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REMOTE MONITORING OF MOLTEN RADIOACTIVE GLASS (U)

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ABSTRACT

An on-line method is described for the near-continuous monitoring of the composition of a molten radioactive waste glass or, alternatively, for signaling a deviation from the target composition of a waste glass. The principle of this method, proposed by A. Schneider in 1986, is founded on the relation between two specific physical properties and composition in a ternary system. Most glasses currently considered as waste forms can be represented as pseudo-ternary system. The pairs of properties especially suited for this purpose are viscosity/density and viscosity/electrical conductivity. A novel viscometry method was developed which uses the remotely determined rise velocity of carefully metered gas bubbles. The monitoring method was tested successfully with simulated Savannah River waste glasses. An integrated probe was conceived for a Joule-heated melter for the on-line determination of viscosity, temperature, density, and liquid level. A computer program calculates the glass composition from the measured data, using information from a previously developed data base.

INTRODUCTION

Glass has been the preferred waste form in many countries practicing or contemplating the solidification of high-level liquid radioactive wastes. Borosilicate glasses have generally been selected because of their relative chemical stability, capability of incorporating various elements and compounds, and long production experience.

The properties of a waste glass are determined primarily by its composition, operating variables during production, and the cooling rate after the glass is poured into the canisters. Leachability, the property of paramount importance, depends greatly on the chemical composition of the waste glass. Great care is taken during the design and construction of vitrification facilities to allow for very precise compounding of the ingredients and for the continuous monitoring of the operating variables. At present, the conformance with composition specifications can only be verified by periodically withdrawing a molten glass sample which is then analyzed in a remotely operated analytical facility. Figure 1 is a schematic diagram of the glass sampler for the Savannah River DWPF melter. It replaces the usual connector between the pour spout and the canister top, since only infrequent sample withdrawal is planned. The sampling, sample transport, and chemical and physical analyses are cumbersome operations because of the complexity of the remotely operated equipment and several days will be required to complete the necessary tests. While these tests are important for the waste qualification protocol, they are of limited value for controlling the continuous glass production process. The application of continuous monitoring methods practiced in the chemical process industry would be very difficult in this instance, because of the large number of chemical elements contained in the glass and the extremely hostile environment of high radiation and elevated temperature.

However, the glass composition can be estimated with sufficient accuracy from the determination of certain physical properties which can be done by remote means [1].

Figure 1. Savannah River DWPF molten glass sampler

ESTIMATION OF GLASS COMPOSITION

Triangular phase diagrams are useful in representing properties of ternary compounds as well as more complex systems which can be approximated as pseudo-ternary compounds. The properties of borosilicate glasses are conveniently represented on a ternary diagram as a function of SiO_2 , Na_2O , and B_2O_3 concentrations. Variation of specific physical properties with composition can be shown, for example, as constant value lines for a given temperature (isopleths) as illustrated in Figure 2 for data found in the literature. By determining two physical properties at the same temperature, one can estimate the corresponding composition for the point where the two isopleths intersect. The precision with which the composition point is located is enhanced if the isopleths do not intersect at small angles. It can be seen in Figure 2 that melt viscosity, electrical resistivity, and density are composition dependent but to a decreasing extent, respectively. It is also apparent that viscosity/density and viscosity/electrical resistivity are suitable pairs, while the electrical resistivity/density combination would produce a large margin of error in the derived compositions.

Figure 2. Isopleths for sodium borosilicate glass at 1100°C

The computer program TERNARY written by Kwansik Choi in Fortran was used to estimate the borosilicate glass composition from two physical properties at a given temperature [2]. In this program polynomial equations are fitted to the isopleths by the least square method. Specific compositions which correspond to the roots of the equations representing the pairs of property values are then obtained, using the Newton-Raphson method. The program was tested with data from the literature for sodium borosilicate glasses. The results shown in Table I indicate a favorable comparison between the composition for which the physical properties were selected and the composition calculated with TERNARY.

TABLE I
Test of Computer Program TERNARY

Composition Taken, mol %		Composition Calculated, mol%	
B ₂ O ₃	SiO ₂	B ₂ O ₃	SiO ₂
20.0	61.9	19.99	62.01
25.0	61.0	24.96	58.95
6.0	78.3	5.29	76.42
2.0	80.7	1.85	80.69
21.7	69.4	22.21	68.68
11.3	81.0	11.36	81.02

A systematic investigation of the effects of variations in composition on certain properties of the Savannah River waste glass was carried out by Schumacher [3]. A simplified schematic diagram of the overall process which will be used in the Defense Waste Processing Facility (DWPF) is shown in Figure 3. The feed to the melter consists of three components: *sludge* (the insoluble portion of the original neutralized high-level waste composed of the hydroxides of Fe, Al, Mn, Ni and containing most radioactive nuclides), *PHA* (precipitated hydrolysis aqueous product), and *Frit 202* (a crushed and classified glass containing B₂O₃, Li₂O, MgO, Na₂O, and SiO₂). While the non-volatile compositions of the three components will remain fairly constant over extended periods, some variability is expected in the ratios between the sludge, PHA, and frit which would cause some deviation from the target composition of 28 wt% sludge, 8 wt% PHA, and 64 wt% frit.

Figure 3. Simplified schematic of the Savannah River HLLW treatment process

Melt viscosities at 1150°C and densities at room temperature for annealed glasses were obtained for twenty one glass melts. It is evident from Figure 4 that the relative orientations of these isopleths are very favorable for the proposed monitoring method.

Figure 4. Melt viscosities and densities of DWPF glass

MEASUREMENT METHODOLOGIES

Many methods are available for liquid viscometry, but the elevated temperature and the corrosiveness of the molten glass have generally limited the choices to the falling ball, flow rate through an orifice, and rotating spindle methods (Brookfield type viscometers). It became evident at the outset of this study that none of the above methods would be suitable for the continuous monitoring of molten glass, especially for remote operation in an intense radioactive field. A new viscometry method was developed which is based on the rise velocity of gas bubbles.

It was known that the rise velocity of gas bubbles in a liquid is a function of the densities and viscosities of the gas and the liquid, the diameter of the gas bubble, and the gravitational constant (Stokes or Hadamard-Rybczynski formulae). Other factors, such as changes in shape and size of the ascending bubble (due to diffusion, chemical reaction, decreasing hydrostatic pressure, and temperature), the surface tension at the gas-liquid interface, and the geometry of the liquid container (wall-effect) will also affect the rise velocity of the bubble, but these effects can be minimized by proper selection of the gas and of the distance over which the bubble velocity is determined.

The experimental setup, shown schematically in Figure 5, consisted of a helium bubble generator which releases a specified mass of helium; two delivery tubes placed so as to release the bubbles at different levels; a system for detecting the arrival of the helium bubble at the liquid-air interface; and a personal computer for controlling the bubble generation and launching cycles, data management (acquisition, processing, and archiving), and diagnostics. The pressures in the launch tubes were measured with transducers and the temperature in the vicinity of the bubble path was determined with a thermocouple. The bubble generator, helium detector, and computer were located several meters from the liquid container.

In the first phase of this study, the system was tested with Cannon Instrument Company S-2000 and S-8000 high viscosity oils (polybutenes). Within the temperature range over which the system was tested (20 to 50°C) the viscosities varied between 10 and 38000 centipoise. In the second phase, bubble rise velocities were obtained for simulated Savannah River waste glass over a temperature range of 1020 to 1100°C. The molten glass was contained in Coors

Figure 5. Schematic of remote monitoring laboratory system.

alumina crucibles placed in a Lindberg high-temperature furnace provided with a Eurotherm 818 communicating temperature controller; the bubble launchers and the thermocouple protective tubes were made of Inconel. The bubble diameters ranged from 0.8 to 2 cm, converted to standard temperature and pressure.

The validation of the BRV viscometry method was made by comparison with data obtained by standard viscometry methods: Cannon-Fenske viscometers for the S-2000 and S-8000 oils (reference viscosities at 25°C were 57 and 240 poise, respectively) and a Brookfield type instrument with a platinum rotating spindle for the glass (reference viscosity at 1050°C was 85 poise). The plots presented in Figures 6 show an excellent correspondence.

Figure 6. Comparison of reduced ($1/BRV$) and reduced viscosities

The densities of the liquids were obtained from the pressures measured at the instants of bubble launchings which are the hydrostatic pressures at two levels separated by a known distance. The results are shown in Figure 7.

Figure 7. Densities obtained by remote measurement

The following empirical formula, derived from several hundred data points, permits the calculation of the dynamic viscosities from BRV measurements, taking into consideration the bubble diameter, the liquid container diameter, and the liquid density [4]:

$$\eta_{BRV} = \frac{100(\rho/BRV)}{4.1122D_b^{-1.4158} (D_b/D_c) + 0.9813D_b^{-2.827}}$$

Applicability range: $0.08 < D_b/D_c < 0.53$

where η_{BRV} = viscosity of the liquid [poise]
 ρ = measured density of the liquid [g/cm³]
 BRV = measured bubble rise velocity [cm/sec]
 D_b = measured bubble diameter [cm]
 D_c = measured inner diameter of container [cm]

The viscosities determined with the BRV method and using the above formula agreed well with the data obtained with standard viscometers. In the case of the Savannah River waste glass the standard error for a large number of determinations was $\pm 6\%$.

CONCEPTUAL DESIGN OF A MONITORING SYSTEM

A concept for an integrated probe for the remote monitoring of molten glass which incorporates the features demonstrated in this study is shown in Figure 8.

The probe made of Inconel 690 consists of two launch tubes, one thermocouple tube, and one gas sampling tube. The heavy duty Inconel 690 tubes are expected to withstand corrosion by molten glass and should not deform as a result of the movement of the molten glass. The cover section of the probe is similar to those used for thermocouple wells and level dip tubes in existing melters. Flexible metal tubes with quick disconnects are used for all connections outside the melter. The probe can be remotely replaced, should this become necessary after the start of hot operations.

The bubble detection method used in this study would be suitable for certain melter types, such as the current model for the West Valley Demonstration

Figure 8. Concept for an integrated glass monitoring probe

Project, where the glass products is air-lifted from a compartment filled by an underflow. For other melters, such as the DWPF unit, the bubble detection method will be modified to avoid interference with the bubble exit from the molten glass which can be caused by the cold cap on the glass surface and by the much lower glass surface temperature due to the tempering effect of the evaporating water. The instance at which the gas bubble reaches a certain level can be conveniently determined with two electrodes with a small AC or DC potential applied across them. The change in impedance will produce a change in the current and this signal can be processed in a conventional manner. The principle of this detection method was demonstrated with glycerol rendered electrically conductive by the addition of a small amount of LiCl. The method is well suited for molten glass which is a conductor and the electrodes consisting of Inconel can be incorporated into the monitoring probe.

CONCLUSIONS

The compositions of ternary or pseudo-ternary mixtures can be monitored by frequent determinations of two physical properties. In the case of molten waste glass, viscosity and density are the properties of choice.

Bubble rise velocity viscometry was shown to be a method comparable in precision and accuracy with established methods. This method is uniquely adaptable to remote operation and the only components in contact with the liquid being analyzed are passive metal tubes. Auxiliary components, which are susceptible to radiation damage, can be located at appreciable distances.

Concepts were developed for integrated monitoring probes compatible with melters of current design. These probes allow the near-continuous determination of viscosity, density, temperature, and hydrostatic pressure. Computer hardware and software were adapted for data acquisition and processing, inter-

face with process controls, and generation of archival materials for quality assurance.

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