THE SAVANNAH RIVER SITE SALT PROCESSING FACILITY: 
AN INDUSTRIAL PERSPECTIVE

Rémi Bera, Marie-Françoise Debreuille 
COGEMA, 1 rue des Hérons Montigny le Bretonneux, 78182 Saint-Quentin en Yvelines, France

Serge Runge 
COGEMA INC., 7401 Wisconsin Avenue, Bethesda, MD 20814, USA

Jean-Paul Moulin, Nathalie Hubert 
SGN, 1 rue des Hérons Montigny le Bretonneux, 78182 Saint-Quentin en Yvelines, France

ABSTRACT

The choice of the chemical processes to be used for the treatment of US defense waste is a clearly identified issue. The selected processes will have to be implemented in a highly radioactive environment, which requires compliance with associated reliability, safety and environmental constraints. Proven process technologies used in the nuclear industry are helpful for the implementation of these chemical processes. The paper presents French extensive experience in the implementation, industrial development and successful application of precipitation, solid-liquid handling, vitrification and solvent extraction technologies, as well as in process integration and layout.

INTRODUCTION

The Defense High Level Waste supernates of the Savannah River Site (SRS) tank farms mainly contain cesium and transuranic waste (TRU) in solution with large quantities of sodium and aluminum. The purpose of the Salt Processing facility is to treat this waste in order to concentrate the radionuclides that will be vitrified, while separating them from the inactive salts (sodium and aluminum) to maintain the volume of highly active glass produced within reasonable limits and ensure high leaching performance for the final residue. Keeping the large quantities of aluminum in solution requires maintaining a very high pH in the supernates.

The separation of cesium is by far the most difficult. It is indeed very challenging because the few chemical processes with an industrial background for the separation of cesium are ineffective in highly alkaline media. The treatment of these supernates therefore requires either a new chemical process or an in-depth modification of an existing one. In addition, the new process had to comply with the vitrification process requirements, such as limits on the amount of certain metals like sodium and aluminum, but also titanium (an important component of the best inorganic ion exchange materials for cesium separation) to be routed to the highly active glass.

The ITP process, which is based on precipitation of the insoluble tetraphenylborate of cesium, had been introduced, but had to be discontinued due to the unexpected high degradation rate of cesium tetraphenylborate and the generation of large quantities of benzene, which is a problem for process safety and chemical releases.
DOE has identified alternative chemical processes to separate the cesium: Small Tank tetraphenylborate precipitation, ion exchange by a new inorganic exchanger (Crystalline SilicoTitanate or CST), caustic side solvent extraction using a new calixarene as extractant, and direct grouting. The chemical process has not yet been selected.

**IMPLEMENTATION OF THESE PROCESSES USING ADEQUATE TECHNOLOGIES: A POSSIBLE BOTTLENECK**

Whatever the chemical process ultimately selected, it will require technologies to be used in a plant submitted to the stringent constraints of the nuclear industry. These technologies have to perform unit operations relevant to the selected chemical process and also have to be efficient, highly reliable and enable maintenance, even though most of the plant will be remotely operated due to the high radioactive content of the waste stream to be processed. They must also comply with safety standards.

As a consequence, the choice of a chemical process is only half the battle. The importance of the selection of process technologies and their implementation should not be underestimated.

In the nuclear industry, it is common knowledge that the reliability, maintainability and a large portion of the safety of a process depend on the technologies used. Reliability, together with maintenance, determine the availability of the process. This parameter is virtually impossible to assess without experience. Proven technologies are therefore invaluable if long and costly developments, including component and full-scale equipment tests, are to be avoided. Some examples of proven technologies developed in France and applied by COGEMA and industrial experience in process integration are discussed below. The objective is to show how they can be used to implement certain chemical processes proposed for SRS and possibly other US defense waste processing.

**RADIOACTIVE SOLID HANDLING AND SOLID-LIQUID SEPARATION TECHNOLOGIES**

*Of great importance are the technologies for operations where solids, particularly highly radioactive solids, are handled in the presence of liquid for dissolution, precipitation, separation or even storage of dispersed solids. These solids can be already part of the liquor to be treated or have been produced to decontaminate the solution either by precipitation of a radionuclide or by adsorption on EIX material. This addresses both possible Hanford pretreatment and SRS supernates treatment, especially the cesium precipitation by sodium tetraphenylborate (TPB) (13).*

**Plutonium Conversion By Oxalic Precipitation, Filtration And Calcination**

An example of such process technology is the plutonium conversion performed by continuous precipitation, filtration and calcination of plutonium oxalate (Figure 1). This process has been reviewed recently (6), (7).

The solution of plutonium (typically 30 to 100 g/l) is adjusted to the tetravalent state and fed continuously, together with the oxalic acid solution, into a vortex-type stirred vessel, the
precipitator, where plutonium oxalate is formed. The pulp is recovered by overflow and fed into a continuous rotary drum filter (with internal feed). The precipitate is separated from the mother liquors, washed and dewatered. The suspension then falls into a screw calciner for drying and calcination before sending the oxide to the conditioning step. The process equipment is housed in glove boxes and is geometrically safe for criticality.

The continuous oxalate process was selected at the beginning of commercial reprocessing. First used in the fifties at the UP1 plant, this process has been operational at La Hague since 1966. The MAPu facility of UP2 was revamped in the early eighties, while the T4 facility of UP3 was started in 1989. The current throughput of both facilities is 48 kg Pu/d. The R4 facility will enter service in 2001 with the same throughput, but with the capability to double it.

Fig. 1. Plutonium conversion by the continuous oxalate process

Since the objective of plutonium separation is to recycle plutonium for MOX fuel fabrication, this process offers unique advantages: it is continuous and yields a constant-quality PuO$_2$ product in terms of homogeneity, specific area, particle size, sinterability and moisture content. MOX fuel can therefore be manufactured with a well-characterized material.

The build-up of americium increases the irradiation level of the plutonium recovered from PWR and BWR spent fuel. In actual plants, even though the equipment is housed in glove boxes, the process is remotely operated under normal conditions and maintenance is performed only after the plutonium has been flushed out. For the R4 facility, a large part of the maintenance will be performed remotely, since equipment requiring maintenance is located outside active areas so most of it can be performed without flushing out the plutonium. Compared with previous facilities, availability will therefore increase.
The safety records of these facilities are excellent. For example, the spreading of radioactive materials is prevented by a double containment system, with a cascade of pressure differentials ensuring dynamic containment; the radioactive doses to workers have decreased to very low levels, since remote handling became routine for normal operation; fire risks are prevented by control of ignition sources, adequate management of combustible materials and physical separation of areas where there is a risk of fire from the rest of the facility.

This process was selected for the COGEMA plants at La Hague and for a plant in Mol, Belgium, which is now shut down. Since some surplus US and Russian weapons-grade plutonium is to be used in MOX fuel, this process has been selected for the proposed Plutonium Finishing Plant of the projected facilities.

The continuous precipitation and filtration of plutonium oxalate benefit from decades of fine tuning. They ensure reliable high throughput of a high-quality product with small remotely-operated equipment. Any waste processing where a precipitation step is projected can benefit from this technology, which is easy to extrapolate since criticality imposes stringent size constraints on the oxalate process that would not be met with any substance other than plutonium or enriched uranium.

*Due to the high level of radioactivity of both SRS and Hanford supernates, they require fully remote-operated technologies. At La Hague plants, the continuous dissolvers and their satellite equipment dissolve nuclear fuels, but also efficiently separate and classify highly radioactive solids, route them to and from storage facilities with leak-tight containment and fully remote operation and maintenance.*
The T1 and R1 facilities of the La Hague plants and solids handling

These facilities and their operation over the last ten years have been described in detail (8), (9), (10). The main purpose of the facilities (Figure 2) is to:

- receive spent fuel, shear it, dissolve the oxide and deliver a clarified liquor to the chemical separation facilities,
- release treated dissolution off-gases to the atmosphere,
- rinse then transfer to the interim solid waste storage, the hulls and end fittings before compaction for final disposal,
- transfer the shearing and dissolution fines to interim tanks and then to the vitrification facility.

In the R1 facility, there is only one set of equipment, while in T1, the process equipment is redundant up to the clarification step. The JNFL plant in Rokkasho has the same head-end facility as T1.

The technology of the dissolver, and of the downstream equipment, can provide some insight on the handling of mixtures of highly radioactive solution (typically around 100 Ci/l) and highly radioactive coarse (hulls) and fine (dissolution and shearing fines) particles (typically around 100 Ci/kg).
The dissolver (Figure 3) sequentially receives the sheared fuel, a mixture of uranium oxide, hulls and shearing fines in a bucket of the wheel, and nitric acid. As the oxide is dissolved, the dissolution liquor overflows from the dissolver through a stilling device. The dissolution gases collected in the plenum of the dissolver are extracted through the gas treatment system (particle and liquid vesicle scrubbing, nitrous fumes recombining and iodine trapping). According to the selected feed rate, the wheel is rotated and sheared fuel is again routed to the next bucket, now in the lowest position. At the top of the wheel, after a half revolution, the loaded buckets discharge the empty hulls to the hull rinser.

The dissolver is equipped with an air-lift which recirculates any hulls (or parts of hulls) that have fallen from bucket to bucket near the discharge position to prevent the build-up of solids in the dissolver.

The dissolver does not discharge dissolution off-gases in its cells, thanks to the hydraulic seals that isolate the cover of the dissolver (as well as the cover of the hull rinser). However, there is no conflict between leaktightness and maintenance operations. If the wheel requires an inspection or maintenance, the dissolution operations are stopped and the dissolver is rinsed, then emptied through a siphon. The cover of the dissolver and the wheel are lifted (Figure 3) and, if necessary,
the rollers (and even the wheel) can be replaced. The dissolver tank, which is made of corrosion-free zirconium material, is not likely to ever be removed, although the operation is possible.

The hull rinser receives the hulls in its lower section and the hulls are lifted to the discharge chute with a reciprocating helical transfer device. A countercurrent water stream washes the hulls.

The dissolution liquors are routed to a pendulum-type centrifuge (DPC-900) operated semi-continuously. The liquors are fed into the centrifuge through a metering device and the fines are separated as the clarified stream overflows from the centrifuge. As soon as a given amount of solution is clarified (corresponding roughly to 4 metric tons of fuel), the feed is stopped, the cake is rinsed (first with nitric acid, then with water) and, ultimately, the fines are transferred through a siphon to the fines storage tank. Provision is made for maintenance of the centrifuge, including complete change-out, which has been performed once in the UP2-400 plant.

The fines storage tank is equipped with coolers and is agitated with an air-fed pulsing device. Ruthenium 106-rich fines in concentrations of about 20 to nearly 100 g/l are stored safely, without settling and aggregation, before transfer to the vitrification plant. As for fission product storage tanks, safety management of such tanks includes redundancy of the cooling system and dilution of the hydrogen produced by radiolysis using an air stream.

These techniques are routinely used to handle highly active solids. They can be applied to the safe handling of any highly active solids, e.g. precipitates of cesium tetraphenylborate or cesium-laden particles of ion exchange materials such as CST.

French vitrification facilities provide another example of fully remote operation and maintenance involving management of high-level waste, including liquids and solids. It is of particular interest for SRS proposed processes by TPB precipitation and ion exchange that both highly active flows can be handled and mixed continuously while keeping the proportion of the final mixture (including a suspension of solids) within stringent limits to ensure the composition and quality of the glass.

The T7 and R7 facilities of The La Hague plants

After the AVM vitrification plant started in 1978 at COGEMA’s Marcoule site, the R7 and T7 vitrification plants at La Hague started operation more than ten years ago and hold the world record for the quantities of vitrified radioactive waste. Information about their design and production records (more than 4,500 metric tons of glass) have been widely published (10), (11).

It is significant that these vitrification plants treat not only fission product concentrates in an acid medium, but also the shearing and dissolution fines separated from dissolution liquors in the T1 and R1 facilities. The fines are pumped from their storage tank and added to the feed system by metering devices to produce a glass whose composition complies with specifications.

The maintenance of the vitrification plants is also relevant for US defense waste management. More than ten years of operation have shown that remote maintenance of the plants is feasible, thanks to the small size of their components and their design. Crucibles have been removed and
replaced, although the average service life of a crucible is now well over 5,000 hours, thanks to improvements in materials and other factors.

*SRS supernates decontamination by solvent extraction has been proposed. This chemical process is very innovative and its implementation for industrial use at such short notice is very challenging. Nevertheless, the solvent extraction technologies are on the contrary fully proven and have been steadily improved up to now for La Hague plants. If the caustic side solvent extraction is selected for SRS supernates treatment, these technologies can guarantee its success.*

**SOLVENT EXTRACTION TECHNOLOGIES**

Solvent extraction technologies have been applied in the nuclear industry since the fifties. The basic principles of mixer-settlers, pulsed columns and centrifugal contactors have now been in use for more than half a century. In the nineties, however, COGEMA implemented new technologies in this field, which proved very useful. The development and operation of annular pulsed columns, for example, has been already described (1).

We will focus only on the reasons why such technology was selected, and the actual results. Criticality safety can be ensured by limiting the mass or concentration of fissile matter or by containing the fissile matter in a “safe” geometry. For the first U-Pu extraction cycle in a reprocessing plant, the risk concerns plutonium. Since industrial-scale mass limitation is impractical, either concentration limitation monitoring or an annular column can address the problem. For UP3, since curium neutron emission makes a plutonium build-up difficult to detect at the extraction and scrubbing steps, pulsed annular columns were selected for these steps, while mixer-settlers were adopted for the U-Pu partition step because curium is mostly removed in the previous steps.

Nevertheless, a further development for UP2-800 introduced pulsed annular columns for the partition step, providing the possibility to process fuels with a high Pu/U ratio. This was made feasible thanks to the fine tuning of the distribution of concentrated tetravalent uranium in an annular geometry (2). The use of annular geometry was not the only innovative improvement introduced for extraction technology. Disk-crown packing was introduced to perpetuate the performance of both the annular columns in the first decontamination cycle and the cylindrical columns for plutonium purification (1). A distillation system was introduced to further increase the separation performance and enhance solvent regeneration (3). After 10 years of operation, the validity of these innovations is evident (4), (5). The decontamination of uranium and plutonium has reached a level close to the theoretical limit; it plays a major role in the drastic reduction of long-lived waste volume, which has been made possible particularly thanks to the excellent performance of the extraction process. The technology selected is insensitive to aging and to the presence of interfacial cruds: it requires little maintenance. As a consequence, only preventive, “out-of-cell” maintenance is necessary.

The process performance data are listed in Table 1 taken from (5).

COGEMA has steadily improved the extraction facilities in its plants. The next facility to be started, R4, will benefit from a variety of innovative features, ranging from the use of a centrifugal contactor to a new design for geometrically safe buffer tanks (6). Specific
developments including microextractor tests have been made to industrialize the centrifugal contactors technology and to control its operating parameters (including temperature).

Whatever the chemical process and the nature of the solvent involved for commercial operation, these technologies will provide significant advantages in terms of performance, maintenance and safety. They will also shorten the development time required.

### Table I. UP3 process performance data

<table>
<thead>
<tr>
<th>Process Unit</th>
<th>Process Item</th>
<th>Actual Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st purification and separation cycle</td>
<td>DF* for fission products</td>
<td>Ruthenium $&gt; 2 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>U-Pu separation</td>
<td>Cesium $&gt; 10^7$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$&lt; 10 \mu g Pu/kg U$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i.e. DF* $&gt; 10^6$</td>
</tr>
<tr>
<td>Uranium cycle</td>
<td>DF* for neptunium</td>
<td>Over 1,000</td>
</tr>
<tr>
<td>Total extraction process DF*</td>
<td>$\beta\gamma$ activity in plutonium</td>
<td>$&lt; 1 \mu Ci/g Pu$</td>
</tr>
<tr>
<td></td>
<td>$\beta\gamma$ activity in uranium</td>
<td>$&lt; 1 \mu Ci/kg U$</td>
</tr>
<tr>
<td></td>
<td>U and Pu recovery ratio</td>
<td>over 99.88%</td>
</tr>
</tbody>
</table>

DF = Decontamination Factor

**INDUSTRIAL PROCESS INTEGRATION EXPERIENCE**

The UP3 design bases were defined at the start of the project to achieve high throughputs and performance goals, while complying with safety standards. They were published long ago (12) and the 10 years of active operation of the modern La Hague plants demonstrate their outstanding validity, as well as a unique experience in implementing them. The lessons learned through this experience are reviewed below.

The separation of functions enables segmentation of process unit operation between separate cells containing equipment with the same activity level in a building (Figure 4), with additional benefits for safety demonstration, in particular for fire hazards and containment of radioactive materials. This is of particular interest for SRS management, especially if the selected process for cesium decontamination is TPB precipitation. The provisions in the original design have also enabled implementation of significant modifications with low personnel dose rates within a short timespan (10).

Most process cells (typically chemical process cells) are maintenance-free, except some specific transfer devices whose wear-prone parts are removed with a special Mobile Equipment Replacement Cask (MERC) without manipulators to maintain containment integrity during removal. Special mechanical equipment is installed in cells specially equipped with manipulators, viewing windows, lining and other features. These arrangements enhance the containment of radioactive materials and facilitate maintenance operations.

This experience in process integration is a powerful tool for decreasing the capital cost of a complex plant: optimal segmentation of the various facilities can be achieved by limiting remote handling facilities for processes where irradiating materials are handled and performing the
separation of non irradiating materials in contact handling facilities. This is particularly true for the Hanford waste management whatever the process technology to be selected.

![Diagram of COGEMA facility](image)

Fig. 4. Typical layout of a COGEMA highly active facility (from [10])

CONCLUSION

COGEMA has more than 40 years of uninterrupted experience in the operation and maintenance of its own process technologies. At the La Hague site, an entirely new plant (UP3) was built at the end of the eighties for spent fuel recycling and has been in service for more than 10 years. A few years later, the UP2 plant was revamped and upgraded to UP3 standards. Both plants are operating smoothly and total production has exceeded 16,000 metric tons, a world record for LWR fuel reprocessing, while radioactive releases to the sea have been reduced dramatically to less than 10% of the 1985 value and the volume of high-level waste produced per ton of reprocessed fuel (including secondary waste) has decreased by a factor of more than 3. The high-level waste on the La Hague site has been vitrified since 1989. Today, the backlog of LWR fuel waste has been processed and the newly generated high-level waste is now processed in line, representing a world record for the quantities of vitrified radioactive waste.

We believe that this industrial experience with highly active plant design and operation can greatly benefit the selection and implementation of a process to treat the SRS supernates and other US defense waste.

REFERENCES


