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Glass ceramics containment matrix for insoluble residues coming from spent fuel reprocessing

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ABSTRACT

Spent fuel reprocessing by hydrometallurgical process generates insoluble residues waste streams called fines solution. Considering their radioactivity, fines solution could be considered as Intermediate Level Waste. This waste stream is usually mixed with fission products stream before vitrification. Thus fines are incorporated in glass matrix designed for High Level Waste. The withdrawal of fines from high level glass could decrease the volume of high level waste after conditioning. It could also decrease the reaction time between high level waste and additives to obtain a homogeneous melt and then increase the vitrification process capacity.

Separated conditioning of fines in glass matrices has been tested. The fines content targeted value is 16 wt%. To achieve this objective, two types of glass ceramic formulations have been tested. 700 g of the two selected glass ceramics have been prepared using simulated fines. Additives used were ground glass. Melting is achieved at 1100 °C. According to the type of glass ceramic, reducing or oxidizing conditions have been performed during melting. Due to their composition and the melting redox conditions, different phases have been observed. These crystalline phases are typically RuO_2, metallic Ru, metallic Pd, MoO_2 and $CaMoO_4$. In view of melting these matrices in an in can process the corrosiveness of one of the most oxidizing borosilicate glass ceramic formulation has been tested. This one has been remelted at 1100 °C in inconel 601 pot for 3 days. The oxygen fugacity measurement performed in the remelted glass leads to an oxidizing value, indicating that no significant reaction occurred between the inconel pot and the glass melt had occurred.

1. Introduction

In present reprocessing plants, insoluble residues coming from hydrometallurgical process are called fines solutions. They are considered as one of the input streams of the high level waste vitrification process. However, their radioactivity level might permit us to classify the fines in the intermediate level waste category. Chemical species included in the fines solution are mainly molybdenum and platinoïds that are partially in their metallic form [1]. Performance of most high level waste vitrification processes are linked to the total amount of molybdenum and platinoïds introduced in the glass melt. In vitrification processes, platinoïds such as ruthenium, palladium and rhodium are known to slow down reaction kinetics between waste residues and glass additives designed to obtain the adequate final glass composition [2]. Thus melting rate of vitrification process can be affected by addition of fines. Platinoïds are not chemically incorporated in the final glass [3]. Consequently, rheological behaviour of the glass melt is modified compared to a single phase glass melt when the platinoïd content is high. Glass melt containing platinoïds is not a perfect Newtonian liquid [4,5] and due to the high density of platinoïds, they could settle according to the melting conditions [6–9]. Molybdenum is the main chemical element contained in fines solution. It is also one of the most dimensioning elements for waste incorporation rate in high level nuclear glass due to its relatively low solubility in borosilicate glass melt [10,11].

The withdrawal of fines solution from the input streams of high level waste vitrification could permit several improvement opportunities for high level waste vitrification process: an increased melting rate and a decrease of the final volume of high level waste.

This strategy requires a development of a performing process for conditioning fines. This paper presents experimental work performed in order to do a preliminary study that aims to demonstrate the feasibility of a simple vitrification process matching the main objectives usually devoted to intermediate level waste containment processes: volume minimization of the final waste, good containment properties, simple and robust process.

In order to define the whole properties necessary to design the glass formulation, a vitrification process is considered preliminary to the glass formulation study. In can process is selected due to its

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robustness and to avoid the pouring phase that could be complicated by a high amount of platinoïds in a glass melter. Glass formulation tests have been also performed in order to assess the possibility of reaching around 15 wt% of fines in a glass. Borosilicate type glass is favoured because of the better knowledge and reliable assessment we have concerning its durability. The constraints linked to the process such as melting temperature and glass corrosivity are also considered.

2. Experimental

2.1. Fines simulation

Characteristics such as composition and particle size distribution of fines which come from clarification unit of reprocessing plant are closely related to the type of the spent fuel, UOX or MOX, its burn up, dissolution and clarification unit efficiency [12]. However, the main characteristics of fines are still the same. The main elements entering the composition of fines are the following:

- molybdenum,
- noble metals such as ruthenium, palladium and rhodium,
- actinides as uranium and plutonium,
- zirconium,
- others: tin, antimony, technetium.

The quantity of fines from the reprocessing plant depends on the type of spent fuel but can be approximately considered as 3 kg/T of spent fuel at 33 GWd/T [12]. A part of these particles is in a metallic form, another part is in an oxidized form. The particle size is considered to be around a few micrometers [2]. In order to assess the vitrification of separated fines, the elements considered are given in Table 1. It is a mix of the main elements generally considered as entering the fines composition. Experiments have been performed in an inactive-lab and fines surrogates have been chosen as indicated in Table 1. Two types of simulated fines mixing named high simulated fines and low simulated fines were considered. For low simulated fines silver is considered as a molar surrogate of palladium and rhodium considering their redox state expected to be 0 [13] and their density. For low simulated fines, technetium and antimony are not considered. For high simulated fines, technetium is simulated by manganese.

2.2. Glass additives

The interest in fines vitrification depends on the ability of glass to incorporate a high enough amount of fines. Considering the elements coming from the fines the most critical elements are noble metals and molybdenum.

Concerning noble metals, they are known to be insoluble in glass melt. They are also known to have a tendency to settle in glass melt. This phenomenon could be increased by a higher content of noble metals in the glass melt. One consequence of noble metal settling is the possible accumulation of noble metals on the bottom of the melter which could also disturb the pouring of the glass. In order to prevent pouring difficulties due to noble metals settling, the choice of an in can process for fines vitrification can be considered. As a consequence, melting temperature should be limited to 1100 °C to guarantee a good performance of the canister. In order to have a good reactivity between additives and the fines stream for such a melting temperature, the form of additives and their composition have to be optimised.

In this study, for enhancing the reactivity, the form of the additives chosen is glass powder. Viscosity of glass additives is also chosen slightly more than 100 dPa s at 1100 °C in order to minimize noble metals from settling and to obtain a rather good homogeneous distribution of noble metals in the canister. In order to verify this point, rheological measurements were performed with a Searle coaxial cylinder viscometer. The stationary platinum–rhodium crucible has an inside diameter of 27 mm; a platinum–rhodium rotor 9 mm in diameter is driven in rotation by a Rheometric Scientific rheometer (LAMY Rheologie) that measures the torque applied by the molten glass. A glass volume of 21 cm^3 is necessary to fill the crucible. The crucible is filled in an auxiliary furnace. This system is able to measure the viscosity over a range between 5 and 2400 dPa s. After filling and cooling, the crucible is placed in the viscometer and heated. The temperature is measured by thermocouple in contact with the crucible. A temperature residence time of 30–45 min is necessary for stabilizing the temperature. The shear stress and corresponding rotor rotation speed are recorded to obtain 240 measurement points at increasing and decreasing rotation speeds during a 5-min period at each test temperature. The shear stress is proportional to the rotation speed, and the liquid viscosity is determined by linear regression between the shear stress and the strain rate. The overall uncertainty on the measured viscosity is less than 10%.

Solubility of molybdenum in glass melt is a major issue in the field of waste vitrification. However, few glass compositions combining good chemical durability and good molybdenum solubility have already been found. Previous studies performed in the context of glass formulation for high molybdenum content solutions enable us to point out two potentially interesting additives composition in regard to our objectives. These glass additives are both borosilicate glass. The first composition referenced GF76 is an

Table 1
Raw materials used for fines simulation.

Elements	Raw material surrogates	
Zr	ZrO_2	Alfa Aesar ~ 325 mesh
Mo	MoO_3	Prolabo
Tc	MnO_2 [(hs)]	Alfa Aesar
Ru	RuO_2	W.C. Heraeus GmbH
Rh	Ag_2O [(ls)]	Prolabo
	Rh [(hs)]	Alfa Aesar < 400 μm
Pd	Ag_2O [(ls)]	Prolabo
	Pd [(hs)]	Alfa Aesar 0.25–0.55 μm
Sn	SnO	Prolabo
Sb	Sb_2O_3 [(hs)]	Prolabo
U	Nd_2O_3	Alfa Aesar
Pu	Nd_2O_3	Alfa Aesar

[(ls)] only for low simulated fines.
[(hs)] only for high simulated fines.

Table 2
Glass additives composition (wt%).

	GF76	GF97
SiO_2	32.56[a]	47.00[a]
B_2O_3	28.05[a]	16.80[a]
Na_2O	14.64[a]	10.20[b]
Al_2O_3	15.23[a]	1.30[c]
ZnO		7.30[b]
ZrO_2		9.00[b]
CaO		7.50[c]
P_2O_5	5.40[c]	
Fe_2O_3	3.60[c]	
MgO	0.52[d]	
Li_2O		0.30[d]
NiO		0.30[d]
CoO		0.30[d]

[a] ±1.0%.
[b] ±0.6%.
[c] ±0.3%.
[d] ±0.15%.