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Glass Composition Development for Stabilization of New York Harbor Sediment (U)

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Glass Composition Development for Stabilization of New York Harbor Sediment - (U)

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APPROVALS

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Glass Composition Development for Stabilization of New York Harbor Sediment - (U)

Summary

Sediment from the New York Harbor must be periodically dredged in order to maintain adequate water depths for navigation. In the past, disposal of the sediment in the ocean was routinely used for discarding the material. Recently, the sediment was found to contain organics and heavy metals which may prevent direct ocean disposal. Methods are currently being evaluated for decontamination and disposal of the sediment. Vitrification is a technology being investigated by the Westinghouse Science and Technology Center (W-STC) for treatment of the sludge. As part of this effort, Westinghouse Savannah River Company (WSRC) - Savannah River Technology Center (SRTC) was tasked with the development of appropriate glass formulations for stabilization of the sediment.

Crucible melting tests were used to identify an "optimized" glass composition for stabilization of the harbor sediment. Criteria to assess the suitability of the glass compositions included: waste loading, homogeneity, raw material cost and melt viscosity. A glass composition satisfying these criteria was developed with a sediment waste loading of 85 wt % (on a calcined waste basis). This was achieved by adding 10 wt % CaO and 5 wt % Na_2O to the dried, calcined sediment. The resulting composition could be melted at 1350° C and produced an acceptable vitreous waste form.

Introduction

Sediment from the New York Harbor must be periodically dredged to maintain navigable water depths for shipping channels. Disposal of the sediment in the ocean was the primary disposal alternative for the material. It was recently discovered that the sediment may contain contaminants such as organic compounds (e.g. dioxins) and heavy metals both at high enough concentrations to disallow direct ocean disposal. The recently revised guidance for dredged sediment disposal, *Guidance for Performing Tests on Dredged Material Proposed for Ocean Disposal* (Draft December 1992), established more restrictive biological and chemical test criteria. This will likely result in an even greater volume of dredged sludge requiring treatment prior to disposal.

Sediment decontamination technologies are being investigated jointly by the Environmental Protection Agency (EPA) and the Army Corps of Engineers. In 1992, authorization was granted by these two agencies to examine and demonstrate technologies to treat the sediment in an environmentally acceptable and cost effective manner. A request for proposal was issued in January 1995 to solicit technologies for harbor sediment decontamination [1]. The initial phase called for bench-scale demonstration of treatment options. Effective bench-scale treatment technologies would be considered for follow-on pilot-scale testing.

Westinghouse Science and Technology Center was awarded a contract for bench-scale testing. The tasks in the bench-scale test program were broken down into two efforts. The first involved pretreatment of dredged material based on Westinghouse's experience in soil washing. This was later determined not to be an applicable technology due to the physical characteristics of the sediment. The second effort involved bench-scale vitrification testing of sediment samples either as-dredged or pre-treated. This initial vitrification trial was aimed at obtaining follow-on support for pilot-scale testing in the Westinghouse Plasma Vitrification System at the Waltz Mill facility. WSRC-SRTC was contracted by W-STC to assist in the bench-scale vitrification testing. The scope of work performed by SRTC included: bench-scale glass formulation testing; characterization of candidate glasses; and assistance in the assessment of the treated product for application as a construction material.

The objective of the SRTC experimental program was to determine an "optimal" glass composition to effectively stabilize the harbor sediment. Criteria to assess the suitability of the glass compositions included: waste loading; additive raw material cost; glass homogeneity; and melt viscosity.. An ideal glass was thought to have a high waste loading, low additive material cost, good homogeneity, and an acceptable viscosity to facilitate processing. Since a plasma vitrification system was designated for production treatment of the sediment, higher temperature glass compositions were examined. A nominal melting temperature of 1350° C was targeted in the crucible tests. This temperature was thought to be high enough to facilitate increased waste loading yet not cause excessive volatilization in the melt. This melt temperature is also readily achievable in the Westinghouse plasma vitrification system.

Glass Formulation Optimization Criteria

Waste Loading: In order for vitrification to be a viable option for treatment of the harbor sludge, processing costs must be minimized. The most effective way to achieve this is to maximize the waste loading in the glass. In this study a premium was placed on waste loading since cost effective processing appeared to be the most significant process parameter. High waste loading must be achieved carefully, however, since excessive loading can interfere with glass processing (e.g. increased viscosity and devitrification) and/or the stability of the final product.

Raw Material Cost: Identifying low cost additives for waste glass formulations is also a valuable way to minimize processing costs. The chemical analysis of the waste indicated that the sediment was primarily composed of silicon and aluminum which can both be characterized as network formers in a glass structure [2]. Fluxing agents would, therefore, need to be added to the harbor sediment to form an adequate glass. Limestone and soda ash were considered the best low cost fluxing agents for this application. Limestone and soda ash introduce, calcium and sodium, respectively, into the glass compositions. Calcium and sodium are considered network modifiers in a glass structure [2]. Network modifiers "loosen" the structure of a glass by creating non-bridging oxygen (NBO) atoms and consequently lower the melting temperature and viscosity of the glass. Sodium (as well as other alkalis) is a "better" network modifier than calcium (and other alkaline earth elements). The rough cost of these materials is $0.01/lb for limestone and $0.06/lb for soda ash. Many other additives are typically added to waste glass formulations to enhance processability and product quality. These include: boron, lithium, iron, magnesium, potassium, and zirconium. The relatively high cost of these additives prohibited their use in these glass formulations.

Homogeneity: Inhomogeneities in a glass melt may cause processing problems and result in a poor glass product. The presence of secondary crystalline phases in a melt can increase viscosity and hinder discharging of the glass from the melter. In extreme cases, crystallization can cause the complete blockage of the melter pour spout or a build-up of crystalline slag on the bottom of the melter. Glass durability can also be decreased by the presence of secondary phases in the glass, since local off-composition areas can have leach rates orders of magnitude higher than the bulk glass. It was a goal of this study to produce homogeneous vitreous waste forms. Since a premium was placed on cost effectiveness minor heterogeneities could be tolerated if they would not interfere with glass processing or the stability of the final product.

Viscosity: The viscosity of a glass melt is an important parameter for effective processing. Extremely low viscosities can lead to excessive melt volatility and corrosion, while very high viscosities can hinder melt homogenization and pouring. Typically, viscosities less than 20 poise and higher than 200 poise are considered unacceptable. In the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS), a viscosity range of between 20 and 100 poise has been specified. In this study, viscosities were estimated for the various glass formulations using several viscosity models. The first model was developed for SRS high-level waste (HLW) glasses and is based on glass structure [3]. This model was developed specifically for HLW borosilicate glasses so the applicability to other glass systems is uncertain. A second generation viscosity model, stemming from the HLW model, was recently developed to better predict viscosities for other waste glass systems [4]. In particular, this model targeted high alkaline earth glass compositions. A final viscosity model, developed from geologic data, was also utilized to estimate the viscosities of the various compositions [5]. As an actual test for melt viscosity, glass pouring behavior upon removal from the furnace was qualitatively assessed.

Experimental Procedure

Compositions for testing were determined using a batch formulation spreadsheet. The spreadsheet calculations were compared to known glass forming regions in the R_2O-CaO-SiO_2 glass system as an initial screening process [6]. Due to the desire to maximize waste loading, some compositions slightly outside the known glass forming region were not initially rejected. The glasses were denoted by their flux additive concentrations. For example, a glass designated 10% CaO/5% Na_2O consisted of 85 wt % harbor sludge (85% waste loading*) with flux additives of 10 wt % CaO and 5 wt % Na_2O. Individual glasses were prepared by mixing reagent grade chemicals and New York Harbor sediment supplied by W-STC according to the spreadsheet calculations. Prior to batching, the sediment was calcined at 700° C for 2 hours in a muffle furnace located in a chemical hood to remove the majority of the organic species. Sodium and calcium were added to the batches as carbonates in concentrations to achieve the desired oxide content in the final glass. The batches were melted at 1350° C for 4 hours in uncovered alumina crucibles and allowed to air cool in the crucibles. The chemical analysis data indicated that a batching error had occurred for one of the glasses. This glass, designated 10% CaO/5% Na_2O #1, had an actual flux addition of 5.8 wt % CaO and 12.7 wt % Na_2O. The targeted composition was later correctly batched and designated as 10% CaO/5% Na_2O #2. A number of the glasses were later remelted at 1350° C in platinum crucibles and poured at temperature into a water bath. Qualitative observations regarding the pouring behavior and the quenching behavior of the glasses were made during this testing.

The glasses prepared in the crucible tests were characterized using the following analytical techniques. A glass sample from scale-up melt tests at Ferro, Inc. was also analyzed using several of these techniques.

X-ray diffraction (XRD) scans were performed on all the glasses in an attempt to identify any crystalline species which may have formed in the melts. A representative sample from each glass melt was ground to -200 mesh and submitted for analysis. The crystallinity detection limit for the technique utilized is 1 volume percent.

The chemical composition of several candidate glasses was determined by chemical digestion followed by various spectroscopic techniques. Two chemical dissolution methods were employed: Na_2O_2/HCl fusion/dissolution and microwave dissolution. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was utilized for the majority of the cation analysis. Atomic absorption spectroscopy (AA) was performed on the microwave dissolved samples for detection of potassium and as a check for sodium concentrations. The resulting elemental concentrations were multiplied by the appropriate oxide gravimetric factors to give the final oxide concentrations in the glasses.

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* Waste loading was determined using the weight of the calcined sludge.

Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) was performed on three of the most promising glasses. Identification of heterogeneities in the glasses was emphasized in this analysis.

The density of two glass compositions was determined using a buoyancy method. The testing was performed in accordance with ASTM C 693 [7].

Results and Discussion of Crucible Study Glasses

Visual Examination of the Glasses

Initially six glass compositions were prepared with varying additive concentrations and waste loadings. These initial glasses had the following flux additions: 10 wt % CaO flux addition (90% waste loading); 10 wt % Na_2O flux addition (90% waste loading); 5 wt % CaO/5 wt % Na_2O (90% waste loading); 15 wt % CaO (85% waste loading); 15 wt % Na_2O (85% waste loading); and 7.5 wt % CaO/7.5 wt % Na_2O (85% waste loading). The glasses were broken out of the crucibles and general observations regarding the homogeneity of the glasses were made. The 10 wt % flux addition glasses (90 wt % waste loading) were generally inhomogeneous with noticeable amounts of crystalline phases or undissolved material present throughout the samples. The glasses with 15 wt % Na_2O and with 7.5 wt % CaO and 7.5 wt % Na_2O appeared to produce homogeneous glasses. The 15 wt % CaO glass had a significant amount of crystalline material or undissolved batch in a layer on the surface of the melt. These observations were consistent with predicted results from the R_2O-CaO-SiO_2 ternary diagram [6]. The normalized compositions of the 10 wt % flux glasses as well as the 15 wt % calcia glass lie outside the known glass forming region for the R_2O-CaO-SiO_2 system [6]. At this point it was apparent that an 85 wt % waste loading (on a calcined basis) could be achieved using flux additions of CaO and Na_2O. Maximizing the CaO/Na_2O ratio in the glasses was the focus of the next efforts. As was pointed out previously, the rough raw material costs for sources of CaO and Na_2O in a glass are approximately $0.01/lb and $0.06/lb, respectively. Therefore, maximizing the CaO/Na_2O additive ratio would result in a significant cost savings in a commercial process.

Two additional glasses were prepared with the following flux additions: 10 wt % CaO/ 5 wt % Na_2O and 12 wt % CaO/3 wt % Na_2O. The composition with 10 wt % CaO and 5 wt % Na_2O (designated 10% CaO/5% Na_2O #1) produced a homogeneous glass with a yellow surface film on the top of the glass. As was previously mentioned, this batch was determined to be misbatched resulting in a composition with approximately 5.8 wt % CaO and 12.7 wt % Na_2O flux additions. When this was realized, this composition was rebatched correctly and designated 10% CaO/5% Na_2O #2. The rebatched glass was generally homogenous with only a minor surface layer containing what appeared to be crystalline or undissolved material. The 12% CaO/3 % Na_2O formulation had considerable amounts of secondary phases present and was deemed unacceptable.

X-ray Diffraction

The nine glasses were ground to -200 mesh and submitted for x-ray diffraction analysis. In cases where a discreet surface layer was present, both the surface layer and base glass were submitted for analysis. The XRD results are listed in Table I. The predominant crystalline phases identified in the samples were quartz and cristobalite. Quartz and cristobalite have the same chemical composition, SiO_2, but have different crystalline structures. These can both be naturally occurring minerals, however, quartz is the more common naturally occurring phase. The cristobalite is likely present due to partial conversion of the quartz during the melting process. In any event, the presence of crystalline SiO_2 indicates a lack of dissolution of the sediment during the melting process. Various other phases were detected in minor concentrations in the XRD scans (Table I).

Following discussions with the W-STC customer, the surface of the 10% CaO sample was also examined by XRD. A metallic-like layer was observed on the surface of the melt in the "large-scale" melt test using the 10% CaO/5 % Na_2O composition at Ferro, Inc. This was similar to that observed in the 10% CaO crucible test, so analysis of the surface layer from this sample was thought to provide insight into the observations from the testing at Ferro, Inc. The XRD scan indicated a significant amount of iron oxide or magnetite was present in the surface layer. This result was later confirmed by observation of magnetic behavior in the sample when brought near a cobalt/samarium magnet.

Viscosity Calculations and Pouring Analysis

Significant variation was observed in the predicted glass viscosities using the various algorithms (Table II). The model developed by Jantzen was specifically designed for SRS high level waste glasses [3]. These glasses have very low alkaline earth concentrations so the applicability to glasses with high alkaline earth concentrations is in question. The model developed by Kielpinski was an augmentation of the Jantzen model with an emphasis on glasses with higher alkaline earth concentrations. This model was, therefore, expected to be a better predictor of the viscosity for the glasses in this study. The model based on geologic data in all but one case predicted the highest viscosities.

All glasses could be poured from the crucibles at 1350° C. As expected, glasses with increased flux additions (i.e. the 85 wt % waste loading glasses) poured more freely from the crucibles. The glasses generally fragmented into small pieces upon quenching in the water bath. In some cases, solidified fibers or cylindrical ribbons were formed during the quench tests. In the 10% CaO/5% Na_2O #2 quench test, a solidified ribbon about 12 inches long was formed. The diameter of the glass necked down from approximately 8 mm to 1 mm over the length of the ribbon.

Density of Glasses by Buoyancy

The results of the previous analyses indicated that the 10% CaO/5% Na_2O and the 7.5% CaO/7.5% Na_2O were the most promising glass compositions. These two compositions were the focus of further analyses including: density; scanning electron microscopy; and chemical analysis. The density of these two glass compositions was determined in accordance with the buoyancy method described in ASTM C 693. The results were as follows:

10% CaO/5% Na_2O #2: $\rho = 2.60$ g/cc
7.5% CaO/7.5% Na_2O: $\rho = 2.61$ g/cc

Scanning Electron Microscopy/Energy Dispersive Spectroscopy

Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy was performed on three samples to locate and identify any heterogenities which may have formed during the melting process. Two areas from the 10% CaO/5% Na_2O #2 melt were analyzed. These areas included the surface layer which appeared to contain a small amount of crystalline species and a small (≈5 mm in diameter) pellet which was retrieved from the bottom of the crucible. Following discussions with the W-STC customer, the surface of the 10% CaO sample was also examined in an effort to gain insight into the observations during the testing at Ferro, Inc. The results of the analyses of these samples are summarized below.

10% CaO/5% Na_2O #2 (surface): The surface of this glass was selectively analyzed to examine for the presence of undissolved silica and other heterogeneities observed in the top layer (≈5 mm) of the solidified melt. The surface was primarily glassy in appearance. EDS scans of large areas of the surface showed the presence of silicon, oxygen, aluminum, calcium, iron, potassium, sodium and magnesium. Although the XRD scans indicated the presence of quartz and cristobalite, no discreet SiO_2 inclusions were detected. In a few isolated areas, there were some hexagonal platelets with small (≈2 μm) equiaxed inclusions (Figure 1). The EDS spectra of these areas indicated that the platelets were primarily iron and oxygen with minor amounts of chromium, nickel and magnesium, while the inclusions or grains on the platelets were primarily iron and oxygen with minor amounts of magnesium and nickel (Figure 1).

10% CaO/5% Na_2O #2 (pellet): SEM/EDS analysis of the pellet indicated it was primarily comprised of iron and sulfur indicating a reduced iron sulfide phase was formed (Figure 2). A smaller volume of glassy material was dispersed within the iron sulfide pellet (dark area in Figure 2). The reducing conditions, indicative of this crucible melt, would not likely occur in a plasma torch using air as the source gas.

10% CaO (surface): The surface layer in this sample was a complicated assemblage of glassy, crystalline and perhaps even metallic phases (Figures 3-6). The low magnification micrograph in Figure 3 illustrates the variations seen in the surface layer and pinpoints regions which were analyzed in more detail. The area displayed in Figure 4 appeared to be primarily glassy. However, scattered throughout the area were small spherical inclusions which were rich in copper. The reduced nature of the melt likely caused the precipitation of these small particles. Three different phases were observed in the area shown in Figure 5. The small spherical inclusions (apparently iron sulfides or phosphides) located near the center of the micrograph were the most unique features of this area. Again the reducing conditions in the melt likely caused these particles to form. The area displayed in Figure 6 may be the magnetite phase (with some atomic substitution) identified in the XRD scan for this sample.

Chemical Analysis

Three glasses from the crucible studies were digested and the chemical compositions determined. Once the results were obtained from the 10% CaO/5% Na_2O #1 sample it was realized that a batching error was made. The glass was re-batched (10% CaO/5% Na_2O #2) and subsequently submitted for chemical analysis. The analyzed compositions and the "predicted" compositions are listed in Table III and Table IV. The predicted compositions are normalized calculations based on the flux additive concentrations and the major components of the chemical analysis of the sediment provided by W-STC. In general, the analyzed compositions agreed well with the predicted compositions.

Analytical Results of Glass Prepared at Ferro, Inc.

The glass composition with 10 wt % CaO and 5 wt % Na_2O flux additions was determined to be the best candidate for large-scale batch testing at Ferro, Inc. A total of 10 kg of glass was produced at Ferro during this phase of the program. A sample of the glass produced at Ferro was sent to SRTC for XRD and chemical analysis.

X-ray Diffraction

An XRD scan was performed on a representative sample of the material from the testing performed at Ferro, Inc. The results indicated that only a minor amount of quartz and cristobalite was present in the glass. The presence of the quartz and cristobalite is again likely due to incomplete dissolution of the sediment into the glassy matrix.

Chemical Analysis

A representative glass sample from the testing at Ferro, Inc. was digested and the chemical composition determined. The analyzed concentrations and the "predicted" compositions are listed in Table V. The chemical compositions closely matched the predicted compositions. The elevated iron concentrations were likely caused by the specimen preparation technique utilized. Prior to submission for dissolution, the glass is ground to -200 mesh in a stainless steel lined grinder. The elevated iron levels (as well as chromium and nickel) were likely due to minor stainless steel contamination in the submitted sample.

Conclusions

New York Harbor sediment was successfully incorporated into glass with a waste loading of 85% (on a calcined waste basis). Lime and soda ash (introducing CaO and Na_2O into the compositions, respectively) were determined to be the most cost effective flux additives. The ratio of CaO/Na_2O in the flux additions was found to be an important parameter in producing a satisfactory glass product. A glass with 7.5 wt % CaO and 7.5 wt % Na_2O flux additions formed an entirely vitreous product. A glass with 10 wt % CaO and 5 wt % Na_2O flux addition represented the maximum CaO/Na_2O ratio where a satisfactory glass could still be produced. This glass was primarily vitreous with only minor amounts of crystalline material in a surface layer on the glass. The relative minor heterogeneity in this glass would not likely affect processing or the final stability of the waste form. This composition was deemed the most appropriate from this study for the vitrification of New York Harbor Sediment in the Westinghouse plasma melter.

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Table I. XRD Results From New York Harbor Sediment Glasses

Sample	Analysis Results
10% CaO	Cristobalite and quartz detected
10% Na_2O	Amorphous; Sodium iron oxide questionable
5% CaO/5% Na_2O	Cristobalite, quartz and sodium chloride detected; Iron sulfate questionable
15% CaO (base)	Amorphous
15% CaO (surface)	Cristobalite and quartz detected
15% Na_2O	Amorphous; Iron aluminum silicate hydroxide questionable
7.5% CaO/7.5% Na_2O	Amorphous
10% CaO/5% Na_2O #1* (base)	Amorphous
10% CaO/5% Na_2O #1* (surface)	Sodium sulfate (not pure) detected
12% CaO/3% Na_2O (base)	Amorphous
12% CaO/3% Na_2O (surface)	Cristobalite and quartz detected
10% CaO/5% Na_2O #2 (base)	Amorphous
10% CaO/5% Na_2O #2 (surface)	Cristobalite and quartz detected
"Metallic Film" on 10% CaO	Iron oxide (magnetite) detected

* This glass was inadvertently misbatched and had an actual flux addition of 5.8% CaO and 12.7% Na_2O

Table II. Viscosity Calculations for New York Harbor Sediment Glasses

	Predicted Viscosity at 1350° C (Poise)		
Sample	Jantzen [3]	Kielpinski [4]	Ghiorso [5]
10% CaO	59.7	638.4	1479.1
10% Na_2O	69.3	421.1	354.8
5% CaO/5% Na_2O	64.3	2037.7	758.6
15% CaO	23.6	112.5	436.5
15% Na_2O	30.0	69.1	81.3
7.5% CaO/7.5% Na_2O	26.6	79.6	204.2
12% CaO/3% Na_2O	25.6	97.7	331.1
10% CaO/5% Na_2O	24.8	89.0	269.2

Table III. Analyzed and Predicted Chemical Composition for NY Harbor Glasses (HCl/Na_2O_2 Dissolution)

	10% CaO/5% Na_2O #2		10% CaO/5% Na_2O #1		7.5% CaO/7.5% Na_2O	
Cation	Analyzed	Predicted	Analyzed	Predicted	Analyzed	Predicted
SiO_2	53.4	55.6	55.2	55.6	53.3	55.5
Al_2O_3	11.9	11.2	10.6	11.2	10.8	11.2
CaO	13.4	14.2	6.4	14.2	8.5	11.2
Na_2O	n/a	7.9	n/a	7.9	n/a	11.0
Fe_2O_3	5.6	6.8	7.2	6.8	7.2	6.8
MgO	2.1	2.2	2.0	2.2	1.9	2.2
K_2O	n/a	2.1	n/a	2.1	n/a	2.1
CuO	0.1	-	0.1	-	0.3	-
MnO_2	0.1	-	0.1	-	0.1	-
PbO	0.1	-	0.1	-	0.1	-
ZnO	0.2	-	0.3	-	0.2	-
BaO	0.1	-	0.1	-	0.1	-
NiO	0.2	-	0.5	-	0.3	-
TiO_2	0.7	-	0.7	-	0.7	-
Cr_2O_3	0.3	-	0.3	-	0.3	-
P_2O_5	0.5	-	0.6	-	0.5	-
Total	88.7	100	84.2	100	84.3	100

Table IV. Analyzed and Predicted Chemical Composition for NY Harbor Glasses (Microwave Dissolution)

	10% CaO/5% Na_2O #2		10% CaO/5% Na_2O #1		7.5% CaO/7.5% Na_2O	
Cation	Analyzed	Predicted	Analyzed	Predicted	Analyzed	Predicted
SiO_2	52.5	55.6	54.5	55.6	53.5	55.5
Al_2O_3	12.5	11.2	11.5	11.2	12.0	11.2
CaO	14.1	14.2	6.9	14.2	9.6	11.2
Na_2O	7.3	7.9	12.5	7.9	9.3	11.0
Na_2O (AA)	6.8	7.9	10.8	7.9	8.0	11.0
Fe_2O_3	6.0	6.8	7.9	6.8	8.2	6.8
MgO	2.1	2.2	2.2	2.2	1.1	2.2
K_2O	1.9	2.1	2.0	2.1	2.0	2.1
CuO	n/d	-	0.1	-	0.3	-
MnO_2	0.1	-	0.1	-	0.2	-
PbO	n/d	-	n/d	-	n/d	-
ZnO	0.2	-	0.3	-	0.2	-
BaO	0.1	-	0.1	-	0.1	-
NiO	0.1	-	0.1	-	0.2	-
TiO_2	0.8	-	0.8	-	0.8	-
Cr_2O_3	0.3	-	0.3	-	0.3	-
P_2O_5	0.5	-	0.6	-	0.5	-
Total	98.5	100	99.9	100	99.3	100

Table V. Analyzed and Predicted Chemical Composition for NY Harbor Glass Prepared at Ferro, Inc.

	HCl/Na_2O_2 Dissolution		Microwave Dissolution	
Cation	Analyzed	Predicted	Analyzed	Predicted
SiO_2	56.6	55.6	56.0	55.6
Al_2O_3	10.3	11.2	11.1	11.2
CaO	12.4	14.2	12.7	14.2
Na_2O	n/a	7.9	7.3	7.9
Na_2O (AA)	n/a	7.9	6.7	7.9
Fe_2O_3	7.2	6.8	7.9	6.8
MgO	2.2	2.2	2.3	2 .2
K_2O	n/a	2.1	1.8	2.1
CuO	0.1	-	0.2	-
MnO_2	0.1	-	0.1	-
PbO	n/d	-	0.1	-
ZnO	0.3	-	0.3	-
BaO	0.05	-	0.1	-
NiO	0.5	-	0.2	-
TiO_2	0.7	-	0.8	-
Cr_2O_3	0.3	-	0.3	-
P_2O_5	0.5	-	0.7	-
Total	91.25	100	101.9	100

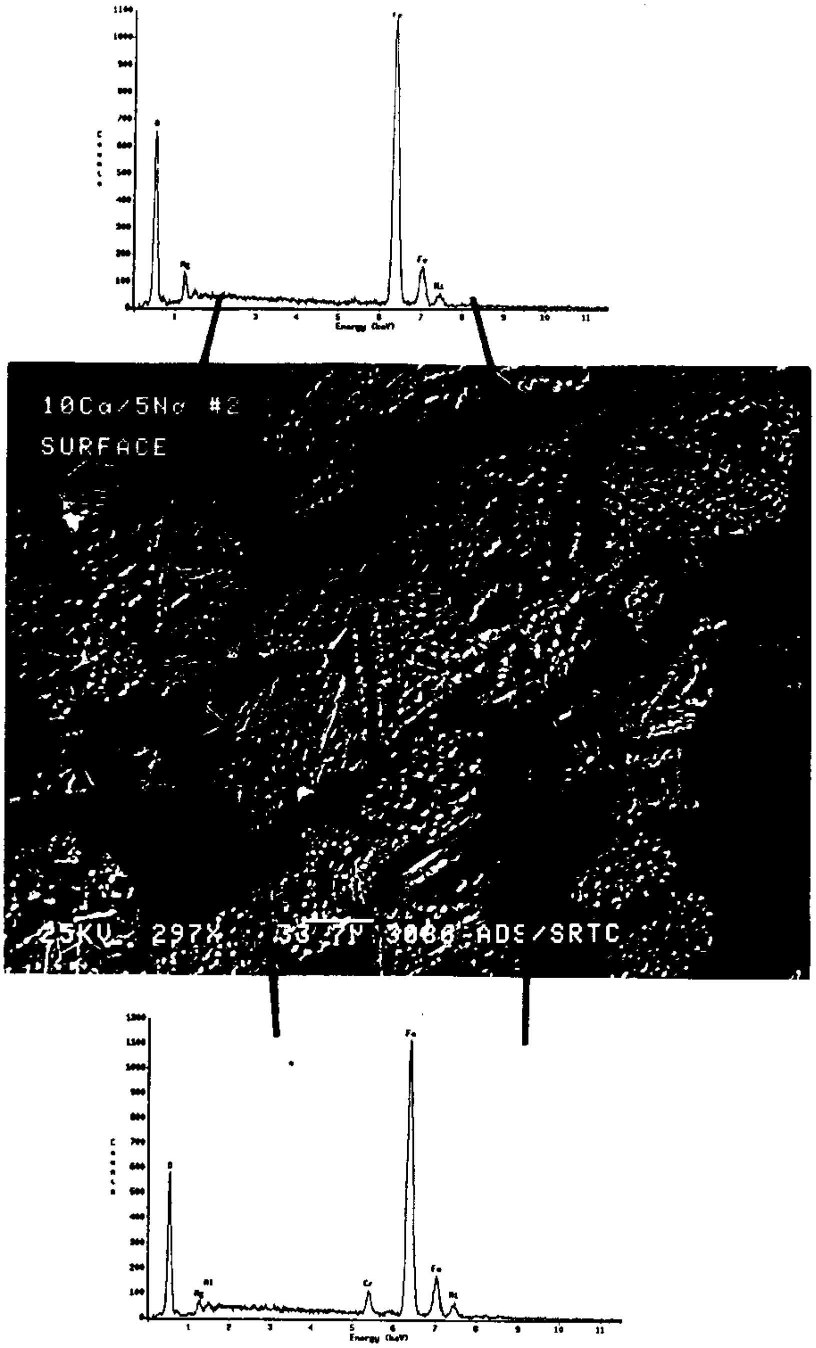


Figure 1. SEM micrograph and EDS spectra of the surface of 10% CaO/5% Na_2O glass.

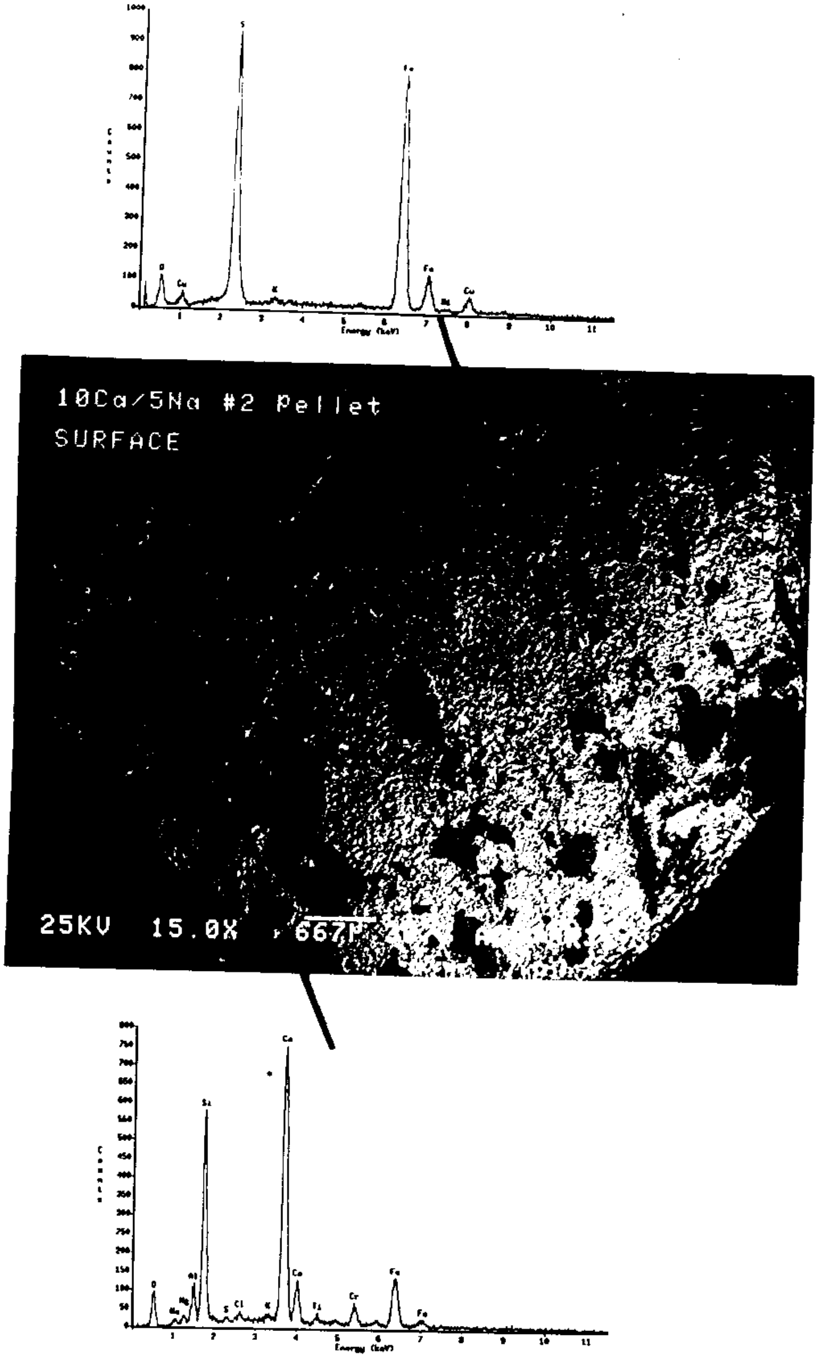
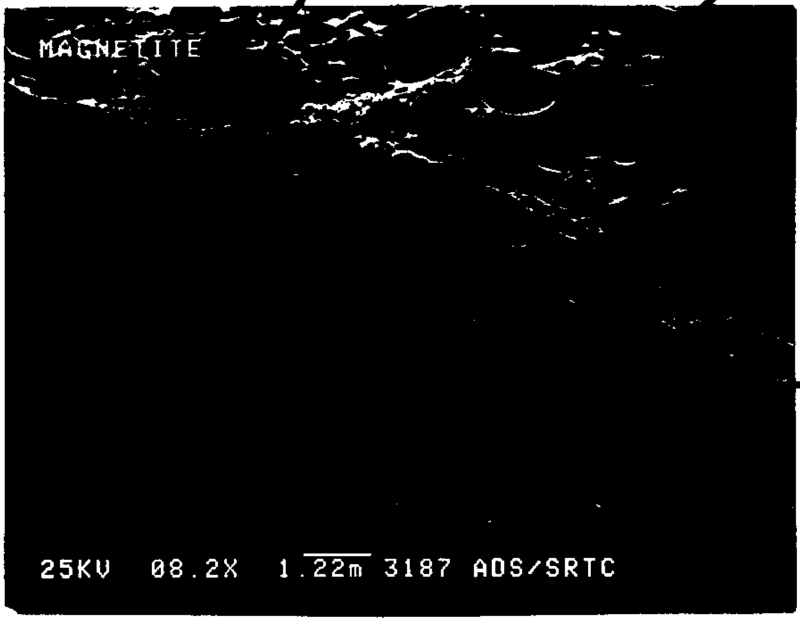


Figure 2. SEM micrograph and EDS spectra of a pellet found in the bottom of the 10% CaO/5% Na_2O glass melt.



SEE FIGURE 5

SEE FIGURE 4

SEE FIGURE 6

Figure 3. Low magnification SEM micrograph of the surface of the 10% CaO glass melt.

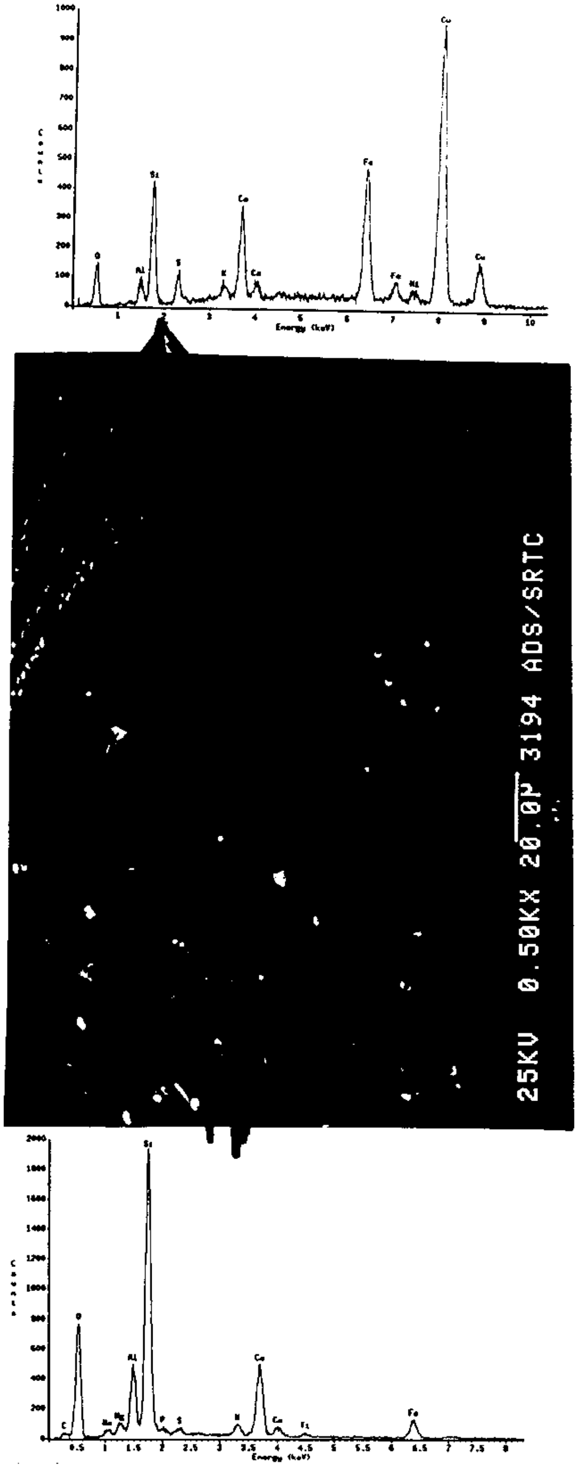


Figure 4. SEM micrograph and EDS spectra of a surface region in the 10% CaO glass.

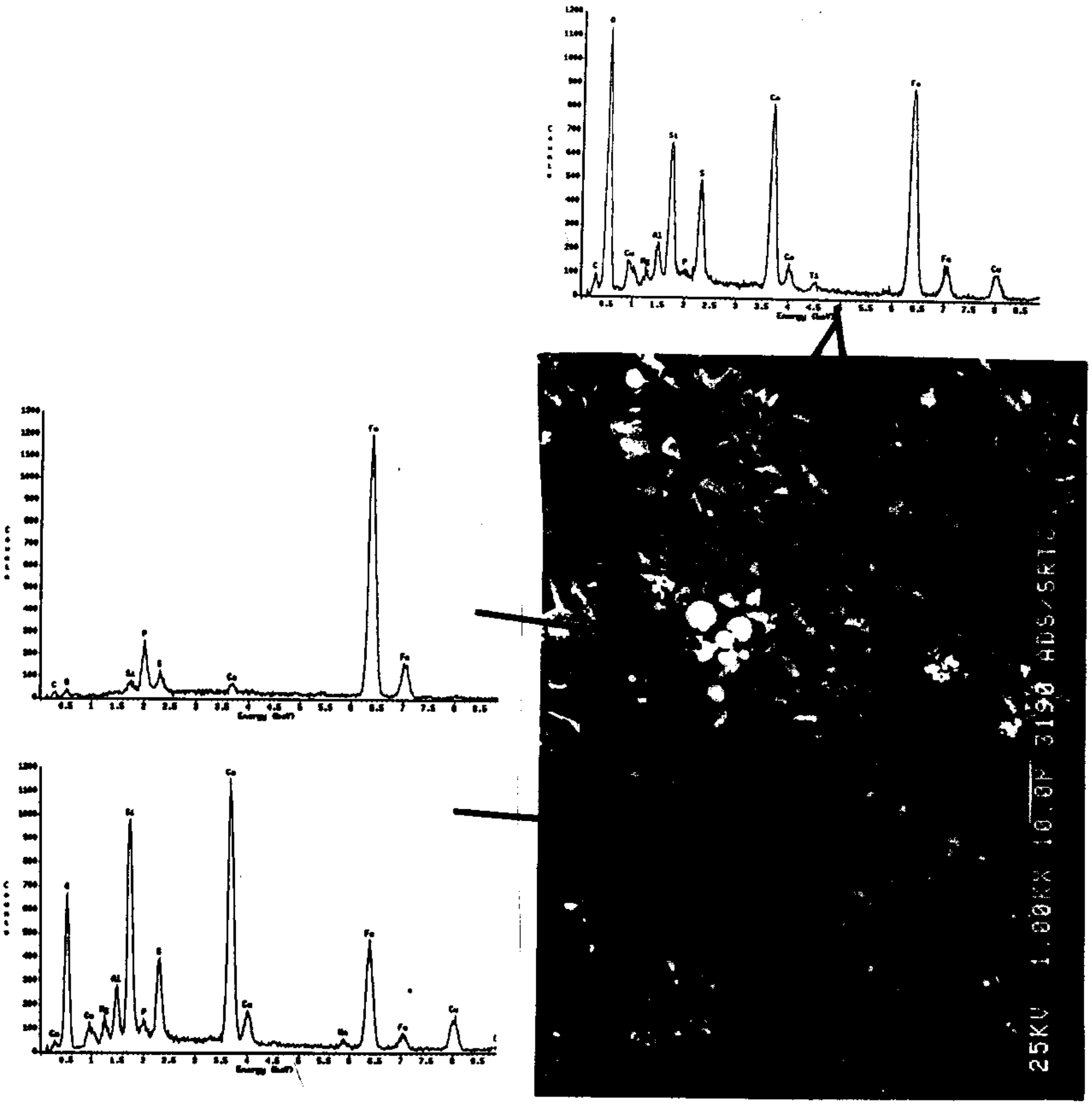


Figure 5. SEM micrograph and EDS spectra of a surface region in the 10% CaO glass.

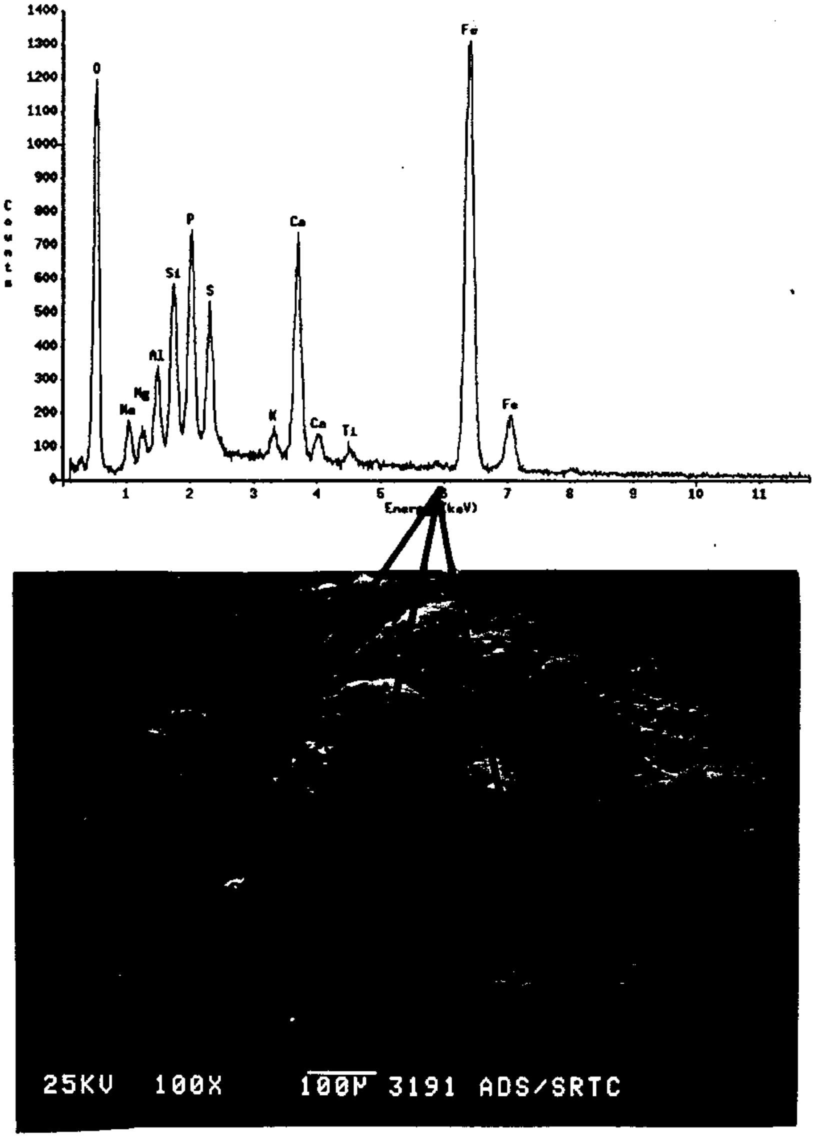


Figure 6. SEM micrograph and EDS spectra of a surface region in the 10% CaO glass.