Mitigation of Yellow Phase Formation at the Rokkasho HLW Vitrification Facility - 10107

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ABSTRACT

The Rokkasho Reprocessing Plant, located in northern Japan, includes facilities for reprocessing spent nuclear fuel and conversion of the high-level waste into a stable glass waste form by vitrification. The vitrification process centers on two, 2.6 m^2 joule heated ceramic melters. The presence of significant amounts of molybdenum in the HLW stream can lead to the formation of a molybdate salt phase ("yellow phase") during vitrification. These salts are undesirable from both melter operations and product quality perspectives. Earlier full-scale mock-up testing with waste simulants suggested that operating protocols that had been developed would be adequate to manage yellow phase formation. However, during inactive and active test campaigns at the Rokkasho plant, yellow phase formation was found to be much more prevalent than was expected on the basis of the mock-up test results. Thus, the objective of the present work was to investigate potential strategies to suppress the formation of the molybdate yellow phase. This work was specifically constrained such that the composition of the final glass product must remain unchanged since it is likely that such a solution would involve the least impact to the design and operation of the facility and therefore could be implemented more easily and more quickly. The principal mitigation strategy that was investigated in the present work employed a reformulation of the glass frit combined with redistribution of some of the components in the frit to the liquid waste stream such that the composition of the final vitrified product remains unchanged. The melting behavior of the reformulated frit and waste simulant with chemical additives was assessed in both gradient furnace and isothermal melting tests. These screening tests were used to down-select preferred modified feed blends that were then subjected to confirmatory testing on a small-scale continuously fed joule heated ceramic melter system. The test results showed that the new strategy successfully prevented yellow phase formation. Based on these results, further testing is ongoing to support the potential implementation of this mitigation strategy.

INTRODUCTION

The Rokkasho Reprocessing Plant is located in Rokkasho Village in northern Japan. The site is operated by Japan Nuclear Fuel, Ltd. (JNFL), a private venture led by the nation's nine electric utilities. The site is an important component in the creation of Japan's closed nuclear fuel cycle. Facilities at the Rokkasho site include the reprocessing plant, spent fuel receiving and storage facilities, the uranium enrichment plant, the low level waste disposal center, the vitrified waste storage center, and the MOX fabrication plant. The nominal capacity of the reprocessing plant is

800 metric tons of uranium per year, which is equivalent to the spent fuel from about forty 1000-MW power plants. High level waste (HLW) from the reprocessing plant will be converted to stable glass in the integrated waste vitrification facility.

The Rokkasho vitrification process centers on two, 2.6 m^2 joule heated ceramic melters. These melters were uniquely designed to treat the specific waste chemistry and high noble metal concentration of the Rokkasho flowsheet. In addition, the waste stream also contains significant amounts of molybdenum. When the concentration of molybdenum is sufficiently high, a molybdate salt phase can form during nuclear waste vitrification [1 - 4]. Such molybdate salts are typically referred to as "yellow phase," since in addition to a variety of other elements they also incorporate chromium, which gives them their yellow coloration. These salts are typically low melting, very fluid at typical melter operating temperatures, of variable density depending on their composition, and undesirable from both melter operations and product quality perspectives. Full-scale mock-up testing with waste simulants suggested that operating protocols that had been developed would be adequate to manage yellow phase formation. Subsequently, over the past two years, the Rokkasho plant has been executing a series of inactive and active test campaigns to ready the facility for full time commercial operations. During the early active test campaigns, yellow phase formation was found to be much more prevalent than was expected on the basis of the mock-up test results. This is believed to be due in part to significant differences in waste composition. In some instances, yellow phase formation interrupted the steady glass discharge from the melter's bottom drain, complicating its operation. As a result of these findings, further measures are being investigated to mitigate yellow phase formation at the Rokkasho facility.

The objective of the present work was to investigate potential strategies to suppress the formation of the molybdate yellow phase during the vitrification of Japanese high-level waste (HLW). Ideally, the preferred mitigation approaches would be those that involve the least impact to the design and operation of the Rokkasho full-scale active vitrification systems. In addition, however, the present work was specifically constrained such that the composition of the final glass product must remain unchanged. While it is possible that, in the longer-term, there may be advantages to modifying the current glass composition, it is likely that a solution that does not change the product glass composition could be implemented more easily and more quickly. Thus, the principal mitigation strategy that was investigated in the present work employed a reformulation of the glass frit in such a way that the composition of the final vitrified product remains unchanged. This was accomplished by redistributing some of the components in the frit so that they are instead added to the liquid waste stream. The basis for this approach is the expectation that the incorporation of certain components in the liquid waste will make them available early in the melting process so that they are able to combine with and "tie up" components that would otherwise form the yellow phase. However, the reformulation must be done in such a way that the general melting properties of the frit, including the overall glass production rate, are not deleteriously impacted. The melting behavior of the reformulated frit and waste simulant with chemical additives was assessed in both gradient furnace and isothermal melting tests. These screening tests were used to down-select preferred modified feed blends that were then subjected to confirmatory testing on a small-scale continuously fed joule heated ceramic melter system.

YELLOW PHASE FORMATION

The HLW stream investigated in the present work is rich in alkali and alkaline earth oxides (Na, Cs, and Ba), molybdenum oxide, rare earth oxides, and several other transition metal oxides (Fe, Mn, Ni, Zr). On an oxide basis the waste simulant used in the present work was composed of approximately 23 wt% Na_2O, 11 wt% each of CeO_2 and ZrO_2, 9 wt% each of MoO_3, Gd_2O_3, and Nd_2O_3, and lesser amounts of a variety of other constituents. The currently adopted processing method introduces glass formers in the form of glass beads.

A sample of the yellow phase collected from a melter discharge during a mock-up campaign in the JNC test facility at Tokai (KMOC) was analyzed by x-ray fluorescence spectroscopy (XRF) and dissolution followed by direct current plasma atomic emission spectroscopy (DCP-AES). On an oxide basis, the sample was composed of about 70 wt% MoO_3, 13 wt% Na_2O, 4 wt% Li_2O, and about 2 wt% each of oxides of Ba, Ca, and Cs, and lesser amounts of a variety of other constituents. The major crystalline phases in the yellow phase identified by x-ray diffraction (XRD) and scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM/EDS) were sodium and calcium molybdates, with minor amounts of cesium and barium molybdates. In addition, a yellow phase composed predominantly of calcium molybdate was observed on the bottom of the KMOC melter as a residue after the glass had been discharged. It is noteworthy that these yellow phases formed in a glass melt in which the MoO_3 content was considerably below its saturation limit, indicating the importance of kinetic effects.

It was hypothesized that the relatively high viscosity of the original glass frit may well impede mixing and reaction between the waste components and the glass and that without rapid mixing and reaction with the glass formers, the alkalis, alkaline earths, and molybdenum oxide in the waste feed would combine to form molybdate salts before being incorporated into the glass melt. Sodium molybdate melts at 686°C, cesium and calcium molybdates melt or decompose at 936°C and 985°C, respectively, and barium molybdate melts at a much higher temperature of 1480°C. Since sodium molybdate would be the most abundant salt from the HLW waste, extensive eutectic melting will occur for barium and calcium salts at around 700°C [5]. As a result, a molten molybdate salt phase incorporating various metals would develop in the melter, even though the overall glass system is not saturated with MoO_3. Once separated, the slow kinetics inhibit the incorporation of the molten molybdate phase into the silicate melt. We have observed and extensively investigated very similar phenomena during the vitrification of high-sulfur wastes, such as the low-activity fraction of the Hanford tank wastes [6 - 10].

Since kinetic effects may be important in the formation of a low-melting molybdate phase, its formation may be significantly affected by the way in which the sodium-molybdenum-rich waste simulant and highly viscous glass frit are introduced. As discussed previously, a constraint on the present work was that the composition of the final glass product not be changed. Consequently, the strategy that was investigated employed modification of the waste-only simulant part by redistributing some of the components in the glass frit so that they are instead added to the liquid waste stream. The basis for this approach is the expectation that the incorporation of certain components in the liquid waste will make them available early in the melting process so that they are able to combine with and tie up components that would otherwise form the yellow phase. However, the reformulation of the glass frit and simulant must be done in such a way that the

general melting properties of the frit, including the overall glass production rate, are not deleteriously impacted.

EXPERIMENTAL

The components to be introduced into the waste simulant part should be selected so that they do not exacerbate the formation of the yellow phase but instead act to compete with molybdenum for alkalis and/or alkaline earths, or bind with molybdenum to form more refractory components before being converted into glass melt. Moreover, in order to minimize the impact of the modification, only a small fraction of the glass frit material should be redistributed and the resultant simulant and glass frit should be processable using the existing melter technology. These prospective composition variations were assessed using a combination of small-scale screening tests, as described below.

The screening tests were performed using a mixture of dried simulants and their matching glass frits (i.e., as modified by the particular redistribution scheme) in isothermal crucible tests, a horizontal gradient furnace, and a vertical gradient furnace. The experimental methods are complimentary in many respects. The gradient furnaces create a thermal environment similar to that in the cold cap, in which the feed materials at different temperatures could change, evolve with time, and interact with neighboring materials that had been evolving at different temperatures. Thus, the reacted feed materials after gradient furnace heat treatment simulate the cross section that might be observed in cold cap samples. In addition, samples generated from the gradient furnace experiments cover wide ranges of temperature in one test. The test, therefore, can be used to quickly identify the critical temperature regions at which more detailed isothermal experiments should be conducted. The isothermal experiments were planned mainly on the basis of the horizontal gradient furnace results, from which a much larger sample was obtained for more comprehensive characterization. The vertical gradient furnace tests were employed as a standardized screening test in the later stages of this work.

In all tests, the waste simulant was mixed with appropriate amounts of the redistributed glass former additives, dried overnight at 110°C, ground to pass 80 mesh sieve, and then mixed with the appropriate amount of the matching glass frit. In all cases, the combination was such as to yield a final product glass of the same composition as the current baseline glass.

The gradient furnace used in this work consists of a horizontal tube furnace that is constructed such that there is a temperature gradient along its length (12 inches). The operating conditions can be adjusted to set the upper and lower temperature limits. After the desired reaction time (1 hour, as used for the isothermal tests), the sample boat was removed, allowed to cool, and sectioned. From previous calibration of the temperature gradient, the horizontal position in the boat could be related to the temperature at that location. The useful range for this work was from 722°C to 980°C over an 11-inch distance. The samples were then removed for analysis by visual inspection, optical microscopy, and SEM-EDS. These tests permit evaluation of the temperature ranges and thermal gradients over which the salt phase forms for each sample. Feed modifications that prevent salt formation or increase the salt-phase formation temperature were considered desirable since that favors ultimate incorporation into the glass melt.

For each isothermal feed conversion experiment, appropriate amounts of the crushed glass frit and dried simulant were mixed before being loaded into a hot ceramic crucible (50 ml alumina) pre-heated to the prescribed test temperature. The crucible was then placed in a furnace for 1 hour at the selected test temperatures (750, 800, 850, or 900°C). At the end of the isothermal test, the crucible was removed from the furnace, allowed to cool in air, and cross-sectioned (dry). The exposed cross-sections of the samples of the partially melted feed pile were examined by visual inspection (by analyzing optically scanned images of whole cross-sections), optical microscopy, SEM/EDS, and x-ray diffraction (XRD). The four temperatures used in the isothermal tests were selected on the basis of the gradient furnace results.

The temperature gradient inside the vertical gradient furnace is maintained by two separate sets of heating elements, both of which are arranged in cylindrical form and aligned along their axis. The inner heater is set at 1150°C, to represent that of the glass pool, and the ambient heater is set at 600°C, representing the melter plenum temperature. A ceramic crucible is used to contain the reacting feed blend. Feed reactions under the controlled temperature gradient are allowed to continue for the designated test duration (typically 30, 60, and 90 minutes) and then stopped by rapid cooling in room temperature air. The top surface of the reacted feed blends are then inspected and photographed. After collection of samples of salt and partially reacted feed blend for further characterization, the crucibles with their feed contents are cross-sectioned (dry) to reveal the conversion progress of feed blends.

RESULTS AND DISCUSSION

Original Feed Blend

The original feed blend (i.e., original glass frit composition without any glass former redistribution) and a variety of modified versions were investigated (all yielding the same product glass composition). A key parameter is the percentage of the glass formers that are redistributed into the waste simulant. A blend that involves the least amount of material redistribution while effectively suppressing yellow phase formation is considered most desirable in terms of minimizing the impact to the feed system.

As shown in the scanned images of the sectioned gradient furnace samples (Figure 1), the yellow phase developed extensively between 820 and 900°C in the partially reacted feed materials of the original feed blend, in general agreement with the full-scale melter tests with the same waste simulant. Over the temperature range, the feed materials evolved from initial reaction and gas evolution, as manifested by vesicles or voids of different sizes and shapes, to partial melting and segregation of yellow phase, to becoming nearly completely molten. Moreover, it is noted that between roughly 920 to 950°C, another salt-like phase (brown in color) was present on the surface of largely molten glass, which was subsequently identified by SEM/EDS as Cs-rich alkali-molybdate.
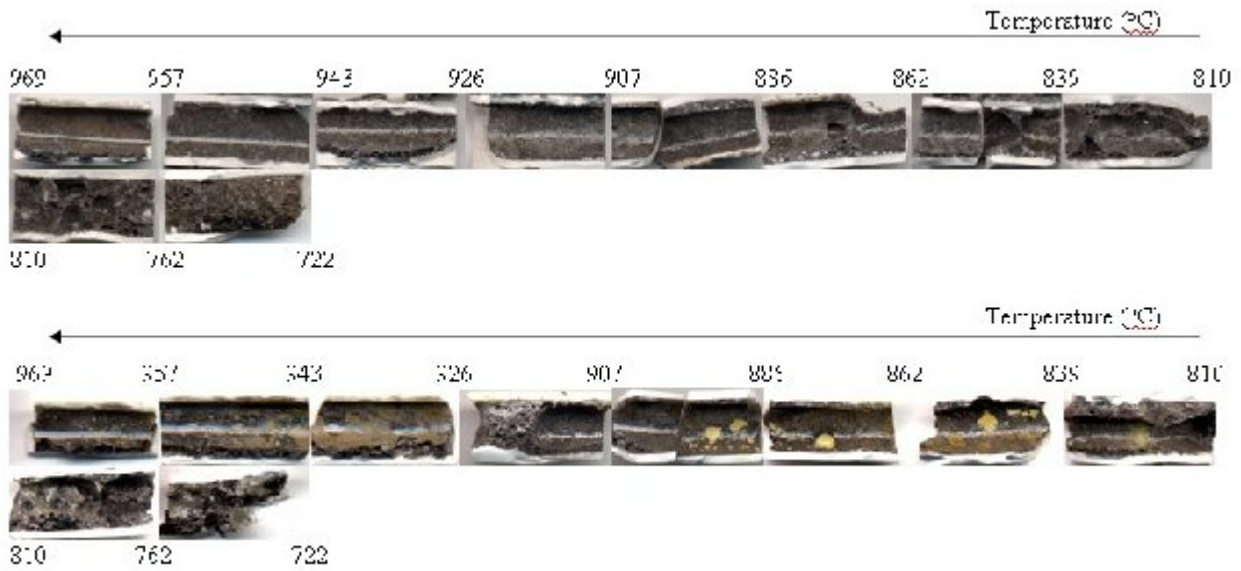
Fig. 1. Optical images of reacted feeds blends after gradient furnace heat treatment for one hour. Top: modified feed blend; Bottom: Original feed blend. The vertical height of the samples is 12 mm.
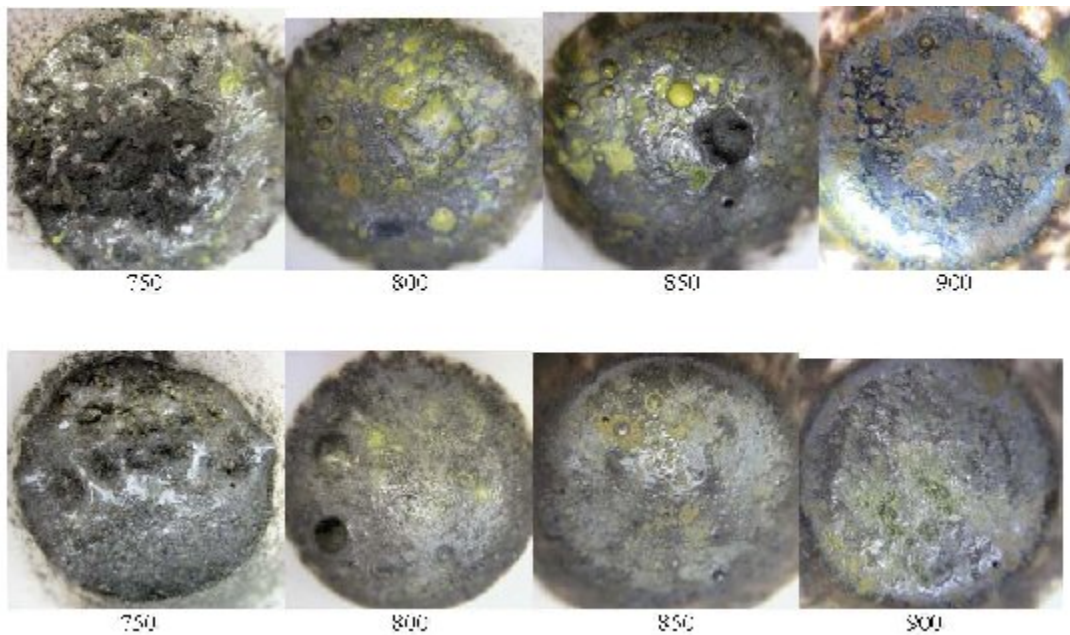

Fig. 2. Optical images of the top views of the reacted feed blends after one hour isothermal heat treatment. Top row: Original feed blend; Bottom row: Modified feed blend.
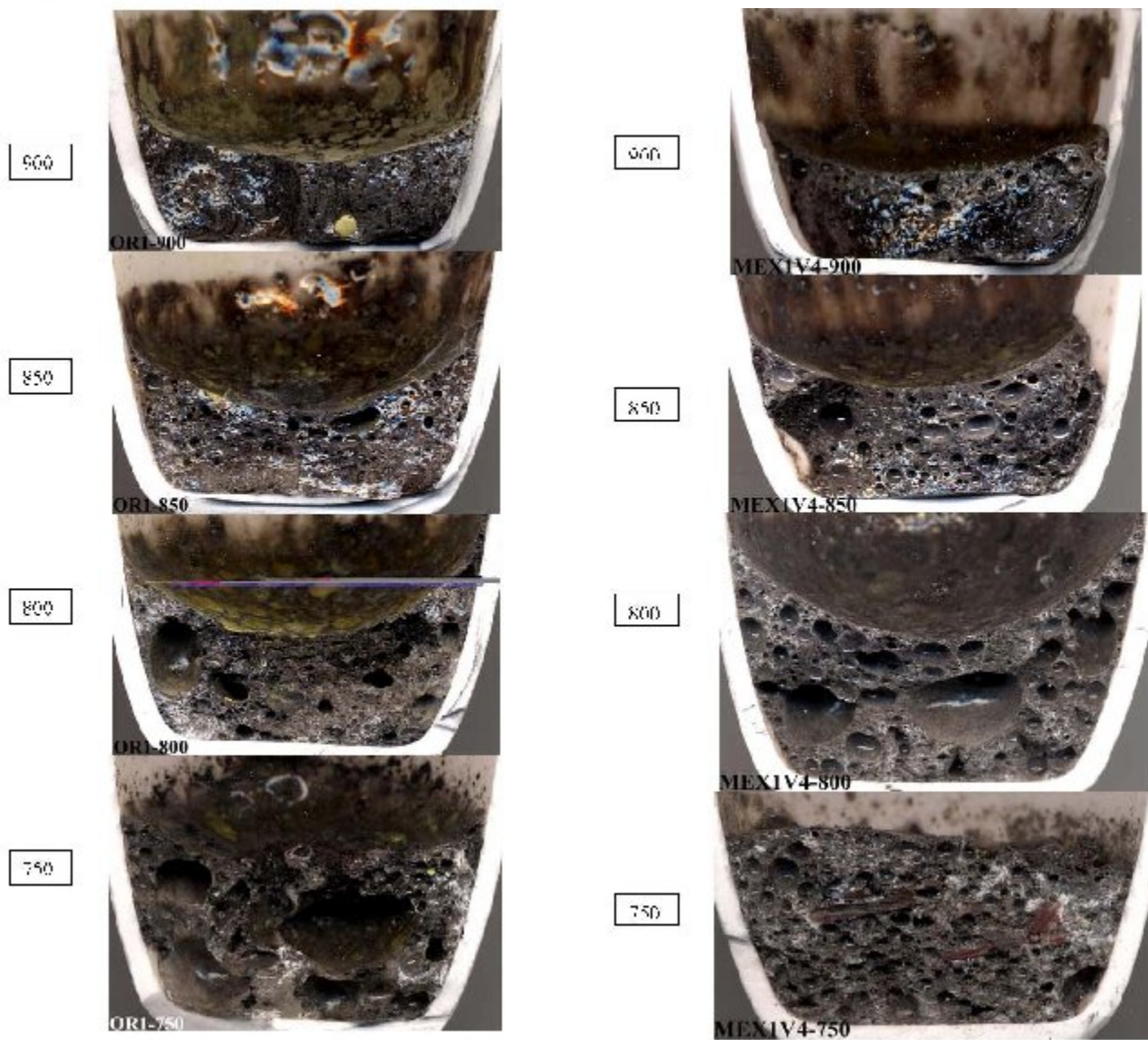
Fig. 3. Scanned images of the cross-sections of the reacted feeds of the original feed blend (left) and the modified feed blend (right) after one hour isothermal heat treatment.

Consistent with the above observations, the yellow phase was abundant on the top surface of the reacted feed materials after being treated isothermally at 800 and 850°C (Figure 2, top). Early signs of yellow phase development are visible at 750°C, and a similar yellow-brown crust formed on the surface of the sample heat-treated at 900°C. The details of the feed conversion are better shown in the scanned images of the cross-sectioned isothermal samples (Figure 3, left), in which foaming was most intense at 750°C, gradually collapsing as melting progressed with increasing temperature. A nearly spherical salt inclusion is easily visible near the bottom of the largely vitreous materials for the 900°C test. XRD analysis shows the presence of Na, Ca, Cs, and Ba molybdates as well as rare earth molybdenum oxides. At 750 and 800°C, alkaline (Na and Cs) and alkaline earth (Ca) molybdates are the major molybdenum phases but the alkaline molybdate phases diminish above 850°C. Figure 4 shows SEM images of the crystalline phases identified on the surface of the isothermally heat treated samples.
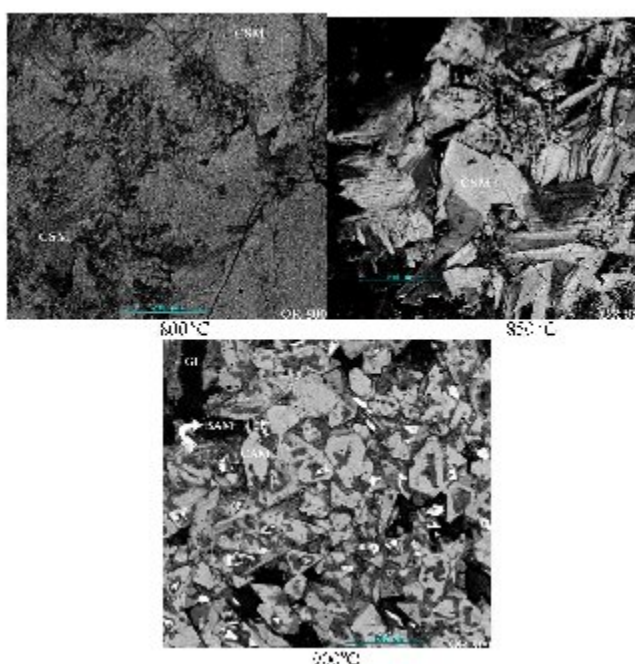

Fig. 4. SEM images of the top surface of the reacted IHI original blend after one hour heat treatment at 800, 850 and 900°C. EDS was used to identify the crystalline phases as labeled (CSM=Cs$_2$MoO$_4$; CAM=CaMoO$_4$; BAM=BaMoO$_4$; GL=vitreous phase).

Modified Feed Blend

Based on the screening test results, one of the preferred modified feed blends involves redistribution of about 6.9 wt% of oxides of Al$_2$O$_3$ and B$_2$O$_3$ from the original glass frit to waste simulant portion. The modified glass frit has similar glass transition temperature but about 50% lower melt viscosity. The modified simulant with additives (added as Al(OH)$_3$ and H$_3$BO$_3$) shows very similar rheological behavior to that of the original waste simulant and almost identical density and pH. Al$_2$O$_3$ and B$_2$O$_3$ were redistributed from the glass frit to the simulant to

compete with MoO_3 for alkalis and alkaline earths from the waste, which in turn should reduce or even prevent formation of the yellow phase during feed conversion.

As shown in the scanned images of the sectioned gradient furnace samples (Figure 1), the redistribution was effective in controlling and preventing formation of the yellow phase that had developed extensively between 820 and 900°C in the test with the original feed blend. Over the temperature range, the feed materials evolved from initial reaction and gas evolution, as manifested by vesicles or voids of different sizes and shapes, to partial melting, to becoming nearly completely molten. It is important to note that no yellow phase was observed visually throughout the whole temperature range from 700 to near 1000°C.

The progress in yellow phase mitigation is also evident from the isothermal tests at all four temperatures. The yellow phase, although still present on the top surface of the reacted feed materials, has been greatly reduced (Figures 2 and 3). As with the original feed blend, gas evolution is evident primarily at the lower temperatures (Figure 3) but no yellow-colored salt inclusion was observed beneath the surface of the reacted feed at any temperature. XRD analysis shows that, similar to the results for the original feed blend, rare earth molybdenum oxide is still present in samples at all four temperatures together with, possibly, other rare earth compounds. From 750 to 850°C, cesium molybdate is probably present as a minor phase. Two of the most notable differences from the original feed blend are: (i) The absence of sodium molybdate, which is the majority component of the yellow phase, and (ii) The possible presence of a barium aluminoborate phase ($Ba_2Al_2B_8O_{17}$, as suggested by XRD pattern analysis). $CaMoO_4$ and $BaMoO_4$ are the major molybdates on the surface of the reacted feed samples from the 800, 850, and 900°C tests. The alkali-molybdate that was observed in the tests with the original blend was not observed.

SMALL-SCALE MELTER TESTS

DM10 Melter System

Based on the results from the screening tests, small-scale continuously fed joule-heated ceramic melter tests were performed with both the original feed blend (as a control) and one of the preferred modified feed blends. The tests were performed on a DM10 melter system. The ceramic refractory-lined melter has an effective melt surface area of 0.021 m^2, and two Inconel 690 plate electrodes that are used for joule-heating of the glass pool. The glass product is removed from the melter by means of an air-lift discharge system. A dual feed system was used to deliver the melter feed into the DM10 melter, where separate containers were used for the HLW simulant and the glass frit. The HLW simulant container was mounted on load cells for weight monitoring, and feed was delivered to the feed tube using a peristaltic pump. Pre-weighed amounts of glass frit were periodically added to a calibrated hopper that was connected to a mechanical screw feeder. The waste simulant and the glass frit were both introduced into the melter through the same water-cooled, vertical feed tube. For operational simplicity, the DM10 is equipped with a dry off-gas treatment system involving gas filtration operations only. Exhaust gases leave the melter plenum through a film cooler device that minimizes the formation of solid deposits. The film-cooler air has constant flow rate and its temperature is thermostatically

controlled. A transition line connects the melter with the first filtration device. Immediately downstream of the transition line are cyclonic filters followed by conventional pre-filters and HEPA filters. The temperature of the cyclonic filters is maintained above $150^{o}C$ while the HEPAs are held above $100^{o}C$ to prevent moisture condensation. The entire train of gas filtration operations is duplicated and each train is used alternately. An induced draft fan completes the system.

Since a key objective of these tests was to assess the extent of yellow phase formation and mitigation, a series of samples were taken before, during, and after the melter tests to determine the extent of secondary phase formation. Separated secondary phases on the melt pool surface were detected by inserting a metal rod into the molten glass pool; secondary phases adhere to the metal rod and can be readily distinguished from the bulk glass. Separated secondary phases on the melter floor were detected by inserting a ceramic tube to the floor of the melter. The tube is connected through a three-way value to an air supply and a vacuum pump; slight positive pressure is supplied while the tube is inserted into the melt, which is switched to suction once the tube is in the sampling position, thereby pulling glass from the bottom of the melter into the tube. Once the tube is removed from the melt pool and cooled, glass removed from the inside of the tube is representative of glass suctioned from the melt pool floor, whereas glass from the outside of the ceramic tube is representative of the surface of the melt pool. Multiple samples of each type were taken.

Original Feed Blend

Following a period to turnover the melt pool inventory, a 65-hour test was performed with the HLW simulant and the original glass frit composition (with no redistributed glass formers). Melt pool temperature throughout the test were close to the target of 1150°C while plenum temperatures ranged from 400 to 550°C once the cold cap was established.

Samples taken prior to the test and midway through were essentially free of secondary phases. Visual observations of these glasses indicated no macroscopic secondary phases were present on the melt pool surface or floor. In contrast, many of the samples taken at the end of the test indicated that secondary molybdate phases were present on the melt pool surface and floor. Figure 5 shows a suction tube sample with the bottom portion of the ceramic tube removed to reveal the glass drawn inside from the bottom of the melter. Yellow streaks are evident along the exterior of the sample. This secondary phase originated from the surface of the melt pool and adhered to the outside of the tube as the tube was removed from the melter. In contrast, the orange-brown material at the far-right tip originated from the melter floor. SEM/EDS analysis of the samples from the outside of the tube focused on two morphologies, referred to as the "yellow" and "mottled brown/gray" areas, respectively. The "yellow" areas were found to consist of sodium and cesium molybdates. The "mottled brown/gray" areas consist of sodium molybdates and cesium oxides. Microscopy on the samples from the glass taken from the inside of the tube indicates that the secondary phases at the melter floor consist of calcium, barium, and sodium molybdates. The higher concentration of alkaline earth molybdates in the melter floor sample is consistent with previous observations from full-scale melter tests with this simulant,

with the denser alkaline earth molybdates settling to the melter floor while the lighter alkali molybdates are found in higher concentration on the melt pool surface.

In summary, therefore, the DM10 melter tests with the original feed formulation reproduced the yellow phase formation that was found in full-scale melter tests and in the small-scale screening tests.

Figure 5. Photograph of a melter suction sample from the end of the test with the original feed blend. The bottom part of the ceramic tube was removed to expose the glass inside. Note patches of yellow phase (originating from the melt surface) and orange-brown material on the far right tip (originating from the melter floor). White material is the ceramic sampling tube.

Modified Feed Blend

After flushing the melt pool to ensure that any secondary phases had been removed (as confirmed by sampling), a second 65-hour test was performed with the HLW simulant with redistributed glass formers and the modified glass frit composition. Melt pool temperature throughout the test was close to the target of 1150°C while plenum temperatures ranged from 525 to 625°C once the cold cap was established. The feed rate was fixed at the same value as employed for the test with the original feed blend.

In contrast to the results from the first test, the series of samples taken at the end of testing showed no discernable yellow phase. There were no signs of secondary phases on the outside of the dip and suctions samples indicating there were no secondary phases on the melt surface. Furthermore, all glass inside the suction tubes was free of any visible secondary phases,

indicating that molybdate phases did not form during the test and settle to the bottom of the melter. The lack of secondary phases in these samples was confirmed by analysis using SEM-EDS.

The lack of secondary phases corroborates the small-scale screening test results and the proposed yellow phase mitigation strategy.

CONCLUSIONS

Yellow phase development during conversion of HLW feed under melter operating conditions has been reproduced in small-scale experiments with mixed feed samples subjected to either an isothermal heat treatment or either horizontal or vertical temperature gradients. The temperature range within which an alkali molybdate dominated yellow phase forms and segregates is around 800 to 900°C, with sodium molybdate as the dominant salt. Once formed, the molybdate yellow phase tends to separate and flow to the surface of the partially molten feed materials due to its lower density, melting point, and viscosity.

The results of the present work show that yellow phase formation during feed conversion can be effectively mitigated *without* modifying the composition of the final glass product. This was accomplished by redistributing a small portion of oxides from the original glass frit to the waste simulant in order to inhibit the formation and segregation of the alkali molybdate yellow phase. However, this must be done in such a way that the modified glass frit composition is still viable. The modified feed blend, with redistributed Al_2O_3 and B_2O_3 and corresponding modified glass frit composition, showed greatly reduced extent of yellow phase formation in small-scale screening tests as compared to the original feed blend and glass frit. These results were confirmed in tests on a small-scale continuously fed joule heated ceramic melter system. These tests confirmed the formation of yellow phase with the original feed blend but showed no yellow phase formation with the modified feed blend, both of which yielded the same product glass composition.

It should be emphasized that the present work was constrained in such a way that the final glass product composition remains unchanged. If that constraint is relaxed, it is quite possible that yet more robust solutions could be developed such that waste loadings could be increased while maintaining suppression of yellow phase formation. Such work is currently in progress. Ongoing work is also addressing the application of the redistribution approach to projected HLW streams with slightly different compositions, the tolerance of this strategy with respect to process variations, and larger-scale testing with a view to near-term implementation at the Rokkasho facility. Longer-term efforts are focused on strategies that may also involve modification of the product glass composition.

ACKNOWLEDGMENTS

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