

**GLASS-CERAMICS IN A COLD-CRUCIBLE MELTER :
THE OPTIMUM COMBINATION FOR GREATER WASTE PROCESSING EFFICIENCY**

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ABSTRACT

Improving the efficiency of nuclear waste immobilization is constantly desired by all nuclear waste management programs world-wide. For high-level and other waste to be vitrified in traditional ceramic Joule-heated melters operated at temperatures up to 1150 °C, process flexibilities including waste loadings are often restricted by this temperature limit as well as the need to consider wastefrom corrosion of refractory linings and electrodes. New melter technologies, such as the cold-crucible melter (CCM), enable processing up to significantly higher temperatures free of many of the limitations of conventional melters. Higher processing temperatures open up the way for wider composition and processing envelopes to be considered for the vitrification process, including the possibility for higher waste loadings.

In many instances the presence of crystals in the final cooled wastefrom is not considered desirable within presently existing glass specifications. For some feed compositions increased waste loadings can lead to the formation of large amounts of crystals, and thus to a significant departure from the ‘glass’ state. Nevertheless it is recognized that, in general, increasing the acceptable volume fractions of crystals in the glass offers the best opportunity to increase waste loading, all other factors being equal. In addition, the deliberate promotion of specific crystalline phases by design may enhance the quality of the wastefrom, for example by partitioning a long-lived radionuclide into a very stable crystalline phase, or by depleting the glass in detrimental elements. In order to explore the potential improvements by harnessing the higher achievable processing temperatures and immunity to refractory corrosion available with the cold-crucible melter, and after promising indications for synroc-based matrices, it was decided to investigate the feasibility of designing and producing via melting new high temperature ‘glass-ceramic’ wastefroms for high level waste immobilization.

The INEEL calcines were selected as example feed compositions. These calcines have a wide range of problematic compositions. They either have high amounts of crystal-forming components, and/or components that lead to corrosive melts, and for good measure, the components in some waste types are quite refractory for vitrification as well. The recent DOE High-Level Waste Melter Review Report concluded that, for the INEEL calcine wastes in particular, the CCM could have sufficient advantages over the Joule-heated ceramic melter to justify its evaluation for direct vitrification of these wastes. Based on the extensive ceramic design experience of ANSTO, in collaboration with the CEA and COGEMA for a CCM implementation, a preliminary set of waste forms has been developed that immobilize long-lived waste actinides into highly chemically durable crystalline phases by design, using refractory crystal-forming components already in the wastes to advantage, while at the same time maintaining a very good overall leach resistance for the glass-ceramics even after “canister centerline cooling” (CCC) heat treatments. This paper presents the results of a 80 kg technological scale test in the CCM of a glass-ceramic formulation for the average Bin Set 2 formulation, at a conservative waste loading of 50 %.

INTRODUCTION

Waste volume minimization is a constant goal for all nuclear waste management programs world-wide. Until very recently, all the existing HLW vitrification programs in the world only considered matrices based on borosilicate glasses, since these had proved to be durable and easy to process in ceramic-lined, Joule-heated or metal-lined, induction-heated melters, at typical operating temperatures of 1100 to 1150 °C. In most cases, only small amounts of

relatively benign crystals were tolerated either in the melters or upon cooling. These borosilicate waste forms proved to be very successful in several industrial HLW vitrification programs, in the United States, Europe and Japan. However, recent studies performed with additional types of wastes, both radioactive and non-radioactive, pointed to the fact that this requirement of avoiding the formation of crystals in the glass matrix led to a (sometimes severe) restriction of waste loading. This becomes particularly evident when new melter concepts, such as the cold-crucible induction-heated melters (CCM) developed in France, are easily capable of overcoming the temperature limit of 1150 °C and, thus, easing one of the often observed processing constraints associated with waste loading improvement. This point has been emphasized, for instance, in the *High-Level Waste Melter Review Report* (1) published in 2001. In parallel, a steady increase of interest and expertise is observed for the immobilization of radionuclides in tailored ceramic phases which can provide very durable and stable crystalline matrices. The deliberate promotion of specific crystalline phases in a glass matrix by design may thus enhance the quality of a glass waste form, for example by partitioning a long-lived radionuclide into a very stable crystalline phase or by depleting the glass in detrimental elements.

The INEEL calcines in Idaho were selected as example feed compositions for this study, since they span a wide range of problematic compositions with high amounts of crystal-forming components and/or components that lead to corrosive melts. In addition, the components in some waste types are quite refractory. Glass-ceramic waste forms have been studied at various times within INEEL over the past 25 years with a view to immobilizing HLW. A comprehensive review of previous efforts (2) details a wide range of proposed waste forms and processing routes, including melting, hot isostatic pressing, and sintering. After promising indications for synroc-based matrices in glass-ceramics via melting routes (3, 4, 5), it was decided to investigate the feasibility of designing and producing via melting new high temperature glass-ceramic waste forms for high level waste immobilization. A collaborative program was launched, combining the extensive ceramic design experience of ANSTO, the radioactive waste glass and process design expertise of the CEA, and the industrial experience of COGEMA.

The whole formulation strategy to be used for this type of program has been defined and investigated. The waste forms were developed to immobilize long-lived actinides into highly chemically durable crystalline phases, taking advantage of the refractory, crystal-forming elements already present in the wastes, while maintaining a very good overall leach-resistance for these and other elements consigned to the glassy matrix. The whole range of variability of the waste composition was accounted for. The requirements for melting in a CCM were also met. From the set of proposed formulations, a representative example was selected for the large scale pilot demonstration. The objective of this demonstration was to investigate the physical feasibility of melting the given composition in a CCM of French design, and to characterize the product and compare it with the laboratory scale melts. The pilot demonstration was performed in December 2002 and detailed characterization of the product is underway.

FORMULATION STRATEGY

Our main formulation strategy was to develop glass-ceramic waste forms at higher waste loadings than generally achievable with borosilicate glasses, having superior chemical durabilities across a wide range of cooling scenarios related to pouring into US canisters, and which have physical properties amenable to high temperature melting in the CCM. ANSTO was specifically in charge of glass-ceramic formulation development in collaboration with the CEA.

The calcine waste compositions

The study focused on average compositions estimated for the calcines stored in the six INEEL “bin sets”, compiled from published data (6). The calcine types are designated zirconia-rich calcine, high alumina calcine, and mixed calcines. The zirconia-rich calcine (Bin Sets 3, 4 and 5) contains high concentrations of zirconia [ZrO_2] and calcium fluoride [CaF_2]. The high ZrO_2 can promote the formation of zirconia crystals at the processing temperature while the very high fluorine can impact negatively on the viscosity and corrosivity of the melt. In contrast, the high alumina calcine comprises about 90% alumina [Al_2O_3] (Bin Set 1). High alumina can lead to refractory and viscous melts that are also prone to the crystallization of aluminous phases such as “magnetoplumbite” [$(Ca,Na,K,Mg,Sr)(Al,Fe,Ti)_{12}O_{19}$], anorthite [$(Ca,Na)(Si,Al)_4O_8$], or even alumina [Al_2O_3], a phenomenon that can lead to an overall poor durability of the product because of the effect such crystallization can have on the composition of the residual glass phase, in similar fashion to the effect on product durability in compositions that lead to nepheline formation. Bin Sets 2 and 6 contain mixtures of the above two calcine types and have average compositions essentially intermediate

between them. Overall, the data in (6) suggest that the high alumina and mixed calcines in Bin Sets 1, 2 and 6 comprise about 40 % of the total volume of waste. Also, in total the calcines hold about 46 kg of Pu.

Requirements for the waste forms

A set of constraints was first defined, to account for industrial, operational, and quality requirements.

The selected waste forms had to be able to accommodate the whole range of waste compositions, with optimized waste loadings. They also had to be processable in the selected technology, a requirement that translated into limits on the viscosity and electrical resistivity of the melt. The powder form of the feed was used because it allowed optimization of the process throughput in a manner appropriately aligned with the nominally powdered form of the actual calcined solids in the bin sets.

The waste forms had to be usable in an industrial context:

- To allow pouring in standard US canisters, and to limit the volatility of some radionuclides, the maximum operating temperature was set at 1300 to 1350 °C.
- As much as possible, it was necessary to minimize the number of different waste form compositional types to treat the whole range of calcine compositions, in order to ease operation and minimize the potential cost of waste form qualification.
- Since, for glass-ceramics, the cooling scenario can impact the microstructure and, sometimes, the quality of the product, the waste form had to be designed to maintain satisfactory quality over a wide range of cooling scenarios, to account for the complex thermal evolution inside a large industrial canister, and to avoid the need of an impractical controlled cooling tunnel, for instance. The baseline cooling scenario used during the formulation development was derived from a CCC (Canister Centerline Cooling) – type curve, but many other scenarios were evaluated, from rapid quenching to very slow cooling (see the section on heat treatments below). The “CCC” cooling scenario used in the laboratory consisted of a decrease from 1300 °C down to 900 °C at a rate of 300 °C/hour, and then a decrease from 900°C to room temperature at 24 °C/hour. This heat treatment lasts about 42 hours.

The waste form quality had to be compatible with disposal into a deep geologic facility such as Yucca-Mountain. Since no clear qualification criteria yet exist for new matrices like glass-ceramics, it was considered that since the selected crystal phases were more durable than the surrounding parent glass, a preliminary quality indicator could be the PCT-B leaching test (7) used as an indicator for HLW glasses. This test would mostly reflect the alteration of the glass phase. The target durability was set such that the measured chemical durability for the waste form via a PCT-B test would be 10 to 100 times greater than that of the EA glass.

Strategy

Since most of the INEEL calcines are very rich in zirconia, we have capitalised on this and designed the formulations to promote the formation of a zirconium-based phase able to immobilize the long-lived actinides. Zirconolite [CaZr(+actinide)Ti₂O₇] was selected as the primary phase for the following reasons: it is a well known phase supported by a huge database proving its long term durability (even on long geological timescales); it is experimentally proven to crystallize in a very wide range of chemically durable glass compositions; it is capable of accommodating more actinides than both zirconia [ZrO₂] and zircon [ZrSiO₄] in a glass environment; and it does not deplete the parent glass in silica, like zircon (this could decrease the glass durability).

The formulation strategy had to take into account the fact that the two major composition types described earlier could be stored together, with layering on various different scales, in some of the bins. It can thus be expected that the composition of each calcine batch may be a more-or-less an intermediate combination of these two major types. It was thus first decided to concentrate initially on producing optimum formulations for the two-end-member compositions (zirconia-rich calcine as in Bin Set 4 and alumina-rich calcine as in Bin Set 1). From this work, only two reference glass ceramics were designed that could accommodate the entire range of calcine compositions likely to be encountered. The decision on which reference glass-ceramic composition to choose for a particular calcine batch would thus be based on which composition gives the highest waste loading. The determining discriminating factor is the alumina content of the batch. The major crystalline phases in both cases are the required phases

zirconolite and fluorite, with some extra zirconia in the formulation for the zirconia-rich calcines. The formulations have been specifically developed with attention to the avoidance of the crystallization of detrimental phases throughout the full range of envisioned canister cooling scenarios. Examples of such detrimental phases that were initially encountered and then subsequently avoided via formulation design include magnetoplumbite-type phases $[(Ca,Na,K,Mg,Sr)(Al,Fe,Ti)_{12}O_{19}]$, nosean $[Na_8Al_6Si_6O_{24}SO_4]$, nepheline $[NaAlSiO_4]$, anorthite $[(Ca,Na)(Si,Al)_4O_8]$, alumina $[Al_2O_3]$, and zircon $[ZrSiO_4]$.

To test the feasibility of this approach, it was applied to the average compositions of the six bin sets. Bin Sets 2 and 6 (“mixed calcine”) were best treated using the high-alumina formulation defined for Bin Set 1, and Bin Sets 3 and 5 were more adapted to the high-zirconia composition defined for Bin Set 4.

Summary of laboratory scale experimental work and results

About four hundred 30 g laboratory scale melting and cooling experiments in platinum crucibles, mostly cooling from temperatures of 1300 or 1350 °C, at various cooling rates, have allowed us to:

- Define process windows and phase boundaries which allow us to tailor additives to maximize waste loadings, while keeping adequate processing properties for the glasses as well as good durability.
- Successfully produce zirconolite-rich glass-ceramics from the average compositions of each bin set. These compositions had been doped with additional amounts of Cs, Sr, Mo and Nd as surrogate “fission products” to ease detection and evaluation of durability.
- Avoid the formation of undesirable phases that could affect durability.
- As part of this development process, about eighty 7-day PCT-B tests (7) were carried out, mostly on CCC-cooled specimens. The durabilities of the optimized glass-ceramics formulated for the average compositions of all the bin sets were 10 to 100 times better than that of the EA glass for B and Na. Normalised concentrations for B, Na, as well as Cs, F, Mo, Sr, Ca, Nd, Cr, Fe, Mn, P, Si, Ti, and Zr were all generally less than 0.2 and usually around 0.1 g/l or lower.

The major phases formed were fluorite $[CaF_2]$ and zirconolite $[CaZr(+actinide)Ti_2O_7]$, with zirconia $[ZrO_2]$ usually present as well, and in some cases minor amounts of rutile $[TiO_2]$. The amounts of fluorite and zirconia present differ depending on whether the glass-ceramic has been designed for the zirconia (and fluorite) rich calcines, or for the high alumina and mixed calcines. These phases are formed at all of the cooling rates that could be investigated in our furnaces (that is, up to 1800 °C/hour), except if quenched onto a steel plate from melting temperatures of 1300 °C or more.

Elemental partitioning conformed to expectations: Nd, the actinide simulate, strongly partitioned to the zirconolite phase. Cs, Sr, B, Mg, Na, K, P, S and Mo remained in the glass. F was in the fluorite and in the glass. Ca was in the glass, fluorite and zirconolite. Zr was mainly in the zirconolite and zirconia. Ti was in the zirconolite, rutile and glass, Cr was in the zirconolite and rutile. Al and Fe were in the glass and zirconolite.

The minor elements such as Cr, Fe, Mg and P as well as S did not appear to have undesirable effects on the properties of the glass-ceramics at the abundance ranges present.

The optimum waste loadings achieved ranged from 28 % for Bin Set 1 to 63 % for Bin Set 5, with densities ranging from 2.8 to 3.1.

SELECTION OF THE GLASS-CERAMIC COMPOSITION TO BE TESTED IN THE CCM

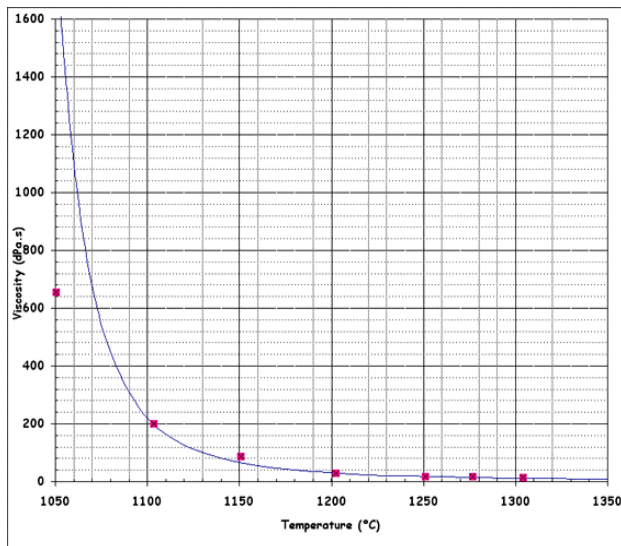
From the abundant data gathered above, it was decided to select the composition corresponding to the average Bin Set 2 contents, since it allowed a demonstration at a conservative waste-loading of about 50 % with a calcine composition that represented a mixture of the two major calcine types. At the same time this composition includes significant levels of aluminum, zirconium and fluorine. Its general characteristics are summarised in Table I.

Table I. Model Bin Set 2 calcine waste composition and the derived glass-ceramic composition used in the CCM test

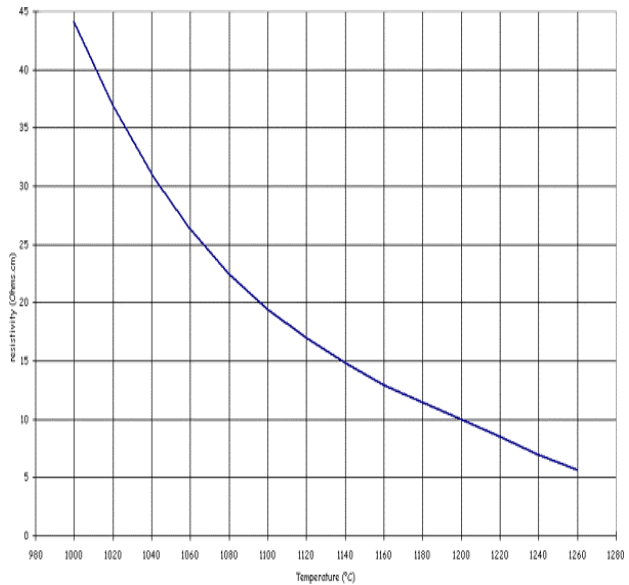
Model Bin Set 2 waste composition (wt. %)		Ceramic composition for the CCM test (waste loading 50 %) (wt. %)	
Al ₂ O ₃	47.5	Al ₂ O ₃	23.5
B ₂ O ₃	1.8	B ₂ O ₃	4.3
CaO	2.0	CaO	5.1
CaF ₂	31.2	CaF ₂	15.4
Cr ₂ O ₃	0.2	Cr ₂ O ₃	0.1
Fe ₂ O ₃	0.2	Fe ₂ O ₃	0.1
K ₂ O	0.2	K ₂ O	0.1
MgO	0.8	MgO	0.4
Na ₂ O	0.8	Na ₂ O	6.9
SrO	0.2	SrO	0.1
ZrO ₂	13.8	ZrO ₂	6.8
PO ₄	0.3	PO ₄	0.2
SO ₄	0.4	SO ₄	0.2
Nd ₂ O ₃ [#]	0.5	Nd ₂ O ₃	0.2
		TiO ₂	8.4
		SiO ₂	28.1

Nd was added as an actinide simulant.

The ultimate phase assemblage for this composition consists of dominant zirconolite and fluorite with minor zirconia. The ultimate volume fraction of crystals at “full” crystallization amounts to about 21 % across an extremely wide range of cooling scenarios after melting at 1300 °C. The measured density (Archimedes) is 2.8 g.cm⁻³. Figs 1a and 1b plot the viscosity and electrical resistivity of this composition upon melting, as a function of temperature. These critical properties were measured at the laboratory scale by CEA during evaluation of the suitability of this formulation for melting in the CCM.



(a)



(b)

Fig. 1. Plots of viscosity (a) and electrical resistivity (b) as a function of temperature for the glass-ceramic composition chosen for the pilot-scale melting demonstration

An account of the crystallization history and crystallization behaviour through a wide range of different cooling scenarios is given in the following sections.

CRYSTALLIZATION SEQUENCE, AND SENSITIVITY OF MICROSTRUCTURE AND CHEMICAL DURABILITY TO COOLING HISTORY AT THE LABORATORY SCALE

Fig. 2 shows an array of SEM micrographs detailing the crystallization sequence for the glass-ceramic composition chosen for testing in the CCM.

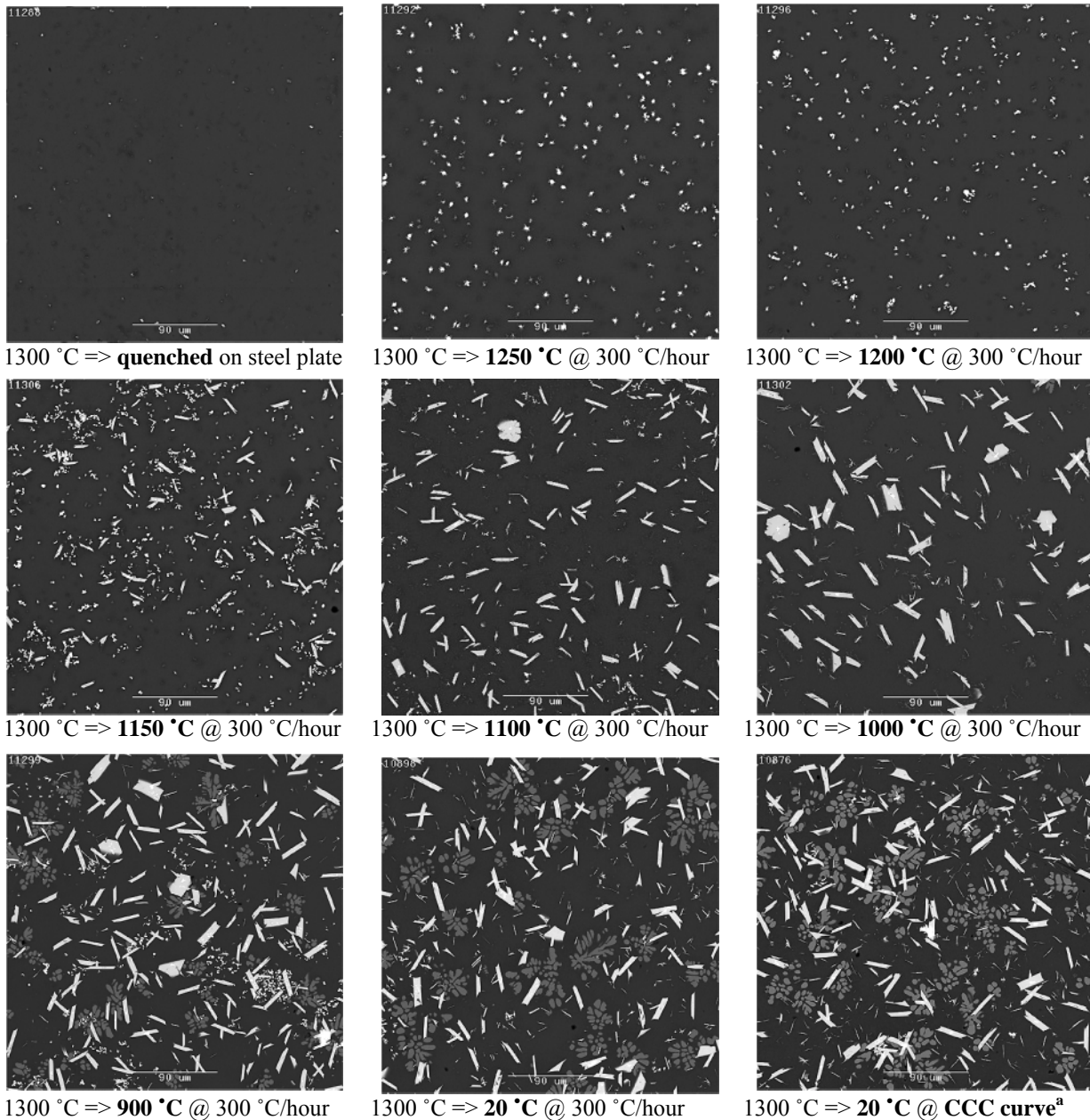


Fig. 2. SEM backscattered electron micrographs detailing the crystallization sequence in 30 g laboratory scale melts of the glass-ceramic composition chosen for testing in the CCM. The first seven micrographs capture progressive development of the phases upon cooling to the indicated temperature, and then quenching. The last two micrographs compare different cooling rates down to room temperature. **zirconolite**: large bright platy crystals; **fluorite**: stumpy gray dendritic growths; **zirconia**: small white specks.

The large matrix of tests that we have done previously in development of this composition shows that the same general crystallization sequence applies across a broad compositional range that envelopes the compositions developed to accommodate all six bin sets. In addition we had found that the formation of the major phases was not very sensitive to the cooling rate. As a consequence this composition is fairly robust and predictable in its crystallization behaviour. The formulations were specifically designed to survive the slow cooling heat treatment of the CCC curve without the formation of extra phases that could affect chemical durability, or low temperature devitrification of the glass. A very wide range of heat treatments and cooling scenarios have been tested at the laboratory scale that bracketed the expected range of thermal histories to be encountered by the product during the pilot tests. Fig.2 shows there is no discernible difference in microstructure between melts cooled and crystallized from 1300 °C to room temperature at 300 °C/hour and melts crystallized on the CCC curve^a. A more detailed illustration of the comparative insensitivity of the final microstructure to a very wide range in cooling rates is presented below in the section comparing microstructures at different cooling rates for the laboratory and pilot scale melts (see Fig. 4). In all, laboratory-scale cooling rate tests were performed at cooling rates from 1300 °C of 24, 60, 300, 600, and 1800 °C per hour.

The main features related to crystallization of these melts, as shown in Fig. 2, are that:

- A small amount of zirconia is the first phase to crystallize.
- Zirconolite crystallization commences from just over 1150 °C and is essentially complete before 1000 °C.
- Fluorite begins to form at just on 1000 °C and its crystallization is largely complete by 900 °C.
- Crystallization is virtually complete by the time the melt cools down to about 900 °C or slightly less.
- No further lower temperature crystallization or glass devitrification takes place, even at the CCC cooling rate of 24 °C/hour below 900 °C.

In addition we have found that the temperature at which the color of the product changes from pale green to pale brown is around 1150 °C. The cause of this pale green/brown color transition possibly relates to changes in iron oxidation state with temperature, such that the pale green color represents Fe²⁺ locked in by faster cooling from elevated temperatures (say above 1150 °C), and the pale brown represents the Fe³⁺ expected upon slower cooling into lower temperatures. However attempts to directly observe the Fe oxidation state in the products to confirm this have so far been inconclusive, probably because of the very small amounts of iron present.

Table II shows PCT-B leaching results for the chosen glass-ceramic composition after cooling from 1300 °C at 300°C/hour to room temperature, and the model CCC curve. The main observation is that, despite the different cooling histories, the results are essentially the same. This is consistent with the identical microstructures for the two samples, as shown in the final two panels of Fig. 2. Typically, normalized concentration values for B and Na are 10-100 times lower than the EA glass values. Similarly, normalized concentration values for other traditionally highly leachable fission product elements such as Cs and Mo are also very low. Further durability testing on the products from the pilot scale tests is planned.

The apparent good chemical durability for the different cooling scenarios in Table II is probably actually directly linked to the similar robustness of the microstructure and phase development for this formulation. For example, the ubiquitous fluorite crystallization removes fluorine from the glass which should increase its durability. As well, the overall silica content of the glass increases as the ubiquitous non-silicate phases in general crystallize. In addition we have specifically designed formulations, using feedback from extensive testing at CCC heat treatments, that do not undergo late-stage crystallization of undesirable phases that are either of low durability themselves (such as nosean for example), or other aluminosilicate phases like nepheline and/or anorthite that consume glass components and direct remaining elements such as Cs and Mo at elevated concentrations into residual glasses having low durability compositions. Another factor that may assist the development of a high durability glass in this wasteform may be the presence of “saturation” levels of Zr and Ti remaining in the glass matrix, even after crystallization of extensive zirconolite. Finally, the zirconolite itself is deliberately introduced because it is an excellent host for the actinides (simulated by Nd).

Table II. Comparison of PCT-B leaching results for laboratory scale melts of the composition chosen for the pilot-scale demonstration. Two contrasting cooling scenarios are compared.

Element	Normalized concentration (g/l)	
	Cooling from 1300 °C @ 300 °C/hour	Cooling from 1300 °C on CCC curve ^a
Al	0.095	0.083
B	0.16	0.15
Ca	0.067	0.053
Cr	0.0311	0.0317
Cs [#]	0.12	0.12
Fe	0.030	0.030
Mg	0.087	0.096
Mo [#]	0.103	0.110
Na	0.097	0.083
Nd	0.000006	0.000033
P	0.10	0.10
Si	0.108	0.087
Sr [#]	0.052	0.049
Ti	0.00052	0.00052
Zr	0.0000047	0.000011
F	0.057	0.053

The melt composition of Table I was actually doped with extra Cs, Mo, and Sr to make these elements detectable in the leaching solutions.

PILOT-SCALE DEMONSTRATION

To ascertain the viability of producing glass-ceramics at an industrial scale, it was necessary to verify the feasibility of processing the material in the CCM melter. The CCM melter, which has now undergone 15 years of development in France for immobilization of HLW, is of a new generation designed to overcome some of the limitations of the presently operating melters. The walls of the melter are cooled to protect them from direct contact with the corrosive melt. This principle also allows melting of the material at very high temperatures, as described extensively elsewhere (8). The melt is Joule-heated by directly inducing current into it, thus avoiding the necessity of transmitting power to the melt from the walls (as with traditional induction heating), or from electrodes immersed in the melt (as with traditional ceramic melters). Since the start of its development, initially devoted to high level waste glasses, this melter has demonstrated its flexibility and opened new perspectives in terms of waste immobilization (higher temperatures, higher waste loadings, new types of wastefoms...). It is also a very compact and modular melter, a fact very favourable to its implementation in a highly radioactive environment. Several pilots of varying sizes and fittings are available and an industrial HLW vitrification unit of this type is now being planned for implementation in the COGEMA La Hague facility (9).

For this initial demonstration, the most fundamental thing to determine was the actual feasibility of heating and melting the starting material in the CCM melter by using direct induction. Another objective was also to verify that the microstructure and quality of the product obtained in this way would match the laboratory melts.

The test was performed on the EREBUS platform rigged at the CEA research center in Marcoule (Fig. 3). This platform, equipped with a 160 kW generator, has totalled more than 5,000 hours of operation without any physical damage. Approximately 50 metric tons of simulated glasses have been produced. The diameter of the melter was 50 cm.

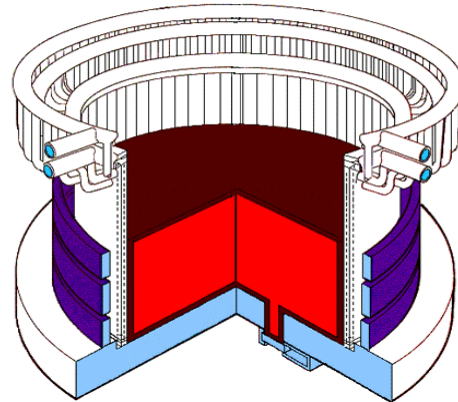
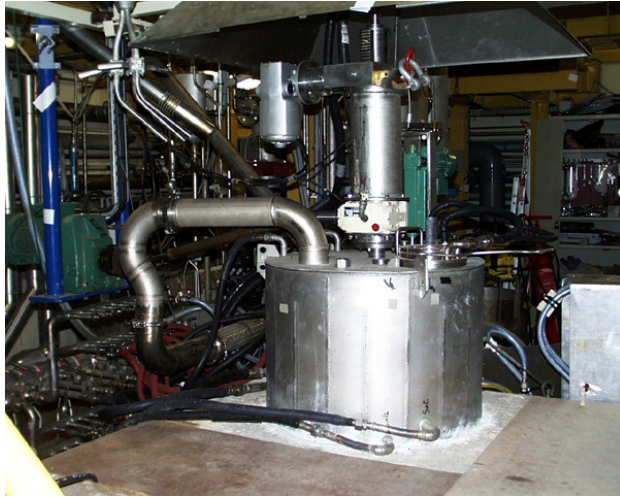


Fig. 3. General view and schematic of the EREBUS platform

Owing to the pilot-scale amount of product to be processed, the stirrer was not necessary. The melter was equipped with a thermocouple measuring the temperature in the hottest part of the melt. No attempt was made in this first test to characterize the off-gas. The starting materials were a mixture of oxides, calcium fluoride, carbonates and sulphates intended as a good simulation of the chemical composition of the calcined waste and postulated additives. The complex waste composition was simplified slightly by replacing very minor components such as potassium with an equivalent of extra sodium, and by replacing the very minor strontium with an equivalent of extra calcium.

The start-up procedure was classical for this type of test, using a titanium ring immersed in about 50 kg of the starting material. The batch melted quite well and was completely molten after two hours. Once at the target temperature (between 1300 °C and 1260 °C), some additional material was added periodically in order to simulate the cold cap that should occur in an industrial facility during feeding. The melt was held at that temperature for a little more than three hours. At that time several samples of about 200 g were taken. One of them was quenched rapidly on a metal plate. Two other samples were transferred to an oven for slow controlled cooling (decrease of 200°C per hour from 1200 °C down to 400 °C, then the furnace ambient cooling rate). The remaining melt was left in the melter after shutting down the power while keeping the cooling system running. This last operation allowed simulating a large mass of material subjected to differential cooling scenarios, a little like what would happen inside a canister. At the location of the thermocouple, the measured cooling rate was around 414 °C per hour down to 900°C. Cooling of the melt was more rapid close to the cooled walls and slower in the parts farther from the walls. These various samples thus span a wide range of cooling scenarios.

Once solidified, the product was removed from the melter for characterization. The material appeared as an ingot with variations in color from pale green to pale brown to white that matched quite well with the color changes seen amongst laboratory scale melts subjected to the various cooling scenarios described elsewhere. The total amount of material recovered amounted to around 81 kg, with a thickness of about 11 cm. A section from top to bottom of this mass was sampled for characterization.

It was concluded from this test that a suitably formulated glass-ceramic based on the INEEL calcines could indeed be melted quite easily in a CCM melter at temperatures that remained compatible with the requirements of industrial processing (below 1300 °C). Furthermore the resulting glass ceramics mimic those produced at the laboratory scale under the same conditions.

Upon dismantling the melter assembly, no evidence of unacceptable entrainment in the off-gas was observed. Some deposits of the powdery feed were found on the cooled dome. No accumulation was observed inside the duct to the washing column. As usual with this type of melter, the product itself did not adhere to the melter walls.

CHARACTERIZATION OF THE PRODUCT FROM THE PILOT DEMONSTRATION, AND COMPARISON WITH CORRESPONDING LABORATORY SCALE MELTS SUBJECTED TO DIFFERENT COOLING RATES

Specimens taken from the pilot-scale melting demonstration were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The microstructure and other characterization results of the pilot samples are very similar to those of the lab-produced samples, whose heat treatments bracketed the heating history of the pilot samples. The correspondence between the product from the pilot demonstration and laboratory scale melts is best illustrated via a direct comparison of the SEM micrographs as shown in Fig. 4.

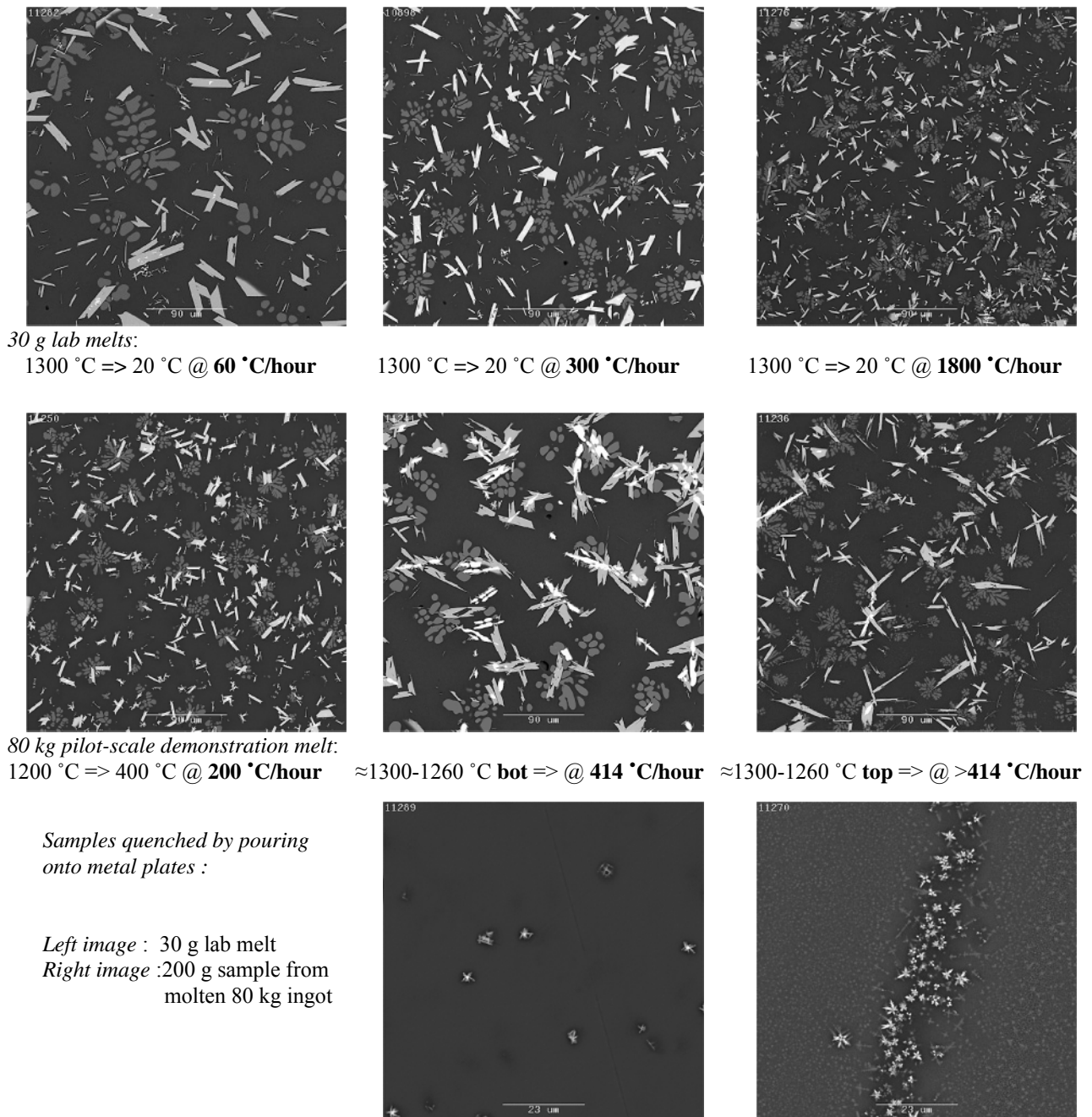


Fig. 4. SEM backscattered electron micrographs comparing samples of the 30 g laboratory scale melts at different cooling rates, and samples from the 80 kg CCM melt ingot with different thermal histories. **zirconolite**: large bright platy crystals; **fluorite**: stumpy gray dendritic growths; **zirconia**: small white even-grained crystals.

Fig. 4 shows the similarity in phases, phase proportions, phase development, and overall microstructure between the 30 g laboratory melts and samples from the 80 kg ingot, across a broad range of thermal histories. The major phases formed were fluorite [CaF_2] and zirconolite [$\text{CaZr}(+\text{actinide})\text{Ti}_2\text{O}_7$], with minor zirconia [ZrO_2] present as well, as was the case for the corresponding laboratory scale melts. That is, all of the intended crystalline phases were produced upon cooling in proportions very similar to in the small scale laboratory experiments.

Fig. 4 also shows that for the samples removed in the molten state there was also a strong similarity in overall microstructure and phase proportions to the laboratory samples with corresponding thermal histories. That is, a 200 g molten sample taken from the molten CCM ingot and transferred to an oven for slow cooling (left hand image in middle row) was essentially the same as a similarly slowly cooled 30 g laboratory test; and samples taken from the main mass of the ingot after ambient cooling, had crystallized *in-situ* with microstructures similar to the laboratory melts. The 200 g sample taken from the molten ingot and quenched differed from a quenched 30 g laboratory melt in that the larger mass of melt from the ingot has a stronger and coarser grained quench microstructure, consisting of abundant quench fluorite, zirkelite [$\text{Ca}(\text{Zr},\text{Ti})\text{O}_4$], and even some stringers of extremely fine grained zirconolite. In fact, in this context, zirkelite can be considered to be a rapid crystallization analogue of zirconolite. XRD shows that the 30 g quenched sample develops the same phases but the crystallites are very much smaller. These differences may only reflect different maximum achievable cooling rates related to the differences in the masses of the melts being quenched.

The color variations observed in the ingot and derivative samples can be explained by reference to the laboratory-scale melts that exhibited similar color differences, depending upon the temperatures that they were quenched from. For this composition the laboratory-scale experiments described earlier suggest that the color changes from pale green to pale brown inside the large ingot probably reflect the local rates at which portions of the melt cooled through 1150 °C. This conclusion also applies to the separate light brown colored slowly oven-cooled sample that was taken from the molten ingot. A white color for these types of compositions, as was seen when the 200 g sample of melt was poured and quenched, is indicative of extremely fine quench crystallization from high temperatures, producing a characteristic milky-looking “phase separated” product filled with dendritic crystallites of fluorite and zirkelite, and even some zirconolite, as already described above and shown in Fig. 4.

PCT-B tests are planned on the actual pilot-scale samples to further more rigorously test the apparent independence of chemical durability to the cooling scenarios, as has already been seen for the laboratory scale melts (Table II). Since the lab-produced samples all show a good resistance to leaching as per PCT-B we expect that the chemical durability of the pilot samples will be similar to those of the lab-produced samples.

CONCLUSION

The work summarized in this paper illustrates the waste loading improvements achievable by reconsidering the waste form criteria and making the best use of the high temperature potential of the CCM technology. For instance, recent formulation efforts published for INEEL calcines (10), targeting glasses and meeting processing criteria adapted to presently operating melters (melting temperature of 1050 °C – 1100 °C), only allowed 40 % waste loading for the Blend calcine -- whose composition was similar to the Bin Set 2 composition used in the present study. Their glass had a significant devitrification potential that could variously manifest itself according to the heat treatment applied. Their report also showed that the observed crystallization did not severely impact the final chemical durability of the glass, which appears to be quite good. In our opinion, by going a step further and proactively taking control of the final crystallization process as part of the formulation drive to higher waste loadings, the formation of tailored desirable crystalline phases could be promoted and undesirable phases avoided. The combination of CCM and glass-ceramics described in this paper opens up industrial-scale opportunities for this kind of approach via higher temperature assemblages containing, among other phases, zirconolite, which is well known for its very good capacity to retain actinides. For the pilot scale work reported in this paper we deliberately chose a conservative waste loading composition. Based on the extensive formulation matrix that we have already developed, as well as what we have learned from this first demonstration, it is possible that satisfactory waste loadings of up to at least 60 % may be achievable for the waste composition listed in Table I.

The formulation work was performed in view of the potential industrial constraints, such as the variability in waste composition and possible variation in cooling scenarios. The resulting formulations were very flexible and allowed coverage of the whole range of compositions inside the six bin sets with only two matrix formulations. The thermal

studies and the characterization of the CCM melt tend to show that a good quality product can be obtained without a requirement for controlled cooling of the canister.

The use of a CCM melter to process these compositions is critical, since it allows higher operating temperatures (necessary to digest the highly refractory components of the waste and to allow the formation of the required phases), and also since it is resistant to corrosion by the very corrosive fluoride-laden melts. Furthermore, the use of such a melter in a direct vitrification option to process the INEEL calcines should allow borosilicate glass-like processing throughputs, but at higher waste loadings.

This first pilot run demonstrated that the proposed feed and additives can be melted easily at the target temperature, and that the product obtained at a significantly larger scale is similar to the laboratory melts. The production of a large sized continuously solid ingot with no cracks also demonstrated that thermal gradients during cooling did not impair the quality of the solidified product.

We hope that this demonstration has provided strong indications of the extended possibilities offered by the CCM, and that the availability of CCM technology stimulates a reconsideration of glass-ceramics as an industrially viable alternative option for high-level waste immobilization, especially as an option for immobilization of the INEEL calcines. It has been shown that the production of such waste forms could be made flexible and compatible with industrial requirements, while using well known melting operations. The quality of the product is remarkably good considering the problematic nature of these waste compositions, with PCT leaching results 10 to 100 times better than EA glass values.

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FOOTNOTES

- a. The model CCC curve we used constitutes cooling from 1300°C down to 900°C at a rate of 300°C/hour, and then a decrease from 900°C to room temperature at 24°C/hour - a 42 hour heat treatment.