Limited Increase of Particle Entrainment in the Off-Gas System of a Cold Crucible Induction Melter Compared with a Joule-Heated Metal Melter for HLLW Vitrification - 11465

P. Gruber, E. Tronche, A. Ledoux, V. Labe, J-F. Hollebecque,
J. Lacombe, C. Ladirat
Commissariat à l'Énergie Atomique (CEA), CEA/DEN/DTCD/SCDV
BP 17171, 30207 Bagnols sur Cèze, France

S. Naline
AREVA NC, Tour AREVA, 1 place Jean Millier, 92084 Paris La Défense, France

ABSTRACT

Fission product solutions arising from reprocessing spent fuel from the nuclear reactors used for electrical production in France are immobilized in six vitrification lines at the AREVA La Hague plant. In 2010, the conventional Joule-heated metal melter was replaced in one of these six lines with a cold crucible melter. The cold crucible melter began vitrifying radioactive effluents produced by rinsing operations in legacy facilities in April 2010. The composition of these effluents requires a containment glass synthesis temperature that exceeds the operating temperatures limits of conventional ("hot") melters. The cold crucible melter technology has three main advantages: melt temperatures well above the current limit, increased glass production capacity, extended lifetime because of the lower wall temperatures. For these reasons the cold crucible melter can subsequently be used to vitrify a wide range of High-Level Liquid Waste (HLLW).

This paper describes the assessment performed to characterize the entrainment of particles or chemicals and/or radioactive species to the off-gas treatment system from a Joule-heated metal melter (JHMM) and from a cold crucible induction melter (CCIM). Vitrification is performed in a two-step process. A calciner is used in each case to dry and calcine the high-level liquid waste, supplying only the dry residue to the melter together with glass frit. The off-gas treatment is identical for both melters.

The paper first describes how the CEA uses its reconfigurable vitrification prototype, a full-scale mockup of a La Hague vitrification line, in support of AREVA to anticipate cold crucible melter operation under radioactive conditions. It describes the process equipment constituting the vitrification line from the melter (using a JHMM or a CCIM) to the off-gas treatment system.

All the differences that contribute to the modification of radioactive particle entrainment from the calciner/melter to the off-gas treatment system are then described.

The results obtained are then discussed concerning the volatility of species produced by vitrification during weekly tests implementing either the conventional melting pot or the cold crucible melter. The distribution of volatile species in the off-gas treatment devices is discussed.

The paper concludes with a discussion of how using the CCIM vitrification process on one of the La Hague vitrification units can achieve an increased vitrification throughput at a higher temperature without any impact on the resulting waste release.

INTRODUCTION

Vitrification of high-level liquid waste is the internationally recognized standard to minimize both the environmental impact of waste disposal and the volume of conditioned waste. Several countries including the USA, France, the United Kingdom, Germany/Belgium, Japan, and Russia have vitrified high-level waste and several more countries are currently examining the implementation of vitrification technology.

In 2010 a cold crucible melter replaced the JHMM in one of the six vitrification lines at La Hague (France). This change made it possible to begin vitrifying the radioactive effluents arising from rinsing operations in legacy facilities, which was not possible with the technology used in the other five lines. The composition of these effluents requires a containment glass synthesis temperature that exceeds the operating temperatures limits of conventional ("hot") melters. The main advantage of the cold crucible melter technology (higher synthesis temperatures, greater capacity and extended lifetime) is that it can be used to vitrify a wide range of high-level liquid waste (HLLW).

This paper describes the CEA's reconfigurable full-scale vitrification prototype corresponding to a vitrification line at La Hague, from the melter (which can be a JHMM or a CCIM) to the off-gas treatment, together with all the differences that affect the entrainment of radioactive particles from the calciner/melter to the off-gas treatment.

It describes the assessment performed to characterize the entrainment of particles or chemical and/or radioactive species to the off-gas treatment system from a Joule-heated metal melter (JHMM) and from a cold crucible induction melter (CCIM).

The volatility of species during a week of vitrification tests using either a conventional melting pot or a cold crucible melter, and the distribution of volatile species in the off-gas treatment devices are discussed. Finally, the performance of the CCIM vitrification process is discussed in the case of the La Hague vitrification facility.

DESCRIPTION OF TEST PLATFORM

Vitrification Pilot Facility

The reconfigurable vitrification prototype (PEV), shown schematically in **Figure 1**, is a full-scale mockup of the vitrification line at La Hague, and is used to qualify the process and the equipment. The feed solution and additives are first supplied to the calciner. The resulting calcine is then mixed with glass frit in the melter. The off-gas treatment unit recycles particle matter and purifies the gas streams, before stack release.

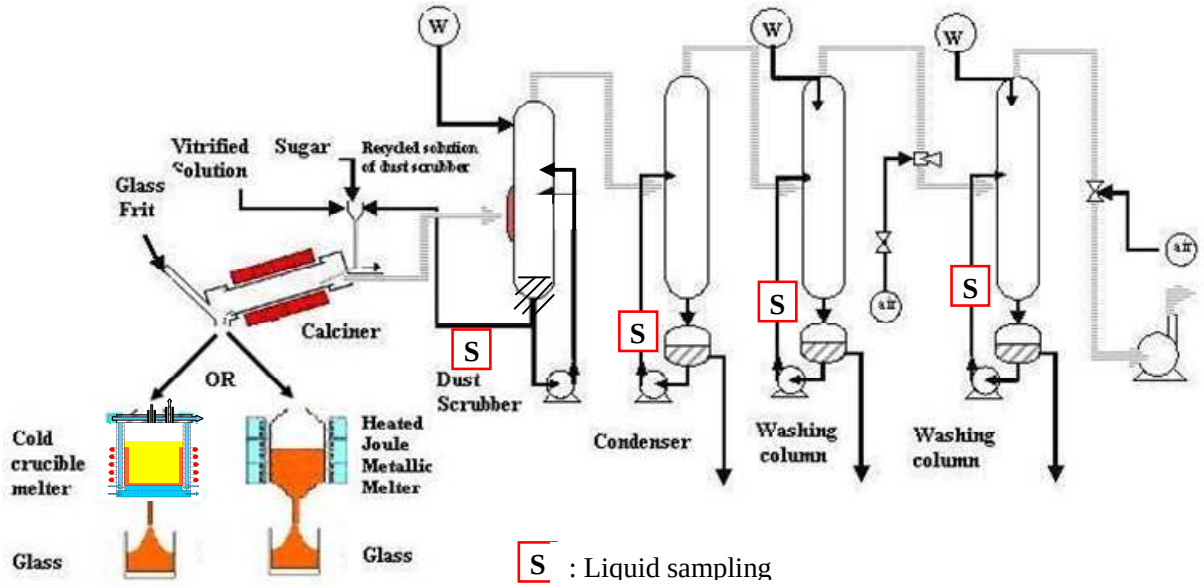

Figure 1. Full-scale vitrification pilot with CCIM or JHMM

The calciner comprises:

- a resistance furnace with four independent heating zones separated by interzone segments,
- a rotating tube,
- an upper end-fitting ensuring leaktightness at the rotating upper end, with connections for exhausting the off-gas to the particle separator and for supplying the liquid input (vitrification feed solution, sugar and recycled solution),
- a lower end-fitting ensuring leaktightness at the rotating lower end and guiding the calcine into the melter.

The calciner is controlled by assigning heating temperature setpoints for the electrical resistors. Temperature sensors were installed on the PEV calciner tube. The calcining performance was observed by monitoring the temperature variations.

Joule-Heated Metal Melter (JHMM) [1]

It comprises:

- four heating inductors supplied via an impedance-matching unit by a medium-frequency (4 kHz) generator,
- inductors for the glass pouring and drain nozzles,
- an dome section connected to the calciner, equipped with stirrers to homogenize the molten glass,
- a tube for measuring the melt level by air sparging, and a few air tubes,
- a video camera for viewing the molten glass (in the inactive pilot),
- temperature sensors in the glass pot and on the melter wall at various heights.

The melter is continuously supplied with calcine and intermittently with glass frit. It is stopped to pour the glass into a canister. The metal melter is heated by Joule effect using electric inductors; the heating system is outside the melting pot and the metal melter directly heats the glass by conduction. This technology is easy to start (even if the metal melter is full or empty), to stop, to maintain or to replace.

Cold Crucible Induction Melter (CCIM) [2]

It comprises:

- an inductor supplied via an impedance-matching unit by a high-frequency (300 kHz) generator with a power rating of 400 kW,
- a crucible or sectorized shell that is transparent to the magnetic field,
- a dome assembly connected to the calciner, and equipped with a stirrer,
- a tube for measuring the melt level by air sparging, and temperature measurement tubes,
- a video camera for viewing the molten glass (in the inactive pilot),
- a sectorized bottom that is transparent to the electromagnetic field, equipped with pouring valves and gaz injectors.

The melter crucible (**Figure 2**) is continuously supplied with calcine and intermittently with glass frit even during pouring. The glass in the crucible is heated directly by eddy currents generated by the inductor surrounding the shell. The currents dissipate power by Joule effect that heats the calcine and glass frit to form the glass melt. The monitored parameters on the melter are the temperature, the stirrer speed, and the gaz flow rate via the injectors.

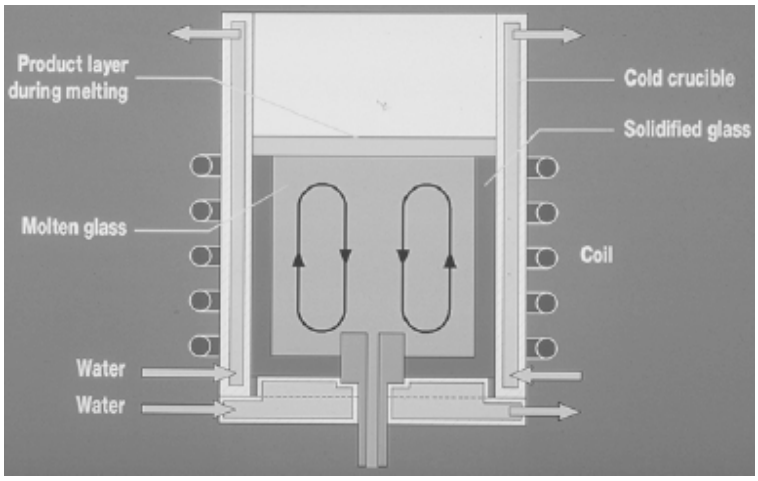

Figure 2, Cold Crucible Melter

Off-Gas Treatment System (OGTS)

The system comprises:

- a dust-scrubber initially filled with demineralized water. It consists of a tank with a baffled column equipped with a backwashing system. The plates are sprayed by an air-lift with solution drawn from the tank, which is heated by pressurized steam in a thermosiphon to maintain the solution stirred and at the boiling point; the solution level is maintained constantly with makeup water. Particulates trapped by the separator are recycled to the calciner inlet by a metering wheel; the negative pressure is regulated by an air ejector at the outlet of the nitrous fumes recombination column;
- a triple-pass condenser with a water-cooled shell. The condensate flow (except for the density) includes the feed flow plus the dust extractor makeup flow;
- a perforated plate recombination column for nitrous fumes;

- a perforated plate scrubbing column with a liquid ring pump constituting the second suction pressure regulation device.

The off-gas treatment must be capable of ensuring a satisfactory decontamination factor in the gas exhausted from the calcining and glass production operations.

Liquid samples are taken periodically from each of the four process devices above to estimate the quantity of volatilized or entrained species (**Figure 1**). Each device is also equipped for level and temperature measurements, and for inlet and outlet pressure measurements.

Control and Monitoring

The test bed is fully instrumented and operated remotely via a programmable logic controller and a digital control system with a multi-screen display. All the process parameters can be monitored, logged, and recorded to provide historical trend information. The control system includes warning thresholds on each critical measurement and automatic shutdown sequences to assure safe operation of the system.

PARAMETERS IMPACTING ENTRAINMENT OF ELEMENTS IN THE OGTS

This section itemizes all the factors in the reconfigurable vitrification prototype line (PEV) that are subject to change and can significantly impact the decontamination performance. A fixed set of these variables is a “configuration”. The variables concern either the hardware technology used or the control parameters.

Melting Pot Technology

As stated in the introduction, we focus here on what can have a significant impact on the decontamination performance of the vitrification line. In this context, the main difference between the Joule-heated metal melter and the cold crucible melter is the glass synthesis temperature, which is higher in the CCIM and is a major factor in the production of volatile elements in the downstream process.

Another major consideration is the presence of a “cold cap”, a layer of glass frit and calcine, above the molten glass, which may limit the release of some elements such as ruthenium. However, this criterion is not considered as a variable because the implications of the presence or absence of a cold cap were not analyzed.

The overall bubbling and sweeping rates are also important, but are taken into account in the hardware variables. The bubbling flow is injected directly into the molten glass and can thus facilitate the volatilization of some elements, while the sweeping rate (augmented by the bubbling flow once it exits the melt) can carry elements from the calcine, for example, to the off-gas treatment.

The values of these parameters are indicated for each technology in **Table I**.

Table I. Bubbling and sweeping flow rates for JHMM and CCIM

Melting pot technology	JHMM	CCIM
Bubbling rate	0.3 - 0.5 m^3/h (at standard conditions) (bubbling tubes)	1.2 to 1.6 m^3/h (at standard conditions) (bubbling tubes)
sweeping rate	4 - 5 m^3/h (at standard conditions) (stirrers, lower end-fitting, glass frit, camera)	7 - 8 m^3/h (at standard conditions) (stirrer, lower end-fitting, glass frit, camera)

Calciner

Two major calciner parameters are sources of contaminant volatilization. The first is the overall feed rate (source term). The second is the flow of noncondensable gas through the unit (leakage rate, bubbling rate and sweeping rate), measured after the NOx recombination column. In the calciner, liquid is evaporated in the high end of the tube whereas in the low end cationic nitrates are transformed into oxydes which form the dry matter. When the tube is rotating, the finest particles can be carried by air process flowrate (sweeping rate, bubbling rate, leakage rate, steam water and nitric fumes) to the off-gas treatment. The noncondensable gas rate represents the effects of the calciner sweeping rate: for a given calcine particle size distribution the amount of particles entrained downstream in the process will vary accordingly. During these tests this gas rate ranged from about 17 to 21 m^3/h.

With these parameters the type of calciner technology was not taken into account. Similarly, the calciner heating adjustment was not considered as a variable.

Configurations Studied – Runs 1 to 4

The vitrification feed solutions tested here included:

- a mixture of a decontamination effluent rich in sodium with a calcination additive, called “Decontamination &Decommissioning (D&D) solutions” [3]
- a commercial Light Water Reactor fission product solution with or without clarification fines rich in platinum group metals, called “Uranium Oxyde (UOX) solutions”
- or some legacy solutions arising from the reprocessing in the 1970s of spent U-Mo-Sn-Al fuels used in gas-cooled reactors, called “UMo solutions” [1] [4].

The complete series of tests with their main production parameters and configurations studied are indicated in **Table II**.

Table II. Test configurations and parameters

Run	Glass	Melter	Glass synthesis temperature	Feed rate	Glass production rate
1	UOX	JHMM	1110°C	109 L/h	25 kg/h
2	UOX	CCIM	1200°C	110 L/h	36 kg/h
3	D&D	CCIM	1240°C	70 L/h	26 kg/h
4	UMo	CCIM	1250°C	110 L/h	45 kg/h

Run 1: This test involved increased calciner throughput (near 110 L/h) associated with diluted UOx solution at the nominal vitrification rate with a JHMM, 25 kg/h.

Run 2: In this test a calcined non diluted UOX solution was vitrified in the CCIM. The glass synthesis temperature was 1200°C and the glass production rate was 36 kg/h.

Run 3: This run was conducted at the nominal vitrification rate for a D&D solution in a cold crucible melter during the test in reference [1]. The glass synthesis temperature was 1240°C with a glass production rate of 26 kg/h.

Run 4: The benchmark test for vitrification of a UMo solution was carried out in a cold crucible melter for a MoO_3 content of 10 wt% in the glass. The glass synthesis temperature was 1250°C with a glass production rate of 45 kg/h.

RESULTS FOR UOX VITRIFICATION: JHMM VERSUS CCIM

The data and findings presented here are based on elemental analysis of the off-gas treatment solutions which allow to access to the decontamination factor, *DF*, of a device for each element which is the radio of inflow to outflow. The data were collected over a period of about 10 years. The methods and their accuracy may have changed in the interim, and the uncertainty on each calculated DF was not determined, but are without doubt quite high. Indeed it depends on analysis accuracy, process functioning conditions, time to take samples… And then, the results are within an order of magnitude of each other.

Computational Method

The decontamination factor, *DF*, of a device is the radio of inflow to outflow. It is calculated for a time *t* as the mass inflow rate divided by the mass outflow rate. All the *DF* values indicated are instantaneous values specific to the moment the sample was taken.

$DF_{C\text{-}V}$ values were calculated for each chemical element for the calcining-vitrification unit:

$$DF_{C-V} = \frac{F_A \times [A] + F_F \times \%_F + F_R \times [R]}{F_R \times [R] + F_C \times [C] + F_{W1} \times [W1] + F_{W2} \times [W2]}$$

where
- F_A volume flow rate of vitrification feed solution
- $[A]$ concentration of the element in the vitrification feed solution
- F_F mass flow rate of glass frit
- $\%_F$ weight percentage of the element in the glass frit
- F_R recycling volume flow rate
- $[R]$ concentration of the element in the particle separator
- F_C condensate volume flow rate
- $[C]$ concentration of the element in the condenser
- F_{W1} overflow rate from NOx column
- $[W1]$ concentration of the element in the NOx column
- F_{W2} overflow rate from the scrubbing column
- $[W2]$ concentration of the element in the scrubbing column

The calcining-vitrification decontamination factor ($DF_{C\text{-}V}$) characterizes the release of each element from the melter + calciner system into the off-gas stream. The causes thus may be either the production of volatile species in the melter or calciner, or the entrainment of particles in the process gas stream.

Discussion of Results

Figure 3 shows the calcining-vitrification decontamination factors ($DF_{C\text{-}V}$) calculated for some of the elements present in the glass frit and in UOX solutions vitrified in the JHMM and in the CCIM.

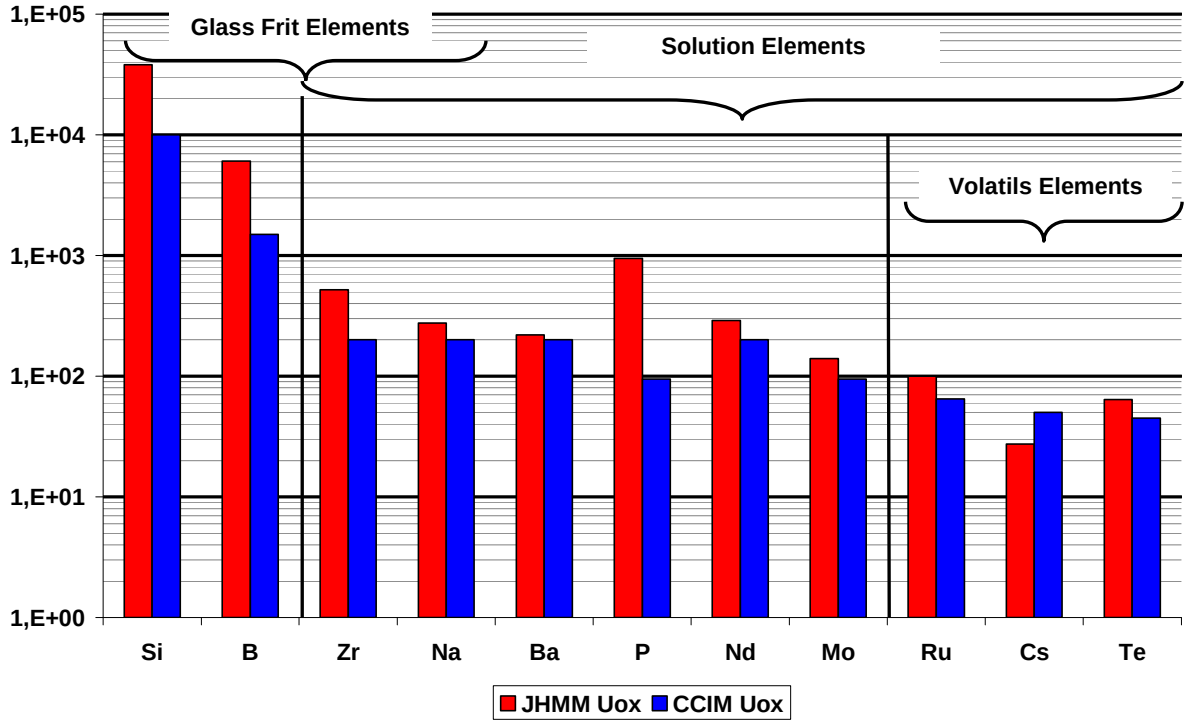

Figure 3. Calcining-vitrification decontamination factors ($DF_{C\text{-}V}$)

It may be noted that, as generally observed, the elements massively retained in the calcining-vitrification process are those that are contained only in the glass frit, such as silicon and boron. This is normal since the frit is feeding at the end of the calciner and is less sensitive to the calciner sweeping rate. These elements are included in solid flakes with dust which is very weakly carried by the gas rates coming from the down of the calciner. In the CCIM, boron has a DF close to 1000, lower than for the JHMM. This element in the glass melt is under the shape of borate BO_4^{X-} associate to alkaline (like Na or Cs) or alkaline-earth metals (like Sr) which can produce volatiles species at high temperature reached by the CCIM. That's why all these elements which are 100 °C higher in a CCIM than in a JHMM are lower retained in the "calcining-vitrification" system. The $DF_{C\text{-}V}$ ranged from a few thousand to tens of thousands in the case of silicon. The $DF_{C\text{-}V}$ values were a few hundred for sodium and zirconium, which are present both in the frit and in solution.

The weakly retained elements are known as volatile elements. Their $DF_{C\text{-}V}$ was below 100 (meaning less than 99% retained) for UOX solutions. The corresponding elements were probably present as volatile species. This is generally the case for tellurium, cesium and ruthenium, for which the $DF_{C\text{-}V}$ values ranged between 20 and 100. The change in technology from the JHMM to the CCIM had no significant impact on the $DF_{C\text{-}V}$ values for these elements in UOX solutions.

Between the strongly retained elements and the volatile elements is a group of intermediate elements making up the remainder of the fission product and corrosion/degradation product surrogates. They include barium, sodium, phosphorus, and neodymium, simulating the actinides and molybdenum. The $DF_{C\text{-}V}$ values for these elements were near a hundred, meaning that more than 99% were trapped in the calcining-vitrification system.

Among the intermediate elements, molybdenum exhibited the lowest $DF_{C\text{-}V}$ values regardless of the melter technology; this was comparable for phosphorus in the CCIM, for which the $DF_{C\text{-}V}$ was lower than for the JHMM. Note that the results obtained with the JHMM in the PEV prototype were consistent with those obtained in the JHMM on the vitrification lines at La Hague.

IMPACT OF THE CCIM ON SECONDARY LIQUIDS RELEASE

As the dust extractor effluents are recycled, the release of vitrifiable elements from the calcining-vitrification-dust extraction system may have an impact on the treatment of the liquid effluent, consisting mainly of condensates.

Figure 4 shows the decontamination factors for the calcining-vitrification-dust extraction system ($DF_{C\text{-}V\text{-}DE}$) for different elements from the frit or UOX solution. This factor characterizes the release of these elements beyond the dust extractor.

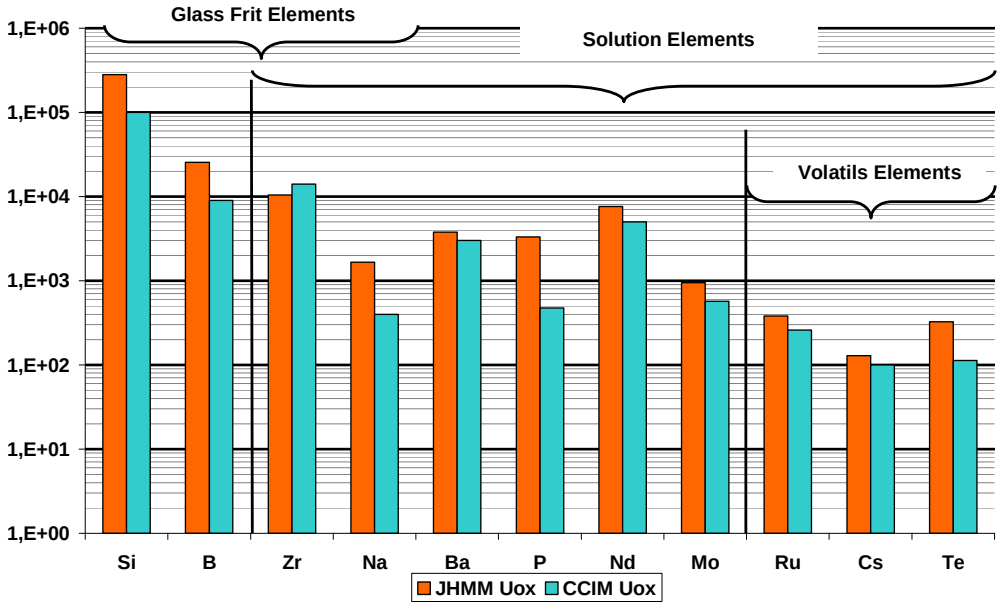

Figure 4. Decontamination factors for the calcining-vitrification-dust scrubber system ($DF_{C\text{-}V\text{-}DE}$)

Figure 4 shows that the volatile elements from a UOX solution, i.e. Cs, Ru and Te, are retained to the same degree by a JHMM or CCIM vitrification system, even though these two technologies differed by the UOX glass production capacity (25 kg/h vs. 36 kg/h), processing temperature (1110°C vs. 1200°C) and bubbling and sweeping rate (4-5 vs 8-10 Nm^3/h). Despite, less than one hundredth of cesium introduced in the process is recovered in the secondary liquids. The condensates produced in a vitrification cell with a CCIM have the same activity of those produced with a JHMM. Also they can be evaporated likewise without modifying capacity. Concentrates can be directed likewise with JHMM to feeding without disturbing the treatment set and the vitrification process.

This observation is valid for all the elements except sodium and phosphorus, which are more affected by the higher process temperature. However their management is less problematic because these elements are not fission products.

Figure 5 shows the decontamination factors for the calcining-vitrification-dust scubber system for different elements from the frit or from UOX, D&D and UMo solutions. This factor characterizes the release of these elements beyond the dust-scrubber for each type of solution.

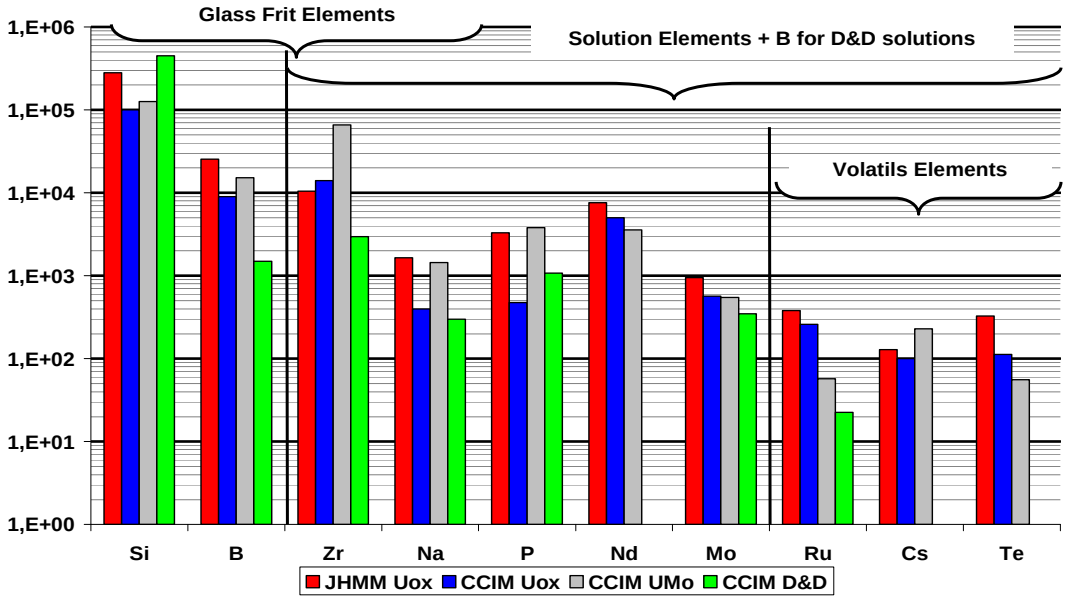

Figure 5. Decontamination factors for the calcining-vitrification-dust scrubber system for different feed solutions

The $DF_{C\text{-}V\text{-}DE}$ values of volatile elements for UMo and D&D medium-level waste solutions are slightly lower than for UOX high-level waste solutions, mainly because of the more thorough fusion but also calcining conditions. However these $DF_{C\text{-}V\text{-}DE}$ values are acceptable for medium-level liquid wastes.

With a CCIM, the three effluents tested (UOX, UMo and D&D) exhibit comparable behavior concerning their release beyond the dust extractor, in proportion with their respective concentrations in the effluent.

Figure 6 shows the decontamination factors for the calcining-vitrification-dust scrubber-condenser system ($DF_{C\text{-}V\text{-}DE\text{-}CO}$) for different elements from the frit or UOX solution. This factor characterizes the release of these elements beyond the condenser.

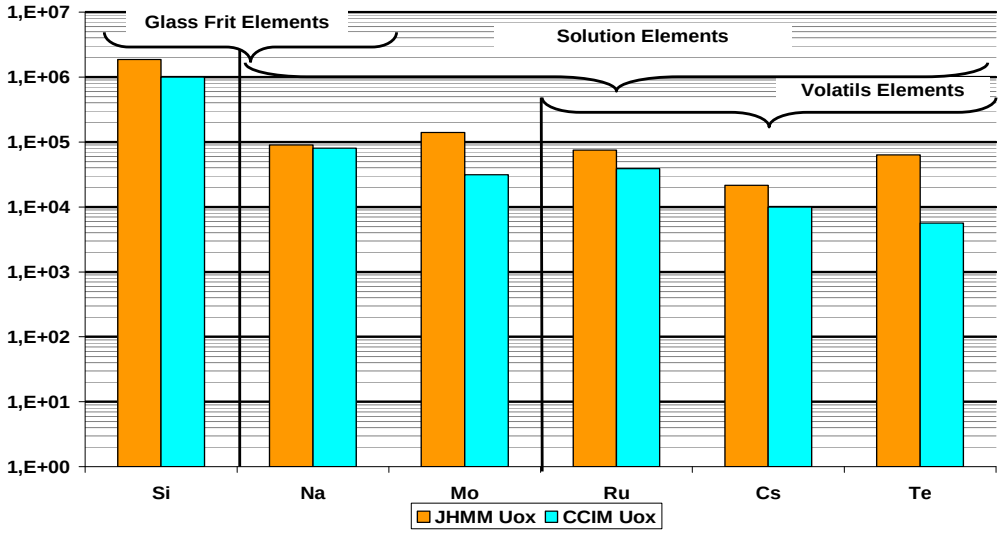

Figure 6. Decontamination factors for the calcining-vitrification-dust scrubber-condenser system ($DF_{C\text{-}V\text{-}DE\text{-}CO}$)

Figure 6 shows t he decontamination factors for the calcining-vitrification-dust scrubber-condenser system ($DF_{C\text{-}V\text{-}DE\text{-}CO}$) is only slightly impacted by the change in technology. Despite the higher capacity, the DF value is comparable in the CCIM with the JHMM : for example more than 99.98% of tellurium, the most volatile element in a CCIM, is trapped before the condenser.

CONCLUSION

This study compares the decontamination factors of volatile elements in the process for different configurations of vitrification :

- with UOX solutions in a joule-heated metal melter (JHMM) or a cold crucible induction melter (CCIM)
- with UMo, D&D and UOX solutions in a nuclearized CCIM

With a Joule-heated metal melter representative of the existing process at La Hague, the calcining-vitrification decontamination performance is satisfactory and is our current benchmark.

The use of a cold crucible melter with a higher molten glass temperature yields decontamination performance comparable to the JHMM.

The findings obtained with a CCIM in the PEV test facility with different feed materials (UOX, D&D and UMo) indicate similar decontamination performance in the off-gas treatment system, with comparable decontamination factors in the calcining-vitrification system and condenser for all three materials.

This comparative study shows that the implantation of a CCIM instead of a JHMM has no impact on the OGTS in spite of increasing of bubbling rate and higher temperature.

REFERENCES

1. R. Do-Quang, E. Pluche, C. Ladirat, A. Prod'homme, "Review of the French Vitrification Program", Waste Management, Tucson, 2004

2. S. Naline, F. Gouyaud, V. Robineau, C. Girold and B. Carpentier, " Vitrification 2010 - A challenging French vitrification project to retrofit a cold crucible inductive melter at the La Hague Plant – 10382", Waste Management, Phoenix, 2010

3. A. Ledoux, J. Lacombe, O. Pinet, J.L. Dussossoy, A. Grandjean, P. Gruber, G. Pruvost, E. Tronche, C. Ladirat, "Methodology of Qualification of CCIM Vitrification Process Applied to the Decontamination Effluent of the La Hague UP2-400 facility - 9142", Waste Management, Phoenix, 2009

4. O. Pinet, JF. Hollebecque, F. Angeli, P. Gruber, S. Naline, "Vitrification of High-Level Solutions Rich in Molybdenum in the Cold Crucible Melter Process – 11502", Waste Management, Phoenix, 2011