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Millimeter-Wave Measurements of High Level and Low Activity Glass Melts Annual Report FY2000

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PROGRESS REPORT

RESEARCH OBJECTIVE

The goals of the research effort are to develop new robust diagnostic tools for glass melt monitoring in a high-temperature, corrosive, radioactive environment, and to advance glass melt chemical modeling to make possible real-time melt characterization via the new sensor capability. Millimeter-wave technology will be applied to the simultaneous measurement of temperature, conductivity, and viscosity for the first time. This new sensor technology will make possible better process control to improve reliability and efficiency of waste glass melters. Also, it will provide new data for bridging the gap between theoretical glass melt models and their relationship to melter performance. The work is closely coupled to the needs of the Defense Waste Processing Facility (DWPF), West Valley Demonstration Project (WVDP), and vitrification efforts at Hanford, Oak Ridge, and Idaho sites. This research is a collaboration between the Massachusetts Institute of Technology (MIT) Plasma Science and Fusion Center (PSFC), the Pacific Northwest National Laboratory (PNNL), and the Savannah River Technology Center (SRTC).

RESEARCH PROGRESS AND IMPLICATIONS

As of the second year good progress has been made in parallel on the various research objectives. Laboratory experiments at MIT have established the feasibility for real-time monitoring of all thee parameters, temperature, conductivity, and viscosity. Also a new potential for molten glass density measurements at high-temperature was discovered. A key milestone in the second year was a meeting[1] with Tank Focus Area representatives at MIT on December 7, 1999 to discuss monitoring priorities and the transfer of this technology to the TFA. Viscosity measurement was identified as the most important need. Experiments following this meeting demonstrated a strong correlation between millimeter-wave molten glass displacement measurements and viscosity. These results imply that robust new sensors for characterizing glass properties *in situ* are possible for improving control of present and future generation melters. Progress is briefly summarized below by the collaborating institution that led the particular developments described. Please see the Appendix for more details.

PSFC (MIT): Experiments continued in the second year with millimeter-wave instrumentation at a frequency of 137 GHz on a laboratory furnace. In collaboration with PNNL a number of different waveguide types, materials, and sizes were tested for interfacing the remote electronics with the molten glass. The two main waveguide types were internally corrugated metal guides and internally smooth non-conducting guides, which can propagate the efficient HE_{11} mode. Inconel 690 was used for testing waveguides of the first type. Performance was good for up to 1150 °C but repeated use up to 1180 °C showed degraded performance due surface corrosion. Silicon carbide (SiC) and mullite ($3Al_2O_3 \cdot 2SiO_2$) were used to test waveguides of the second type. Though tests of high resistively SiC samples indicated this would make a good dielectric waveguide, the vendor for this material could not produce a high resitivity tube. Mullite on the other hand proved to be a very effective millimeter-wave waveguide material. It has been successfully used in repeated measurements to 1300 °C, both above and immersed into the molten glass with millimeter-wave transmission efficiencies of 93% in the present setup. The implication of this result is that robust access for millimeter-wave sensors into glass melters in an oxidizing environment is now well established.

[1] Participants: Bill Holtzcheiter, Frank Thomas III, *from SRTC;* Tom Thomas, *from INEEL*; Glenn Bastiaans, *from Ames*; S. K.. Sundaram, *from PNNL*; Paul Woskov, John Machuzack, Kamal Hadidi, and Paul Thomas, *from MIT*

A number of experimental runs with two different Hanford glasses have been carried out to develop the measurement techniques using both the Inconel and mullite guides. The measurement of temperature and emissivity has been shown. The feasibility of viscosity measurements has also been established by sealing the waveguide with a window and connecting to a pressurized source of gas. The rate of flow of molten glass in the waveguide, in response to a pressure transient, has been shown to be dependent on glass viscosity. Furthermore, the magnitude of the liquid glass displacement for a given pressure is dependent on the liquid density. Data for a Hanford glass mix over a temperature range of 1000 - 1300 °C and corresponding viscosity range of 3,000 - 100 Poise has been acquired. The viscosity measurement development work is currently ongoing to optimize measurement methods and techniques, and to obtain additional data on other glasses.

PNNL: Work at PNNL has focused on molten glass conductivity – chemistry relationships and supporting the experiments at MIT. This year PNNL supported MIT in design and fabrication of different waveguides for this application.

Electrical Conductivity: A high-accuracy coaxial-cylinders technique was adapted successfully to measure the conductivity of waste glass melts. Characterization of 3 Hanford glasses, 6 DWPF glasses, and 5 privatization glasses was completed. Conductivity of the 2 Hanford glasses and 1 DWPF glass was predicted using 1) first-principle process-product model, developed by Jantzen[2] and 2) empirical mixture models, developed by Hrma et al.[3]. Preliminary comparison of the predictions with the measured value showed promise for developing a good conductivity-chemistry relationship. Further development of this relationship is in progress.

Redox: The coaxial-cylinders technique was modified to include a stabilized zirconia reference electrode. This modified probe will be used to measure redox of the waste glass melts from the glass test matrix, using square-wave voltammetry. A modified version of Rapidox® probe will also be used. These results will be compared.

Additionally, a symposium on "Millimeter/Submillimeter-Wave Technology – Materials, Devices, and Diagnostics" was organized on the occasion of the Spring 2000 Meeting of the Materials Research Society on April 24, 2000 at San Francisco, in collaboration with international researchers in this area. An electronic Proceedings is being published. Please see more details in the Appendix.

SRTC: Research at SRTC has focused on the development of an advanced based control system that would use information from in situ measurements of millimeter wave emissions from molten glass to determine the glass properties. The current process control strategy in the Defense Waste Processing Facility uses analytical measurements of the compositions of the feed components along with an assessment of the uncertainties in the analysis and in the process variables such as batch volumes to ensure that acceptable glass will be made downstream from the blend tank. This is a feed forward control strategy. Direct measurement of glass properties offers the possibility of feed back process control where the measured product properties are used to optimize the control of the system. The millimeter wavelength radiation profile data would be used into a process model that account for uncertainties in the measurements and system response

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[2] C. M. Jantzen, "First Principles Process-Product Models for Vitrification of Nuclear Waste: Relationship of Glass Composition to Glass Viscosity, Resistivity, Liquidus Temperature, and Durability," pp. 37-51 in Nuclear Waste Management IV, Editor: G. G. Wicks, D. F. Bickford, L. Roy Bunnell, Ceramic Transactions, Volume 23, The American Ceramic Society, Westerville, Ohio, USA, 1991.

[3] P. R. Hrma, G. F. Piepel, P. E. Redgate, D. E. Smith, M. J. Schweiger, J. D. Vienna, and D. –S. Kim, "Prediction of Processing Properties for Nuclear Waste Glasses," Ceramic Trans. 61, 505-513 (1995).

to minimize the amount of frit added to the glass. Unlike the current control strategy, the new control strategy uses information about the composition of the blend tank, the melter feed tank, and glass already in the melter to determine an optimum glass blend. The glass produced by this strategy is potentially a more nearly optimal composition than it is currently possible to obtain. Future work will focus on quantifying the benefits of such a feedback control system and will also consider measurements in the presence of disturbances such as temperature fluctuations to the system.

APPENDIX

ADDITIONAL FY2000 PROGRESS

EMSP-TFA COLLABROATION: The project team attended the National Workshop for the Environmental Management Science Program in Atlanta to share current research on the Millimeter-Wave Measurements Project with DOE sponsors and other scientists /researchers in the EM Science Program. All three partners, MIT, PNNL, and SRTC met to discuss the current status of the Millimeter-Wave Measurements (MWM) project and plans for future work. A key issue brought out at the National Workshop was the need to demonstrate practical applications of EM Science sponsored programs. With respect to this need, it was decided to plan a demonstration of the MWM pyrometer capability for temperature profiling in a real melter production environment. SRTC then took the lead in arranging such a demonstration. To most efficiently use the funds allocated for the MWM project, SRTC decided to augment an existing project for Idaho National Engineering and Environmental Laboratory (INEEL) to examine vitrification of High Level Wastes (HLW) from the Idaho Nuclear Technology and Engineering Center (INTEC). This INEEL, SRTC, and PNNL project involves pilot testing at the Clemson Environmental Technology Laboratory (CETL) using an Envitco EV-16 melter. These tests are designed to examine the vitrification process for simulated HLW from INTEC. The MWM technology was presented to the SRTC lead for the INEEL project, who expressed an interest in using it to measure surface temperatures across the melt pool. There was also an interest in measuring any cold cap formed during the INEEL EV-16 runs. An agreement was made where a demonstration of the MWM pyrometer would be allowed during EV-16 runs conducted during the first week of August 2000. At that point, the MIT and PNNL partners met at CETL with their SRTC counter-parts to discuss how to implement the demonstration of the millimeter-wave pyrometer . A consensus was reached that the millimeter-wave pyrometer would be incorporated in the EV-16 melter to provide a temperature profile of the melt pool surface as well as some indication of cold cap coverage. This required modifying the EV-16 melter slightly by adding a port on the melter side through which to pass a rotatable waveguide. MIT will provide the electronics for the millimeter-wave pyrometer during the demonstration. Future demonstrations of the MWM capabilities for viscosity and conductivity measurement are also planned based on what is learned during this first demonstration and on other available melter campaigns.

Some research was done at SRTC to identify the advantages of using the Millimeter-Wave Measurements (MWM) technology to directly measure melt viscosity in the Defense Waste Processing Facility at SRS. During DWPF processing of Macrobatch 2 which consisted of a blend of Savannah River Site's (SRS) High Level Waste Tanks 51 and 42, the predicted viscosity of the DWPF glass was very close to its upper limit of 100 poise. This hard viscosity constraint is necessary to allow processing of the DWPF glass, i.e. the ability to pour and properly mix the melt pool. In response to this encroachment on the high viscosity limit, SRTC developed an in-house technique for measuring glass viscosities at melt temperatures. A Harrop, high-temperature viscometer was developed to examine the viscosity of several glasses in the Macrobatch 2 compositional range. As a result of this study, it was found that uranium might affect the melt viscosity as seen in Macrobatch 2. There is preliminary evidence that glasses without uranium have a predicted viscosity greater than the measured viscosity and glasses with uranium have a predicted viscosity lower than the actual measured viscosity. This uranium effect was only observed in the sludge-only processed glasses and not the coupled sludge-PHA glasses. This SRTC study showed the need for a better prediction of the DWPF glass viscosity.

The DWPF melt viscosity prediction comes from a first principle model developed by SRTC[4] based upon the $(SiO_4)^{-4}$ tetrahedra linkages in glass. Alkali or alkaline earth elements depolymerize the $(SiO4)^{-4}$ linkages in glass (SiO_2) and every mole of M_2O, where M is a monovalent cation like Na, Li, Cs, or K, causes two non-bridging oxygen bonds to form. From other glass data examined, it was also deduced that every mole of Fe_2O_3 formed two non-bridging oxygen bonds, every mole of Al_2O_3 created two bridging oxygen, and every mole of B_2O_3 created one non-bridging oxygen. Based on the information collected during this study, the following non-bridging oxygen term was defined that explained the majority of the viscosity data correlation:

$$NBO = \frac{2*(M_2O + Fe_2O_3 - Al_2O_3) + B_2O_3}{SiO_2}$$

Using this first principle approach, the viscosity prediction can be expressed as:

$$\log(h) = A + \left(\frac{1}{T} + NBO\right) \bullet B$$

where A and B are constants based upon the empirical fits of the glass viscosity data and T is the temperature of the glass. The composition dependence comes through the Non-Bridging Oxygen (NBO) term. To account for uncertainty in this model, Scheffe type confidence bands (CB) are calculated as:

$$CB = s_r \sqrt{p \bullet F_a\left(p, n-p\right)} \bullet \sqrt{\left(1 \quad \frac{1}{T} \quad NBO\right) \bullet \left(X^T X\right)^{-1} \bullet \left(1 \quad \frac{1}{T} \quad NBO\right)^T}$$

where s_r is the root mean square of the regression fit, $F_\alpha(p,n-p)$ is the F-statistic for a model with p parameters and n-p degrees of freedom for an uncertainty interval of $100*(1-\alpha)\%$, X^TX is the product moment matrix for the regression fit, superscript T refers to transpose, and the other terms (1 1/T NBO) represent the specific point where to evaluate the confidence bands. So the viscosity prediction with uncertainty bands becomes:

$$\log(h) = A + \left(\frac{1}{T} + NBO\right) \bullet B \pm CB$$

Since DWPF operates at a constant temperature of 1150°C, the above equation reduces to a quadratic that can then be solved for upper and lower limits on the viscosity in terms of the Non-Bridging Oxygen term NBO. These NBO limits can then be translated into limits on the individual oxide terms. Therefore the processing constraints on viscosity of between 20 and 100 Poise are translated into compositional limits. These viscosity compositional limits are then factored in with other compositional limits of the Product Compositional Control System (PCCS)[5] such as liquidus temperature, glass durability, homogeneity, to find an acceptable compositional blend space for the DWPF sludge waste, frit, and PHA (if present).

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4 "The Relationship between Glass Viscosity and Composition: A First Principles Model for Vitrification of Nuclear Waste", C. M. Jantzen, Westinghouse Savannah River Company, Presentation at American Ceramic Society Annual Meeting, Dallas, TX, April 24, 1990.

5 "DWPF Waste Glass Product Composition Control System," K. G. Brown, R. L. Postles, Westinghouse Savannah River Company, Ceramic Transactions: Advances in Fusion ad Processing of Glass, vol. 29, 1993.

The Millimeter-Wave Measurements viscosity monitor could provide a better estimate of the on-line viscosity, thus eliminating or reducing the uncertainty in the viscosity model discussed above. This reduction in uncertainty in the viscosity prediction could allow for a larger blend space or increase the processing region for the DWPF sludge waste. This enhanced prediction of viscosity then could lead to better control of the melter. Instead of depending on a batch-wise prediction of the viscosity, a continuous on-line measurement of the viscosity would be available through the MWM instrumentation. Process control decisions could be based on what the current viscosity is measuring as opposed to a predicted value. To explore these potential control enhancements, experiments are planned in the next fiscal year for demonstrating the on-line viscosity capability of the MWM technology.

In addition to the usefulness of an on-line measurement of viscosity, on-line temperature profiling of the MWM technology would be valuable for DWPF in determining cold cap size and distribution. Currently DWPF does not have a readily available technique for measuring cold cap coverage. Cold cap coverage is important in that it affects the overall melt production rate and thus impacts DWPF's primary task of disposing of High Level Waste by a set schedule. Cold Cap coverage can influence how much melter feed is allowed in and at what intervals to avoid violating processing constraints, like the lower plenum vapor space temperature. The lower plenum vapor space temperature interlocks the melter feed if it drops below a certain value that would prevent combustion of the incoming feed materials. The MWM technology may also be of help with this process-limiting behavior by measuring the plenum vapor space temperature on-line. The current vapor temperature measurement is delayed due to a thick thermowell in which a thermocouple is housed. The safety interlock tied to this thermowell-measured plenum vapor temperature may then be artificially limiting the melter feed when the true vapor space temperature is higher than what is indicated. The on-line vapor temperature measurement capability of the MWM technology still needs some development but could be of significant use to DWPF. An attempt will be made in FY01 to develop this vapor temperature measurement technique.

Another added benefit of installing the Millimeter Wave Measurements instrumentation in DWPF would be the ability to measure temperatures at different depths in the melt pool. This capability could be used to help determine melter hot and cold spots. Identification of these hot and cold spots would help tell if the heating electrodes are functioning properly and if the melt pool is well circulated. In the same manner, the MWM could be used to measure viscosity at different melt pool depths. The ability to measure all these glass properties would help the melter run more smoothly and help insure a steady production rate. There is a belief that the millimeter-wave waveguide could also be used to measure melt density on-line. This ability would further enhance the operation and control of the melter.

In the coming fiscal year, more melter demonstrations of the MWM technology are planned. SRTC will coordinate these demonstrations at the Clemson Environmental Technology Laboratory as well as at the Mini-Melter facilities at SRS. SRTC will also provide Harrop, high-temperature measured melt viscosities of several DWPF type glasses to verify the millimeter-wave viscosity measurements.

SYMPOSIUM: The symposium AA on “Millimeter/Submillimeter Wave Technology – Materials, Devices, and Diagnostics” turned out to be an international event with presentations from UK (2), France-Finland-Italy (2), Russia (2), Japan (3), and USA (8 with one co-authorship from Canada), totaling to 17 presentations covered in two sessions. The first session on characterization and diagnostics started with an expert overview of millimeter and submillimeter wave components by Chris Mann from The Rutherford Appleton Laboratory, UK. Paul Woskov from Plasma Science and Fusion Center at Massachusetts Institute of Technology and S. K. Sundaram from Pacific Northwest National Laboratory elaborated the application of millimeter wave technology to diagnose high temperature processes under harsh environments using robust waveguides and novel designs. They presented millimeter wave data for simulated high-level nuclear waste glasses that will be processed in a melter (vitrification) for safe disposal. Charles Oleson from Oleson Microwave Labs emphasized the importance of calibration for 110-325 GHz vector network analysis. This was followed by description of vector measurements for dielectric characterization by Phillippe Goy from AB Millimetre, France. Vladimir Lyubchenko from Russian Academy of Sciences presented the potential of the millimeter wave imaging for civilian applications. Joe Ogita from Kanagawa Institute of Technology and Takeo Katoh from Mitsubishi Materials Corporation both from Japan summarized the application of UV/millimeter wave technique to characterize the subsurface damage of silicon and hydrogen-implanted silicon.

The second session on material components and devices started with an overview of millimeter wave solid state devices from Neville Luhmann's research group from University of California at Davis. J. G. Fleming (Sandia National Laboratory) and T. W. Crowe (University of Virginia) elaborated fabrication and characterization of different diodes for application in the millimeter/submillimeter wave technology. Steve McKnight from Northeastern University accounted the application of planar ferrite materials. Vladimir Lyubchenko (in lieu of V. V. Meriakri) from Russian Academy of Sciences showed how millimeter waves could be used to measure water content and to monitor moisture in different materials. Robert Freer from University of Manchester, UK reviewed the microwave dielectric ceramics for communication application. D. K. Verma (University of Central Florida) presented data on arsenic sulfide glasses used for this application as a waveguide.

Fourteen manuscripts received so far are under review. The Proceedings will be published by the Materials Research Society once the peer review is completed.