WSRC-MS-97-00850

Americium/Curium Vitrification Pilot Tests - Part II

CONF-980521--

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MAY 13 1998
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A document prepared for 100TH ANNUAL MEETING OF THE AMERICAN CERAMIC SOCIETY at Cincinnati, OH, USA from 5/3/98 - 5/6/98.

DOE Contract No. **DE-AC09-96SR18500**

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A paper for publication in the Proceedings of the International Symposium on Waste Management Technologies in Ceramic and Nuclear Industries
The 100th Annual Meeting of The American Ceramic Society
Cincinnati, Ohio
May 3-6, 1998

This paper was prepared in connection with work done under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

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ABSTRACT

Isotopes of americium (Am) and curium (Cm) were produced in the past at the Savannah River Site (SRS) for research, medical, and radiological applications. These highly radioactive and valuable isotopes have been stored in an SRS reprocessing facility for a number of years. Vitrification of this solution will allow the material to be more safely stored until it is transported to the DOE Oak Ridge Reservation for use in research and medical applications. A previous paper described operating results from the Am-Cm Melter 2A pilot system, a full-scale non-radioactive pilot facility. This paper presents the results from continued testing in the Pilot Facility and also describes efforts taken to look at alternative vitrification process operations and flowsheets designed to address the problems observed during Melter 2A pilot testing.

INTRODUCTION

Approximately 15,000 liters (3,600 gallons) of solution containing isotopes of americium (Am) and curium (Cm) are currently stored in F-Canyon Tank 17.1. These isotopes were recovered during plutonium-242 production campaigns in the mid- and late-1970's. The continued storage of these isotopes was identified as an item of primary concern in the Defense Nuclear Facility Safety Board's (DNFSB) Recommendation 94-1. Currently, there are no existing SRS facilities that can be used to stabilize this material for safe interim storage and transportation to the heavy isotopes program at the Oak Ridge National Laboratory (ORNL). An analysis of several alternatives resulted in the recommendation to stabilize the Am-Cm solution in a high-lanthanide glass. The Multi-Purpose Processing Facility (MPPF) in the F-Canyon at SRS will be used for the vitrification process. Pretreatment operations will be performed in existing canyon vessels to separate actinides and lanthanides from other priorities (primarily iron, aluminum, and sodium) subsequent to the vitrification operation.

In 1994, a study was performed to determine the most attractive disposition option for the solution of Am and Cm that is currently stored in the F-Canyon. Vitrification in the form of a high-lanthanide glass was selected as the most attractive option. The Savannah River Technology Center (SRTC) was charged with developing the vitrification flowsheet, designing the prototype equipment, and demonstrating integrated system operations. The vitrification operation was originally planned to be performed in a platinum-rhodium (Pt-Rh) bushing melter that will be fed an Am-Cm liquid-frit combination. A Pt-Rh bushing melter was chosen because of its small size and its shape (which could be needed for future criticality requirements if other radioisotopes such as plutonium were subsequently vitrified in the same system). Platinum-rhodium bushing melters are commonly used in the glass industry, especially in the manufacture of fiberglass. In these industrial applications, however, either molten glass or dry feed is delivered to the bushing. There has never been a bushing melter that was designed for the additional requirements of slurry feeding. Slurry feeding greatly increases the level of difficulty for glass melting, as higher power requirements are needed at the upper portion of the bushing. An off-gas system is also required to treat any volatile or entrained components coming out of the melter. In addition, the numerous remote operation requirements for this radioactive feed had never been attempted before. The SRTC effort has demonstrated proof of concept with over 250 hours of integrated melter system operation. Significant progress has been made on the development program, however, several technical issues have arisen that require additional development in order to ensure confidence for reliable remote operation. These issues deal primarily with demonstrating reliability of the feed system and with design and operation of the bushing melter. A previous paper[1] discussed initial development activities in the Am-Cm Melter 2A bushing melter pilot system. This system was installed and operated at SRS in 1997. As a result of the issues associated with remote operation, a decision was made in early 1998 to focus the development on a batch process operated in an induction-heated vessel. This paper discusses the development of the batch process and compares operation in the induction melter to the original bushing melter system.

PROCESS DESCRIPTION

Bushing Melter System

The Melter 2A system is a full-scale pilot plant of the actual system to be installed at the SRS. The basic operation involves feeding a surrogate Am-Cm nitric acid feed solution, along with glass forming frit, in a carefully controlled mass flow ratio into the vapor space of a resistance heated Pt-Rh bushing melter operating at approximately 1350-1450 °C (depending on the glass composition used). The glass flows from the bottom of the melter by gravity through a drain tube and into a stainless steel canister. The canister will then be sealed for later transport to ORNL.

As the melter is fed and the liquid is vaporized, the expanding gases are drawn into the off-gas treatment system through a film cooler by a steam jet. The steam jet, coupled with a control air purge that is introduced into the off-gas system between the film cooler and the steam jet, maintains a target melter plenum pressure that is negative with respect to ambient pressure. The vapor exiting the steam jet enters a quencher where it is cooled and scrubbed of particulate entrained into the off-gas system during melter feeding. The condensate drains to the off-gas Condensate Overflow Tank (COT). Overflow from the COT goes into a 55-gallon bounce tank. The vapor exits the top of the COT and is drawn through a high efficiency mist eliminator (HEME), a high efficiency particulate air (HEPA) filter pre-heater and a HEPA by an air jet. The pre-heater raises the off-gas temperature above the dew point prior to entering the HEPA filter to prevent condensation in the HEPA. The air jet discharges the treated off-gas to the atmosphere through a stack. A schematic diagram of the bushing melter vitrification system is shown in Figure 1.

Batch Melter Process

A batch melter process is currently under investigation as an alternative to the bushing melter system. Flowsheet development for this process is underway. Additionally, a pilot facility is under construction and will be operational in early-1998. In this process, the nitric acid-based Am-Cm solution or surrogate is transferred into a reaction vessel. Eight-weight percent (8 wt.) oxalic acid is added to the solution to precipitate the rare earths as oxalates. The precipitate is allowed to settle and the excess liquid is decanted. A dilute oxalic acid wash solution (0.10M) is added to remove excess contaminants (e.g., Fe, Cr) and reduce the acidity of the feed. The precipitate is again allowed to settle and the washwater is decanted. The resultant slurry is mixed and then gravity fed to a cylindrical Pt-Rh vessel that is induction heated. The proper amount of frit is added to result in a final glass composition containing 35 weight percent of the Am-Cm solution. Depending on the frit particle size used, the frit addition can be made to the precipitation vessel prior to the transfer to the vessel or can be preloaded in the melter vessel. A simplified schematic of the batch process equipment is shown in Figure 2.

The oxalate precipitate/frit slurry is added to the melter vessel while holding at a between 100 and 150 °C). This temperature is held until the bed has dried. The vessel temperature is then raised at rate of ~4 to 8 °C /min to a glass melting temperature of ~1350-1380 °C.

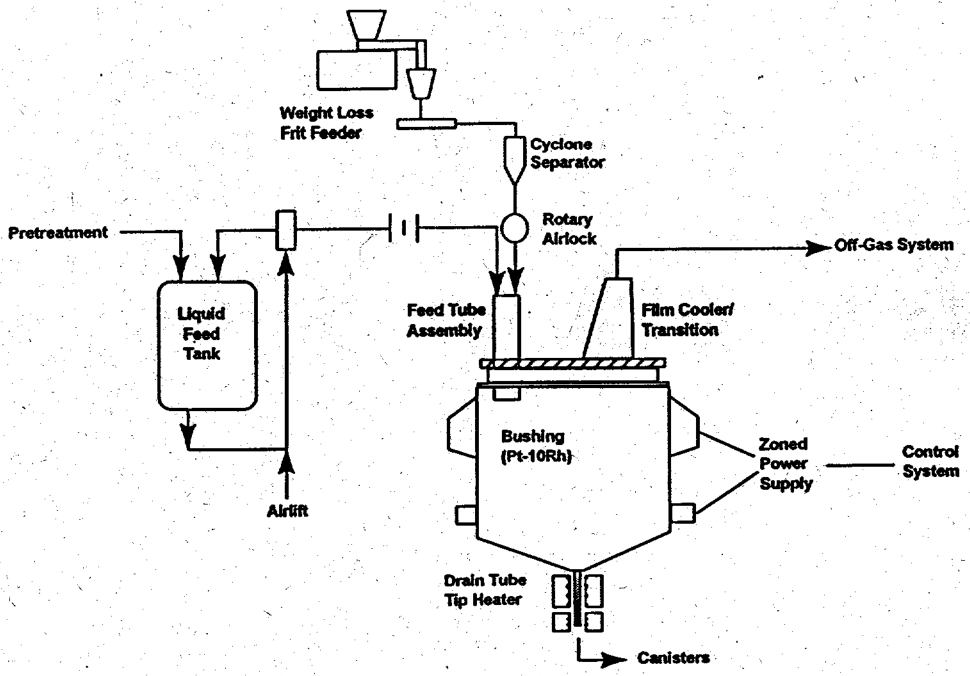

Figure 1 - Schematic Diagram of Bushing Melter System

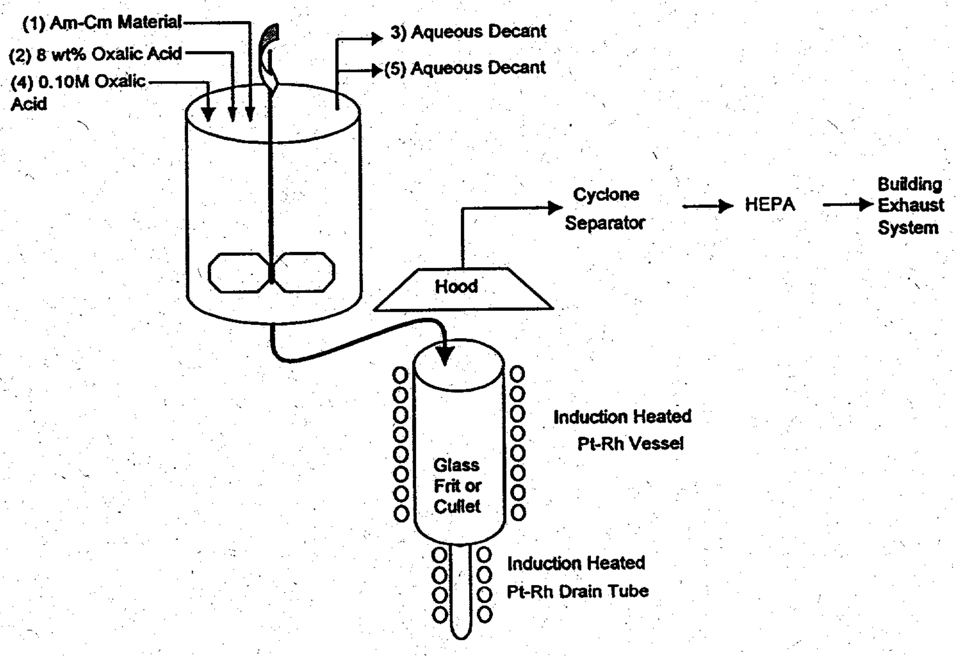

Figure 2 – Schematic Diagram of Batch Melter Process

During this temperature increase, the remaining nitrate is evolved and the oxalate precipitate decomposes to the associated rare-earth oxides. The melt is held at temperature for approximately 1-4 hours to ensure adequate mixing of frit and oxides and is drained from the bottom of the melter by gravity through a drain tube and into a stainless steel canister. The vessel is sized so that a single charge fills a single canister. The canister will then be sealed for later transport to ORNL.

DEVELOPMENT AND OPERATING ISSUES

Bushing Melter System

Significant achievements have been made in the development of the bushing melter system, however, the R&D effort has identified systems and components requiring further development prior to initiating final design for reliable and remote operation in the MPPF. Many of these issues were discussed in the preceding paper,[1] that described early pilot facility experience with the Melter 2A system. Additional work was performed in late-1997 to address the issues identified during the early testing. While progress was made during this phase of testing, significant issues remained. These issues are summarized below.

- Feed System
  Reliable performance of this system has not been achieved in the Pilot Facility. In order to achieve the low flow rates (2 liter/hr), while maintaining acceptable melting rates, the liquid feed system contained small orifices and small diameter tubing (0.05"). This system has been susceptible to plugging and required frequent mechanical cleaning, a procedure that will be difficult to adapt to the MPPF environment. Addressing these concerns was likely to require substantial modifications to existing components. Evaluation of alternative technologies was likely to significantly increase the scope of the development program. The preferred alternative technology, slurry feeding, was greatly complicated by the low feed rate requirement.

- Melter System
  Splatter and deposition observed in the melter plenum in the Pilot Facility was greater than that expected. As the liquid was fed into the melter, a significant amount was ejected into the plenum area of the melter (note: the surface of the melt pool was approximately 3" from the off-gas entrance under normal operating conditions). This liquid deposited in the cooler areas of the plenum where the rare-earth nitrates would decompose to form rare-earth oxides. These oxides were not melted in the cool temperature regions of the plenum. On several occasions, this splatter was sufficient to plug the off-gas system and the liquid feed tube.

  Additionally, both Melters 2A and 2B failed prematurely. In both cases, the failure occurred at the base of the lower electrical connection 'ears' indicating a structural deficiency in the design of Melter 2A and 2B. A newly designed melter was procured which addressed some of the structural design issues of Melters 2A and 2B, however, the failure of these melters raised concerns regarding the long-term structural integrity of the bushing in its current slab-like geometrical configuration.

- Off-Gas System
  Splatter and plugging problems were also observed in the off-gas system. The earlier paper[1] discussed plugging of the HEME and HEPA filter and the off-gas sampling performed to better understand this phenomenon. A redesign of the system to provide increased scrubbing of particulates was proposed. A more significant issue was the splatter of material onto the entrance of the off-gas system in the area of the film cooler that resulted in plugging of the film cooler

and subsequent pressurization of the melter system. Pressurization of the melter is undesirable due to the potential to contaminate clean areas of the MPPF.

The combination of the splatter/deposition issue and the melter life concerns was likely to lead to a significant redesign of the current bushing system. Additionally, some of the earlier requirements that led to the design of the bushing melter system were relaxed. For example, the requirement that the equipment be of critically safe geometry (which led to the use of the slab bushing melter) was removed by demonstrating that the Am-Cm solution was infinitely safe. The other primary requirement that led to the bushing system design was the desire to achieve fairly high production rates (several kilograms per hour) in the system. This led to the current liquid feed system, which was originally designed for a continuous feed and pour system. The throughput requirement resulted from the potential to utilize this system for production campaigns other than Am-Cm where significant quantities of glass will be produced. Since the Am-Cm campaign will only generate approximately 330 kg of glass, the throughput requirement was removed.

The problems encountered during the development of the bushing melter system , coupled with removal of some of the original processing requirements, made it prudent to evaluate alternative processes.

Batch Melter System

As discussed earlier, efforts are underway to develop a batch processing operation performed in a cylindrical induction-heated melter. This work has been ongoing since November 1997. To date, efforts have focused on developing a process flowsheet and installing a prototypical melter system in the pilot facility. The batch melter system and process addresses many of the issues associated with the bushing melter and greatly simplifies the process, making it desirable for remote operation. A summary of the advantages of the batch melter system is provided in Table 1.

Table 1. Comparison of Slab Bushing Melter Problems/Issues to Batch Melter Potential

System/Equipment/ Process	**Slab Bushing Melter**	**Batch Cylindrical Induction Melter**
Melter System	• Melter Life	• Less Stress (Unrestrained, Cylindrical) • Easier/Inexpensive to Replace Vessel
Melter Feed System	• Challenging Low Liquid Feed Rate • System Pluggage	• Batch Process - Higher Flow Rate • Reduced System Pluggage
Off-Gas System	• Film Cooler Entrance Pluggage • Complex Control Scheme	• Simple, Hood Design • 'Decoupled' Offgas System
Melter Pour System	• Drain Tube Pluggage (Devitrification) • Drips & Stringers	• Melt & Drain -- Single Canister -- Less Time in Devitrification Zone • Mechanical Drain Valve Possible • Option to Operate as 'In-Can' Melter
Primary Disadvantages/Issues	• *Melter Life* • *Feed Pluggage* • *Off-Gas Pluggage* • *Drain Tube Pluggage*	• *Increased Manipulator Handling* • *Slightly Longer Campaign* • *Potential Slurry Feed/Dry Feed Development*

Development of the batch process and associated equipment is being accomplished by a combination of lab-scale tests and pilot system testing. Lab-scale tests are accomplished in Pt-Rh crucibles in muffle furnaces. Pilot system testing is being accomplished in a cylindrical, resistance-heated vessel that was installed to develop glass drain tube operations (known as the Drain Tube Test Stand, DTTS). This facility is representative of the Cylindrical Induction Melter (CIM) being installed; the primary difference being in the heating mode (resistance heating vs. induction heating). The lab-scale and DTTS tests are being used to refine the flowsheet in preparation for testing in the CIM facility which will qualify equipment for eventual installation in the MPPF.

Significant progress has been made on flowsheet development since beginning this effort. Initial testing has demonstrated the ability to produce glass that meets acceptance standards. The primary issues encountered to date relate to controlling decomposition of the oxalate during the heating cycle. The decomposition reaction generates CO and CO_2 that can result in expansion of the powder bed. Volume expansion is undesirable because it may limit the amount of glass that can be produced in a single batch; the batch height will have to be controlled so that the material is contained within the Pt-Rh vessel at all times. Additionally, initial testing resulted in the formation of bubbles in the glass melt at temperatures in excess of 1200 °C. The cause of these bubbles remains under investigation, however, preliminary analysis of the evolved gases indicates that the composition is rich in O_2 and CO_2.

Two possible sources of gas generation at these high temperatures are:

(1) Thermal reduction of CeO2 (or other multivalent oxides), and/or
(2) Decomposition of carbonates.

CeO_2 is known to reduce at high temperatures in a lanthanide borosilicate glass. Recent studies at PNNL indicate an 85% reduction of CeO_2 (+4 to the +3 state) at 1300 °C. With this reduction, O_2 would be liberated. Given that CO_2 is one of the high temperature gases detected by the GC/MS during the quartz crucible runs, one possible source of the CO_2 could be the interaction of O_2 liberated from the CeO_2 reduction coupled with residual carbon from oxalate decomposition. Tests are ongoing to confirm this hypothesis. Additional details of the characterization of the melt dynamics in this system will be described in a later paper.

Decomposition of "high temperature" carbonates may provide a second potential source of CO_2. X-ray diffraction patterns of oxalate precipitate calcined at 500 °C indicated that presence of "rare-earth" carbonates. Based on this data, one possible mechanism would be the conversion of the rare-earth oxalates to carbonates and ultimate thermal decomposition of the carbonates to oxides liberating CO_2. XRD patterns of the oxalate after calcination at 1300 °C for 2 hours indicate only rare earth oxides.

Glass Formulation

The original glass formulation selected for stabilizing the Am-Cm solution was based on a Loffler glass composition. This glass was chosen based on the fact that the base glass composition is high in lanthanides (La_2O_3) making it a logical choice to stabilize lanthanide materials. The general formulation for this glass (known as Frit 1000) is shown in Table 2.

Frit 1000 met the initial requirements placed on the glass composition as shown below:

- Able to incorporate up to 40 weight percent Am-Cm material,
- Viscosity in the range of 5-15 poise at operating temperature (necessary to pour through the drain tube configuration), and
- Maintain recoverability of the Am-Cm material when dissolved in HNO_3.

Table 2. Simplified Formulations for Glasses Considered for Am-Cm Stabilization

Oxide	Frit 2000	25SrABS-F
SiO_2	44.2	33.7
B_2O_3	9.20	13.5
Al_2O_3	6.05	24.9
La_2O_3	7.12	25.0
PbO	24.38	---
BaO	9.02	---
SrO	---	2.9

However, Frit 2000 required operation at temperatures in excess of 1450 °C. After one of the early Am-Cm bushing melters failed due to overtemperature, there was a desire to evaluate frits with lower liquidus/melting temperatures. A strontium aluminum borosilicate glass was identified as a potential candidate. The composition of this glass (known as 25SrABS-F) is also shown in Table 2. Based on successful testing of the 25SrABS-F glass in the laboratory, it was selected as the baseline composition for initial evaluation in bushing Melters 2A and 2B. However, during early testing of Melter 2A, severe foaming was encountered when the melter began to be fed with a nitric acid solution and SrABS-F frit. Subsequent testing focused on developing an understanding of the cause for the foaming and compositionally characterizing the foam layer using the reference frit, 25SrABS-F.

Analysis of samples of the foamy, porous cold cap formed by feeding the 25SrABS-F frit with liquid nitric acid surrogate feed indicated the presence of rare earth oxides. Mass spectrometry analysis of gas trapped in the pores of the cold cap samples detected nitrogen and oxygen. The foaming mechanism that was postulated from this information was the decomposition of the rare earth nitrates. This decomposition liberates NO_x gas, which is trapped in the viscous cold cap. This foam layer then acts as an insulating blanket, which in turn reduces the melting efficiency of the bushing. If feeding is continued, the bushing cannot melt the additional feed and the entire melt pool becomes covered with a cold cap. This theory is backed by the finding that the addition of just nitric acid to an SrABS glass melt pool produced a thin, non-porous oxide layer due to the extraction of the lanthanides from the glass. This extraction first converts the rare earths to a nitrate form and then quickly decomposes these nitrates to an oxide layer on the glass surface. This decomposition results in the liberation of gases, which then attempt to rise out of the melt pool/cold cap. Without a cold cap, however, there was no viscous layer to trap these gases, and therefore these rare earth oxides were re-dissolved into the glass fairly rapidly.

Based on the less than adequate results with the 25SrABS-F frit in Melter 2A, a decision was made to reevaluate the use of B2000 frit in the bushing melter system. This frit composition did not produce a porous, cold cap, but the lead in the composition was significantly volatile at the melter operating temperature (1450 °C) and caused plugging in the off-gas system. Modifications were being made to the off-gas system to accommodate the increased volatility when other processing problems led to the decision to abandon the slab-bushing melter system.

Due to acceptable processing experience with the B2000 frit in Melters 2A and 2B, it was selected as the 'reference' frit composition for initial testing of the batch processing flowsheet. Early testing on this flowsheet suggested, however, that the B2000/surrogate system was subject to rapid devitrification in the drain tube of the Pt-Rh vessel. The drain tube functions as a 'freeze-valve' to hold the glass in place by application of forced cooling air on the tip of the tube. As a result, there exists a region where the glass in the drain tube is below the liquid temperature of the glass. Initiation of the glass pour is accomplished by interrupting the cooling airflow allowing the tube to heat up. As the tube heats up, the glass melts and flow begins. If there is a region of substantial devitrification, it is difficult to initiate flow. This was observed when B2000/surrogate glass was held in the melter for periods in excess of 24 hours. Laboratory testing indicated that complete devitrification occurred after periods of 24 hours in the B2000/surrogate system. At the same time, it was recognized that the change in process flowsheet made it possible to reexamine the use of the SrABS glass composition; the new flowsheet removes much of the NO_3^- which was shown to produce unacceptable foaming during the melting operation. Testing of this system had shown that its crystallization properties are more favorable to operation of the drain tube than the B2000/surrogate composition. Testing to date has shown acceptable performance with the SrABS glass composition in the batch flowsheet; it is now the 'reference glass' composition.

SUMMARY

Significant progress has been made in the development of a vitrification process and equipment for stabilization of the Am-Cm solutions at the Savannah River Site. Equipment problems, primarily associated with developing the confidence for operation in a remote environment, have resulted in programmatic changes from a semi-continuous process in a slab Pt-Rh bushing melter to a batch process in a cylindrical induction heated melter. Testing and development of the batch process and equipment is in progress. Initial results described in this paper suggest that this process variation is more readily adaptable to remote processing environments.

ACKNOWLEDGEMENTS

This paper was prepared in connection with work done under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

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[1] M. E. Smith, A. P. Fellinger, T. M. Jones, C. B. Miller, D. H. Miller, T. K. Snyder, M. E. Stone, and D. C. Witt, "Americium/Curium Melter 2A Pilot Tests (U)," Submitted for publication in the *Proceedings of the International Symposium on Waste Management Technologies in Ceramic and Nuclear Industries,* The 100th Annual Meeting of The American Ceramic Society, Cincinnati, Ohio, May 3-6, 1998.