DEVELOPMENT AND EVOLUTION IN FRANCE IN THE CONDITIONING OF LOW AND MEDIUM LEVEL WASTE FROM REPROCESSING PLANTS

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GENERAL FEATURES

This paper mainly deals with the liquid and solid low and medium level wastes arising from the industrial reprocessing of spent nuclear fuels. Since the industrial fast breeder fuel reprocessing has only been scheduled for the last decade of this century, information on this subject will, of course, be very short and rough.

Data already given for low and medium liquid wastes produced during LAWR fuel reprocessing usually range from 20 to 100 m^3/MTHM. If a concensus can be reached for LLW (20-50 m^3/MTHM[a]) the discrepancy is very large for medium level wastes since figures from 0.1 to 60 m^3/MTHM have been given formerly. In fact, activity limits for the waste classification will differ according to national practices: 100 Ci/m^3 being often taken as a maximum for average activity in MLW and 5 Ci/m^3 for LLW (wastes with lower activity than 5.10^{-2} Ci/m are considered as "dubious"). Solid wastes produced by the reprocessing plants are estimated between 2 and 8 m^3/MTHM, including low level refuses, failed equipment, filters and solid waste issued from solidification of LLW and MLW concentrates. These figures do not take into account any biological shielding for such solid wastes.

Before giving french data and estimates for the new reprocessing lines, we would like to point out some explanations for such a large discrepancy between figures already given.

First and main point is the load factor of the plant: if each section of the reprocessing plant is running properly and with a minimum of stop and go, then the wastes arising would be close from the forecast and of limited amount. If many troubles occur, needing more decontamination works and concentration steps for fissing materials recovery in diluted solutions, then not only the low and medium level wastes would increase in volume and activity during the year, but the reprocessed fuel amount will decrease and the volume of waste per MTHM may then reach as much as 300 m^3/MTHM. Assuming that waste production is the same during normal operation as when the plant is in shut-down, decontamination or restarting phases, it is easy to show that the low and medium waste volume per MTHM is about doubled when the

[a] MTHM: Metric Ton of Heavy Metal

plant capacity is halfed. Since normal operation without troubles reduces waste production, a factor of 3 is possible between these two extreme conditions, the average taking into account 200 days/year of normal operation and 100 days for repair, flushing and decontamination.

LIQUID WASTE TREATMENT STATIONS

Some special points must be noticed, since they have been taken into account for new projects in France.

The collecting system for wastes: in order to avoid mixing of different level wastes, it is necessary to install as many separative networks as possible. Drain floor network is specially concerned, the corresponding wastes being very often "dubious" wastes instead of "active" wastes. One can easily save from the active part of the station STE 3 a lot of these wastes, specially if online activity measurements are used.

The recycling of process wastes is often proposed for helping to reduce the volume of active wastes. This can be done quite easily for distillate, when chemical composition is well defined and activity controlled, but this practice must be limited in order to avoid multiple interactions likely to disturb the chemical process of separation or to induce corrosion problems in sensible parts of the plants.

The process for low and medium level waste treatment could be different according to the allowed activity to be released in the biosphere (the release being dependent of the location of the plant (on sea shore or inland). Salt content, volatility of radionuclides, activity level of the wastes will also be taken into account for the selection of the process to be used.

As a general indication, evaporation shall be preferred for high decontamination factor, with MLW at high salt content and nonvolatile radionuclides. Chemical precipitation shall be used when salt content is high (for limitation of solid wastes to be embedded) or when high decontamination factor is not required. Operation cost will then be lower than with evaporation. For low activity and very low salt content, organic ion exchange without regeneration, giving directly a solid waste, ready for embedding, is intended to be considered.

Global risk to be considered can be divided into three separate fields:

- Operational risks for operators during running of the reprocessing plants.

- Surrounding risks for populations living in the vicinity of the plant or farther on, and due to atmospheric, sea releases.

- Long term hazards for people living in the vicinity of solid wastes disposal, in case of groundwater pollution.

A general evaluation with cost and detriment analysis criteria is very difficult and not yet achieved.

The main data about the new waste treatment station now in detail project phase, for the new UP2 800 and UP3 A plants in La Hague (1600 MTHM/year) are the following:

MLW

10 m^3/MTHM	solution	(~0.5 M/L NO_3H)	< 60 Ci/m^3/
0.1 m^3/MTHM	resins in water	(~40% decanted resins)	< 300 Ci/m^3/

LLW

45 m^3/MTHM	solution	(~0.3 M/L NO_3H)	< 3 Ci/m^3/

More than 90% of $\beta\gamma$ activity is due to Cerium, Ruthenium and Cesium. Total activity would be around 500 Ci $\beta\gamma$ per MTHM.

The main steps for chemical treatment foreseen in STE3 LA HAGUE are the following:

SEPARATE STORAGE of wastes in five tanks, each one corresponding to a liquid waste production of 3 days or one week, according to their activity level (LLW or MLW). Each tank is interchangeable and alternately in filling (two tanks) preparation or treatment (one tank remaining spare).

CHEMICAL TREATMENT (one line for both LLW and MLW). After solvent separation by decantation, radionuclides are, one after other, precipitated by various specific reagents, with increasing pH, the last reaction being a floculation.

So, the Antimonium, Ruthenium, Cobalt, Cerium, Zirconium, Niobium, Actinides, Cesium and Strontium are insolubilized, step by step, in different tanks, one feeding the following, with special chemical addition and pH control at each stage. A final decanter allows the separation of the floculate (4 to 16% in volume) from the overfloat to be performed.

FILTRATION: The overfloat is sent to a precoat filter and then, after activity control, to the sea discharge by pumps in operation during tides (each discharge would concern about 300 m^3 with an activity level of about 0.1 Ci/m^3).

With chemical precipitation, gross FD expected are from 50 to 100 for $\beta\gamma$ and 1000 for α. This is enough for reprocessing plants sited near ocean like La Hague, where the total release of activity could reach 10-20,000 Ci/year. For Marcoule (south of France, along Rhone River) the activity released is only about 1000 Ci/year. At least for medium level wastes, an evaporation step is then necessary.

For fast breeder reactors, the forecast for medium and level wastes are of about 200 m /MTHM (about three times more than for LWR fuels). Since the chemical process is not very different, explanations that can be given for the difference are:

- Scale of the plant (FBR capacity in MTHM, usually ranges from 5 to 10 times less than LWR).
- Need for interrun flushes due to the alternate reprocessing of axial bundles.

EMBEDDING PROCESS DEVELOPED IN CEA GROUP

The need for solidifying high level wastes (works on vitrification starts in 1960, as soon as fission products compositions were available) was soon extended in France to low and medium activity liquid wastes.

Bitumen first, thermosetting plastic, and concrete have been developed in France and some consensus appear now that each of these processes is well adapted for a given situation. This situation not only deals with each waste specifically, but also with the container used for overpack and also with the kind of storage to be used later on for disposal. This global evaluation being necessary but also uneasy.

BITUMEN: this process is used in MARCOULE for the medium level sludges issued from UP1 reprocessing plant, since more than 15 years. Same process, but with one stage evaporation step, is intended to be used in LA HAGUE for embedding the sludges coming from LLW and MLW treatment station (STE 3) and organic resins from storage pool water treatment.

Two lines shall be used, with an evaporation capacity of about 220 L/H of water per line.

A total amount of 4000 drums (55 gallons each one) will be produced per year, with an average activity of 1 Ci/liter.

In order to increase safety during intermediate storage, asbestos-cement drums could be used. The filling of a 110 gallon drum has been recently tested in Marcoule.

Since extruder is used in Marcoule plant and foreseen in La Hague, blown bitumen is used but direct distillation bitumen is also used in Saclay for laboratory waste embedding, using a falling film evaporator. The embedding conditions need to be carefully defined, after many analyses and security checks and verification of the radiation resistance, gas radiolysis release, volume expansion under water and leachability measurements made on radioactive blocks. Organic additives like solvent must be strictly limited in order to control long term release of actinides. Containers and overpacks as well as backfilling materials to be used in the final storage must be carefully selected in order to be used as efficient barrier for avoiding actinides release of reprocessing wastes.

Sludges embedded in bitumen can reach 40 to 45% in weight of the final product, and organic resins in bitumen 45 to 50% of the embedded bitumen. Diffusion rate in demineralized water (according to AIEA tests) is in the range of 10^{-5} to 3.10^{-8} cm/day for $\beta\gamma$ emitters and of 10^{-8} to 3.10^{-9} for α emitters.

Due to their α content, these embedded bitumen blocks need special attention for their container or overpack. Their ultimate storage in France, shall be a geological disposal, the preliminary engineering studies concerning this storage shall be initiated soon, when the inventory of α wastes concerned by this storage are completed.

CONCRETE

If concreting of low level wastes is a common practice in France for reactor wastes, the use of this technique is not yet established for liquid reprocessing wastes.

Research and development works have been initiated since about five years, by CEA (SACLAY and MARCOULE) and by SGN, in order to gain laboratory and pilot experience for concreting several kinds of wastes. Among the problems met, we shall point out: the leachability of many salts, including those with radionuclides like cesium; the need of pretreatment in order to transform as much as possible soluble salts into insoluble form, to absorb them with additives, mainly for keeping back radionuclides.

Among the properties of the concreted wastes, a compromise shall be found between mechanical strength, final volume of the block and leachability of the final product.

Formulation without or with a minimum amount of sand or filler will be useful in order to limit the volume of the concrete blocks, without reducing compression strength.

Considering that the potential cesium release could be quite high, a delaying line with an asbestos-cement container with an inner plastic liner, as developed in France by EVERITUBE for low level waste storage, would be very helpful.

For daily operated concreting stations, a batch process would be preferable, the mixing of liquid wastes and cement taking place inside the container itself, the shaft being preferably recoverable but losable if necessary.

Alternately, a continuous process is now being developed by SGN for the case of weekly stopping of the unit (during weekend for instance).

This two step system starts with a continuous reactor (mixer and evaporator) for pretreatment and overconcentration of the waste. This first equipment feeds the continuous mixer where cement and additives are introduced, mixed with the concentrated slurry, and then poured into the container. Flushing of equipment is reduced or supressed for short interruption of operation (one or two days), the mixture remaining in the mixer being adjusted so as to avoid cement settling during the stopping period.

THERMOSETTING RESINS

Embedding of dried wastes with thermosetting resins has been developed by CEA in Grenoble and used for waste embedding in this nuclear center since many years.

This batch process, already described can use either unsaturated polyester resins or epoxy resins; for embedding dried concentrates or organic ion exchanger.

Quality control of the end products includes fire tests, freezing-thaw cycles, leachability test after and before irradiation and radiolysis gas evolved until 5.10^9 Rad.

The use of thermosetting resins in the reprocessing field would apply to use bead resins, powdered resins, solid wastes and specific wastes such as lead iodide. For each of these wastes, feasibility studies have been carried out and for some applications, development works have been undertaken.

Bead Resins

Atmospheric drying or centrifugation is only required before embedding but special resins formulation are needed so as to limit peak temperature during setting of the large blocks (55 gallons). Remaining composition water will secure dimensional stability of the drums, even with a flooded storage. Special fillers allow a good homogeneity to be reached and any cracks to be avoided.

Cationic, anionic or mixed bed bead resins have been used for such embeddings, with a few percent of free water remaining in the ion exchangers.

Powdered Resins

Laboratory tests have shown proof of the quality of such embedded products, which is about the same as that of bead resin blocks. Fifty five gallon drums have been prepared with powdered resins including 70% water.

Solid Wastes

A conditioning station has been built in La Hague for the decommissioning of Cesium contaminated equipment. Fillers are mixed with thermosetting resins so as to decrease the price of raw materials and also to limit shrinkage and temperature during polymerization. Before their dismantling, equipment are recovered with a plastic film applied by electrostatic spattering of epoxy resins (without solvent). An easy fixation of the contamination is got, with a 95% paint deposition on metallic pieces.

Fifty-give gallon containers can be prefabricated with the same thermosetting resin as for embedding wastes. Research works have shown that 2 cm of pure resin layer around the embedded waste is a very efficient barrier against water penetration, and, consequently leachability. A similar thickness of pure resin is put on the top of the containers after their filling. Continuous preparation of the inactive embedding mixture is quite easy and is done during operation.

Lead Iodide

A new process with lead iodide production is intended to be used in UP3. Dry intermediary storage of PbI_2 is a possible solution but thermosetting resins embedding is also investigated. Leachability tests are under progress with very good prospects, compared with cementation of the same compounds.

These four examples show the various application fields of this process at least well adapted for ion exchanger resins and metallic equipment embedding, when severe quality criteria are required for the storage.

COMPARISON OF THE PROCESSES

As indicated before, the three processes for embedding wastes must be considered as tools allowing to decide what solution is the best for each specific case, taking into account the whole situation: safety of the process, location of the plant, leachability rate and diffusion during the final storage.

Bitumen and thermosetting resins are similar for the volume reduction. If bitumen is a burnable material, thermosetting resins need a preliminary drying of concentrates, which could be uneasy for radioactive products.

Long term stability of plastic resins, as well as concreted wastes are not a fact of experience.

Concrete seems the best material for tritium wastes and for low level wastes.

Except for some ceramic materials, leachability, even very low, could be significant during geological disposal needed for α wastes. The best way to avoid this long term release would be to limit the amount of leaching water around the solid wastes and to prohibit the storage of complexants. This means to take special care for chemicals used during reprocessing and during decontamination of equipment.

If all corresponding data are not available today, enough is known for undertaking a general evaluation and appreciation of the different embedding techniques in connection with the overpack and backfilling (if any) and with the possible geological storages for disposal (or sea disposal for special cases as tritium and iodine wastes).

SOLID WASTES
(Low and Medium Activity)

As seen before, the average volume of solid wastes produced from LLW and MLW ranges from 0.5 m^3/MTHM (bitumen) to 1.5 m^3/MTHM (concrete). Other solid wastes range from 3 to 5 m^3/MTHM, according to the size and load factor of the reprocessing plant, with the following splitting:

(a)	Refuse to be compacted	60%
(b)	Combustible trash	25%
(c)	Failed equipment	15%

If compaction is only used for volume reduction of these wastes, (a and b) final volume will be reduced to 1.5-3.5 m^3/MTHM (according to initial volume, size of the drum and kind of pressing machine). Total volume to be stored will then be ranged from 2.5 m^3/MTHM (hulls and end caps being not included in this evaluation).

These figures can be slightly reduced from 0.5 to 1 m^3/MTHM if incineration is used for combustible trash.

For La Hague reprocessing plant, the expected value for direct production of solid wastes is 4 m^3/MTHM. Since incinerator is not yet decided, the final figure, with bituminization and compaction is of 3 m^3/MTHM. With incinerator, this volume would be reduced to 2.5 m^3/MTHM.

It is obvious that the decision for the storage shall not only depend on economical consideration but rather on safety. As a matter of fact, after high temperature combustion, α wastes become oxidized and insoluble and more more complexant remains in the stored wastes.

As far as the conditioning of solid wastes is concerned, direct embedding is scarcely the right solution. In fact, failed equipment follow decontamination way, with conventional reagents (water, nitric acid, sodium hydroxide), even if their repair is obviously impossible. This is done in order to declassify the future storage container (below 0.1 Ci/T of α, the package could be sent to a shallow land burial instead of geological disposal for α wastes).

When this low activity level can be reached, preconcreted asbestos-cement containers, with internal liner can be possibly used without direct embedding of metallic pieces. For higher activity level wastes, concrete embedding in tight containers shall be preferred.

Volume reduction by compaction is widely used for non-combustible low level wastes and improvements can be done with powerful press on condition that no liquid remains in the solid wastes.

Plutonium recovery is obviously expensive but shall be done as much as possible, due to safety consideration (specially for high level combustible wastes or for α wastes enclosing complexant chemicals).

In that way, an incinerator is strongly advisable for safety reasons needed for long term storage of such wastes; even if incineration of large volume of low α wastes is delayed or cancelled for economical reasons. For La Hague reprocessing plant, the option for incineration is still pending.

Many technical choices remain difficult, due to the problems in connection with the sorting of wastes and their activity measurement. Accountability of fissile materials still remain to be improved and leachability tests of heterogeneous materials embedded for a long term storage, questionable.

Moreover, even if it is not yet critical, the dismantling of old radioactive installations will take more and more extension in the future. It will be wise to take this operation into consideration, not only for the sizing of technological wastes station but also for the storage capacity of disposal.

BUREAU FOR EVALUATION AND CONTROL OF CONFINEMENTS (BECC)
A USEFUL TOOL WITHIN THE WASTE MANAGEMENT STRATEGY

To face the rapidly growing importance of the radwaste management problems, the CEA has decided three years ago, the creation of the BECC. Main objectives of this Bureau are:

- The definition and the selection of criteria for waste confinement evaluation.
- The establishment of characterization or qualification procedures before homologation and agreement.
- The evaluation of the efficiency of conditioning processes.

This office is taking a part in the CEA waste management strategy and is also involved in international cooperation actions.

Characterization programs engaged with low and medium activity wastes under the coordination of BECC, are summarized below:

Long Term Leaching Resistance of Bitumized Reprocessing Sludges (Marcoule)

A long term full scale (200 l drums) leaching test is performed on a real bituminized product prepared in Marcoule with two steps extruder machines. The specific initial activity for the main radionuclides are (in Ci/m^3):

^{239}Pu	: 0.14	^{137}Cs	: 8.2
$^{241}Am + ^{238}Pu$	: 0.13	^{90}Sr	: 0.26

The released fractions observed during the first period of 500 days of dynamic leaching are:

Days	Cumulative fraction released		
	^{137}Cs	^{90}Sr	^{239}Pu, ^{241}Am
100	$2.8\ 10^{-4}$	$1.5\ 10^{-4}$	$<4\ 10^{-6}$
200	$5.2\ 10^{-4}$	$7\ \ 10^{-4}$	"
300	$8\ \ 10^{-4}$	$1.2\ 10^{-3}$	"
400	10^{-3}	$1.6\ 10^{-3}$	"
500	$1.1\ 10^{-3}$	$1.8\ 10^{-3}$	"

It is intended to continue this test at least 2 years before destructive examination for after test controls (diffusion repartition of active and inactive materials...). The leachates are examined for determination of the physico-chemical nature of the leached compounds.

CHARACTERIZATION OF BITUMINIZED WASTES (SLUDGES - SPENT ION EXCHANGERS FOR THE FUTURE WASTE TREATMENT PLANT (LA HAGUE)

The characterization program is engaged on the following parameters: homogeneity, swelling, mechanical properties, biological behavior and radiolysis effects.

Thermal effects on long term properties of bituminized wastes is scheduled for the end of 1982, in connection with examination of influence of these effects on leaching.

Characterization of Hulls Embedded With Cement

For the new reprocessing plants in La Hague a characterization program has been engaged in 1980 on zircaloy hulls embedded in cement.

The cement + waste formulation have shown: no free water, no voids and very complete immobilization.

After six months of leaching tests with active samples, the Pu leached can be expressed as:

$$\frac{\Sigma a_n}{A_o} \quad \frac{\text{(leached activity)}}{\text{(initial activity)}}$$

is comprised between 5.10^{-6} and 10^{-5} with hulls and is less than 10^{-8} with dissolution fines.

Radiolysis tests (with active samples in 1 bar atmosphere of helium) show a low yield of H^2 and tritium, after six months tests.

CONCLUSION

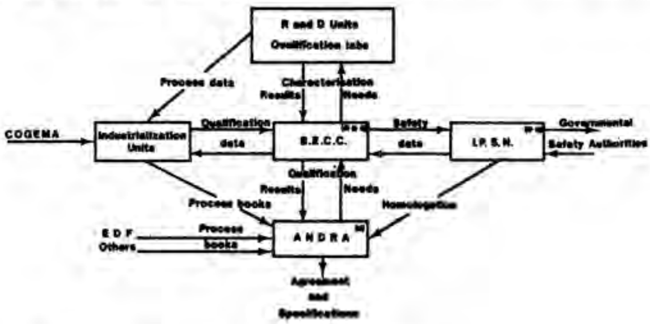
The various endeavors undertaken in France show that special care has been brought, since the beginning, to the wastes of low and medium activity.

The trend was first to help the operation staff of reprocessing plant to solve their daily waste management problems. Today, the outcome of the choices made in that field begin to be foreseen.

The knowledge of the different processes implemented is now in progress, due to interdisciplinary works on various fields: embedding, interactions between wastes and matrix, between containers and surrounding media, nature of leachates, backfilling, ion migration in soils and to the biosphere.

Technical and economical feasibility studies, taking into consideration not only the investment costs but also operation costs are now in progress in Europe as well as in the USA, allowing a better evaluation of the total cost of various scenarios.

This knowledge must also be used to give more adjusted explanations to populations, and enlarge the acceptability of the reprocessing of nuclear fuels, for the public opinion.



(*) A N D R A : National Agency for Radioactive Waste Management
(**) I.P. S.N. : Institute for Nuclear Protection and Safety
(***) B.E.C.C. : Bureau for Evaluation and Control of Confinements

Fig. 1. Role of the BECC(***).