DIRECT VITRIFICATION OF LOW- AND MEDIUM-LEVEL RADIOACTIVE WASTE: REVIEW OF TECHNOLOGICAL DEVELOPMENT AND MAIN RESULTS

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ABSTRACT

The CEA and SGN are actively engaged in an ongoing research effort to apply the vitrification process to low- and medium-level waste such as the ion exchange resins and combustible wastes produced in nuclear power plants. Laboratory-scale tests at a feed rate of 100 g·h^{-1} conducted with encouraging results showed that direct vitrification at the surface of the glass melt is effective for the destruction and disposal of such waste. Orientation tests were then undertaken in a small-scale pilot unit (15 kg·h^{-1}) using an induction-heated cold crucible melter (CCM) 300 mm in diameter to provide data on the physical and chemical process conditions (glass temperature, excess oxygen, pressure drop, electrical parameters) as well as data concerning the CCM off-gas stream (gas temperature, CO, NO_x, CO_2, O_2 concentrations, particle matter fraction and composition). Additional tests were conducted to design an industrial off-gas treatment system, using a high-temperature filter to determine its efficiency on particle matter in the CCM off-gas stream.

The results of these tests and technological development work will be implemented in a larger pilot plant with a capacity of up to 50 kg·h^{-1} using a 550 mm diameter CCM to be built in Korea, and scheduled to begin operating in 1999. This paper describes the orientation and additional tests performed in France by the Commissariat à l'Énergie Atomique (CEA) and outlines the major process options selected for the Korean pilot facility. The cost effectiveness of this process and its potential applications to other types of nuclear power plant waste are also briefly described.

INTRODUCTION

Cold crucible melting technology has been shown to be useful for the destruction and disposal of voluminous low-level radioactive wastes, including combustible waste and organic ion exchange resins. In some cases these resins can pose a difficult packaging and disposal problem. Cold crucible melting technology was therefore investigated to determine its feasibility for direct vitrification of the resins: thermal decomposition of the organic structure on the glass bed, simultaneous combustion and incorporation of the radionuclides and noncombustible constituents into glass. The objective is to achieve combustion and vitrification of the inorganic residue simultaneously and directly in the molten glass. This process is of particular interest for plastic and cellulosic wastes as well as ion exchange resins, which are currently conditioned in cement or polymer matrices representing a significant waste volume for disposal.

Several difficulties must be overcome before direct vitrification becomes a viable process:

- The combustion off-gases are generally chlorinated in the case of plastic wastes such as polyvinyl chloride, and generally sulfated in the case of resins, many of which are sulfonated. The CEA and SGN have acquired considerable experience in incinerating highly chlorinated plastic wastes. The sulfate must be extracted in the off-gas stream to prevent the formation above the glass of a yellow phase that generally traps the radioactivity, which is no longer immobilized in the glass. Special precautions had to be taken when direct vitrification was implemented.

- Hot gases containing chlorine or sulfur may lead to severe corrosion when handled in hot equipment. The cold crucible process provides an ideal solution to this problem.

- A final difficulty is the dust content in the combustion off-gases. The radioactive particles must be trapped before the off-gas treatment, and a solution must be developed to recycle the dust back to the CCM.

Laboratory-scale tests and technological tests were therefore conducted for each wasteform in a pilot facility equipped with a CCM to develop suitable solutions to these problems, to compile the data necessary to design a CCM pilot facility for combustible waste processing, and to demonstrate the technological and economic advantages of the direct vitrification process.

PRELIMINARY LABORATORY TESTS

Laboratory tests of direct vitrification of ion exchange resins on a glass melt were conducted by the CEA and SGN at Marcoule in a bell-type furnace capable of reaching temperatures of 1200°C. The furnace included an alumina crucible containing the molten glass, an afterburning chamber to ensure complete combustion of the gas stream, and an off-gas treatment system. The entire facility (**Figure 1**) was installed in a fume chamber.

The laboratory test results demonstrated the feasibility of incinerating and vitrifying ion exchange resins in a single operation, and provided qualitative results on resin behavior during vitrification: combustion mode and main vitrification parameters (temperature, atmosphere, etc.).
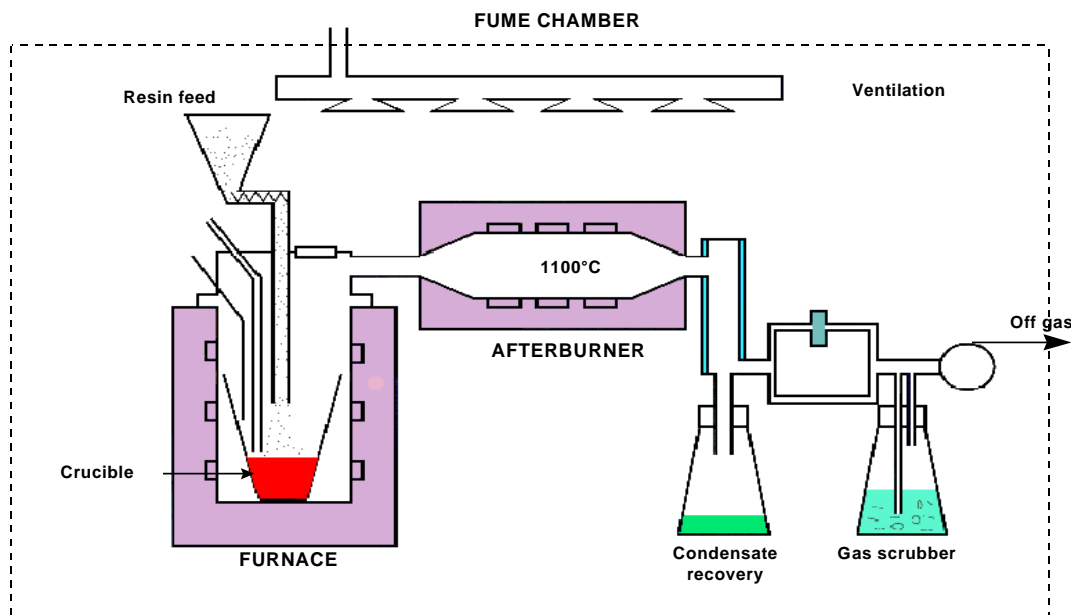

Figure 1. Laboratory facility for ion exchange resin treatment tests

TECHNOLOGICAL TESTS

Following the satisfactory results obtained at laboratory scale, direct vitrification orientation tests were conducted at technological scale using a direct induction-heated cold crucible 300 mm in diameter, an electrically heated afterburning chamber and a system designed to ensure cooling, particle separation and chemical scrubbing of the process off-gases (**Figure 2**). Gas composition and particle size measurements were also carried out.
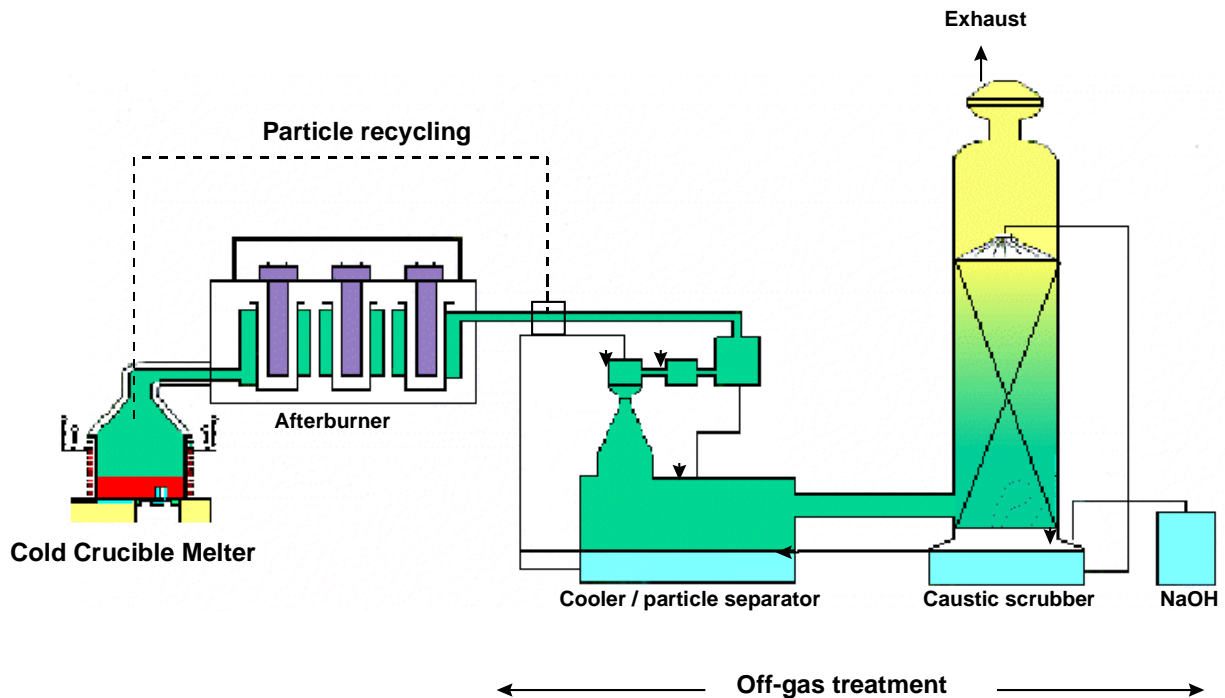

Figure 2. Pilot facility for ion exchange resin treatment tests

Ion Exchange Resin Tests

The tests performed on ion exchange resins alone provided valuable information on the physical and chemical operating conditions (process atmosphere and temperature) and on the IER processing capacity of the cold crucible. The process atmosphere must be oxidizing to avoid glass reduction by carbon from the resins and combustible waste; all the tests were carried out with 25% excess oxygen. The glass surface temperature was limited to about 1200°C in order to limit radionuclide volatility during combustion on the glass melt. The capacity of the 300 mm diameter cold crucible melter is 12 kg·h^{-1} with resins and 15 kg·h^{-1} at the maximum flow rate. Continuous analysis of the off-gases (CO, CO_2, O_2, NO_x, SO_2, dust content) from the cold crucible and afterburner confirmed the advantages of afterburning and allowed optimization of the off-gas treatment system.

During direct resin vitrification at 10 kg·h^{-1}, the gas temperature in the CCM off-gas line was about 400°C to 500°C (cf. experimental gas temperature record in **Figure 3**) and the flow rate was 23 Nm^3·h^{-1}.
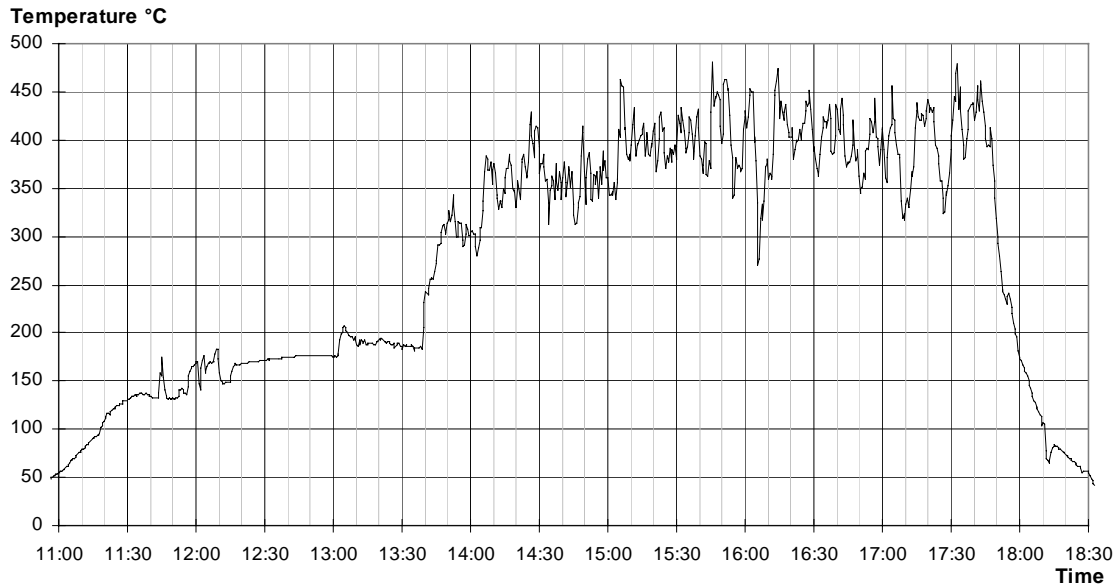
Temperature °C

Figure 3. CCM off-gas temperature record

The following composition was measured at the CCM outlet port:

- CO   : 190 ppm (but 950 ppm during the startup phase)
- C_xH_y : 10 to 50 mg·m^{-3} (but 200 mg·m^{-3} during the startup phase)
- CO_2 : 15%
- O_2 : 25%
- NO   : 2000 ppm
- H_2O : 53%
- SO_2 : 0.6% to 1.6%

The C_xH_y and CO concentrations are indicated in **Figure 4**. Afterburning was only useful during the start-up phase. The concentrations following afterburning were several times lower than these values.
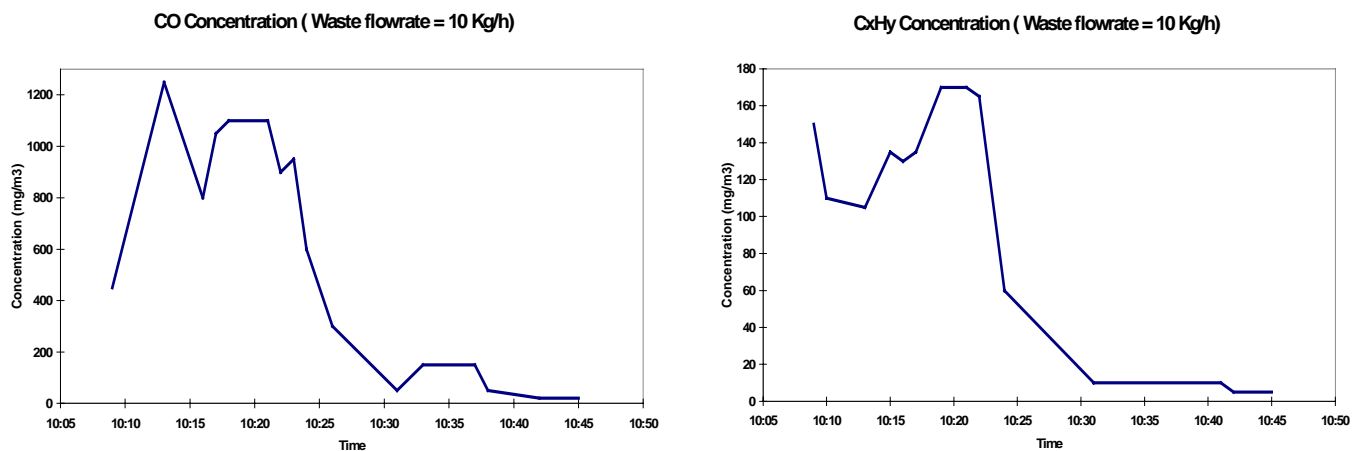

Figure 4. Off-gas CO and CxHy concentrations versus time

The particle content ranged from 1 to 10 $g \cdot Nm^{-3}$ depending on the type of resin (Duolite or Amberlite), the water content (dry resins or wet resins) and the type of vitrification additive (borosilicate or not) used for the test. The particle size distribution (**Figure 5**) included 10 to 15% of particles exceeding 3.1 µm in diameter, and 85 to 90% of particles below 3.1 µm (10% < 0.36 µm). The particles consisted mainly of $CoLi(SO_4)_3$ when the resins were loaded with Cs and Li, and $NaSO_4$ for pure resins. Only removable dust was found on the cold crucible wall.
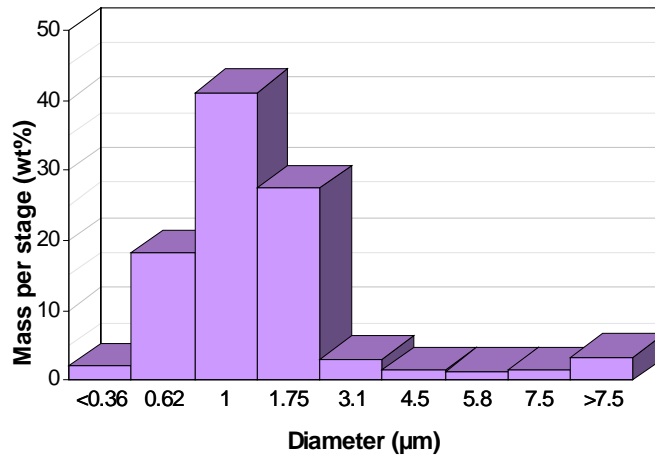

Figure 5. Particle size analysis
(CCM off-gas stream; flow rate 10 $kg \cdot h^{-1}$)

The cobalt distribution was determined during technological tests: 93% of Co remained in the glass, resulting in a cobalt decontamination factor of 34.

It must be noted that the tests were conducted with a high content of surrogate (Cs, Co) to simplify analysis, although this does not correspond to radionuclide waste composition. Tests are continuing to provide further data in this area, and particularly to recycle the dust into the glass in order to obtain an acceptable overall decontamination factor.

The glass obtained during the tests did not include a separated yellow phase containing molten salts (sulfate lake), but the glass was highly reduced by carbon from the resins. The glass composition must therefore be modified to address this problem.

Combustible Waste Tests

Combustible wastes containing up to 50% PVC were also tested at this stage. The test capacity of 7 $kg \cdot h^{-1}$ did not represent the maximum value. The pilot unit was limited by the oxygen flow rate, making it impossible to increase the waste feed rate.

High-Temperature Filter Tests

Additional direct vitrification tests were conducted at the same technological scale, using a high temperature filtration pilot (**Figure 6**) between the cold crucible melter and the afterburner. Satisfactory results were obtained, and the filter efficiency was between 99.6% and 99.8% at 200°C. The high-temperature filter decontamination factors were 2000 for Co and 4000 for Cs.
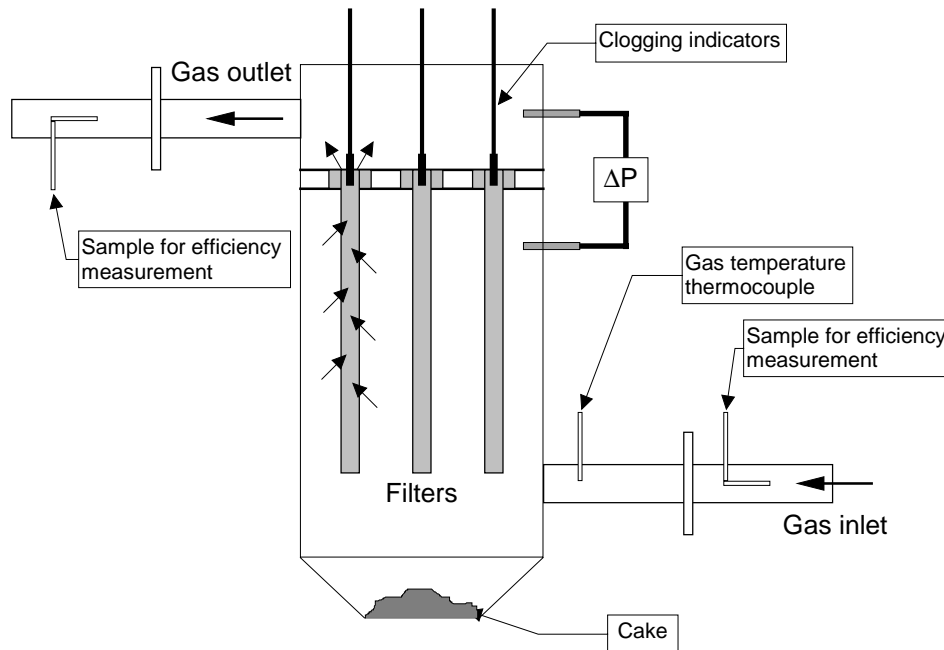

Figure 6. High-temperature filtration pilot schematic

DESIGN OF A CCM PILOT FACILITY FOR COMBUSTIBLE WASTE

The cold crucible pilot plant with a 550 mm diameter melter will have a capacity of about $30 \text{ kg}\cdot\text{h}^{-1}$ ($50 \text{ kg}\cdot\text{h}^{-1}$ maximum) requiring an off-gas system rated for $150 \text{ Nm}^3\cdot\text{h}^{-1}$. The pilot plant will include an advanced off-gas treatment system in order to conduct an extensive research and development program for future applications with ion exchange resins, combustible solid waste and borated concentrates.

The main process line will consist of the following components:

- Two melter *feed lines*. Waste will be supplied to the CCM by a metering screw conveyor, while glass frit will be fed via a transfer system comprising a hopper, a vibrating table to convey the frit to the bucket, and a weighed bucket used to dump the desired mass of glass frit into the melter via a transfer lock consisting of two valves.

- The *cold crucible melter*: a water-cooled assembly of stainless steel segments forming a cylindrical structure 550 mm in diameter. The cooling temperature is about 110°C at a pressure of 2 bars.

- The *off-gas treatment system*. CCM off-gas includes a large particle fraction when burning resins, high SO_x content when burning cation resins, high water content when burning wet resins, and high HCl content when burning waste containing PVC. In order to prevent dust from reaching the afterburning chamber, the CCM off-gas stream will be prefiltered across a cleanable high-temperature filter designed to trap volatile radionuclides (mainly cesium). The afterburner then heats the off-gas to 1100°C for a minimum residence time of two seconds to burn any residual carbon in the form of CO or

complex hydrocarbon species C_xH_y. The exhaust gas is quickly cooled by full quenching, and scrubbed with a sodium hydroxide solution to eliminate SO_x and HCl. The scrubber outflow laden with sodium and cesium salts is sent to a final conditioning process.

In an industrial facility operating with radioactive materials, the off-gas is released after it is ducted across HEPA filters; this assumes that fine aerosols have been eliminated from the scrubbed gas stream by an efficient demister, and that the gas has then been reheated. Finally, in order to ensure low NO_x and dioxin emission in all cases, the off-gas may be routed through a catalytic converter in which any remaining dioxins and furans in the heated gas are destroyed and the NO_x is converted to N_2 by injection of ammonia.

TECHNICAL AND ECONOMIC FEASIBILITY STUDIES

The vitrification of low-level waste from nuclear power plants mainly concerns organic products such as ion exchange resins and combustible solid waste. Scrap metal and concrete are not considered, as the volume reduction factor is not high enough to demonstrate the cost effectiveness of the application.

For ion exchange resins, a cement grouting process usually increases the initial waste volume by a factor of 2 to 3. When IER are vitrified, the volume reduction factor is in the range of 50 to 100, depending on the mineral load—which is quite small (on the order of 1 wt%)—and on the waste loading ratio in the glass. The difference between the final conditioned waste volume, and accordingly on the disposal cost, is therefore high enough to offset the higher capital cost of the vitrification technology.

Direct vitrification also yields high volume reduction factors for combustible solid wastes, as the mineral load is relatively small and also contains some major glass components such as silicon.

Other types of waste routinely produced in nuclear power plants (including oil, sludges, decontamination solutions and borated concentrates) are also suitable for vitrification. For borated concentrates, the maximum boron oxide content in the glass (20 wt%) does not provide a significant difference in terms of the volume reduction factor compared with conventional conditioning processes such as cement encapsulation. The volume reduction factor is higher for the other wasteforms, but the amounts of waste to be treated are usually small. In both cases, the process is cost-effective when the facility used to process the organic product can also be used for these additional wastes, making a dedicated facility unnecessary.

LLW vitrification is cost-effective when the overall waste processing cost (including the return on investment and the operating, maintenance, transportation and disposal costs) is lower than with another process. Such calculations must be performed on a case-by-case basis as they depend largely on national data (disposal and labor costs) and national requirements such as waste acceptance criteria for disposal. The economic assessments performed to date have yielded positive results.

The development of LLW waste vitrification is thus based on the treatment of organic materials and some liquid waste to benefit from the use of a single facility. Scrap metal and concrete debris have been intentionally disregarded since the necessary additional plant capacity cannot be offset by a corresponding waste volume reduction. Slag is the final wasteform for mixed (metallic and nonmetallic) waste processing. The qualification of such a matrix and compliance with national acceptance criteria for waste disposal may also be an issue under these conditions.

CONCLUSION

Orientation tests demonstrated the feasibility of direct vitrification of organic products such as ion exchange resins and dry combustible solid waste. Test also showed that direct vitrification was advantageous for the treatment of organic materials, and provided valuable data on operating conditions and off-gas treatment. The tests corroborated the capacity postulated for the technical and economic feasibility studies, confirming the cost-effectiveness of the process.

Based on these tests and on technological developments, a larger pilot plant with 550 mm diameter CCM will be built in Korea, and should begin operating in 1999.

Direct vitrification has been investigated primarily for the disposal of ion exchange resins, but the same pilot facility could also handle liquid waste and other combustible solid wastes.

Further research is necessary on recycling particle matter and volatile radionuclides in the cold crucible, on characterizing the resulting glass material, and on specifying a glass matrix suitable for processing various categories of combustible waste according to the actual detailed needs of Nuclear Power Plant operators.