Management of Radioactive Ashes after a ^{137}Cs Source Fusion Incident

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Abstract. As a consequence of an accidental fusion of a ^{137}Cs source in a stainless steel production factory , part of an oven and the refrigeration circuit were radioactively contaminated. This incident generated the following radioactive wastes: 40 m^3 of contaminated water, used in the cleaning process, 2000 T of ashes with low-medium activity level, and 150 T of fusion material. Reducing the volume of radioactive ashes to be managed or declassifying them would be very beneficial from the economical and radiological point of view. The aim of this work is the treatment of these ashes in order to declassify them as radioactive waste and, therefore, reduce waste volume to be disposed. Lixiviation has been found to be the most suitable treatment to remove ^{137}Cs from the ashes. This paper describes the experimental assays accomplished to establish the most appropriate extraction solution and the optimal procedure to extract the ^{137}Cs from the radioactive ashes.

1. Introduction

The origin of this work was the incident occurred in 1998 in ACERINOX, a stainless steel production company placed in Cádiz (Spain), where a ^{137}Cs source was accidentally melted in one of the ovens. As a consequence of this, several companies were radioactively contaminated: ACERINOX S.A.; PRESUR (*Planta Metalúrgica de Demostración de Prerreducidos del Sur S.A.*), which recovers metals from Acerinox powder; the inorganic industrial waste inertisation plant of EGMASA (*Gestión Medioambiental S.A.*) in Huelva (Spain), which inerts powder and slag from Acerinox; and the Inert Recovery Centre (IRC-9) in Huelva (Spain) where the inert products are disposed.

The *Nuclear Safety Council* (CSN) of Spain carried out an action plan to decontaminate the affected companies. Some of the radioactive wastes generated in this decontamination process were sent to El Cabril in Córdoba (Spain), a storage site managed by ENRESA where low and medium level radioactive wastes are disposed. The Acerinox incident did not have significant radiological consequences for either working personnel of the contaminated companies, or the rest of the population or the environment, since appropriate legal and technical procedures to reduce accident probability had been established before this incident.

In ACERINOX, the melting of the ^{137}Cs source contaminated the foundry material, the refrigeration circuit and part of one oven. The later decontamination process generated 40 m^3 of ^{137}Cs containing water with an average activity higher than 300 kBq/L, 2000 T of ashes of low-medium activity level, and 150 T of contaminated foundry material. The Chemical and Nuclear Engineering Department of the Polytechnic University of Valencia (UPV), in collaboration with LAINSA company, carried out the treatment of the contaminated liquid by means of a reverse osmosis plant [1,2]. By the application of this technology, around 36 m^3 of water were decontaminated. The remaining 4 m^3 were treated by evaporation, obtaining a final concentrate waste volume of 1 m^3.

In relation to the radioactive ashes, they are still stored at different places: at the stainless steel company (ACERINOX), at the inert material recovering centre (IRC-9) and at the low-medium radioactive waste storage site in El Cabril. Getting a volume reduction of the ashes to be managed or declassifying them as radioactive waste would be very beneficial from an economical and radiological point of view. The aim of this research is to determine the most suitable treatment of the ashes in order to declassify them and, therefore, reduce waste volume to be disposed in El Cabril. This paper describes the experiments carried out to assess the viability of lixiviation to accomplish ash decontamination.

2. Decontamination of radioactive solid wastes

2.1. Treatment options

The most common ways of decontaminating ^{137}Cs containing soils are the following:

- Adsorption with zeolites or diatomaceous earth. This treatment consists of incorporating the adsorbent, which is encapsulated in a semipermeable material, to the contaminated soil. The adsorbent has to be uniformly distributed along the soil so as to assure a good performance of the process [3]. This treatment is not very efficient and it is exposed to climate inclemency. Furthermore, radioisotope adsorption is much higher near the surface than in depth.

- Phytoremediation, which consists of using some plants that have the ability of selective adsorption of soil ions by the roots, incorporating the ions to the vegetative cycle of the plant [4,5]. This process has the disadvantages of being random, the plant turns into a radioactive waste, and it has been only applied to vegetative soils, not to other kind of systems.

- Lixiviation or solid-liquid extraction, which consists of extracting the radioisotope with an appropriate solvent. The radioisotope is incorporated to the liquid stream that must be treated later to remove it.

2.2. Selection of the most suitable treatment

After assessing the three alternatives described previously, it has been found that lixiviation is the most suitable treatment for ^{137}Cs removal from Acerinox radioactive ashes. The main advantages of this process are the following:

- Decontamination takes place in an industrial plant where performance parameters can be easily and immediately controlled.
- The process is easy to automate, which reduces working people exposition to radiation.
- Additives can be used to favour extraction and thus improve process production.
- The process can be integrated in a more complex system for treating liquid and solid radioactive wastes in a continuous way.

The main disadvantage of lixiviation is that it requires the use of good quality water. However, this drawback can be minimised by treating the liquid stream by means of membrane technology (reverse osmosis). This membrane treatment would allow the reusing of most of the water in the extraction process.

3. Experimental

3.1. Radioactive ashes characteristics

Before carrying out the lixiviation experiments, the radioactive ashes generated in the incident of ACERINOX were characterised microscopically. FIG. 1 shows a micrograph of a sample of the ashes that was obtained by a scan electronic microscope. It can be seen that they consist of a group of metallic granules of different sizes.

FIG. 2 shows a superficial microassay of the same ash sample, where it can be appreciate a significant presence of Fe, Zn and Cr in the radioactive ashes. The quantification of the different elements indicated in FIG. 2 can be seen in Table I.
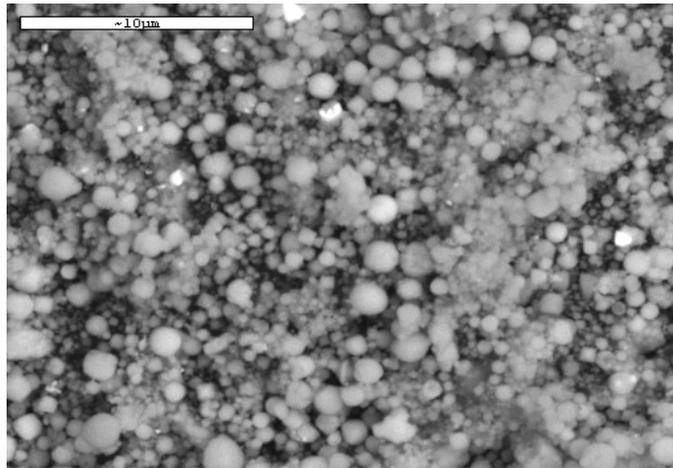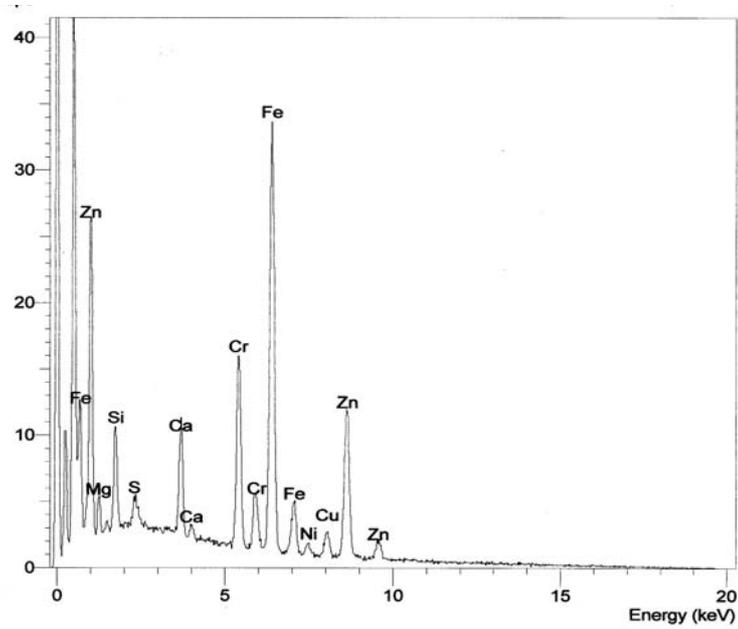
FIG. 1. Micrograph of the radioactive ashes

FIG. 2. Superficial microassay of the radioactive ashes

Table I. Element concentration in the radioactive ashes

Element	Concentration (%)
Ni	1,42
Mg	1,93
Si	3,53
Ca	4,17
Cu	4,37
Cr	12,38
Zn	34,21
Fe	38,00

3.2. Extraction solutions

Three different extraction solutions were tested in order to choose the most suitable one to remove ^{137}Cs from the ashes:
1. Distilled water
2. Bidistilled water
3. Demineralised water

These extractor solutions were selected bearing in mind the following criteria:
*   the high solubility of caesium in aqueous solutions,
*   the price of the solutions, which is relatively cheap in all cases,
*   the favourable characteristics from the point of view of health and safety.

The main characteristics of these extractors can be seen in Table II.

Table II. Characteristics of the extractors used in the experiments

Extractor	pH	Conductivity (μS/cm)
Distilled water	5,26	3,4
Bidistilled water	5,20	0,1
Demineralised water	3,95	0,1

Besides using these pure solutions, three additives were tested in some experiments in combination with the aqueous bases:
a) Oxygenated water
b) Citric acid (5 %)
c) ClCs (100 - 500 mg/l)

The aim of citric acid addition is to increase caesium solubility by reducing the pH value of the solution. The reason for having chosen this acid is because, in case it was the selected extractor and bearing in mind the later treatment of liquid stream by membrane technology, it is not aggressive to reverse osmosis membranes. ClCs was selected following the results obtained by Baeza et al. [6].

3.3. Experimental procedure

Two sets of experiments were carried out with the radioactive ashes. Firstly, some experiments at ambient temperature were performed in order to asses the extraction efficiency of each solution (with or without additive). This efficiency was measured by the radioactivity removal, and it was also qualitatively determined bearing in mind the following conditions:
*   Ease of mixing the ashes and the extractor solution.
*   Time required for settling.
*   Ease of separating the solid and the lixiviate after the extraction.

Once these experiments were finished, one solution (with or without additive) was selected as the most suitable one. The second set of experiments was carried out with that selected solution at different temperatures to define the optimal process conditions like temperature and extraction time.

FIG. 3 shows a general diagram of the experimental procedure followed in all the experiments.
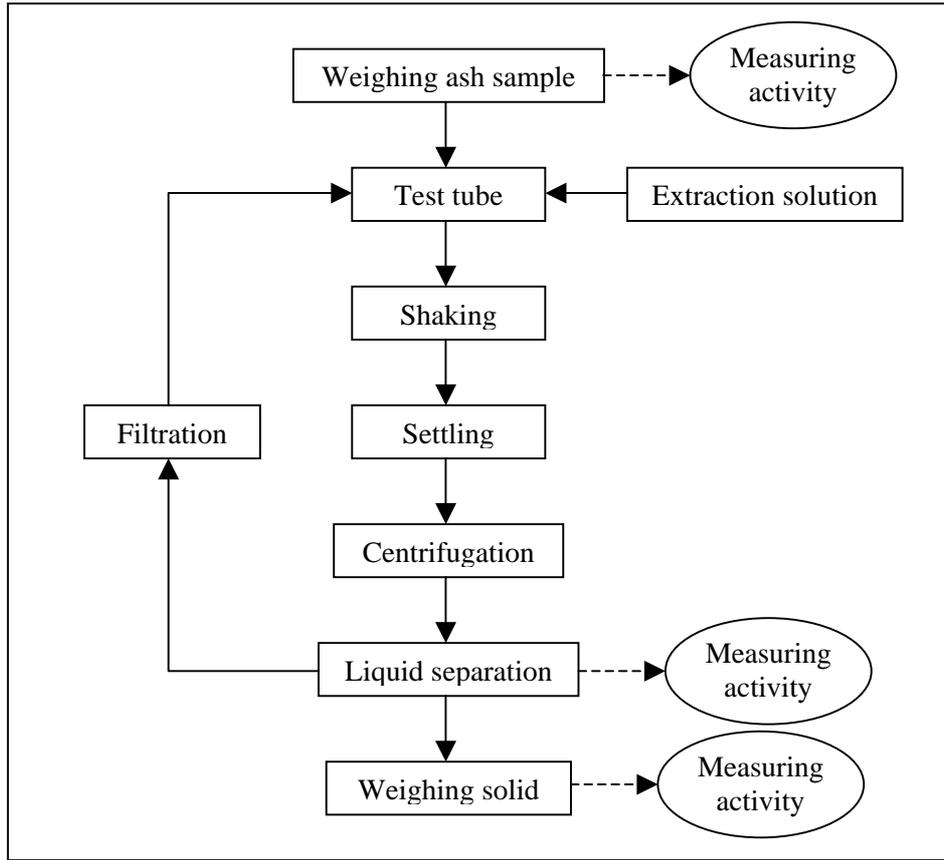
FIG.3. Experimental procedure for ^{137}Cs extraction from radioactive ashes

All the ash samples used in the experiments had a weight between 30 and 75 grams, with a radioactivity within the range 30 – 300 Bq/g. The radioactivity level depended on the quantity of caesium present in the sample, since it is not uniformly distributed in the ashes.

Radioactivity measurements were carried out at the Environmental Radiation Laboratory of the UPV, by means of a NaI scintillation solid detector activated with thallium and a multichannel analyser, both from SILENA company. Activity measurements were done to the ashes before the extraction process, and to the liquid and the solid after being separated (FIG. 3). The pH value and the conductivity of the separated liquid were also measured.

4. Results and discussion

4.1. Selection of the most suitable extraction solution

Table III shows the characteristics of some of the experiments carried out at ambient temperature to select the best extraction solution. Some of the results of activity removal obtained in these experiments can be seen in Table IV. The parameter E_{rel} represents the relative efficacy, calculated by the following expression:

$$E_{rel} = \frac{Act_{liqMi}}{Act_{0Mi}} \times \frac{Act_{0std}}{Act_{liqstd}} \tag{1}$$

where

Act_{0Mi}	Initial activity of the solid (ashes) before the extraction (Bq/g);
Act_{liqMi}	Activity of the lixiviate after the extraction (Bq/mL);
Act_{0std}	Initial activity of the sample of ashes taken as standard for comparison (Bq/g);
Act_{liqstd}	Activity of the lixiviate obtained from the standard sample (Bq/mL).

Table III. Characteristics of the first set of experiments

Sample	Initial activity (Bq/g)	Extractor solution
M1	168,4	Distilled water
M2	230,9	Demineralised water
M3	189,7	Distilled water with citric acid
M4	168,8	Bidistilled water
M5	192,6	Distilled water with ClCs
M6	262,4	Distilled water with oxygenated water

Table IV. Radioactivity removal and relative efficacy in the first set of experiments (std = standard)

Sample	1st lixiviate		2nd lixiviate		3rd lixiviate		4th lixiviate		ΣE^{rel}
	Bq/mL	E_{rel}	Bq/mL	E_{rel}	Bq/mL	E_{rel}	Bq/mL	E_{rel}	
M1 (std)	22,67	1,00	7,47	1,00	3,96	1,00	5,19	1,00	4,00
M2	19,81	0,64	8,97	0,87	4,58	0,84	4,54	0,64	2,99
M3	25,98	1,02	12,87	1,53	1,95	0,44	4,04	0,69	3,68
M4	20,47	0,90	13,47	1,80	4,05	1,02	9,33	1,79	5,51
M5	31,58	1,22	14,58	1,71	3,79	0,84	11,09	1,86	5,63
M6	21,92	0,62	12,35	1,06	2,89	0,44	5,69	0,70	2,82

According to the presented results, it can be said that the best extraction solutions with regard to activity removal were distilled water with ClCs and bidistilled water, with a total relative efficacy values higher than 5,50 in both cases, after four extractions. The distilled water with ClCs was chosen as the most suitable extraction solution for ^{137}Cs removal since its decontamination factor was the highest one. Several experiments with the selected extractor proved that the best concentration value of ClCs to be added is within the range 100 – 200 mg/L, and that it is much more effective in the first extraction, so it is not worth its addition in the following extraction stages.

Another conclusion of these experiments is that 4 extraction stages are enough, within the tested radioactivity range, to remove most of the original activity from the ashes (efficiency around 90%). The addition of another stage is unnecessary because the residence time would be too long for a very small radioactivity removal. An appropriate length of each extraction stage is around 5 hours, resulting in a total extraction length of 24 hours, approximately.

Some experiments were performed with the selected extractor and with/without the addition of citric acid in order to assess the possible improvement of the extraction due to the additive. Table V shows the characteristics of two of the experiments carried out, and Table VI presents the results of those experiments.

Table V. Characteristics of the experiments with/without citric acid

Sample	Initial activity (Bq/g)	Extractor solution
M7	46,4	Distilled water with ClCs
M8	172,6	Distilled water with ClCs and citric acid

Table VI. Radioactivity removal and relative efficacy in the experiments with/without citric acid

Sample	1st lixiviate		2nd lixiviate		3rd lixiviate		4th lixiviate		ΣE^{rel}
	Bq/mL	E_{rel}	Bq/mL	E_{rel}	Bq/mL	E_{rel}	Bq/mL	E_{rel}	
M7 (std)	8,52	1,00	7,59	1,00	1,84	1,00	0,99	1,00	4,00
M8	22,99	0,723	29,90	1,06	8,19	1,19	5,22	1,42	4,39

According to the results of Table VI, the addition of citric acid improves radioactivity removal. However, the experimental process resulted much more complicated since the addition of citric acid forms a kind of emulsion that is quite difficult to filtrate and manage. As a consequence of this, the addition of citric acid was discarded.

4.2. Temperature influence

To finish the experimental procedure, one experiment at different temperature was performed in order to assess the influence of this parameter in radioactivity removal. The experiment was carried out using distilled water with ClCs as an additive and it began at a temperature of 20ºC, which was increased to 30ºC throughout the assay. The extraction evolution was followed by measuring the conductivity, since it is proportional to the activity and it is much quicker and easier to measure [7]. FIG. 4 shows the results of this experiment.
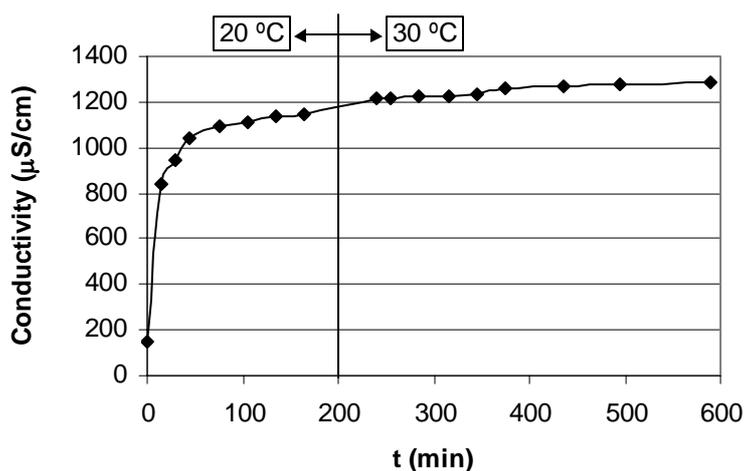

FIG.4. Conductivity evolution in the experiment at different temperatures

It can be seen in this figure that the tendency of the curve at 30ºC is very similar to the one at 20ºC, which means that temperature increase in that range does not significantly affect ^{137}Cs extraction. Therefore, extractions will be done at ambient temperature.

5. Conclusions

According to the obtained results, the following conclusions can be stated:

- The most suitable solution to carry out ^{137}Cs extraction from Acerinox radioactive ashes is distilled water with ClCs as an additive in the first extraction, with a concentration within the range 100-200 mg/L.
- The bidistilled water performs also successful results as extractor, always adding ClCs in the first stage.
- The addition of citric acid is not interesting from the point of view of solid filtration.
- Four extraction stages are enough to remove around 90% of the original activity, when it is below 60 Bq/g. The length of the complete extraction process is estimated around 24 hours.
- Temperature increasing does not improve ^{137}Cs removal, so it is better to work at ambient temperature.

Acknowledgements

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