TREATMENT AND CONDITIONING OF THE HLLW STORED AT ENEA's REPROCESSING PILOT PLANTS

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ABSTRACT

At the ENEA reprocessing pilot plants some 115 m^3 of aged first cycle reprocessing aqueous waste are stored, produced during the reprocessing of MTR , CANDU and Elk River spent fuels. A preliminary chemical treatment to separate the high active fraction and the cementation of low active fraction is selected. The chemical processes, developed both on hot laboratory scale and on inactive pilot plant scale, are described.

The plant under design, to be realized at the EUREX site, will be suitable to implement the described processes, allowing the cementation of the low level fraction with a mobile unit.

A small size vitrification unit, based on the ceramic melter technology, is considerated for conditioning the high active sludge fraction.

INTRODUCTION

At the ENEA reprocessing pilot plants some 115 m^3 of aged HLLW are stored, coming from reprocessing MTR fuel (88 m^3), CANDU fuel (24 m^3) and Elk River fuel (3 m^3).

The main chemical and radiochemical characteristics of these wastes are shown in Table I.

Solidification of these HLLWs is planned in order to fulfill the specific requirements established by the Safety Authority, taking into account the criteria set up in a Technical Guide, issued in 1985 in the matter of radioactive waste disposal.

Vitrification was first considered and developed on inactive pilot scale in the late seventies, since future industrial needs were expected for HLLW treatment at that time (1).

More recently, an extensive R&D activity has been carried out on laboratory scale with real waste and in a cold pilot plant with simulated waste (2, 3, 4, 5, 6), in order to select a suitable technique for conditioning the waste, taking into account its peculiarity (small volume, low beta/gamma activity, significant content of alfa radionuclides, large content of inerts) and the Italian scenario (nuclear industry phasing-out). A chemical pre-treatment to separate the high active fraction and to allow the cementation of the low active fraction has been considered. This process has been envisaged in order to produce cemented drums acceptable for surface disposal. Besides a simplified vitrification unit is under consideration for conditioning of the high active fraction.

SELECTIVE SEPARATION PROCESSES

Processes of selective separation of the radionuclides have been developed for the HLLWs in order to achieve the separation of the waste into two fractions:

1. a small volume of sludge which contains most (99 %) of the radioactivity; this fraction can be vitrified by a small size vitrification plant;
2. a large volume of alkaline solution which contains almost all the inert salts; this fraction can be cemented for surface disposal.

The processes developed on hot laboratory scale and on inactive pilot plant scale are described below.

Separation Process For HLLW-MTR

The MTR waste was produced in the early 70s during a reprocessing campaign of Material Testing Reactor irradiated fuels at the EUREX plant (Saluggia, Italy). This waste contains a large amount of Al together with Fe, Hg, NO_3- and a small amount of other elements. At the present the radioactivity is mostly due to Cs-137, Sr-90 and Transuranium elements.

The selected process includes the following steps (7):

1. Alkalinization, carried out with a concentrated solution (10 M) of sodium hydroxide in order to allow:
   neutralization of the free acid;
   a final pH > 13 for the solubilization of Al as aluminate;
   removal of Sr and Actinides by coprecipitation with ferric hydroxide.
2. Cs removal by selective precipitation, using NaTPB (sodium-tetraphenyl-borate). This step is able to provide an high decontamination factor for cesium, thus allowing a full decontamination of the solution in a single batch precipitation.
3. Double step solid-liquid separation by decantation, the first one in the same precipitation reactor, the second one into a decanter, where is possible to accumulate the slurry of several batches to improve the thickening. In addition the supernatant from the reactor and from the decanter can be centrifugated in order to increase the separation of the solid particles; the experimental tests have shown this operation not so necessary indeed.

The main DFs achieved with this process are: Cs-DF > 1000, Sr-DF = 100, TRU-DF (transuranium elements) > 1000 .

From the experimental results a production of 3-4.5 m^3 of sludge is expected (depending by the thickening); the average expected composition is shown in Table II.

Figure 1 shows the envisaged process flow sheet for a batch of 0.5 m^3 of HLLW-MTR. It is planned to carry out campaigns of 20 daily batches of 0.5 m^3 of HLLW, followed by a slurry thickening stage.

TABLE I

Main Components of the ENEA's HLLWs

HLLW		MTR	CANDU	Elk River
density	(kg/m^3)	1200	1150	1100
H+	(M)	1.2	1.2	1.8
Fe	(kg/m^3)	0.49	0.46	2.1
Hg	(kg/m^3)	1.18	-	-
Al	(kg/m^3)	32	-	-
SO4=	(M)	0.015	0.01	-
NO3-	(M)	4.33	1.8	1.8
U	(kg/m^3)	5 E-3	90	0.01
Th	(kg/m^3)	-	-	0.8
Pu-241	(GBq/m^3)	15	570	0.03
Pu-alfa	(GBq/m^3)	6	23	-
Am-241	(GBq/m^3)	0.15	570	-
Cm-244	(GBq/m^3)	3.7 E-5	44	-
Sr-90	(GBq/m^3)	1.14 E+4	2.18 E+4	1.0 E+5
Cs-137	(GBq/m^3)	1.28 E+4	3.66 E+4	1.0 E+5
Total alfa	(GBq/m^3)	6.15	640	1.9
Total activity	(GBq/m^3)	4.8 E+4	1.2 E+5	4.0 E+5

TABLE II

Main Components of the HLLW-MTR Sludge

density	1200-1300	kg/m^3
Fe	10-15	kg/m^3
Al	10-12	kg/m^3
Na	60-70	kg/m^3
Hg	5-15	kg/m^3
SO4=	0.2-0.3	kg/m^3
NO3-	80-100	kg/m^3
-TPB	5-10	kg/m^3
Cs 137	200-350	TBq/m^3
Sr 90	200-300	TBq/m^3
Pu 241	300-450	GBq/m^3
Total alfa	100-200	GBq/m^3
Total Activity	800-1300	TBq/m^3

Separation Process for HLW-CANDU

The HLLW-CANDU was produced in the early 80s during a reprocessing campaign of CANDU spent fuel at the EUREX plant. Since with the applied extraction process the depleted uranium was separated in the first cycle raffinate along with the fission product, this waste contains a large amount of Uranium (90 kg/m^3).

In this case the process also achieves the coprecipitation of Sr and transuranium elements with ferric hydroxide and Cs precipitation as CsTPB, but the alkaline agent is Sodium Carbonate, which allows to mantain U in solution as complex. Laboratory tests have in fact shown that coprecipitation of uranium would make the slurry quite bulky and not easily

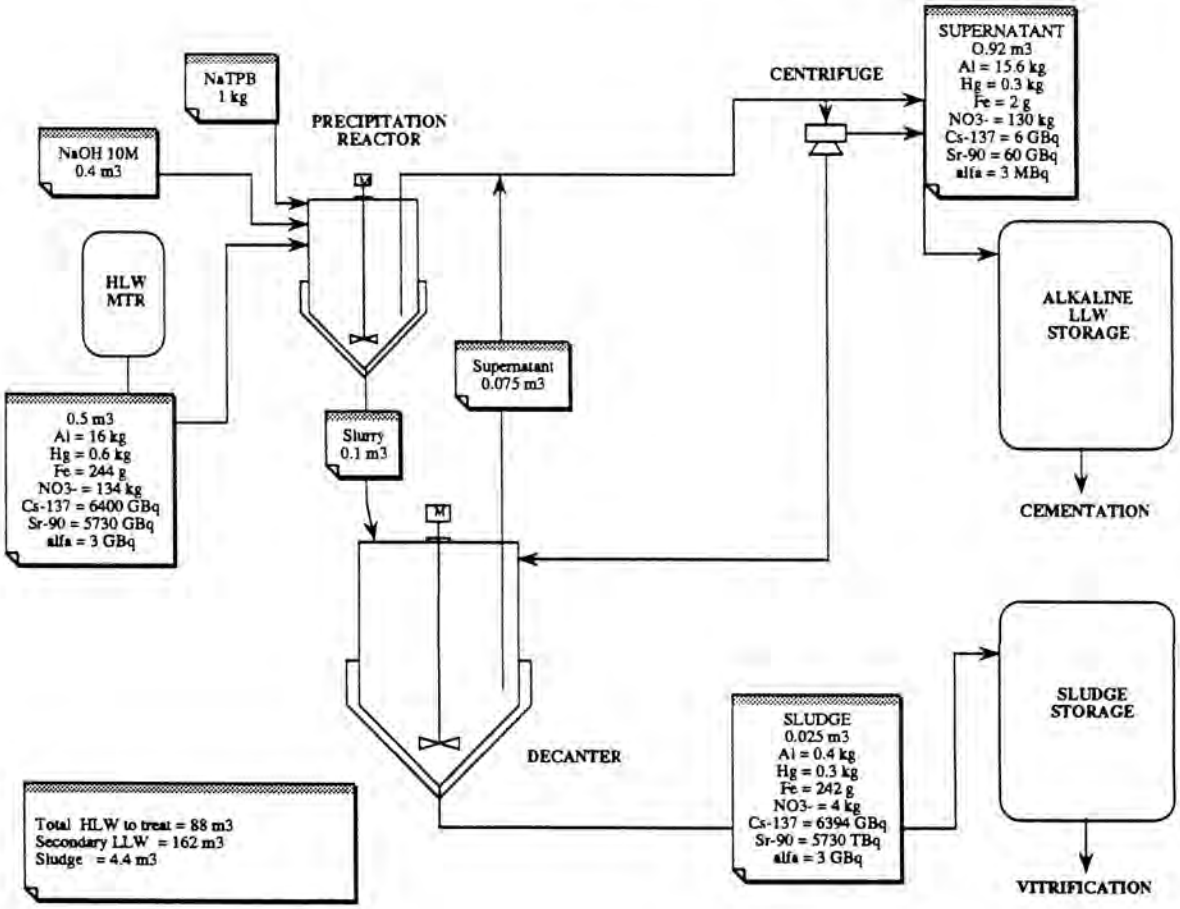

Fig. 1. Process flow-sheet for treatment of HLW-MTR.

thickened and removed. Besides, in order to achieve a satisfactory DF for Pu, Am-241 and Cm-244, the precipitation has to be carried out in two steps, varying the pH conditions; for each step the solid-liquid separation procedure is the same as for MTR process.

The main DFs achievable with this process are: Cs-DF- > 1000; Sr-DF = 5-10 ; TRU-DF = 500-1000.

A production of 1.5-2.4 m^3 of sludge (depending from the achievable thickening) is estimated with the average composition indicated in Table III.

The process flow sheet is shown in Figure 2 for a batch of 0.2 m^3 of HLLW-CANDU, referred to the worst results for thickening. It is planned to carry out campaigns of 20 daily batches of 0.2 m^3 of HLLW, followed by the thickening stage of the accumulated slurry.

Separation Process For HLLW-Elk River

This waste was produced in late seventies by the ITREC plant located at Trisaia (Southern Italy) during a reprocessing campaign of twenty U-Th spent fuel elements coming from the U.S. reactor Elk River. Due to the small amount (3 m^3) this solution will be transported to the EUREX site and mixed with the HLLW-MTR before the chemical treatment. That will not significantly change the HLLW-MTR composition and the chemical treatment parameters.

TABLE III

Main components of the HLLW-CANDU Sludge

density	1200-1300	kg/m^3
Fe	20-30	kg/m^3
Na	20-30	kg/m^3
U	15-20	kg/m^3
SO4=	0.2-0.3	kg/m^3
NO3-	30-50	kg/m^3
-TPB	10-20	kg/m^3
Cs 137	400-700	TBq/m^3
Sr 90	200-300	TBq/m^3
Pu-241	6-9	TBq/m^3
Total alfa	7-11	TBq/m^3

CEMENTATION OF THE LOW ACTIVE FRACTION

After solid-liquid separation the supernatant from HLLW-MTR treatment, containing almost all the aluminium and nitrates, and the supernatant from HLLW-CANDU treatment, containing the U and nitrates, can be cemented, while the sludge may be conditioned by vitrification.

The selected cementation process is the in-drum mixing type. The 400 liters drum, containing pre-weighed dry cement fed by a screw feeder, is moved to the cementation station on a roller way. After chemical adjustment the low-active fraction is transferred batchwise by pump to the mixing station and fed

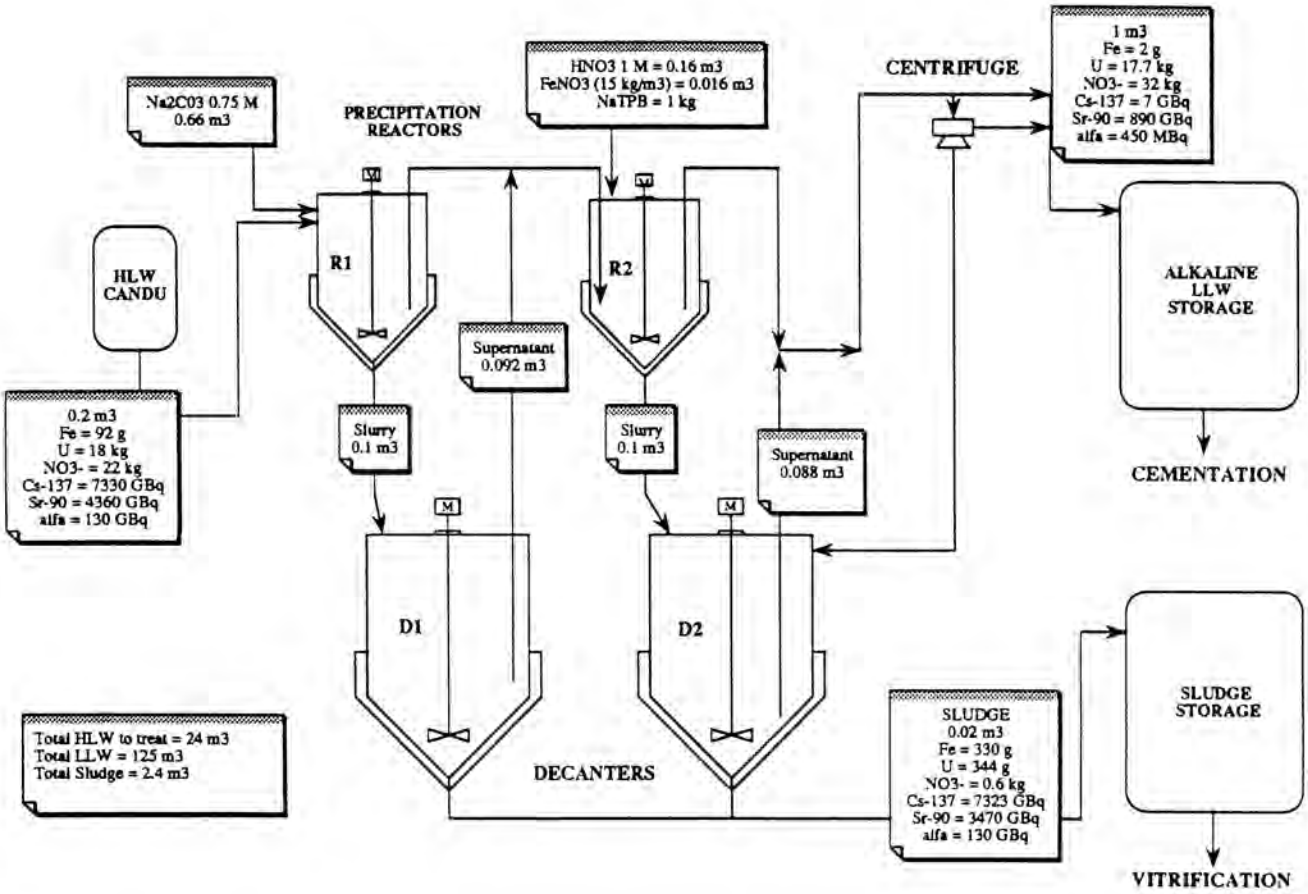

Fig. 2. Process flow-sheet for treatment of HLW-CANDU.

into the drum along with possible additives. After mixing process, carried out by a lost-blade stirrer, the drum is parked on a roller way to allow the matrix setting and a first hardening. To complete the conditioning process, the drum is capped with inactive grout, provided that the cement matrix is under specification. Following one day setting time, the package is weighed, monitored for contamination and dose rate and sent to the on-site interim storage.

The cementation of the about 160 m^3 low level alkaline waste coming from the treatment of the HLLW-MTR should produce more or less 340 m^3 of cement.

The cementation of the about 125 m^3 low level alkaline waste coming from the treatment of the HLW-CANDU should produce more or less 240 m^3 of cement.

VITRIFICATION OF THE HIGH ACTIVE FRACTION

The vitrification process is still under feasibility study. Due to the limited quantity of high active sludge to vitrify, a very small unit, based on the ceramic melter technology, is under consideration. The preliminary estimation for design and construction of the vitrification section has been completed.

According to the presented data, the amount of the high-level waste slurry to be vitrified is:

- from HLLW-MTR: 4.5 m^3 maximum
- from HLLW-CANDU: 2.4 m^3 maximum

A direct feeding of the slurry to the ceramic melter is considered.

Vitrification of the Slurry from HLLW-MTR

The major constituents of the HLLW-MTR waste residue as oxides are Fe_2O_3, Al_2O_3, Na_2O.

Based on a 10 wt% loading of the waste glass with waste calcines, a slurry feed rate of 4 l/h is assumed to keep the melter dimension as small as possible. The selected process data of the vitrification are the following

- Slurry feed rate to melter 4 l/h
- Glass production rate 6 kg/h
- Glass frit rate to melter 5.4 kg/h
- Specific radioactivity of the glass 380 GBq/kg (Cs/Sr, average)
- Time for production of 1 canister 67 hours (400 kg glass capacity of the can)
- Total amount of glass 6750 kg (max)
- Number of canisters (400 kg) 17

Vitrification of the Slurry from HLLW-CANDU

The major constituents of the HLLW-CANDU waste residue as oxides are Fe_2O_3, Na_2O and some Uranium oxide. The radioactivity of the slurry is higher than the HLLW-MTR slurry, while the expected solid oxide residues is about half.

Based on a 10 wt% waste glass loading, the selected process data design are as follow:

- Slurry feed rate to melter 4 l/h
- Glass production rate 3.13 kg/h
- Glass frit rate to melter 2.82 kg/h
- Specific radioactivity of the glass 1500 GBq/kg (Cs/Sr, average)
- Time for production of 1 canister 127 hours (400 kg glass capacity of the can)
- Total amount of glass 1880 kg (max)
- Number of canisters (400 kg) 5

PLANT DESCRIPTION

The plant to be realized at the EUREX site is presently at the preliminary design stage. The facility will include the following units:

1. Chemical treatment unit;
2. Cementation unit;
3. Vitrification unit.

Chemical Treatment Unit

This unit includes:

- a feed tank for HLLW batch storage (V = 1 m^3);
- two reactor tanks for precipitation (V = 1 m^3);
- two decanters for sludge thickening (V = 2 m^3);
- a centrifuge;
- a low level alkaline effluent storage tank (V = 6 m^3);
- a high active sludge storage tank (V = n.a.).

The unit will operate on a weekly basis, producing a batch suitable for a weekly operation of the cementation unit.

Cementation Unit

The cementation unit, which will also treat the LLW presently stored at the EUREX site (150 m^3), includes

- a feed tank for storing a weekly batch of supernatant;
- a cementation unit based on the MOWA technology;
- transfer and curing systems for cemented packages;
- station for quality control, grout sealing, and final measurements on cemented packages;
- cemented packages interim storage.

The expected throughput of the cementation section is 25 cemented packages (400 liter drums) a week (about 6 m^3 of treated liquid waste). The produced packages will be suitable for surface disposal, according to the italian policy.

Vitrification Unit

The vitrification unit, which will require a cell of 4 m length, 4 m depth, 5 m height (estimated size), includes three main units:

- Melter;
- Slurry and Frit Feeding System;
- Off-gas System;

The size and the features of the ceramic melter are presently under consideration. The design of this component should be developed with the assistance of a qualified supplier.

The feeding system should consist of the following major components:

- feed tank for slurry;
- pumping system for introducing feed rate-controlled the slurry into the melter (because of the low flow-rate a displacement pump should be used instead of an air-lift);

- glass frit feeding system for introducing frit particles batchwise into the melter.

The off-gas system includes a jet-scrubber (for removing dust and condensate all the steam in the off-gas), a NOx-column, a glass fibre filter, a HEPA-filter and a blower.

INSTALLATION

At the present two approaches are being evaluated for the installation of the treatment and solidification sections of the facility:

- a new building at the EUREX site, in the area surrounding the storage tank farm;
- installation of the chemical treatment and vitrification units into the EUREX cells, following the dismantling of the existing process equipment, while the cementation could be carried out in an external area, by a mobile unit.

The two options have been developed at the preliminary design stage; the selection of the second one, which is technically feasible and economically attractive, requires a revision of the scheduled decommissioning plan for EUREX plant. A final decision on that point will be made within 1992.

WORK IN PROGRESS

At the moment the experimental work is completed for the MTR Separation Process, while the last adjustment is being performed for the CANDU Separation Process.

The qualification for the cementation "recipe" is being carried out for the low level fractions, as well as the study for the glass matrix suitable for the sludge fractions.

The preliminary design for the integrated plant in which to perform the waste treatment is being worked out on the basis of the experimental data.

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