FRENCH PRACTICE AND TRENDS IN THE TREATMENT AND CONDITIONING OF PWR LIQUID EFFLUENTS AND SOLID WASTES

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INTRODUCTION

From the early stages of the development of the nuclear industry in France, it has been decided to avoid radioactive effluent release by treatment, conditioning and storage of the wastes. It was not possible, when choosing this option, to reach the optimum from the beginning for the whole management system. The selection of a treatment process requires a precise knowledge of the nature, the composition and the arisings of radioactive wastes and these data are only available when commercial size reactors are in operation. To solve this problem, a close collaboration has been developed between the nuclear station operators and the R & D laboratories in charge of studying new treatment methods. This cooperation is a fruitful permanent exchange giving precise data about the waste, results of treatment operation on the industrial units, allowing modifications in the installations to improve their efficiency and sometimes, resulting in new trends for the research program.

Obviously, this collaboration must also be conducted in close connection with the other concerned organizations. With those in charge of disposal, since it is unwise to treat and condition the waste without a definition of disposal acceptance specifications and with those in charge of safety problems to define the criteria to take into account in the development of processes. It is on such a collaboration basis that EdF and the DEA are optimizing the management of the nuclear station wastes which is presented in this paper.

PRESENT RESULTS - TRENDS

The selection of an optimal process for radwaste management requires a careful analysis of the different steps: treatment of liquid effluents, conditioning, transport and disposal. This analysis must be carried out with a triple preoccupation: to develop safe processes, to minimize the final waste volume, and to lower the capital and operating costs.

A PWR nuclear station give rise to three main types of wastes:

- liquid effluents
- process wastes (filters, evaporator concentrates, spent ion exchangers)
- technological wastes (metallic pieces, plastic sheets...)

Table I. Annual Arisings of Radwaste.

Waste	1 reactor 900 MWe	1 reactor 1300 MWe
Evaporator concentrate	25 m3	35 m3
Spent ion exchangers		
- low activity	9 m3	12 m3
- medium activity	5 m3	5.5 m3
- high activity	5 m3	7.5 m3
Decontamination drains	2 m3	2.5 m3
Filters	20	30
Technological wastes	150 m3	200 m3

Until now, EdF has been immobilizing the process wastes in a hydraulic binder matrix. This choice was dictated by economical reasons and feasibility of operation; it is now questionable and the new strategy applied by EdF is developed later on in this paper.

Nevertheless, it may be of interest to precise that at the time being, EdF is immobilizing the wastes with Portland cement mixtures in reinforced cylindrical concrete containers with an external volume of 1.25 or 2 m3 and with a useful volume from 0.14 to 0.95 m3. The technological wastes are compacted with a press in 200 l steel drums.

To reduce the final volume and to minimize the operating costs, EdF has engaged a study and testing program on liquid waste treatment and conditioning processes:

- For liquid waste treatment, a comparison has been made between thermal evaporation ion exchange, chemical precipitation and forced air evaporation.

- For the conditioning, it has been studied the feasibility and the economical interest of: drying of concentrates, fixed or mobile solidification system with hydraulic binder in steel drums of 400 l, different processes of solidification in polymers with mobile stations, bulk transport to a central conditioning station.

Simultaneously, EdF has engaged a qualification program to assess the characteristics of the solidification products.

LIQUID EFFLUENT TREATMENT

Primary Effluent Treatment

The liquid effluents of a PWR nuclear station are treated in two circuits: primary circuit with only primary tritiated hydrogenated water and "used effluent circuit" with aerated water coming from the different drains and the other types of contaminated water (floor drains, laundry wastes, decontamination and chemical effluents).

We can see on Fig. 1 the flow diagram of primary effluent treatment of a 1300 MWe station (3rd generation called N.4 project). After the ion exchange decontamination step, the liquids are treated in a double function apparatus: evaporation and degassing are carried out in a single step. This treatment has been verified feasible and leads to an appreciable economy.

Spent Effluent Treatment

In the Fig. 2 is summarized the flow diagram of "spent effluents treatment". For the presently operating stations, 900 MWe or 1300 MWe, the decontamination of the more active liquids (residual drains and certain floor drains) is performed with a thermal evaporator. For the other effluents, their specific activity level is generally very low and they are only filtered before control and release; if their activity does not allow this treatment, they are treated with the thermal evaporator.

The treatment of these "spent effluents" is the most important source for the process waste: the concentrates represent about 70% of the whole production (if the filters of nuclear auxiliary circuit are excluded). To minimize this production, studies and test operation in industrial operating stations have been engaged. For the operating stations, the only possibility is the application of ion exchange; for the projected stations, chemical precipitation, forced air evaporation and drying of evaporator concentrates are also considered.

The extension of ion exchange application has been experienced in a pilot plant at the FESSENHEIM station were the

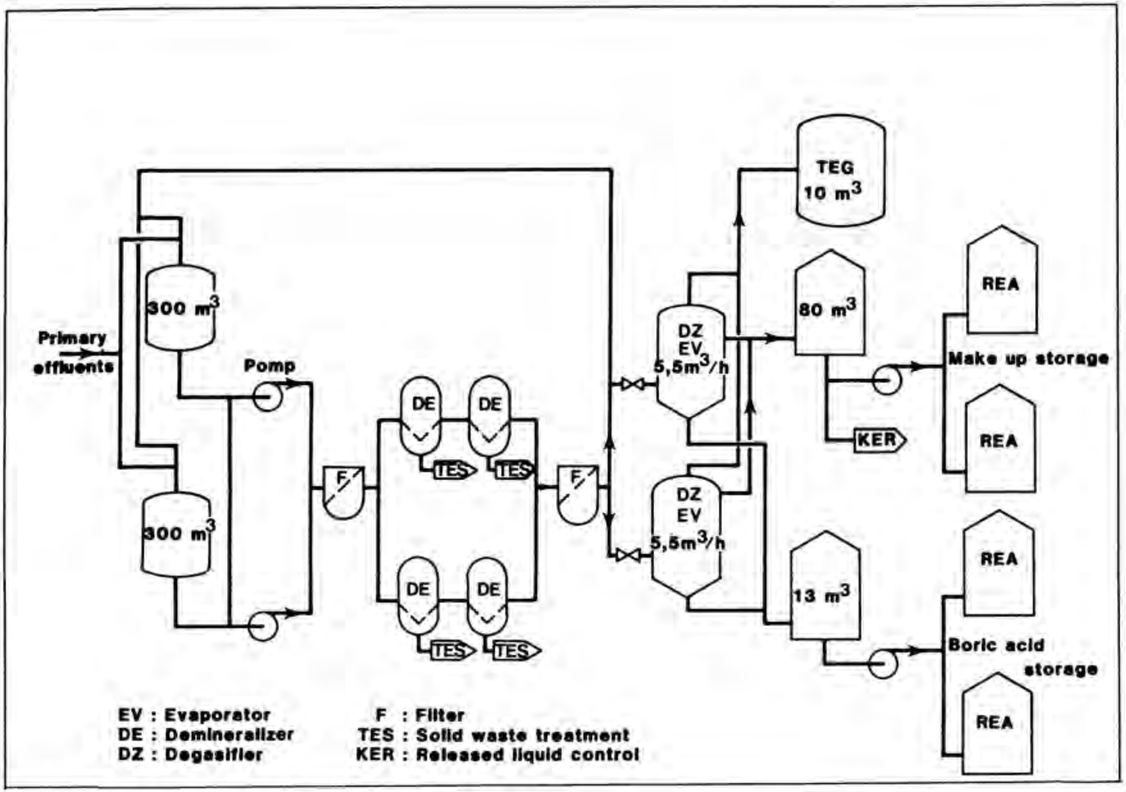


Fig. 1. Primary Effluent Treatment 1300 MWe.

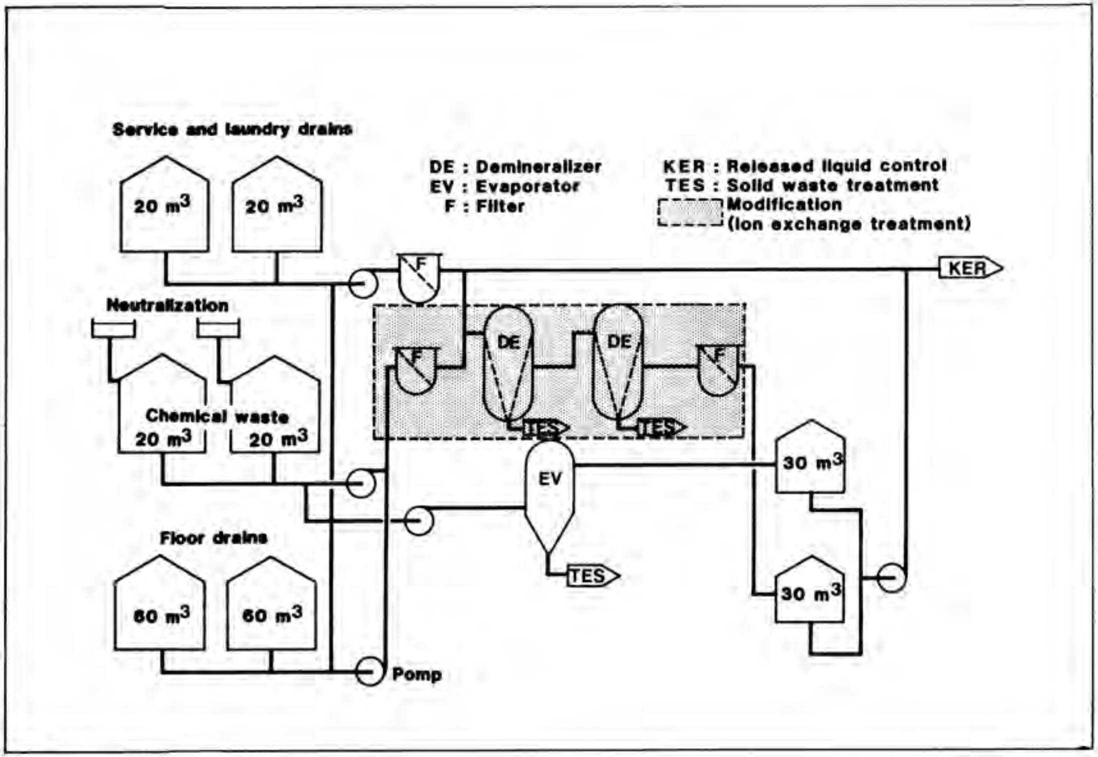


Fig. 2. Liquid Waste Treatment.

feasibility, the efficiency and the economical interest have been demonstrated. The results may be summarized as follows: for the treatment of 2,390 m3 of effluents the production of spent ion exchangers was 3.25 m3. If these effluents were treated by thermal evaporation, production of 48 m3 would have been observed. Taking into account the drumming efficiency (0.3 for spent resins and 0.4 for concentrates), the volume reduction gained is 11. The decontamination factor, with an efficient filtration ahead of the demineralizers is above 10^3. EdF has decided to apply this treatment, which is in halftone in Fig. 2, to all the existing or future stations, beginning with FESSENHEIM and BUGEY. In the stations, a selection of the more suitable filters is engaged: standard paper cartridge, precoat filter recoverable, carved disks filters recoverable. Results of this study is expected mid 1983.

The drying of concentrates has been proved uneconomical compared to ion exchange and has not been retained for application. The chemical precipitation has been studied for EdF by the CEA in CADARACHE and an industrial unit is operating in a continuous long term campaign since February, 1982. The decontamination factors required are: 8 for cobalt and manganese, 100 for cesium and 40 for the gross gamma activity. Through the operating performances EdF will decide future application for the 1300 MWe reactors of the third generation (N.4) as a complement or instead of the ion exchange treatment.

Forced Air Evaporation

This process has been studied and developed by the CEA. Its main interest is to avoid any release of treated liquid. At the time being, 2 units are in operation on a 250 l/h of evaporation basis. The Fig. 3 is giving a picture of such an evaporator which ensures the transfer of the evaporated water to an unsaturated air stream. The contamination of the air leaving the evaporator is generally $<1.10^{-13}$ Ci/m3. EdF is interested by this technique for the nuclear stations sites where the availability for dilution of released liquid is low. Taking into account the results obtained by the CEA with real effluents from nuclear stations, EdF has decided the installation of a pilot plant in CHINON. The main features of this pilot are: evaporation rate: 1m3/h, length: 13 m, width: 9 m, height: 8m. Total evaporation area: 1392 m2 - flow rate of air stream: 104 000 m3/h - operating temperature (inlet): 40°C.

CONDITIONING OF SOLID WASTES

Initially, when EdF started with its nuclear program, the immobilization matrix chosen was based on hydraulic binder. The

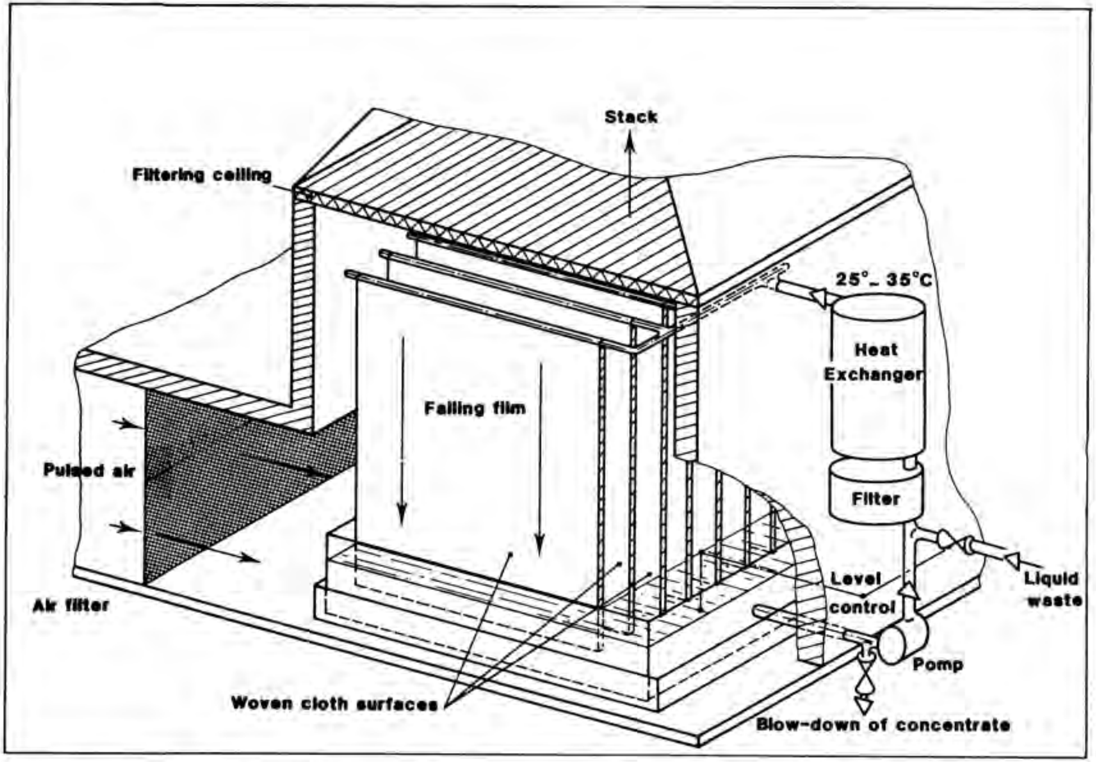


Fig. 3. Forced Air Evaporator.

early formulations retained were selected according to a mechanical criterium: compressive strength. To fulfill the requirements of the ANDRA (National Agency for Radioactive Waste Management) summarized in specifications, EdF has engaged a wide program to set up new advanced embedding formulations with the CEA and its subsidiary SISA (Société Industrielle de Stockage et d'Assainissement). The priority was given to spent ion exchangers immobilization; but to face the possibility of unsuccessful qualification results, EdF has at the same time decided extension of spent resins storage capabilities and the creation of a special circuit allowing the operation of mobile solidification stations using polymers.

Conditioning in the 900 MWe Stations

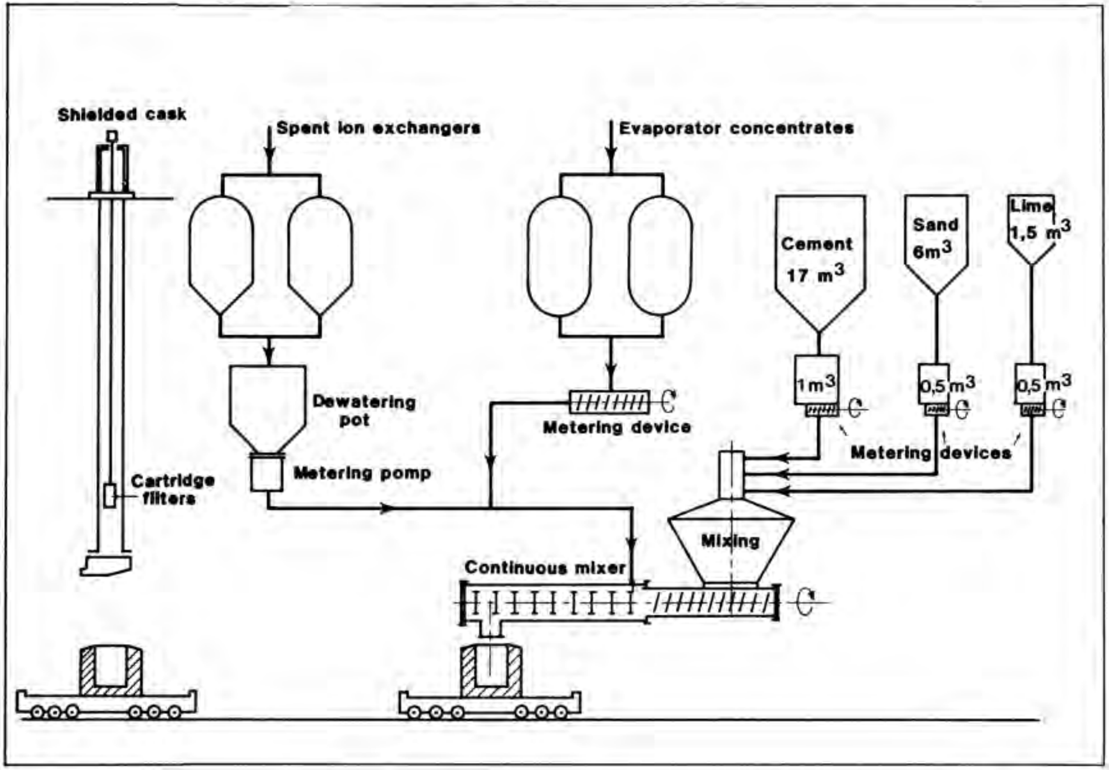
For two reactors there is a common auxiliary building which ensures the storage of spent ion exchangers and concentrates and where is operating a concrete solidification station. The filters are immobilized in reinforced concrete containers with a ready to use grout (cement + sand + water premixed). The process wastes are immobilized by in drum mixing with lost blade using dry materials (lime + sand + cement) the usual specific activity observed is <1 Ci/m3 for evaporator concentrates, <4 Ci/m3 for low activity resins, 60 and occasionally, up to 600 Ci/m3 for the high activity resins.

A special care is taken to prevent the swelling effect of the immobilized product: a thin metallic coating with 1 to 2 mm spacing is placed inside the container before its use.

Conditioning in the 1300 MWe Stations

The conditioning described in the above section has the disadvantage of a lost container with a relatively high cost for preparation and for disposal. Moreover the dosing or metering devices do not allow a satisfactory drumming coefficient and the process cannot accept all types of containers.

These reasons have led EdF to estimate the economical interest of a conditioning method using 400 l steel drums filled by a continuous mixing system which are transported to the disposal site inside recoverable shielding made of steel or case iron, 5 to 15 cm thick. The Fig. 4 summarizes the whole scheme of the installation which exhibits the originality of dewatering metering system allowing a continuous feed of waste with a well known water content and a very simple, low cost, easy to maintain continuous mixer.


Shielded cask
Spent ion exchangers
Evaporator concentrates
Cement
17 m^3
Sand
6m^3
Lime
1,5 m^3
Dewatering pot
Metering pomp
Metering device
1 m^3
0,5 m^3
0,5 m^3
Metering devices
Cartridge filters
Mixing
Continuous mixer

Other Processes Investigated - New Trends

For obvious economical reasons EdF has taken into consideration the solidification mobile stations and the comparison of their interest to the results obtained with fixed station like these operating until now. The principles are summarized on the Fig. 5 which shows the order of magnitude of the spent resins storage for an auxiliary building common to 4 reactors (1300 MWe).

If used with hydraulic binders, the capital cost is lower than with fixed installation, but the overall cost is not significantly different. If used with polymers, the capital and operating costs are higher compared to both fixed or mobile solidification stations with hydraulic binder. A short economical comparison will be given later in the report.

Another system is also investigated: bulk transport to a central solidification facility. This method is in favor of EdF according to the following advantages:

- volume reduction of waste to transport between nuclear stations and conditioning and disposal site.

- better adaptation of treatments to be applied according to the nature and specific activity level of the wastes (i.e., corrosion products contaminated waste of low activity could be put in decay without further conditioning).

- better possibility to take into account progress in conditioning techniques in a central facility.

- lower investment and operating costs.

- likely better quality insurance in a central facility due to experience of operating teams and easier quality control.

According to a preliminary study of PEC (PEC Engineering Cy) for EdF, a cooperation is undertaken with CEA to investigate more deeply this concept study to obtain, early in 1983, the elements for a decision which can lead to industrial application in 1985.

The question for EdF is: what is the conditioning process to develop until 1985 and eventually later if the bulk transport is not applicable?

EdF had initially retained the conditioning with mobile stations; but the characterization studies have shown that spent

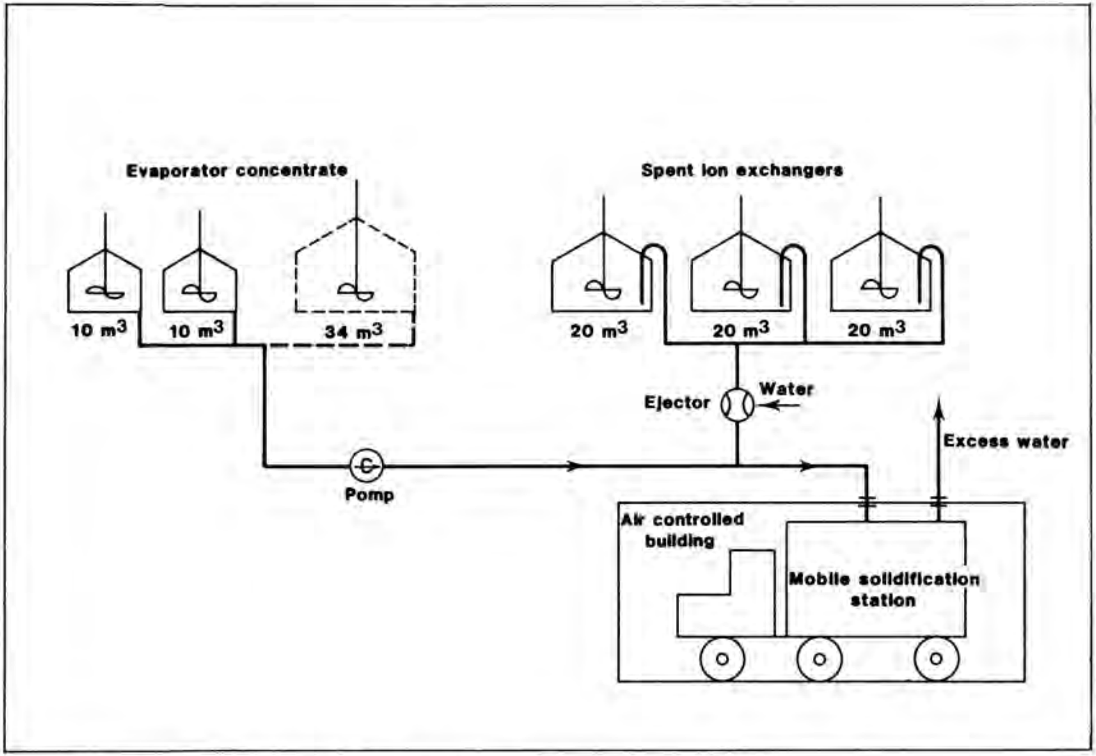


Fig. 5. Solidification With a Mobile Station.

ion exchangers immobilization with hydraulic binder is giving a waste form nonacceptable from the leaching of cesium point of view. Consequently, it was necessary to choose another product which offers better leaching properties. The only available operating station in Western Europe with industrial experience was based on the STEAG process. (G.N.S). STMI (Société de Travaux en Milieux Ionisants, a CEA subsidiary) was asked to buy and operate that type of mobile station. The first active operation with the new station is foreseen for April 1982, with spent ion exchangers. For evaporator concentrate EdF has decided to use its own fixed existing solidification plants or mobile stations (STEAG or TRANSNUKLEAR) with hydraulic binders.

Concurrently, other tests and studies are in progress to estimate the applicability of the DOW CHEMICAL process and the CEA process described below.

Summarizing its position, EdF is hoping to be authorized to bulk transportation of the waste and, for the near future, is using mobile station where the different processes remain in competition (STEAG: polymer or concrete, TRANSNUKLEAR: concrete, DOW CHEMICAL and CEA: polymers.

CEA Solidification Process with Polymers

This solidification process has been investigated and developed in the CEA at the Nuclear Research Center of GRENOBLE where there is one installation operating on active concentrates and spent ion exchangers since several years. A second industrial plant has been realized for SENA (Société d'Energie Nucléaire des Ardennes) where a PWR 300 MWe is in operation.

The Fig. 6 shows the flow diagram of the process. The evaporator concentrates are treated to insolubilize cesium, strontium and cobalt; then they are dried and crushed to give a powder with <6 % H_2O. The spent ion exchangers, until now, were treated for complete saturation with NaOH, but recent improvements have shown that this pretreatment is not necessary. The powder or the dewatered ion exchange resins are mixed in a steel drum with the monomers and with the polymerization reagents. Two kinds of polymers are used: polyesters and epoxides. For the cartridges filters, they are placed in a basket in the drum which is filled by the mixture of polymers + additives. The gelification occurs within 3 to 4 hours and the hardening needs 1 to 2 days, the maximum hardness being obtained in 7 to 10 days. The ratio of waste to polymers is: 45/55 for powders, 50/50 for spent ion exchangers. The maximum temperature increase in 200 l. drum is lower than 80°C. The CHOOZ solidification unit has started its active operation in January 1981. After one year of experience,

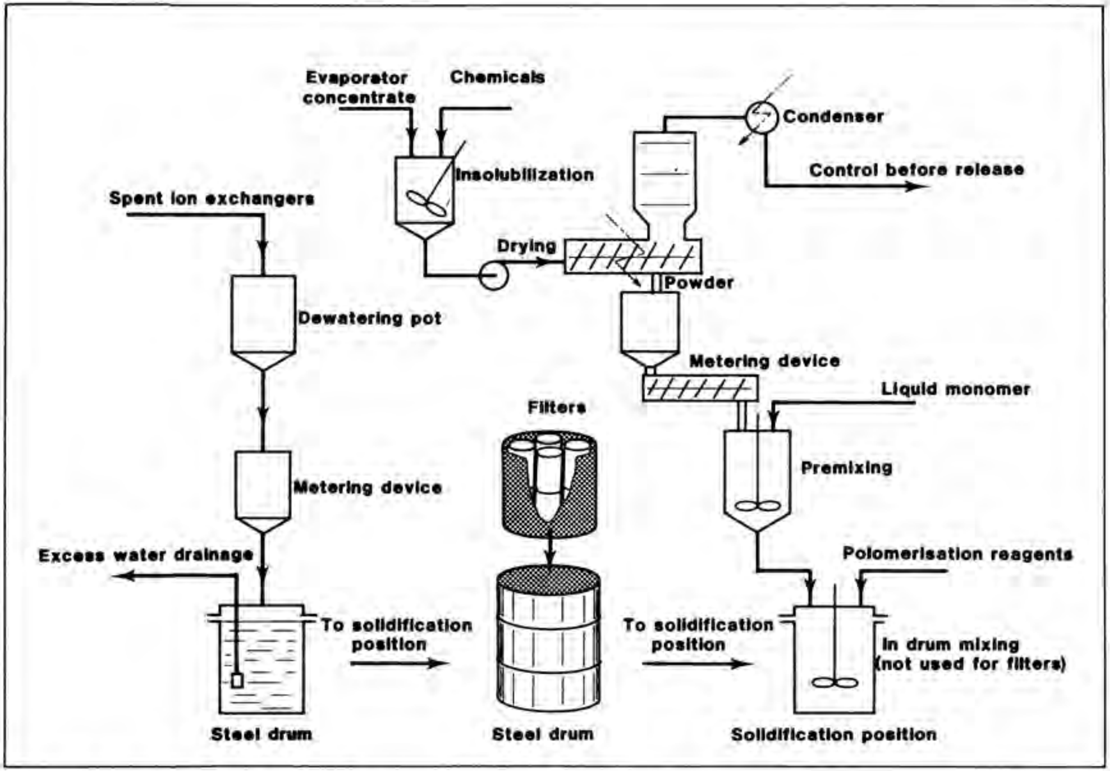


Fig. 6. CEA: Solidification Process.

it seems that despite a small overcost, the solidification with epoxide is easier, safer and give better products.

A mobile station using a continuous waste-monomers mixing device is presently studied and will start in operation in the CEA at the end of 1982.

CHARACTERIZATION OF SOLIDIFIED WASTES

ANDRA (French National Agency for Radioactive Waste Management) created in November 1979, has defined the different constraints for waste packages in view of their acceptance in the "Centre de Stockage de la Manche" (C.S.M). For this disposal center ANDRA has edicted specifications which are, at the time being, only applicable to waste packages with matrices of hydraulic binders in reinforced concrete containers.

Among the required characteristics, one of the most important is the leaching resistance. This property is expressed in terms of annual fraction released by leaching during the first year ($\frac{\varepsilon a_n}{A_o}$ where εa_n is the sum of the incremental activity leached during the first year and A_o is the initial activity for each concerned radionuclide.) The yearly maximum acceptable values are:

^{60}Co : $<2.10^{-3}$ ^{137}Cs: $<1.10^{-2}$

^{90}Sr : $<2.10^{-4}$ α emitters
($T > 50$ y) $<2.10^{-6}$

To fulfill these requirements, a characterization program has been undertaken in close collaboration with EdF, CEA (ANDRA, BECC, Bureau for Evaluation and Control of Confinements) and more recently with the support of the Commission of the European Communities.

Evaporator Concentrates from PWR Solidified with Concrete

A full scale leach test on an industrial block is in operation for more than two years to estimate the active release under dynamic continuous leaching. The formulation used for the tested product was the following for a 200 l. final volume of solidified material: concentrate $\sim$80 l ($\sim$100 kg), $Ca(OH)_2$ 12 kg, quartz sand $\sim$130 kg, Portland cement CPA 55 R $\sim$210 kg. The density of the product is 2.3-2.5. (The cement block was removed from the steel drum).

The specific activity of the main radionuclides is (in Ci/m3):

^{54}Mn : 3.5.10^{-2}
^{58}Co : 0.4.10^{-2}
^{60}Co : 4.1.10^{-2}
^{90}Sr : 5.9.10^{-2}
^{134}Cs : 4.5.10^{-2}
^{137}Cs : 4.6.10^{-2}

We can see, Fig. 7, the evolution of the released fractions for ^{60}Co, ^{90}Sr, ^{137}Cs and inactive Na^{+} ions. The block remains apparently unaltered after 2 years except a visible deposit of calcium carbonate. The leaching water chemical composition is similar to that one of the ground water in the disposal site.

Improved formulations are now in pilot and industrial testing to improve the retention for cesium; the most promising are pouzzolanic or slag cement mixtures. Their complete characterization is undertaken, including: fall and fire resistance, mechanical and physical properties, leaching in dynamic conditions, ageing in the presence of real ground soil and water from the disposal site.

PWR Wastes Solidified with Polymers (Polyester or Epoxides)

The main physical properties measured are summarized in the Table II.

Table II. Physical Properties of Waste Solidified With Polymers.

Waste	Evaporator concentrates		Spent ion exchangers	
Matrix Property	Polyester	Epoxides	Polyester	Epoxides
Density	1.45	1.38	1.15	1.05
Compression resistance(bars)	~700	~900	180	190
Firing weight loss (%) (30 min - 800°C)	6-7	6-7	10-15	10-15

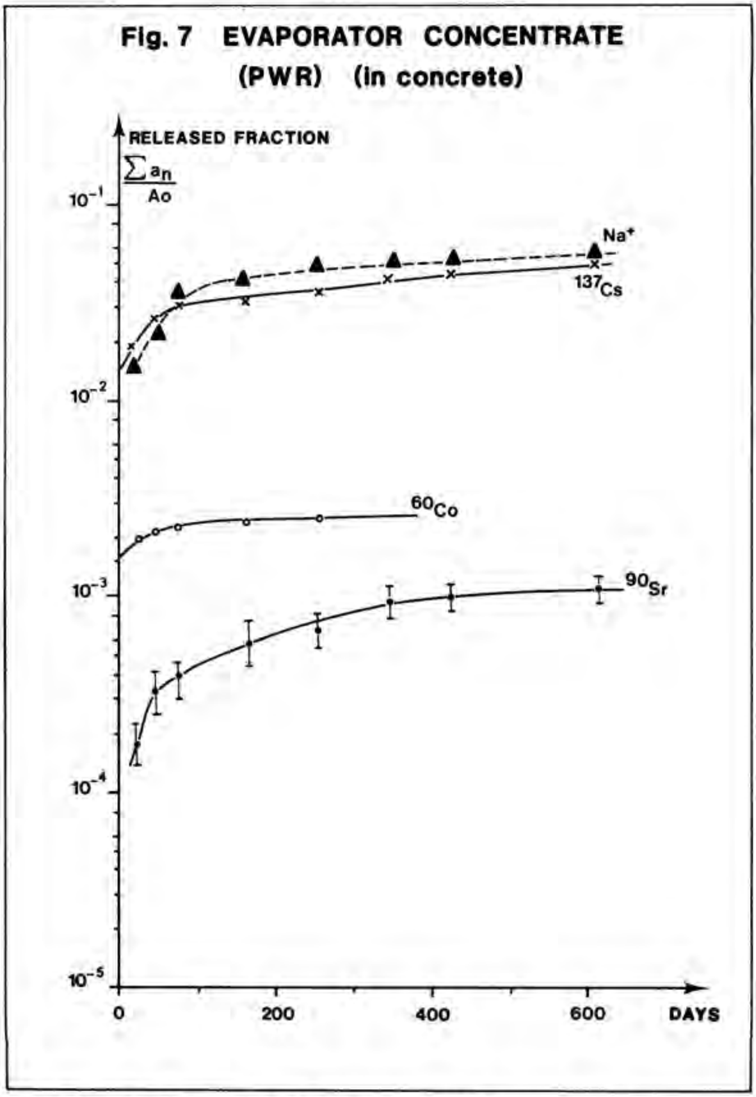


Fig. 7. Evaporator Concentrate (PWR) (in concrete).

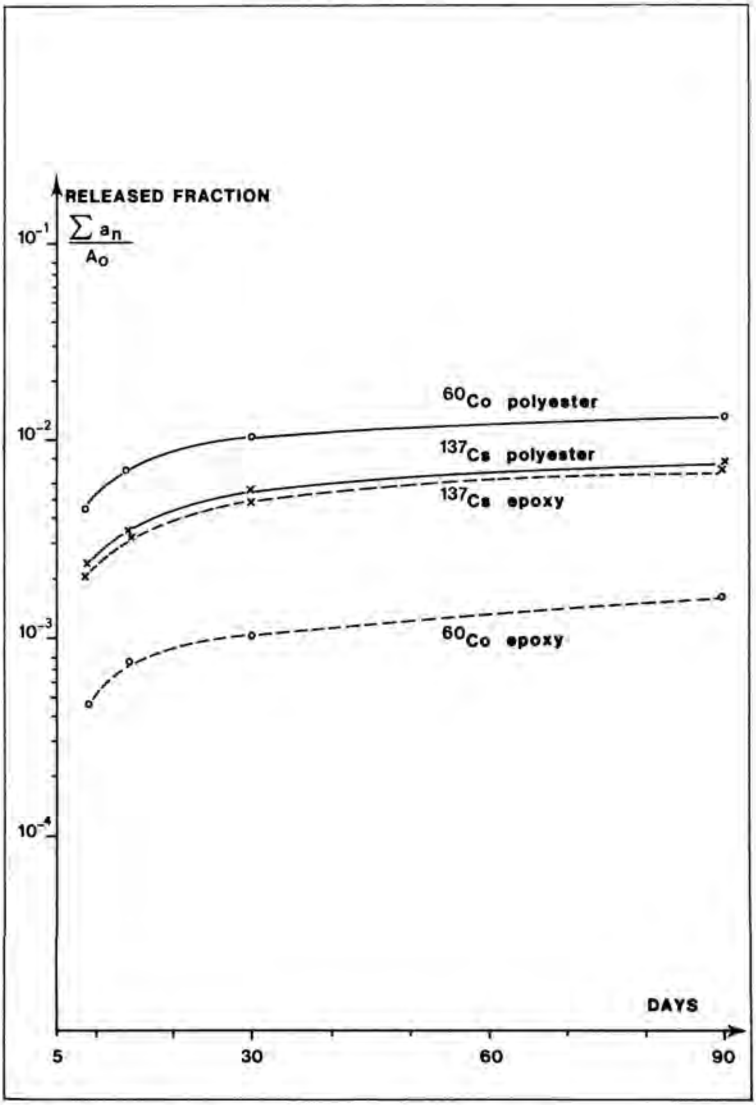


Fig. 8. Spent Ion Exchangers (PWR)(in polymers).

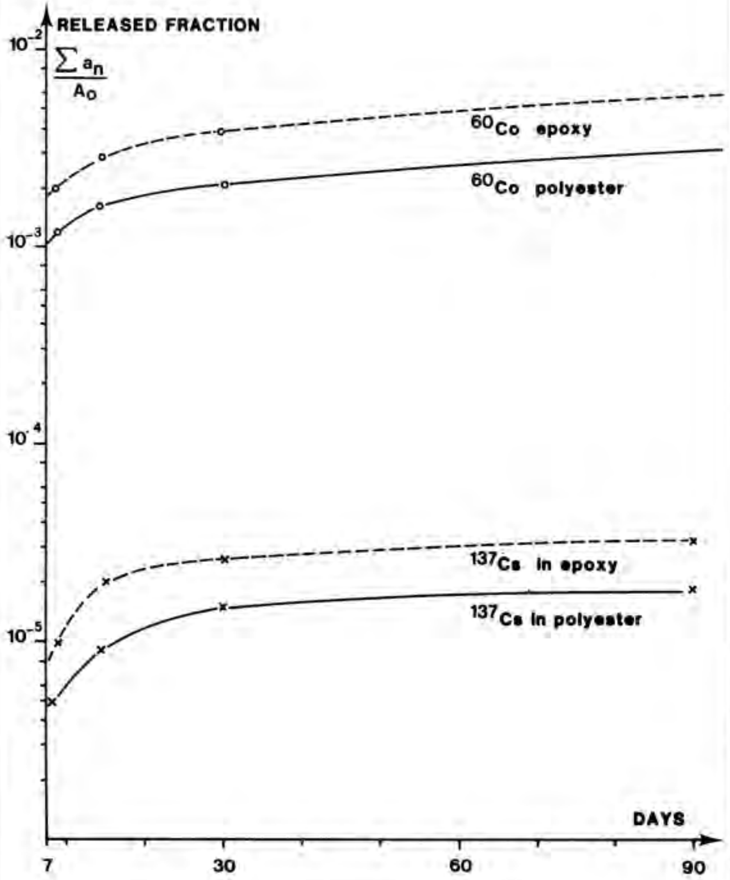


Fig. 9. Evaporator Concentrate (PWR) Dried (in polymers).

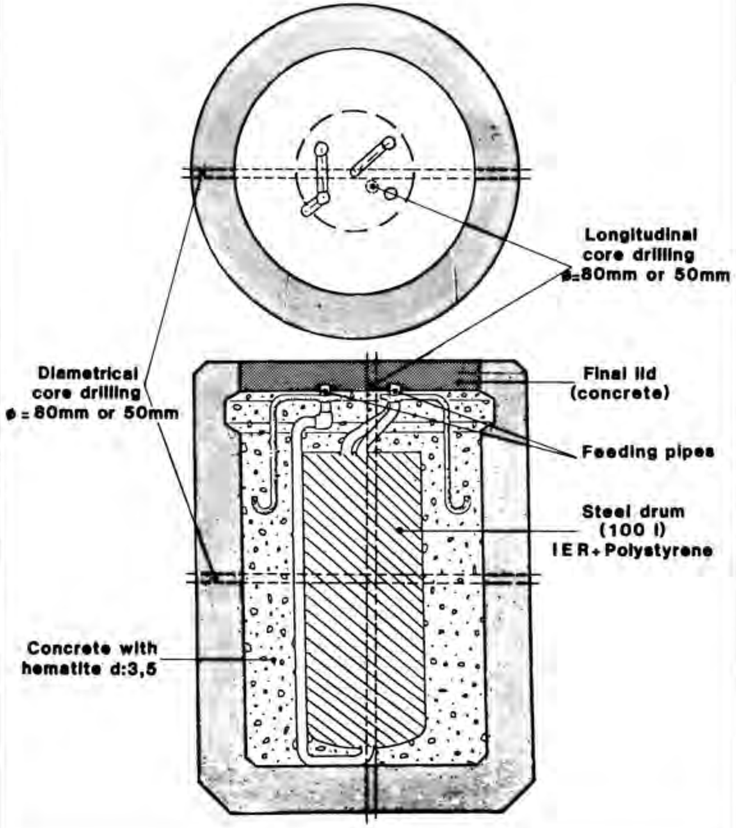


Fig. 10. Container Filled With Spent Ion-Exchangers and Polystyrene (mobile station).

The macro structural homogeneity was observed by cutting more than 30 inactive drums; it was excellent, with no voids.

The leaching resistance is tested on 4 industrial active real blocks (200 l), the steel drums having been removed. The average initial specific activity of the final waste forms is (in Ci/m3):

Evaporator concentrate		Spent ion exchanger	
^{60}Co	0.08-0.12	^{60}Co	0.05-0.07
^{137}Cs	0.12-0.15	^{137}Cs	0.9 -1.1

We can see on Fig. 8 and Fig. 9 the results observed during the first 90 days leaching period. It is clear that the insolubilization of ^{137}Cs is very efficient in the case of evaporator concentrate, but the leach rates of ^{60}Co are higher than expected and improvements of the conditioning operations have been undertaken. The resulting products will be submitted to the same characterization program.

ECONOMICAL ASPECTS OF WASTE TREATMENTS

The costs indicated below are expressed in french francs, basis in January 1981, excluding TVA (added value taxes).

Comparison of Economical Interest Between Mobile Solidification Station and Fixed Installation Both Using Hydraulic Binder Matrix

Two cases have been considered:

- Purchase of the equipment and working under controlled services operation.

- Controlled services operation only.

In the comparison, material, transport and storage costs have not been taken into account, since they are the same for the two cases. The mobile station has been supposed to serve 8 reactors (4 pairs) and 4 fixed installations (each serving one pair of reactors. The waste production treated is based on the arisings given in Table I.

In terms of total cost it does not appear a decisive economical advantage, taken into account the possible margins of error for the given evaluations. There is only an appreciable reduction of capital cost for the controlled services operation.

Table III. Economical Comparison Between Fixed and Mobile Solidification Stations Using Hydraulic Binder (in 10^6 FF)

Cost elements	Fixed unit	Purchase of mobile unit	Mobile unit (controlled operation)
Capital cost	31.1	30.9	18.1
Operating cost	3.5	2.7	11.4
Total	34.6	33.5	29.5

Comparison Between Three Types of Solutions: Fixed and Mobile Station With Hydraulic Binder (STEAG/STMI and Mobile Station Using Polystyrene

The difficulties encountered for the qualification of the embedded products containing spent ion exchangers in hydraulic binder have led EdF to decide in favor of polymer embedding. An economical study has been conducted on the basis of 1 PWR, 1300 MWe with the arising of spent resins given in the Table I and where the "spent liquid effluents" are treated by ion-exchange as shown in Fig. 2.

Table IV. Comparison of Cost Elements for 1 m3 of Spent Ion Exchange Resins Solidified in Hydraulic Binder or in Polystyrene (in 10^3 FF)

	Hydraulic binder solidification		Polystyrene solidification (STEAG/STMI)
	Fixed	Mobile unit	
Amortization	34.4	17.9	11.4
Manpower	3.3	7.8	11.2
Raw material	6.7	6.7	36.0
Transport	12.0	12.0	9.0
Storage	16.2	16.2	18.5
Total	72.6	60.6	86.1

The cost for polystyrene solidification with a mobile unit is respectively ∿20% higher than with a fixed installation and ∿50% higher than with a mobile unit, both using hydraulic binder. An optimization study of the STEAG/STMI equipment should allow a substantial decrease of the operating cost, but it is already ascertained that the cost with a mobile unit with hydraulic binder shall not be approached.

SAFETY ASPECTS

For any choice in conditioning processes and disposal method, a complete safety analysis has to be conducted. With such an analysis, it is possible to evaluate the potential consequences of the management, including disposal, to make an assessment of the risk and finally, to judge the level of safety obtained.

In FRANCE, we have chosen shallow land burial for disposal of solid wastes coming from nuclear power plants. But it is possible to adapt the other barriers and particularly the conditioning matrix and the container.

As we saw in previous sections of this paper, many processes have been developed in FRANCE. All processes are not applicable to all categories of effluents; but some processes are applicable to several categories. In this case, it is interesting-and in accordance with the recommendations of ICRP- to compare the incidence of each process on safety evaluation. It is also the case for the various possibilities of implementing a specific process. For instance, there are many possible compositions of concrete: choice of quality of cement, proportions of various compounds... Some characteristics of the product obtained will have direct consequences on safety analysis: for instance, leaching rate, long term behavior of the matrix. But other ones may have indirect influence. It is the case for volume reduction. As a matter of fact, it is easier and not so expensive to improve the qualities of the second barrier and eventually of the third one for a smaller volume of wastes.

Of course, many other factors have to be taken into account in choice of the process, especially economical factors, status of the development of the process. But it is useful and possible to take into account safety aspects. To do so, it is important to have a close cooperation between all concerned people: waste producers, disposal agency, staff in charge of R&D studies, people responsible for safety assessment. Such a cooperation has to be set up as soon as possible to avoid any research or any decision conducting to a dead-end.

CONCLUSION

The management of the PWR stations radwastes is a relatively complex system. The variation in composition of the different types of effluents and solid wastes involves the possibility of different management schemes. By another way, and for other nuclear wastes, various treatment and conditioning processes have been developed in FRANCE. The initial selection made by EdF was immobilization with hydraulic binders. This choice was an acceptable option which is permanently improved by R&D studies. The results of these studies are not only better confinement qualities but also better adequation of the processes and in certain occasion spectacular improvement of the volume reduction such as this factor 11 obtained when using ion exchange instead of evaporation.

All these studies are also aimed to give to the safety authorities and to the storage responsible people the elements allowing a complete safety analysis of the disposal sites. It is obvious that the studies made in that frame such as diffusion of radionuclides in different matrices or physico-chemical nature of the released compounds are also applicable to all kinds of conditioned nuclear wastes.

But, of course, and first of all, these research studies are directed toward the optimization of the nuclear station radwastes management to obtain safer processes, better volume reduction factors and minimization of capital and operating costs. According to our experience, we consider that the cooperation between research teams, operators of storage organizations and safety authorities is the best way to reach the management system optimization. This cooperation allows the harmonization between the economical constraints and the safety requirements which are not in contradiction when they have been studied simultaneously and from the beginning of the research work.