,Fe²⁺,Al)(Si,Al)₂O₆ crystallized.

Cr(VI) was converted into Cr(III) upon vitrification at 1500°C. It was found that increased CrO₃ loading promoted the formation of spinel, but inhibited the crystallization of augite.

The TCLP Cr leaching of the resultant products were all on the order of 0.01mg/L, far below the EPA regulatory limit of 5mg/L. The hardnesses of the water-quenched and the furnace-annealed samples were about 600 and 800 KgF/mm², respectively.

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