THE FIRST STEP IN THE FINAL SHUTDOWN OF THE UP1 PLANT: RINSING WITH CHEMICAL REAGENTS

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ABSTRACT

The COGEMA UP1 reprocessing plant commissioned at Marcoule, France in 1958 handled roughly 20,000 metric tons of fuel from gas-cooled and research reactors. The commercial reprocessing activities of the UP1 plant ended in December 1997.

CODEM , a joint venture created by the former users of the UP1 plant, including the utility Electricité de France (EDF), the French Atomic Energy Commission (CEA) and COGEMA, was established to fund and supervise decommissioning of the plant. COGEMA was selected as the industrial operator of the decommissioning project, which is scheduled to span a period of about 40 years.

COGEMA, with its CODEM partners, had made the decision to proceed to a "Final Shutdown" of the plant within a few years after the end of commercial operation. Final shutdown is intended to remove remaining fissile matter and highly radioactive materials, as well as some equipment, from the plant to ease the plant monitoring requirements compared with those applied when the plant was in operation.

A two-step approach has been devised, including first the rinsing of the equipment with selected reagents in order to decrease the radiation exposure rate and contamination risk enough to allow further mechanical decontamination operations, such as high-pressure water scrubbing and equipment cutting.

The reagents to be used and the methods employed to optimize their use in terms of quantities and sequence of use were selected by leveraging available experience, and by setting up a large-scale R&D program to test reagents both for general decontamination and for hot spots. This program also included treatment of the decontamination waste to demonstrate that this waste could be made compatible with solidification facilities of the UP1 plant, i. e., vitrification in the AVM facility and bituminization.

The R&D results are described, as well as the initial results of plant decontamination.

INTRODUCTION

The French Atomic Energy Commission (CEA) selected Marcoule, located near the Rhône river in south-eastern France in 1952 to become the first industrial nuclear site. As a consequence, the first French reprocessing plant, UP1, was built in Marcoule. Following commissioning in 1958, it was initially used to produce fissile materials for the national defense program.

In 1976, a major change occurred: the CEA's industrial operations, including at UP1, were transferred to COGEMA and commercial activities were initiated in the UP1 plant. The plant began reprocessing fuel from the natural uranium, graphite moderated, gas-cooled reactors (GCRs).

In the following years, UP1 was supplemented by new facilities: the *Atelier de Vitrification de Marcoule* (AVM), the first industrial vitrification plant in 1978, a new decladding facility for GCR fuels (MAR 400) in 1983 and a new liquid waste treatment facility (STEL) in 1985.

After shutdown of the last GCR power plants, production in the UP1 plant terminated at the end of 1997. UP1 has reprocessed 18,600 metric tons of spent fuel in 40 years of operation.

DECOMMISSIONING UP1: THE INDUSTRIAL ORGANIZATION

The former users of the plant— the utility Electricité de France (EDF), the CEA (on its own behalf and for the French Ministry of Defense) and other COGEMA clients, at government request, established a "client structure" known as CODEM. The purpose of CODEM is to handle overall management of the UP1decommissioning project, including final shutdown, onsite waste retrieval and repackaging, surveillance and dismantling.

CODEM is a joint venture set up on July 1, 1996 with the following partners: CEA, EDF and COGEMA [1]. In turn, CODEM has chosen COGEMA as the prime contractor and industrial operator of the decommissioning operations. COGEMA contracts the design and management task to a consortium including SGN, EDF and Technicatome.

The decommissioning project includes three main phases:

- Final shutdown. These operations involve remote rinsing of equipment with various reagents to reduce the radiation level and fissile material content, followed by contact cleaning. The organization of this step is therefore very similar to that of production. The main objective of this decontamination is to achieve radiological conditions low enough to promote the decrease of occupational exposure, the minimization of waste volume and therefore cost minimization, as quickly as possible.
- Retrieval and repackaging of onsite waste. The Highly Active Liquid Waste (HALW) is already conditioned as canisters of glass thanks to the successful operations of the AVM vitrification plant. The Intermediate- and Low-Level Liquid Waste (ILLW) has been solidified and conditioned in bitumen drums. The site also retains spent fuel structural waste, as well as technological and miscellaneous other waste. This waste has to be recovered, characterized, sorted and, in some cases, processed and/or repackaged and shipped either to an onsite interim storage facility or to a disposal site.

- Dismantling and surveillance of plant facilities. This step concerns the reprocessing plant and its ancillary facilities (in particular liquid waste treatment, solid waste conditioning, and interim storage). Its objectives are to decommission the facilities to AIEA stage 2 (ICPE status of French regulations), to eliminate the radiologically restricted access areas, and to set up suitable surveillance provisions.

SCOPE OF THE FINAL SHUTDOWN OPERATIONS

The objective of the final shutdown operations is to optimize the costs and feasibility of the future dismantling operations. The final shutdown operations are intended to remove remaining fissile matter and highly radioactive materials, as well as some equipment, from the plant in order to ease its monitoring requirements compared with those applied for an operating plant. The main objective is to achieve this status within a five-year period, first by rinsing the equipment with various chemicals until the radiation and contamination risks are low enough, and second by cutting and opening to perform further mechanical decontamination operations, such as high-pressure water scrubbing. The first step, the chemical rinsing, generates the largest amount of HA and IL liquid waste. As a consequence, its second objective is to minimize the solid waste produced by treating this liquid waste. The HA and IL liquid waste can be routed:

- Either to the AVM vitrification plant, after treatment and concentration by evaporation and incorporation into glass stored in canisters.
- Or to the liquid waste treatment facility (STEL), where it is processed by coprecipitation, converted into sludge that is incorporated into bitumen and stored in drums.

The glass produced by the AVM plant is ideal for HA Liquid Waste, but the amount of many chemicals, including sodium, is strictly limited in glass, leaving bitumen as the only other choice. Therefore, the minimization of bitumen production is based on the use of lessons learned from experience, R&D on vitrification-friendly reagents and careful arrangement of rinsing sequences.

Immediately after the end of reprocessing operations, the plant was "rinsed" by circulation of the reagents currently used for the reprocessing operations. Preparation for the final shutdown of UP1 also required establishing a policy for decontamination of the plant with quantitative objectives. In order to decontaminate the plant by rinsing the equipment with chemical reagents, a strategic plan was devised.

After "mapping" radiation levels in the plant, the objectives were to determine:

- Which reagents could be used, both for general decontamination and for eliminating the hot spots.
- Which criteria must be applied to select among potentially usable reagents, allowing for constraints related to compatibility with vitrification and other waste solidification routes and criticality risk minimization.
- Which reagent must be used first and which one had to be used at the end of the process, both to minimize the volume of waste incompatible with shallow land disposal and to prevent corrosive reagents from being used on poorly decontaminated equipment, in order to avoid spilling radioactive liquors due to leakage.

These objectives were achieved by:

- Leveraging available experience.
- Setting up a large-scale R&D program to test reagents both for general decontamination and for hot spots.
- Using the R&D results to devise a plan for employing the selected reagents optimally with regard to their quantities and sequence of use in order to minimize the volume of waste and the amount of releases.

The lessons learned comprise D&D already performed (or part of it) on facilities:

- Either belonging to COGEMA (one of the UP1 dissolvers has already been thoroughly cleaned, following removal and replacement with a new one [2]).
- Or belonging to the CEA, such as the D&D performed on the PIVER pilot vitrification plant [3].

In addition, experience gained through complete final shutdown of the Eurochemic reprocessing plant at the Mol site in Belgium was also applied [4].

R&D PERFORMED FOR UP1 FINAL SHUTDOWN

Objectives:

The R&D program included two main parts:

- The first was devoted to optimizing the quantities (volume, concentration, temperature, duration of application) of well-known reagents like caustic soda on samples of contaminated parts from the plant, and to testing alternative reagents less likely to increase the volume of glass produced. It included innovative features like testing of gels and foams containing various reagents to clean the upper parts of tanks without very large volumes of reagent.
- The second was devoted to decontaminating hot spots. It relied on an investigation of the chemical composition of the hot spots and the selection of reagents likely to attack them efficiently, as well as testing these reagents on inactive compounds.

This R&D also included treatment of the decontamination waste to demonstrate that this waste could be made compatible with solidification facilities of the UP1 plant, i. e., vitrification in the AVM facility and bituminization.

The experimental work included:

- Optimization of the first decontamination steps based on successive rinsing with "mild" reagents, nitric acid and caustic soda.
- Tests with corrosive reagents, fluoride ions and cerium IV for further decontamination.
- Tests with reagents that target insoluble deposits, organic acid and permanganate, and other substances.

After preliminary tests performed on specially made contaminated surfaces, most of the benchmark tests have been performed on stainless steel rods which were used as electric probes in the first codecontamination extraction cycle of UP1. The main radiological pollutant of these rods is ruthenium 106.

"Mild Reagents": Successive Nitric Acid and Soda Washing

The successive acid and alkaline rinsing operations have been optimized, with the results shown in Table I. The parameters to be optimized were the concentration of reagents, temperature and duration of the operation. The key parameter is the overall amount of caustic soda used for a given result.

The results indicate that the most efficient cycle is performed at 50°C. It consists of a succession of washings with nitric acid, caustic soda and then nitric acid again, with roughly equal concentration for these reagents (5 molar each). The optimum acid rinsing duration is one hour and the optimum alkaline duration is two hours.

Table I: Laboratory Test Results

Test + Reagents	T °C	Initial ^{106}Ru KBq/cm^2	Residual ^{106}Ru KBq/cm^2	Equivalent removed thickness* μm	Ru DF
MRS** = "Mild reagent" sequence	50	5990	600	0	10
MRS + [NaOH 1M+$KMnO_4$ 0.1M] + HNO_3 4 M	50	5640	3	0	1.88×10^3
MRS + [NaOH 1M+$KMnO_4$ 0.1M] + [HNO_3 2 M+Ce^{IV}0.05 M]	50	6280	0.2	7.5	3×10^4
MRS + [NaOH 1M+$KMnO_4$ 0.1M] + [HNO_3 2 M+HF 0.2 M]	50	5830	0.06	6	0.97×10^5
MRS + [HNO_3 2 M+HF 0.2 M]	50	7430	0.003	33	2.5×10^6
MRS + [HNO_3 2 M+Ce^{IV}0.05 M]	50	5990	0.007	22.2	8.5×10^5

* Thickness evaluated by the measured mass loss

** "Mild reagent" sequence (MRS) = 3 washings: HNO_3 5 M + NaOH 5.5 M+ HNO_3 5.5 M

"Corrosive Reagents" for Further Decontamination

The efficiency of hydrofluoric acid and cerium IV has been demonstrated. Optimal decontamination dictates recommending an erosion of 2 to 10 μm.

The corrosive properties of cerium IV are well known and it has already been used for decontamination purposes in nuclear power plants [5]. R&D mainly concerned the electrogeneration of cerium IV from solutions of cerium III and the destruction of the excess of cerium IV. Hydrogen peroxide readily reduced the cerium IV.

The tests with mixtures of nitric and hydrofluoric acids show that the nitric acid concentration must be kept below 4 mol/l to prevent passivation, and that it is highly recommended to use a concentration of hydrofluoric acid at least above 0.1 mol/l to avoid an unwanted induction delay for effective decontamination. After decontamination, the corrosive solution is neutralized by adding aluminum ions to complex the fluoride ions. It has been noted that the Ru DF obtained by nitric hydrofluoric acid mixtures is higher if performed after a "mild decontamination" operation than if the hydrofluoric rinsing is performed directly.

Reagents Targeting Insoluble Compounds

Even though nitric hydrofluoric acid mixtures offer good efficiency against ruthenium deposits, specific reagents have been tested for ruthenium. Potassium permanganate is efficient, as shown in Table 1.

Antimony is very poorly soluble in a nitric medium and antimony deposits were expected in the head-end of the plant. Various organic chelating acids were tested, and tartaric acid proved to be efficient for antimony dissolution and decontamination. Since the "standard" test rods were not significantly contaminated with antimony, parts of fuel baskets from the CEA's APM pilot plant were used to test the decontamination from actual material.

INITIAL RESULTS OF UP1 FINAL SHUTDOWN

Objectives: Radiological Status and Operational Dosimetry

The final shutdown objective was to meet the following criteria for at least more than 90% of the approximately 500 rooms and cells:

- Radiation exposure rate < 0.4 mSv/h.
- No hot spot above 10 mSv/h on contact with equipment.
- Atmospheric contamination below the detection limit.
- Labile surface contamination < 100 Bq/cm^2 for α emitters.
- Residual plutonium mass less than 10 g per equipment item.

These objectives were achieved for half of all the rooms and cells by the end of 1999.

The history of the amount of plutonium and $\beta\gamma$ emitters extracted from the plant is detailed below.

Prior to final shutdown of the plant, extensive rinsing was performed just by keeping it running, without introducing new spent fuel. Table II shows the results for HA facilities (chemical decladding, both continuous and batch dissolution and extraction cycles), and IL facilities (plutonium conversion and scrap recovery facilities).

Table II: Decontamination Performance of Preliminary Rinsing in HA and IL Facilities

	Extracted βγ Activity (TBq)	Solubilized plutonium (g)
HA Facilities	900	950
IL Facilities	-	3300

In 2001, the "mild reagents" rinsing was also finished. The results are shown in Table III.

Table III: Decontamination Performance of "Mild Reagents" Rinsing in HA and IL Facilities

	Extracted βγ Activity (TBq)	Solubilized plutonium (g)
HA Facilities	1200	2200
IL Facilities	-	900

The nature of the isotopes present in the waste has shifted from ruthenium in the beginning to antimony 125, which is known to be poorly soluble in nitric medium.

Current work is focusing on deposits found in the dissolvers, mainly zirconium and molybdenum, as well as some plutonium. These deposits have been tentatively identified as zirconium molybdate, a compound known to precipitate at its boiling point and which contains plutonium as a minor component [6]. Since there is not enough molybdenum in the fission products of spent GCR fuel, the molybdenum of the precipitate is likely to be the molybdenum of the U-Mo alloy used to manufacture certain fuels. These deposits are efficiently dissolved, either by using nitric hydrofluoric acid mixtures (dissolving zirconium, molybdenum and plutonium) or by successive rinsing using first caustic soda (dissolving molybdenum) and then nitric acid (dissolving zirconium and plutonium).

CONCLUSIONS

Final shutdown operations for the UP1 reprocessing plant were initiated in January 1998. The shutdown procedures were prepared by analyzing the experience acquired during plant operation or during previous decommissioning operations, and by assessing results of a development program to optimize the duration and efficiency of the operations, and to limit the occupational doses and waste production.

Progress in meeting the final shutdown objectives is well underway. The first step consisting of chemical rinsing using "mild reagents" has produced excellent decontamination performance. The current step is devoted to further decontamination of hot spots. When the hot spot and deposit treatments are finished, the decontamination will be completed by opening the equipment and cleaning with mechanical devices, including high-pressure water jets.

In mastering the final shutdown of a reprocessing plant, COGEMA will have demonstrated a new skill.

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