Incineration-vitrification of a mixture of zeolites, diatoms and ion exchange resins using the SHIVA process

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Abstract. The Advanced Incineration-Vitrification Hybrid System (SHIVA) process is well suited to treat organic and mineral waste, with high alpha contamination management capabilities. It allows, in a single reactor, waste incineration by a plasma burner and ash vitrification in a cold wall direct glass induction melting system. The SHIVA trial demonstrates the successful processing of an inactive waste stream analogue that contains a mixture of mineral and organic ion exchange media. The waste loading attains a promising value of 38 wt.% and a glass wasteform is obtained. Further, the microstructure, chemical composition, and chemical durability of the wasteform are characterised.

1. Introduction

The Thermal treatment for radioactive waste minimisation and hazard reduction (THERAMIN) project is a European Commission programme, which is jointly funded by the Horizon 2020 Euratom research and innovation programme and various European nuclear waste management organizations (WMOs). The THERAMIN project is being conducted between June 2017 and May 2020. Twelve European WMOs and research and consultancy institutions from seven European countries are participating in THERAMIN. The overall objective of THERAMIN is to provide improved, safe, long-term storage, and disposal of intermediate as well as low-level wastes that are suitable for thermal processing. The work programme provides a vehicle for coordinating research in the entire European Union and demonstrating technologies, which are designed to improve the understanding and optimisation of the application of thermal treatment in radioactive waste management programmes across Europe. Additionally, this project will facilitate the development of technologies to increase their Technology Readiness Level (TRL).

In the framework of the THERAMIN project, studies were carried out by the French Alternative Energies and Atomic Energy Commission (CEA) on the incineration-vitrification of mixed inactive waste, which contains inorganic and organic ion exchange media using the Advanced Incineration-Vitrification Hybrid System (SHIVA) process. SHIVA combines heating methods by employing transferred arc plasma and direct induction; the waste incineration is carried out above the plasma torches and the molten glass is heated by the induction generator.

2. Description of the SHIVA process

The SHIVA process (Figure 1) uses cold wall direct glass induction melting and plasma burner technologies. It is therefore an incineration-vitrification process well suited for organic wastes.

SHIVA consists of a water-cooled, stainless steel cylindrical reactor, which is equipped with a flat coil at the bottom and a transferred arc plasma system in the reactor chamber. The SHIVA bottom

structure is built to be transparent to the electromagnetic field such that the glass is directly heated by the field, while the cylindrical shell is not. The plasma torches were developed to minimise their maintenance requirements, in particular, the graphitic consumable electrodes are fed automatically. As oxygen is used and no secondary chamber is present, the gas treatment is simple and compact. It consists of an electrostatic tubular filter and a gas scrubber. The dust in the filter is recovered in a bottom ashtray for recycling. The glass is drained from the cold crucible.

SHIVA was designed to treat organic waste, potentially with a high chloride or sulphur content. The waste can be in solid or liquid form. SHIVA is not compatible with metallic waste nor does it have a separate metallic phase during treatment. The technology is specifically designed to operate in a hot cell for high or intermediate-level wastes. The small size and internal cold walls of the vessel were chosen for high alpha contamination waste capabilities. The SHIVA process is at TRL 5-6 as a full-scale inactive pilot, which has been tested by the CEA since 1998 for various wastes.
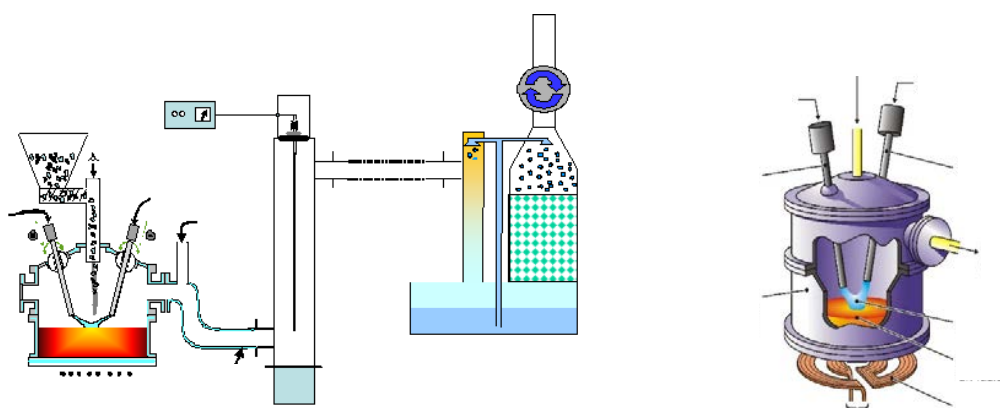

Figure 1. (a) Simplified diagram of the SHIVA process and (b) artist's view of the reactor.

3. Trial information

3.1. Feeds

The waste selected for the trial was a 25 kg mixture of inactive inorganic and organic ion exchange media composed of zeolites, diatoms, strong acid ion exchange resins (IERs) and strong base IERs (Table 1). The zeolites originated from crushed natural zeolite rock composed of 60 ± 5 wt.% chabazite, having a high specific surface area > 100 $m^2 \cdot g^{-1}$, and a cation exchange capacity of 2 meq·g^{-1}. Diatomite, being a highly porous material, is usually used as a filtration and clarification medium once cleaned and crushed. The IERs were styrene divinylbenzene copolymers with a strong acid site $–SO_3^-H^+$ for cation exchange (≥ 1.90 eq·L^{-1} H^+ form) and a strong base site ($–N(CH_3)_3^+OH^-$) for anion exchange (≥ 1.20 eq·L^{-1} OH^- form). The IERs contained 50 wt.% of water.

Table 1. Waste feeds for SHIVA trial.

Waste	Fraction (wt.%)	Quantity (kg)	Supplier and reference
Zeolites	45	11.3	SOMEZ Siliz® 14, ZN-024-14
Diatoms	44	11.0	LAFFORT Diatomyl® P0
Strong acid IERs	5.5	1.4	LENNTECH Amberlite™ IRN77
Strong base IERs	5.5	1.4	LENNTECH Amberlite™ IRN78

Vitrification was accomplished by the addition of 40 kg of glass frit whose composition is provided in Table 2. It should be noted that in the first approach, the vitrification was carried out with a known and available glass frit that responds well to induction. Its composition could be optimised for this specific waste as a result of a formulation study.

Inputs were therefore composed of 38.4 wt.% waste and 61.5 wt.% glass frit. It should be noted that ion exchange media were not exchanged with solutions containing radionuclide surrogates prior to the trial. Therefore, IERs were completely burned. The theoretical composition of the wasteform (Table 2) can be calculated from the theoretical compositions of the glass frit, zeolites, and diatoms, and the amounts of these materials that are introduced into the process.

Table 2. Compositions (expressed in oxide weight percentages) of glass frit, zeolites, diatoms and the wasteform (calculated and analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and energy dispersive X-ray spectroscopy (EDS)). The seven main oxides of the wasteform are written in bold. Note that IERs were completely burned in the process.

Oxide	Glass frit	Zeolites	Diatoms	Wasteform		
				Calculated	Analysed by ICP-OES	Analysed by SEM/EDS
Al_2O_3	5.2	17.0	3.0	**7.2**	**5.6**	**5.7**
B_2O_3	14.7	-	-	**9.8**	**12.1**	n.a.[a]
CaO	4.1	5.5	0.5	**3.8**	**4.2**	**3.9**
CoO	0.7	-	-	0.5	0.6	0.6
Fe_2O_3	4.0	2.5	1.6	**3.4**	**4.2**	**4.0**
K_2O	-	4.5	0.2	0.9	0.5	0.6
Li_2O	2.0	-	-	1.3	1.5	n.a.[a]
MgO	-	1.3	0.3	0.3	0.2	0.4
Na_2O	10.0	-	2.3	**7.1**	**8.7**	**8.0**
Nd_2O_3	7.3	-	-	**4.9**	**6.2**	**6.1**
NiO	0.5	-	-	0.3	0.4	0.3
SiO_2	46.6	51.5	91.1	**57.2**	**50.7**	**52.2**
TiO_2	-	-	0.5	0.1	0.6	0.5
ZnO	2.5	-	-	1.7	2.3	2.1
ZrO_2	2.4	-	-	1.6	2.2	2.1

[a] n.a.: not analysed because boron and lithium are not detected by EDS.

3.2. Heating systems

To ensure complete mineralisation of the waste and guarantee its incorporation into the vitreous matrix, the two modes of heating — induction and plasma torches — were used simultaneously during the waste feeding operations.

- The induction heating system was started at the beginning of the trial and was maintained throughout its duration to maintain a molten glass bath at the bottom of the SHIVA reactor. The induction was started using a titanium starter ring and the generator power was incrementally increased from 40 to 90 kW.
- The sleeves and electrodes of the torches were fed with argon during the start-up phases, and with a mixture of argon and oxygen ($\approx$ 10 L·min^{-1}) during the waste introduction periods. The electrodes were pushed a few millimetres at every hour to compensate for their wear.

3.3. Course of the trial

Before the start of the trial, the reactor was pre-filled with 40 kg of glass frit. The waste feed was introduced to the upper part of the reactor; this was achieved during three 8-hour feeds by using a feeding hopper and a worm screw at an average feed rate of 1 kg·h^{-1}. This sequencing was used to facilitate a daytime operation for the waste incineration.

For this demonstration, no maximum was sought in terms of processing capacity and waste loading in the vitreous matrix. These parameters would be higher for industrial scale processing.

4. Characterisation of the produced wasteform

The end product of the process was a glass that is macroscopically homogeneous. To be characterised, the wasteform was broken into pieces and a sample was selected by quarter splits (Figure 2).

Figure 2. Wasteform sample (≈ 10 cm long) from the SHIVA trial.

4.1. Microstructure

From a fraction of the Figure 2 sample, a polished cross section was prepared by embedding in an epoxy resin and polishing with diamond abrasive cloths and suspensions before coating with a carbon deposit. Scanning electron microscopy (SEM) (Zeiss Supra™ 55, acceleration voltage of 15 kV) shows a homogeneous material at the micrometric scale (Figure 3 (a)). Another fraction of the sample was crushed and analysed by X-ray diffraction (XRD) (Phillips X'PERT Pro, Bragg-Brentano θ-2θ diffractometer, Cu-Kα$_1$ radiation, 40 mA-40 kV). The pattern acquired between 10° and 90° (2θ) shows no diffraction peak characteristic of the presence of crystalline phases and has a diffuse scattering characteristic of vitreous materials (Figure 3 (b)). The matrix is thus vitreous and amorphous.
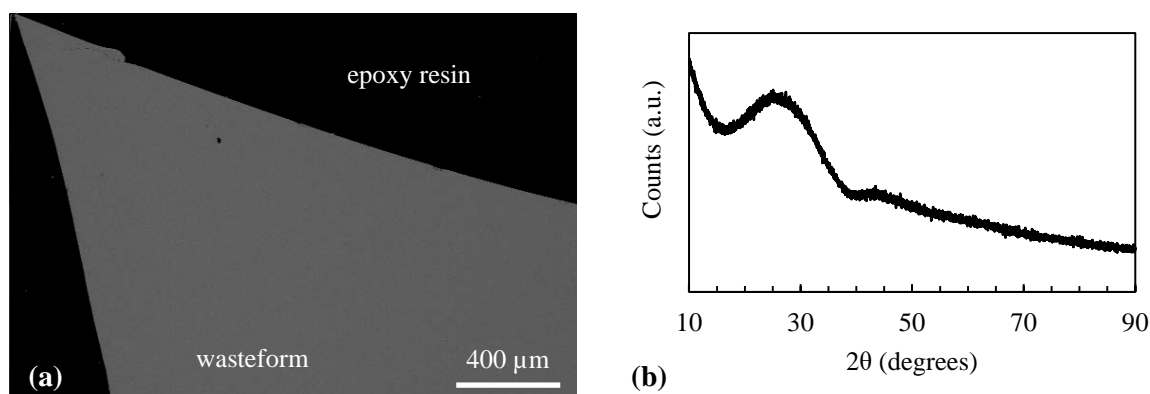

Figure 3. (a) SEM image and (b) XRD pattern of the wasteform.

4.2. Chemical composition

The calculated theoretical chemical composition of the wasteform, shown in Table 2, is checked by two methods: (*i*) complete dissolution of the material followed by solution analysis by ICP-OES and (*ii*) analysis by EDS coupled with SEM. Using EDS, six regions of interest were analysed with similar results (standard deviation ≤ 0.3). The values presented in Table 2 are the average of the six measurements. Since boron and lithium are too light to be analysed by this method, the composition is normalised using the theoretical contents of these two elements.

The analysis of the glass composition by the two techniques provides consistent results. The glass contains mainly SiO_2, B_2O_3, Al_2O_3, Na_2O, and Nd_2O_3 that represent ≈ 85 wt.% of the glass composition. These contents are of the same order of magnitude as those of the inactive surrogate of the French reference high level nuclear wasteglass R7T7. Differences are noted between the theoretical and analysed compositions. They can be explained by an inhomogeneous incorporation of the waste into the matrix or some carryover of the powdery waste in the off-gas treatment system.

4.3. Chemical durability

The chemical durability of the material was studied according to a protocol adapted from the PCT-B standardised test [1]. After crushing the material, 125–250 μm powder was placed in contact with pure water with a glass-surface-area-to-solution-volume ratio (S/V) of 10 m^{-1} at 90±2 °C in unstirred perfluoroalkoxy (PFA) reactors. The powder specific surface area of 280 g·cm^{-2} was estimated by adsorption of krypton on the sample surface (Micromeritics ASAP 2020) according to the Brunauer–Emmett–Teller theory [2]. Solution samples, taken at regular intervals, were filtered with a cut-off of 0.45 μm, acidified with ultrapure grade HNO$_3$ and analysed by ICP-OES (Thermo Scientific iCAP™ 6000 Series). The concentrations were used to calculate normalised mass losses $NL_i = C_i/(x_i \times S/V)$, where C_i is the concentration of the element i, and x_i is the mass percentage of i in the glass (using the analysed sample composition: $x_{Al} = 0.030$, $x_B = 0.038$, $x_{Ca} = 0.030$, $x_{Li} = 0.007$, $x_{Na} = 0.065$, $x_{Si} = 0.237$). The alteration rate, $r = dNL_i/dt$, was calculated by linear regression.

The stoichiometric dissolution of the glass during the first days (Figure 4 (a)) gradually becomes non-stoichiometric with a retention of Ca and Al of 4% and 30%, respectively, (relative to B) after one month. The rather unusual shape of the curves $NL_i = f(t)$ — in particular, B release is not showing a drastic rate drop — is explained by the conjunction of two phenomena: (*i*) the effect of the pH variation on the rate of hydrolysis and (*ii*) the effect of the formation of a surface layer on the alteration rate. The pH increases from 7 to 8.5, which is the value at which it stabilises. This variation causes the increase in the rate of hydrolysis (v_0) of the vitreous matrix. This effect of pH is illustrated by the grey dashed curve on Figure 4 (a), calculated according to: $v_0 = k_+ \times C_{H^+}^n \times \exp\left[-E_a/(R \times T)\right]$, where k_+ is estimated from the NL_B value at day 1 (0.12 g·m^{-2}), n is the pH dependence coefficient, E_a is the apparent activation energy, R is the ideal gas constant, and T is the temperature. In this calculation, $n = 0.4$ and $E_a = 76$ kJ·mol^{-1} are assumed to be equal to those of the R7T7 glass. The progressive divergence between the calculated and the experimental data is explained by the decrease of the alteration rate with the formation of a surface layer.
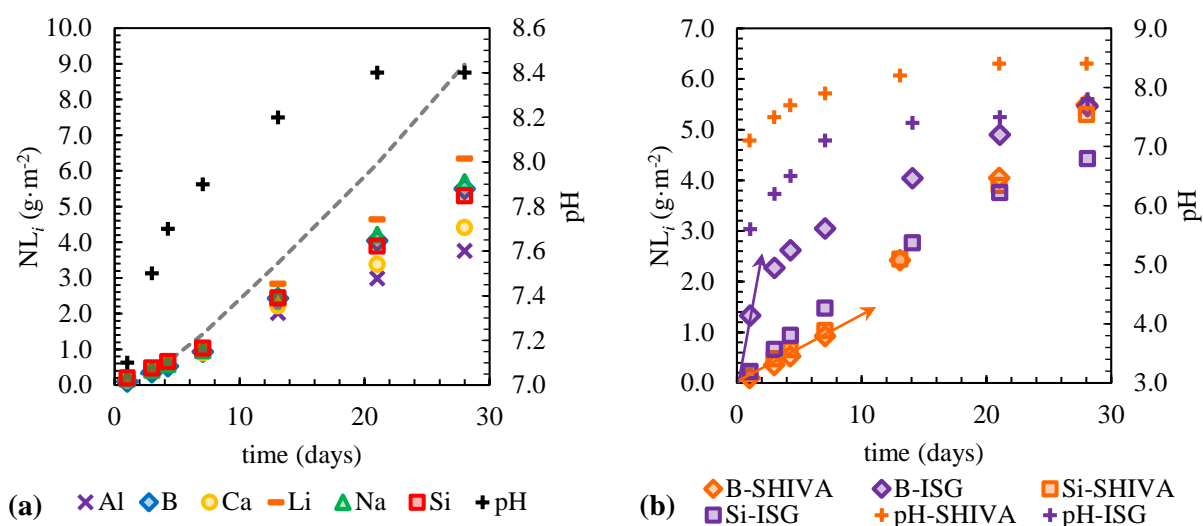

Figure 4. (a) Evolution of NL and pH during wasteform leaching. (b) Compared evolutions of NL and pH during the leaching of ISG and SHIVA-produced wasteform. The arrows are a guide for the eyes to estimate the minimum hydrolysis rate of the matrices.

Comparison of these results with those acquired for the reference International Simple Glass (ISG) [3, 4] altered under the same conditions (Figure 4 (b)) shows a similar (and classical) evolution of the pH of the solutions, with release of alkali species leading to an increase of solution pH. The pH stabilizes at values close to 8 at 90 °C under these experimental conditions of low S/V ratio. The hydrolysis rate

of the ISG is higher by approximately one order of magnitude than the rate from SHIVA-produced sample. The dissolution of the ISG is prematurely non-stoichiometric and coincides with the formation of an alteration layer. Due to the diffusion of elements through this alteration layer, the alteration rate of ISG drops earlier than for the SHIVA-produced wasteform. Drawing conclusions about the long-term behaviour of this wasteform would require further investigation.

5. Conclusions

The SHIVA trial conducted in the framework of the THERAMIN project demonstrated the success of the process for the thermal treatment of a mixture of organic and mineral waste composed of zeolites, diatoms and ion exchange resins. The waste loading of 38 wt.% is high and could be increased in the future. The activity of maximising the waste load and the processing capacity was not attempted during this feasibility trial. The final product consists of an amorphous glass, which is primarily composed of SiO_2, B_2O_3, Al_2O_3, Na_2O, and Nd_2O_3. Differences are observed between the theoretical composition of the glass and the composition analysed by two different techniques; this is probably due to low convection in the melter and some carryover of the powdery materials in the off-gas treatment system.

Leaching tests conducted at 90 °C and a low glass-surface-area-to-solution-volume ratio show that the hydrolysis rate of SHIVA-produced wasteform is significantly lower than that of the reference International Simple Glass (ISG). Drawing conclusions about the long-term behaviour of the wasteform would require further investigation, but these results can be regarded as encouraging. Finally, the vitreous nature of the matrix and the presence of boron, which is known to be a tracer for the alteration [5], render it possible to apply proven methodologies to this matrix for elucidating its chemical durability and long-term behaviour.

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