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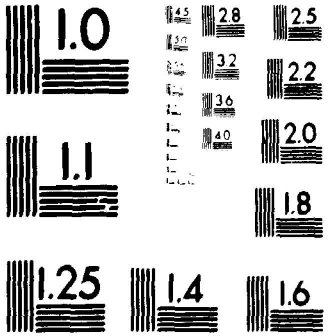

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ENEA

COMITATO NAZIONALE PER LA RICERCA E PER LO SVILUPPO
DELL'ENERGIA NUCLEARE E DELLE ENERGIE ALTERNATIVE

CHARACTERIZATION OF SOLIDIFIED RADIOACTIVE WASTES PRODUCED AT MONTALTO DI CASTRO BWR PLANT WITH REFERENCE TO THE SITE STORAGE

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RT/COMB/85/5

Testo pervenuto nell'ottobre 1985

International Seminar on Radioactive Waste Products.
JULICH (RFT), 10-13 June 1985

Summary

The cement solidification of the Montalto di Castro BWR plant radwastes has been studied both from the point of view of the mixture formulation and of the product characterization. Five radwaste types and mixtures of them have been taken into consideration, determining the best chemical formulations starting from the compressive strenght as leading parameter. The solidified products have been characterized from the point of view of the freeze and thawing resistance, the water immersion resistance, the leachability, the dimensional changes and the free standing water. All the tests have been performed taking into account the real site conditions, so the leaching tests and the water immersion tests have been carried out using sea water and table water as leachant.

Riassunto.

In questo lavoro vengono presentati alcuni risultati riguardanti gli studi effettuati sulla cementazione dei rifiuti radioattivi che verranno prodotti nella centrale di Montalto di Castro, studi riguardanti sia la scelta delle formulazioni cementizie che la caratterizzazione dei prodotti finali. Sono stati presi in considerazione cinque tipi di rifiuto e loro miscele, determinando le migliori composizioni sulla base della resistenza a compressione scelta come parametro guida. I prodotti finali sono stati caratterizzati dal punto di vista della resistenza ai cicli gelo-disgelo, della lisciviabilità, delle dilatazioni volumetriche, della resistenza all'immersione prolungata, della presenza eventuale di acqua libera. Tutti i test sono stati effettuati tenendo presente le condizioni reali del sito, e così i test di lisciviabilità e di immersione prolungata sono stati condotti impiegando acqua di mare e acqua di falda come mezzo lisciviante.

1. INTRODUCTION

Three nuclear power plants are at present in operation in Italy, while a fourth stopped its activity some time ago. A new 1000 MWe BWR plant is under construction at Montalto di Castro and its operation is foreseen at present to begin on 1990.

The liquid and the wet radioactive wastes produced at Montalto di Castro will be solidified by means of a continuous cementation plant provided by the Italian firm Castagnetti SpA, which is also responsible of the good exploitation results.

In order to guarantee the attainment of a safe and satisfactory management of the radwastes which will be there produced , a collaboration has been established betweeen ENEA and Castagnetti SpA /1/, centered on the formulation and the characterization of the cement products.

2. RADWASTE TYPE AND COMPOSITION.

The radioactive wastes that will be cemented at the Montalto di Castro BWR plant are the following:

- evaporation concentrates;
- exhausted Powdex ion exchange resins;
- mixed bed exhausted ion exchange resins;
- sludges from the traveling belt filter;
- concentrates from the decontamination and the laundry.

The chemical composition of them, as simulated for the characterization work, is shown in the Table I.

The evaporation concentrates must be stored at temperatures higher than 40 °C, in order to avoid the sulphate crystallization. As concern the other waste types, the wastes coming from the travelling belt filter are nearly solid , due to the relatively low water content after filtration. The laundry concentrates are in form of a very dense sludge composed of detergents and cotton wool water embedded.

In general for the simulated waste preparation the same chemicals used at the Italian power plants have been employed.

The overall production per year of the radioactive wastes is estimated to be the following:

Evaporation concentrates:	740 m^3
Powdex Ion Exchangers :	17.1 Tonn
Bead Resins :	66.4 Tonn
Filter Sludges :	13.8 Tonn
Laundry Concentrates :	1.4 Tonn

TABLE I. Chemical composition of the Montalto di Castro radioactive wastes.

Evaporation Concentrates	Na_2SO_4	25 %	w/w
	NaCl	3.5 %	--
	Carbonates,phosphates,silicates	0.5 %	--
Powdex ion exchangers	Dry Powdex	30 %	w/w
	Fe_2O_3 (Crud)	6 %	--
	H_2O	64 %	--
Bead Resins	Montedison Kastell C383 SM (Dry)	24 %	--
	" " A503 SM (Dry)	27 %	--
	H_2O	49 %	--
Travelling Belt Filter Sludges	Diatomeceous Earths	41.6 %	--
	PAO Termokimik	4.2 %	--
	PCH " "	4.2 %	--
	H_2O	50 %	--
Laundry Concentrates	Solka Floc	16 %	--
	Rolfon 230	4 %	--
	H_2O	80 %	--

In order to overcome the problems due to the transfer of some waste type, and to optimize the overall reduction factors, the waste solidification by the cementation plant will be operated on mixtures of the different waste types, excluding the laundry wastes, according to the following scheme:

- Cement + Evaporation Concentrates
- Cement + Evaporation Concentrates + Powdex Resins
- Cement + Evaporation Concentrates + Bead Resins
- Cement + Evaporation Concentrates + Filter Sludges
- Cement + Laundry concentrates

The cement that will be used for the solidification will be the Portland 425 or the Pozzolanic 325 type alternatively, both being easily available and reliable as concern the supply.

3. PRODUCT FORMULATION AND CHARACTERIZATION

The cement solidification of the radwastes described before requires a preliminary product formulation study and a careful product characterization, in order to comply from one side with the requirements that will be officially established by the Italian Regulatory Body (DISP) and presented in an other session of this Seminar, and from the other to optimize the volume reduction factors. Moreover, taking into account the need to store on site for longtime the conditioned wastes, as it is the Italian situation at present time , the characterization tests must be referred in our opinion to the actual Montalto di Castro site characteristics.

The cement mixture selection has been done by means of the evaluation of the experimental results obtained in the characterization work, using firstly the compressive strenght after 28 days as screening parameter. The other characteristics which have been studied are the following:

- temperature peak during the setting;
- freeze and thawing resistance;
- water immersion resistance;
- leaching resistance;
- free standing water;
- dimensional changes.

3.1 Compressive Strenght

The compressive strenght of the solidified blocks has been determined according to the UNI Italian Standard Test for the concrete compressive strenght evaluation /2/. Three cubic samples, 10 cm high, have been employed for each composition to be tested, and a Tecnotest compression apparatus has been used for the measurements. The compressive strenght determinations have been done, for each formulation, on samples cured for 28 days , before and after immersion for 90 days in the Montalto di Castro table water and in the Montalto di Castro sea water, as well as before and after 30 freeze and thawing cycles between -40 °C and +40 °C at 90% of relative humidity. In Table 2 the phisico chemical characteristics of the Montalto di Castro table water are shown.

TABLE 2. Phisico-chemical characteristics of the Montalto di Castro table water.

pH	6.60	Conductivity	1.180μScm^{-1}
CO_2	50 mg/l	Organics	23.07 mg/l
Suspended solids	52 mg/l	SiO_2	17 mg/l
Total hardness	350 mg/l	Ca	270 mg/l
Mg	80 "	Na	127 "
K	19.75 "	Fe	5.52 "
Mn	0.21 "	NH_3	N.D.
Cl	90 "	SO_4^{-2}	48.8 mg/l
SO_3^{-2}	1.0 "	NO_3^-	14.08 "
NO_2^-	0.191 "	PO_4^{3-}	N.D.

3.2 Peak temperature

The peak temperature is the maximum temperature value reached by the cement drum during the hardening phenomena. It is experimentally determined in laboratory by measuring and recording the maximum temperature reached by 1 liter of cement mixture placed in an adiabatic system. The adiabatic system simulates the real conditions existing at the center of the cement drums.

The peak temperature should be kept as low as possible, and in any case must be lower than 100 °C, in order to avoid the water evaporation and excessive shrinkages producing cracks in the cement blocks.

3.3 Leaching resistance

The leaching resistance has been determined according to the ISO Standard Test /3/, at room temperature and using as leachant the Montalto di Castro table water . The leachability determinations have been performed using Co^{58}, Sr^{85}, Cs^{137} as tracers, and only the most significant cement formulations have been leach-tested, being this investigation reserved to formulations already positively tested from the other point of views.

3.4 Free standing water.

The solidified cement blocks must be free of standing water after setting. The presence of free standing water has been controlled according to the following procedure /4/ : about 20 grams of cement mixtures are placed, just after preparation, in 25 ml sealed containers. After 1, 2 and 3 days the containers have been opened and the free standing water, not chemically bonded to the solid structure, if present, collected, weighed and recorded.

4. RESULTS.

4.1 Evaporation Concentrates.

This waste type has been solidified both in Pozzolanic 325 Cement (CPZ 325) and in Portland 425 Cement (CPT 425), in the following Waste/Cement ratios: 0.66, 0.8, 1.0.

In the Table 3 the results obtained in the characterization of these compositions are shown, while in the Fig.1 the compressive strenghts are reported.

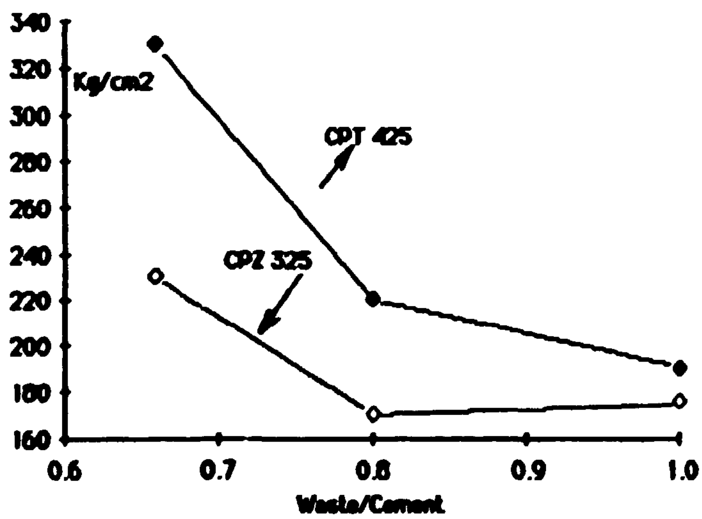

FIG.1 THE COMPRESSIVE STRENGHT OF EVAPORATION CONCENTRATES INCORPORATED IN PORTLAND AND POZZOLANIC CEMENT.

TABLE 3. Characterization results of the evaporation concentrates incorporated in Portland and Pozzolanic Cement.

Cement	CPZ 325			CPT 425		
Waste/Cement	0.66	0.8	1.0	0.66	0.8	1.0
Free water	No	No	No	No	No	No
R after 28 days	230	170	175	330	220	190
R at 90 d of sea water immersion	180	220	130	165	110	destr.
R at 90 d of table water immersion	200	220	120	270	125	destr.
R after 30 freeze-thawing cycles	170	ND	100	340	destr.	ND
% Vol.changes at 28d	+0.7	+0.2	+1.2	-0.3	-0.2	-0.1
Idem after 90d sea water immersion	+2.1	+1.0	+2.8	+3.7	+2.0	destr.
Idem after 90d table water immersion	+0.8	+0.5	+2.6	+3.4	+1.6	destr.
Idem after 30 freeze-thawing cycles	+0.75	--	+1.05	0	--	--
Temp. peak (°C)	78	67	64	84	75	73

The peak temperature evolutions in the cement mixtures during the setting process are shown as an example in the Fig.2 . From the curves shown in this figure it is possible also to evaluate the time required for the cement setting, and this information could be usefully integrated with the results of the Vicat measurements.

By evaluation of the results shown in Table 3, the Pozzolanic Cement CPZ 325, at the ratio waste/cement=0.8 , has been selected for the solidification of the evaporation concentrates, and only this mixture has been tested from the point of view of the leaching resistance. The results of the leaching resistance measurements are shown in the Fig.3 and the Fig.4 as referred to the leaching factors of Sr^{85}, Co^{58} and Cs^{137} and to the cumulative leached fractions of them respectively.

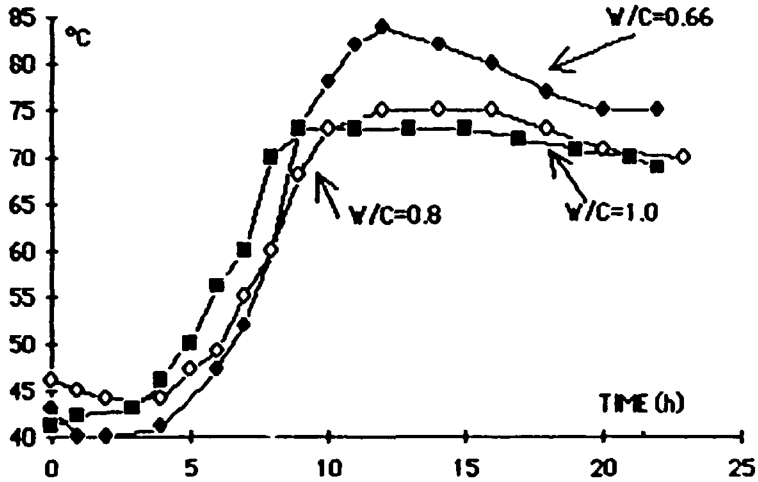

FIG. 2 PEAK TEMPERATURES OF THE CPT 425 INCORPORATING EVAPORATION CONCENTRATES.

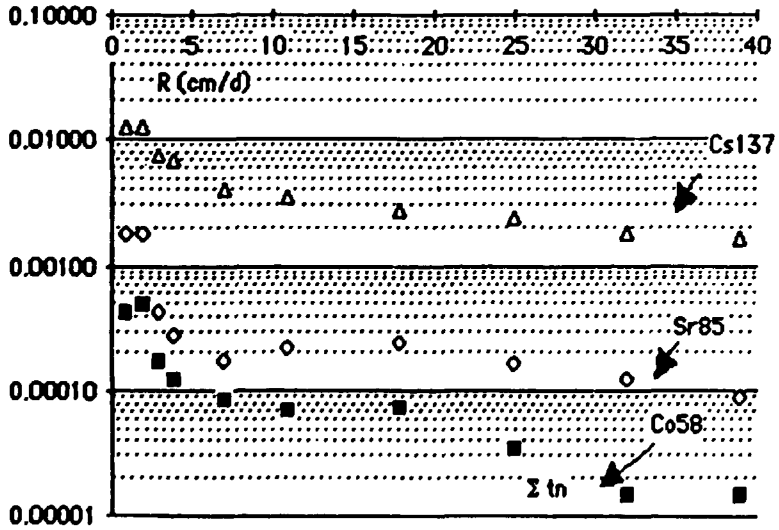

FIG.3 CS137, CO58, SR85 LEACHING FACTORS OF EVAPORATION CONCENTRATES INCORPORATED IN CPZ325 (W/C=0.8)

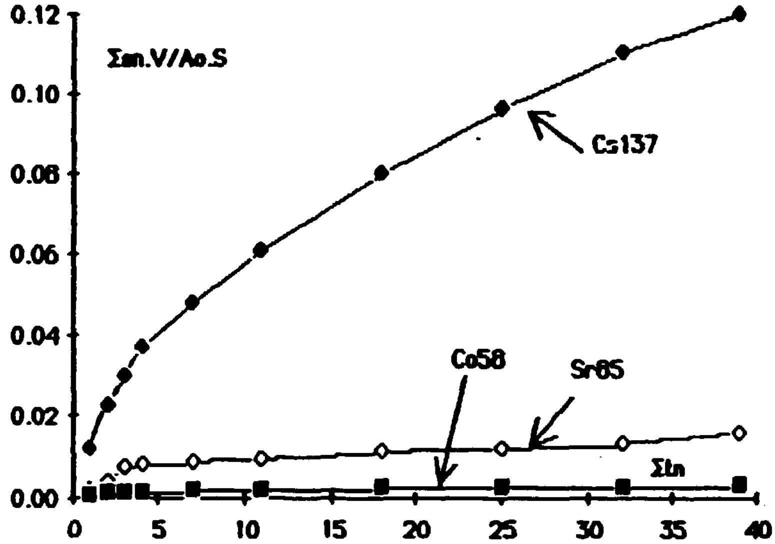

FIG.4 Sr85,Cs137 AND Co58 CUMULATIVE LEACHED FRACTIONS OF EVAPORATION CONCENTRATES IN CPZ325 (W/C=0.8).

4.2 Evaporation Concentrates + Powdex Resins

The solidification study of this waste type has been performed on samples prepared at Powdex/Cement ratios of 0.28 ; 0.42 and 0.56 , maintaining in any case the ratio Evaporation Concentrate/Cement = 0.8.

The samples corresponding to Powdex/Cement = 0.56 showed very poor mechanical properties just after preparation. The other formulations on the contrary have been characterized and the results of this work are shown in the Table 4.

The best formulation seems to be the pozzolanic cement CPZ325 incorporating the waste at Evaporation Conc./Cement=0.8 and Powdex/cement= 0.28 ratios. The other mixtures either show poor compressive strenght and large volume changes after water immersion, or completely disaggregate.

The leaching resistance behaviour of this solidified product, determined according to the procedure already described, is shown in the Fig.5 and Fig.6 as referred to the leaching factor R and to the normalized leached fraction respectively.

TABLE 4. Characterization results of Evaporation Concentrates + Powdex Resins incorporated in Portland and Pozzolanic Cement.

Cement	CPZ 325		CPT 425	
Evap.Conc./C	0.8	0.8	0.8	0.8
Powdex/C	0.28	0.42	0.28	0.42
Free water (1d)	No	No	No	No
Compressive Strenght at 28d (Kg/cm^2)	120	75	150	65
Idem after 90d sea water immersion	85	Destr.	Destr.	Destr.
Idem after 90d table water immersion	100	55	Destr.	Destr.
Idem after 30 freeze-thawing cycles	85	Destr.	Destr.	Destr.
% Volume change at 28d	+1.94	+7	+0.8	+8
Idem after 90d sea water immersion	+3.6	-	-	-
Idem after 90 d table water immersion	+3.6	+9.4	-	-
Idem after 30 freeze-thawing cycles	-1.1	--	--	--

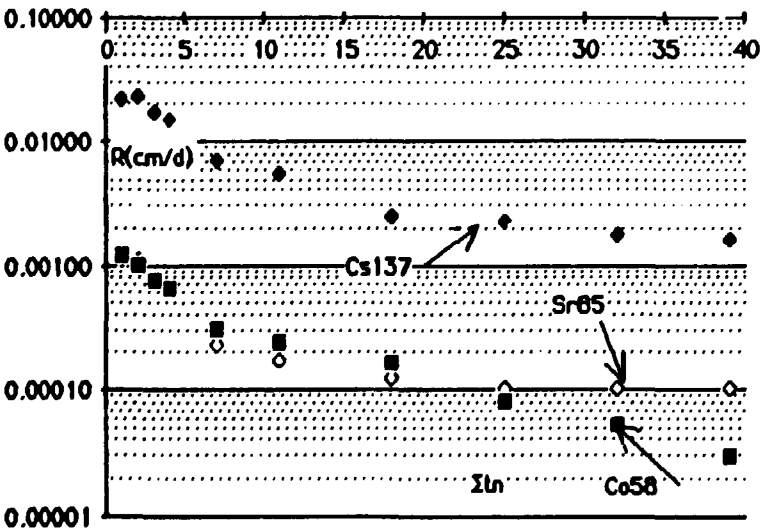

FIG.5 CS137, SR85 and CO58 LEACHING FACTORS OF EVAPORATION CONCENTRATES+POWDEX INCORPORATED IN CPZ325.

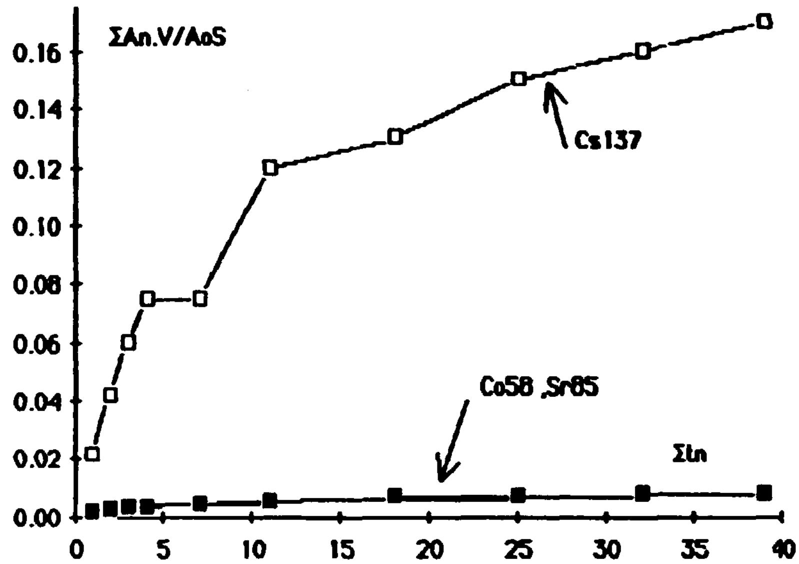

FIG.6 CS137,CO58 AND SR85 CUMULATIVE LEACHED FRACTIONS OF POWDEX INCORPORATED IN CPZ 325.

4.3 Evaporation Concentrates + Bead Resins.

A screening analysis, taking into account only the compressive strenght, has led to the results shown in Table 5. Four Bead Resins/Cement ratios have been considered : 0.2 ; 0.4 ; 0.6 ; 0.8 , for all of them the ratio Evaporation Conc./Cement being 0.55.

From the compressive strenght and volume changes results, the best mixture seems to be Bead Resins/Cement=0.2 . The characterization work, which is at present in progress, is being performed indeed only on this composition.

The leaching resistance of this solidified products is shown in Fig.7 and Fig.8, as referred to the leaching factors and to the cumulative released activity fractions respectively.

4.4 Evaporation Concentrates + Filter Sludges.

The mixture composed of diatomeceous earths and cement could be very difficult to be omogeneously stirred, if the final volume of the solidified product is to be maintained as low as poss!ble, and indeed a minimum

TABLE 5. Preliminary tests on bead resins incorporated in cement.

Evap.Conc./CPZ325	0.55	0.55	0.55	0.55
Bead Resins/CPZ325	0.2	0.4	0.6	0.8
Compressive Strenght at 28d (Kg/cm^2)	150	95	80	55
Volume change % at 28 d	+0.8	+1.5	+3.6	+7.6

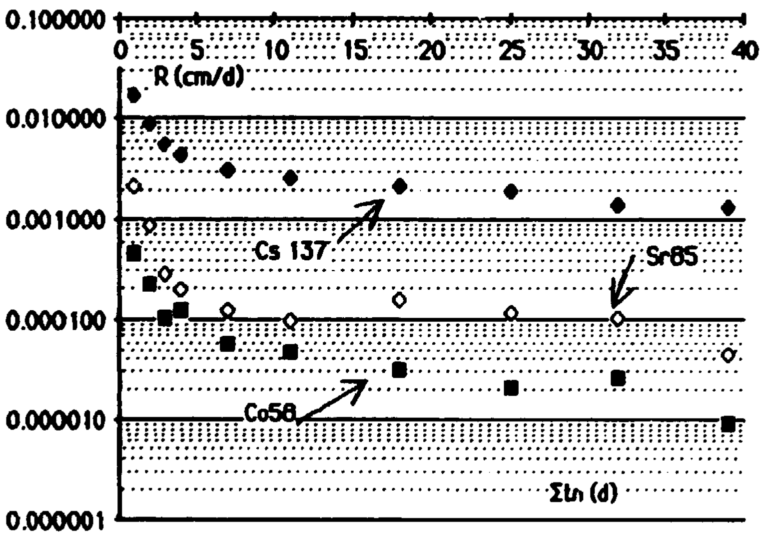

FIG.7 CS137, SR85 AND CO58 LEACHING FACTORS OF BEAD RESINS + EVAPORATION CONC. INCORPORATED IN CPZ325.

amount of additional water can be added. From this point of view the ratio Filter Sludges/Cement = 0.6 can be considered the maximum allowed to be employed. In any case the added filter sludges amounts could be in the ratios 0.3 and 0.6 (Waste/Cement w/w) when the Evaporation Conc./Cement ratio is 0.8.

The characterization results of these formulations are shown in the Table 6, from which it appears that the composition filter sludges/CPZ325 = 0.3 could be considered the best one, as it shows good

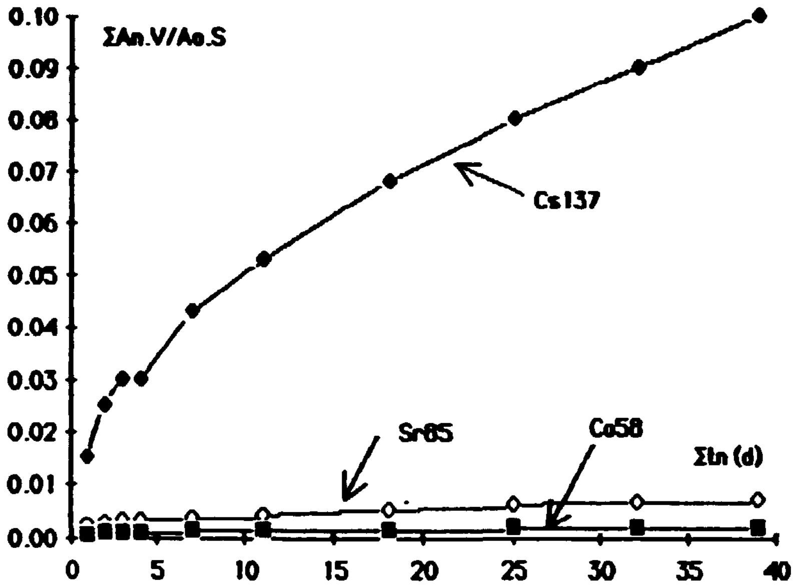

FIG.8 LEACHABILITY OF BEAD RESINS INCORPORATED IN CPZ325.

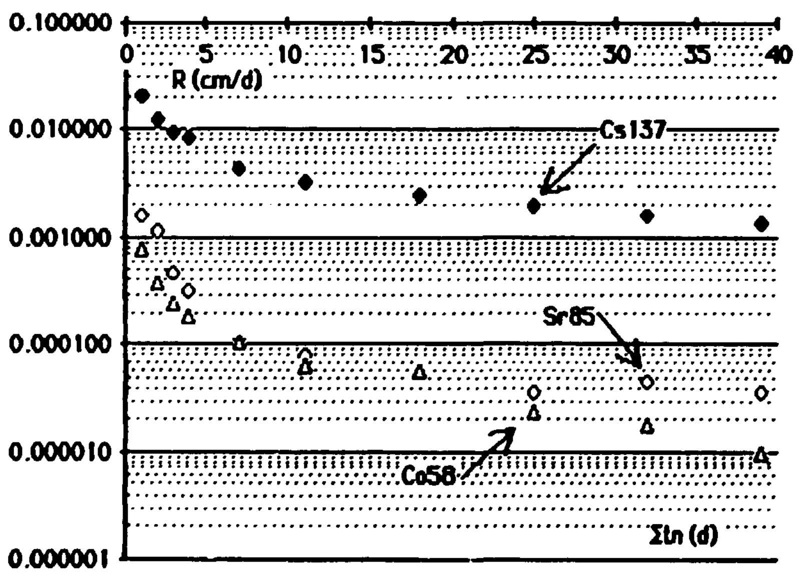

FIG.9 LEACHING FACTORS OF FILTER SLUDGES IN CPZ325.

compressive strenghts and minimum volume changes also after longtime water immersion.

The leaching behaviour of this composition is shown in the Fig.9 and

Fig.10 for the leaching factors and the cumulative leached fractions respectively.

The Co^{58} leaching release appears to be particularly low and, as it has been shown in the case of all other solidified wastes, it is much lower than Cs^{137}.

4.5 Laundry Wastes

The laundry wastes solidification by cementation appears to be very difficult from the process point of view, due to the high detergents and organics contents in the liquid. Moreover the waste contains a large amount of cotton and fabric fibers , which are water embedded and difficult to homogenize. Several types of antifoaming chemicals are being tested at present, and the characterization work is in progress.

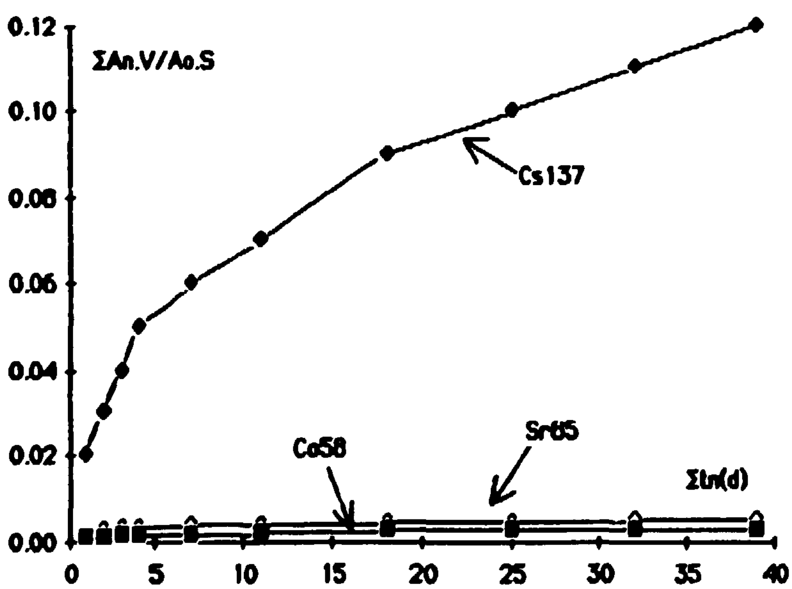

FIG.10 CUMULATIVE LEACHABILITY OF FILTER SLUDGES IN CPZ325.

TABLE 6. Characterization results of Evaporation Concentrates + Filter Sludges incorporated in Portland and Pozzolanic Cement.

Cement	CPZ 325		CPT 425	
Evap.Conc./C	0.8	0.8	0.8	0.8
Filter Sludge/C	0.3	0.6	0.3	0.6
Free H_2O at 1d	No	No	No	No
Compres. Strenght at 28d (Kg/cm^2)	155	120	190	170
Idem after 90d sea water immersion	180	175	90	ND
Idem after 90d table water immersion	210	170	175	ND
Idem after 30 freeze-thawing cycles	175	165	180	ND
% Volume change after 28d	+0.6	+1.2	-0.25	ND
Idem after 90d sea water immersion	+0.9	+0.9	+0.6	ND
Idem after 90d table water immersion	+1.4	+1.2	+1.3	ND
Idem after 30 freeze-thawing cycles	+0.7	+1.0	+1.5	ND

5. CONCLUSIONS.

Although a lot of informations do exist in the literature as concern the radwaste solidification by cementation, and although several research programs are going on also at international level on this subject, many difficulties arise when the waste management concern an integrated radwaste system. This is the case of a nuclear power plant, like the Montalto di Castro BWR plant for example, where several waste types should be mixed and conditioned together in order to optimize the overall operations and the volume reduction factors.

The technical informations required to solidify such radwaste mixtures either are not available in the literature, or do not exist at all.

Having these considerations in mind, the work presented in this paper intended to contribute to the enlargement of the radioactive waste treatment technical knowledge.

With reference to the obtained results , some considerations could be drawn :

- the pozzolanic cement appears to be better than the portland cement in all cases, as it is well known. In addition to this, the product amelioration due to the diatomeceous earth mixing could be mentioned;

- the sea water and the table water longtime immersion do not seem to produce much different effects, less than in the case of the Powdex wastes;

- the solidified product characteristics seem to be able to comply, at a first approach, with the requirements under consideration by the Italian Regulatory Body (DISP).

The work at present is still in progress and, mainly as concern the laundry wastes, some more time will be needed in order to be completed.

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Edito dall'ENEA, Direzione Centrale Relazioni.
Viale Regina Margherita 125, Roma.
Tipografia «La Casa della Stampa» - 00019 Tivoli (Roma)