The Solidification of High-Level Radioactive Wastes

by John R Grover

Since the earliest days of nuclear energy, the management of radioactive wastes has been a major concern, both for the public and those engaged in the industry, particularly with regard to the release of radioactive materials to the environment and possible risks of contamination. The largest quantity of radioactivity is contained in irradiated nuclear fuel. If present doubts about the safeguards aspects of fuel reprocessing are overcome and the irradiated fuel is reprocessed to recycle the fissile material, the management and disposal of the high-level waste will become a major task as the world nuclear generating capacity increases over the next few decades

Reprocessing involves the dissolution of the irradiated nuclear fuel, usually in nitric acid solution, and the removal by solvent extraction of the plutonium and unburned uranium. The remaining solution, containing more than 99 9% of the non-volatile fission products, together with some additional constituents from cladding materials, traces of unseparated plutonium and uranium, and most of the transuranic elements, constitutes the high-level waste.

This liquid waste is usually concentrated by evaporation and stored as an aqueous nitric acid solution in high-integrity stainless steel tanks. Experience with tank storage has been good, but persisting with this practice would involve continuing technical supervision and periodic replacement of tanks over the centuries. While liquid storage can be considered acceptable for some decades, with the expansion of nuclear power, it is generally agreed that in the longer term it is better to replace liquid storage by an alternative system based on solidification of the waste.

The conversion of the high-level waste to a solid has been studied for the past twenty years. Large pilot scale operations of both the calcination and vitrification processes have been successfully demonstrated and more advanced processes are currently being developed.

As part of the IAEA programme in the waste management field, the Agency's Secretariat prepared a document which surveyed the existing technology. This was reviewed and revised by an Advisory Group meeting convened in Karlsruhe, in the Federal Republic of Germany in 1977, and has now been published as the Technical Reports Series No 176 "Techniques for the Solidification of High-Level Radioactive Wastes"

This paper summarizes the highlights of that report, covering mainly the basic features of the many processes that are being developed to illustrate the wide variety of potential solutions to the problem The paper concludes with a review of the current status and

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future prospects for waste solidification in the wider context of the management of wastes in the nuclear fuel cycle. For detailed descriptions of the processes, the plant design, operation, maintenance, scale-up potential, flexibility and safety aspects the reader should consult the relevant sections in the Technical Reports Series No 176

Basic Features of Solidification Processes

The primary aim of any solidification process is to convert the high-level waste solution to a product that is less mobile, requires less surveillance and is more suitable for final disposal. This product should satisfy certain criteria. e.g., it should maintain its mechanical integrity, have a good resistance to irradiation; adequate thermal conductivity and, ideally, a very low leach rate. Under the present state of knowledge, glasses and ceramics are considered suitable for final disposal

The basic solidification processes are illustrated in Figure 1. The simplest procedure is firstly evaporation, followed by denitration (or "calcination") of the waste solution to form a calcined product which can either be in granular or solid form. (Calcines are considered only as interim products as they do not sufficiently fulful all the above criteria) However, the granular calcines can be mixed with additives and melted to form a glass or ceramic product. An alternative route is to mix the additives with the waste solution and evaporate, denitrate and melt, to form a glass or ceramic product in one step Another variant is the use of an adsorption process followed by a high temperature treatment to produce a ceramic product. During the past few years, attempts have been made to improve the properties of the products by further treatment, such as the incorporation of the calcine or glass into a coated particle or metal matrix to improve the leach resistance and thermal conductivity.

About 30 different processes have been developed over the past twenty years and they can conveniently be classified into four groups by their stage of development.

1. Processes which have been demonstrated, but are no longer in routine operation.
2 Processes in active operation or being constructed and commissioned to handle the waste from industrial reprocessing plants.
3. Processes in an advanced stage of development.
4. Processes in the early development stage

Group One Processes

The first process to be developed in which the waste was incorporated in glass was at Chalk River, Canada, where the waste solution was mixed with a nepheline/syenite/lime mixture and fused at 1350°C. Radioactive samples of this glass were buried in the soil in 1960 and the leaching of nuclides has been studied ever since This was closely followed by the FINGAL process, developed at Harwell, UK, where a borosilicate glass containing 25–40 wt% of waste (as oxides) was produced at 1050°C.

During the early 1960's many solidification concepts were studied in the USA and three of these were chosen for demonstration in the Waste Solidification Engineering Prototype (WSEP) plant which operated at Richland, Washington from 1966 to 1971.

Experience from both the UK and USA operations in the late 1960's is being used for further developments, both in those and other countries.

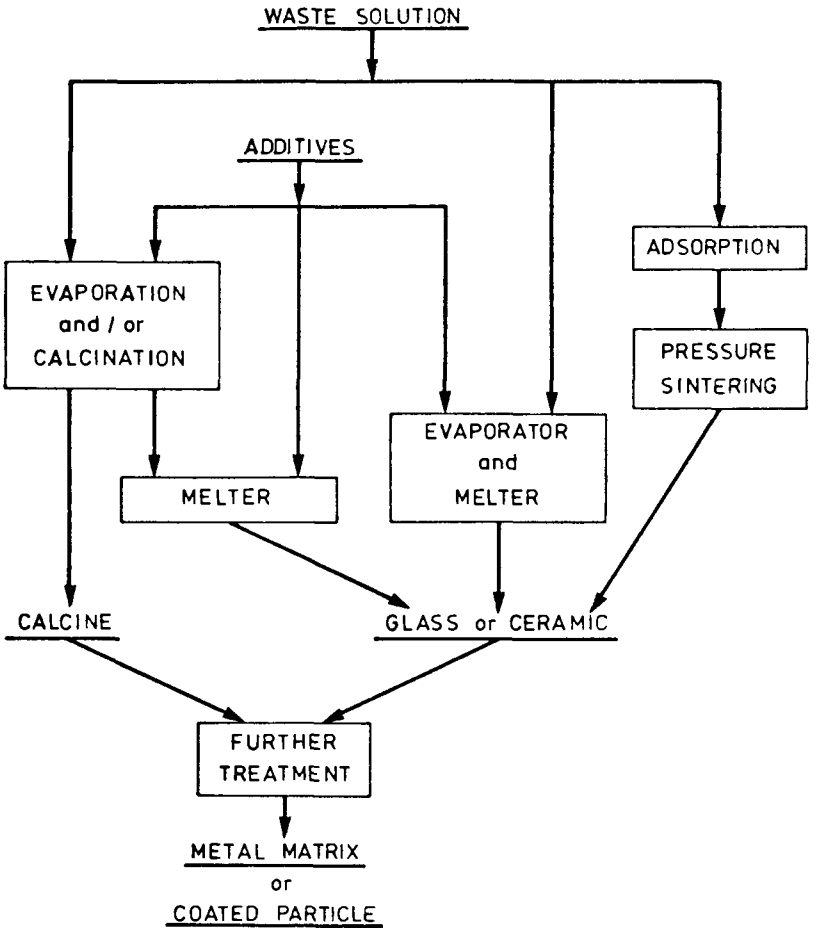


Figure 1. Basic Solidification Processes

Group Two Processes

Only four plants have been operated or are being constructed to handle the waste from industrial reprocessing plants. Since 1963, waste containing approximately 70 megacuries of radioactivity from the USAEC's Idaho Chemical Processing Plant has been solidified by fluidized-bed calcination. In this process, the waste solution is sprayed into a fluidized-bed and calcined at 400–500°C to produce a granular, free flowing product which is stored in large, air-cooled bins in underground vaults. A new plant is currently under construction and will be commissioned in 1980. This is now the only plant producing a calcine product, which is considered acceptable for the conditions at the site. The wastes that are handled result from the reprocessing of highly enriched fuel elements which have only 0 1–1.0% of the specific radioactivity and heat generation rate of commercial power reactor wastes.

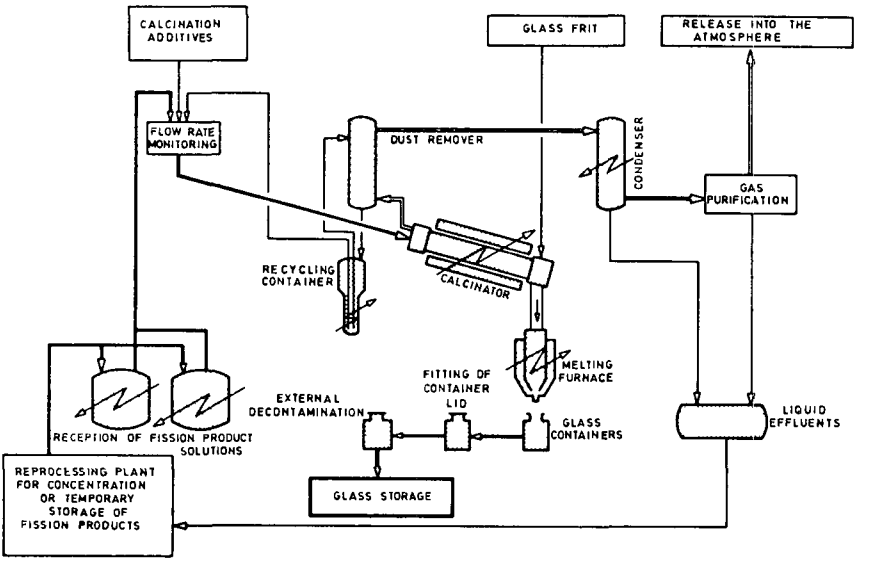
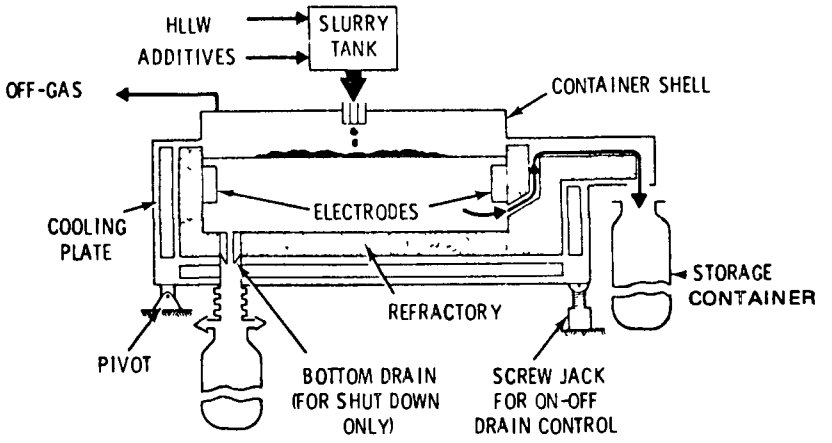


Figure 2: Simplified flowsheet of vitrification plant at Marcoule (AVM)



Melting Cavity Dimensions	0.86 m wide, 1.22 m long, 0.71 m deep
Outside Dimensions	1.95 m wide, 2.13 m long, 1.62 m high
Glass Depth	0.48 m

Figure 3: Direct Liquid Fed Ceramic Melter

In France, the PIVER pilot plant operated from 1969 to 1973 to convert waste containing 5 megacuries of radioactivity from the Marcoule reprocessing plant into a borosilicate glass. The waste was mixed with a glass frit, calcined to 300°C and then the temperature was raised and the mixture melted. The molten product was then transferred from the processing vessel to a storage container. It was found that this could be repeated up to 30 times before the processing vessel had to be replaced. This process has now been superceded by a two-stage continuous process (AVM) which has just commenced radioactive operation. The AVM plant consists of a rotary calciner coupled to a melting furnace The simplified flowsheet is shown in Figure 2. The calciner has a nominal capacity of 40 litres/h and the vitrification unit a maximum capacity of 20 kg of vitrified product per hour. All wastes arising at Marcoule are to be vitrified in this plant and a similar plant is to be constructed at La Hague (AVH) for the high-level waste arising from that reprocessing plant.

A plant which is based on a semi-continuous pot glass process, involving calcination followed by melting in the processing vessel and subsequent casting of the glass in a storage container, is under construction at Tarapur in India. It will commence active operation in 1980.

Group Three Processes

A number of processes are in an advanced stage of development in the UK, USA, the Federal German Republic and the Soviet Union.

The HARVEST development programme in the UK, which is a scale-up of the FINGAL process, will lead to the construction of a full-scale active plant at Windscale, planned for the late 1980's. This is a single-stage batch process in which the waste solution and glass making additives are fed to a cylindrical vessel, up to 61 cm dia, and the evaporation, denitration and melting occur in the same vessel to produce a borosilicate glass.

A range of processes are currently under development in the USA, of which the two most promising are the spray calciner/in-can melter and the direct liquid-fed ceramic melter. The spray calciner was one of the processes evaluated in the WSEP plant. Liquid waste is atomised at the top of a chamber, heated to 750°C, and the droplets are dried and calcined as they fall through the hot zone At the bottom they are mixed with frit and fall directly into the final container which is situated in the melter furnace The contents are fused and the container is then transferred to storage.

A second US process uses a ceramic melter in which the melting energy is supplied by passing an alternating current between electrodes immersed in the glass Initially this unit was coupled to a fluidized-bed calciner in which the waste solution was calcined. The calcine was then mixed with a powdered glass frit and the mixture dropped onto the molten glass in the ceramic melter. This proved a very successful unit and smooth operation was demonstrated at high throughput, so tests were carried out in which the waste solution was mixed with the glass frit and fed directly to the ceramic melter. While throughputs were not so high, the operation of the single-step process was successful so that a scaled-up version is now being demonstrated. To empty the molten glass from the ceramic melter, the latter is tilted slightly to pour the glass into the storage container When the container is full, the melter is tilted back to terminate draining. (See Figure 3).

Similar ceramic melters are also being developed at Karlsruhe in the Federal Republic of Germany and in the Soviet Union. In the Karlsruhe unit, the waste solution/frit mixture is sprayed onto molten glass Emptying is through an outlet in the lower side of the unit which is normally plugged by an electrode, and which for discharge purposes is heated and partly removed. The Russian unit is fed directly with liquid (not sprayed), and is one of the few processes that produces a phospate glass instead of a borosilicate glass.

Two other processes are being developed in the Federal Republic of Germany Gelsenberg, A.G., in collaboration with the Eurochemic Company, is developing the PAMELA process in which the waste solution is first concentrated and denitrated, then vitrified. The melt is converted to glass granules or beads which are then incorporated in a metal matrix. This process has a number of important differences compared with those described so far. The granule production is a continuous process in which sampling and quality control of the product can be easily carried out The final metal matrix product has a much higher thermal conductivity so larger blocks can be produced, and at the same time the temperature of the product in storage can be lower.

The FIPS process, being developed at Julich in the Federal Republic of Germany, is a two-stage process in which the waste solution with glass frit is dried on a drum drier and the material is scraped off and falls into a melter container.

Group Four Processes

A number of other processes are in the early stage of development, some of which are very similar to those already described. Only those in which there is a significant difference will be mentioned.

The LOTES process is being studied at Eurochemic for wastes with high aluminium content. These are converted to a granular aluminium phospate ceramic in a stirred bed reactor at 550°C and then incorporated in a metal matrix at 350°C, thus avoiding the high temperatures of the vitrification processes

Workers at the Sandia Laboratory in the USA, and in Japan and Sweden are developing processes based on the adsorption of the waste on inorganic ion-exchange materials which are then sintered.

In the USA, the technology of coated particle fuels is being adapted to produce impervious coatings on particles of calcined waste, such as those produced in a fluid bed calciner. The coated particles can then be incorporated in a metal matrix

Off-gas Treatment Systems

Most of the solidification processes involve evaporation and denitration In addition to steam and oxides of nitrogen, the off-gases usually contain some carryover of fine particulates and volatile radionuclides The treatment system must trap all radioactive carryover and ensure that any discharge to atmosphere is within acceptable limits

In general, the off-gases from the solidification unit pass either through a filter first or directly to a condenser or wet scrubber. The condensate or scrub liquor is fed to an evaporator-fractionator The concentrate from the evaporator is recycled to the feed to the solidification unit and the vapours from the evaporator are scrubbed so that the water and

nitric acid distilled off can be reused The off-gases from the fractionator are further scrubbed and pass through a final filter before discharge. In some cases, a special ruthenium filter is used.

The off-gas system on the Idaho waste calciner facility is rather more complex as the throughput is up to 100 times higher, mainly due to the large volume of fluidising air used. A unique system was used on the FINGAL plant where the off-gases were passed through high efficiency filter-adsorbers before condensation and high decontamination factors were achieved by dry filtration.

Current Status and Future Prospects

A waste solidification process has to operate with very high levels of radioactivity and involves high temperatures This combination is one of the most difficult to be met in the management of nuclear wastes. While much experience has been gained in handling the radioactivity levels in the fuel dissolution, reprocessing, high-level waste evaporation and tank storage, the added combination of handling radioactivity at high temperatures imposes severe demands on the plant design and on the skill of the operators.

During the past fifteen years experience has been gained from the operation of a number of pilot scale facilities – PIVER, FINGAL, WSEP – and also the Idaho WCF, and over 100 megacuries of radioactivity have been successfully incorporated into a solid product. An industrial scale plant has just commenced operation in France (AVM) and a number of others are under construction to handle the wastes from commercial reprocessing facilities.

In parallel with the process development, much work has been done to develop and evaluate the long-term properties of the solidified products. After the early work on calcination, most of the effort was devoted to glasses and ceramics, both borosilicate and phosphate. During the later 1960's, the experimental studies began to show clearly that better long-term stability could be obtained with borosilicate glasses and ceramics for most of the waste compositions likely to be of interest in the future A detailed analysis of the properties of the many candidate products being evaluated will be published in the IAEA Technical Reports Series, under the title "Characteristics of Solidified High-Level Waste Products".

Taken together, this new technical report and Technical Report No. 176 indicate that adequate technology exists for the design and construction of a solidification facility for high-level radioactive waste and that the product should be suitable for long-term storage and disposal

However, it is clear that further improvements will arise from the current research and development programmes in many countries. These programmes include improvements to the process technology, the standardisation of product criteria and economic aspects. Increasing confidence will be gained in the ability of the various products to withstand the long-term effects due to radiation, heat and the repository environment.

For the future, more information will become available as a result of this research and development effort Other processes, systems and product types will reach maturity during the next ten years, thus increasing the confidence that all the high-level wastes arising in the future can be solidified in an appropriate way, which is an essential step in their long-term management.