

TECHNIQUES OF TREATMENT OR CONDITIONING FOR WASTE ARISING FROM ^{131}I PRODUCTION

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ABSTRACT

Distillation, evaporation/crystallization, direct immobilization and some chemical processes like precipitation and reduction were studied as techniques of treatment or conditioning for waste arising from ^{131}I production. The description of all techniques studied, as well as evaluation and discussion of the results are presented.

1. INTRODUCTION

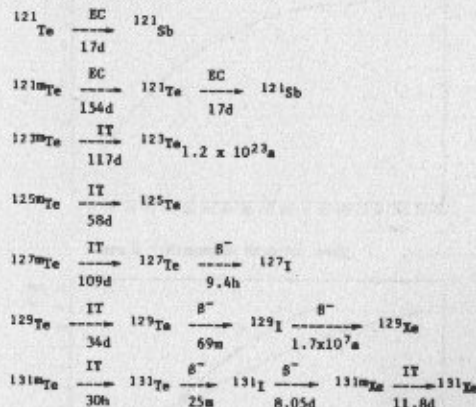
The growing demand of radioactive isotopes of iodine, particularly the ^{131}I , has been justified by its large use in medicine, mainly in the field of thyroid diagnostic and therapy. Due to this fact, ^{131}I has become one of the most important isotopes in radioisotopes production centres (1).

The nuclear processes for the production of ^{131}I involve, either the irradiation of uranium with the recovery of ^{131}I from the resulting fission products, or extraction of ^{131}I from irradiated tellurium.

More frequently, the target elements utilized are tellurium compounds (2), and after irradiation two extraction methods are used to separate the ^{131}I : dry distillation, in which the iodine is distilled directly through the heating of irradiated target and wet method, which adjust chemically the irradiated target for later distillation.

At the Radioisotopes Production Department of Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP) the ^{131}I is produced by thermal neutron irradiation of tellurium oxide (TeO_2) for 252 hours (8 hours per day), in a neutron flux of $10^{13} \text{ n.cm}^{-2}.\text{s}^{-1}$. The resulting isotopes from this irradiation and their

respective decay products are:



After irradiation, the ^{131}I is extracted by wet method using the following process: TeO_2 is dissolved in a sodium hydroxide (NaOH) solution, oxidized to tellurate (TeO_4^{2-}) with hydrogen peroxide (H_2O_2). The H_2O_2 in excess is decomposed using molybdate (MoO_4^{-2}). The resulting suspension is acidified and dissolved with sulphuric acid (H_2SO_4), and then the ^{131}I is

distilled.

For each processed batch, one litre of radioactive waste is generated, totalizing approximately 100 litres per year. The waste is composed basically of tellurium isotopes, residual iodine and molybdate ions in a 5M sulphuric acid solution, with an activity concentration of 259 GBq.L⁻¹ at the moment of collection.

Nowadays, the procedure adopted to treat this waste is collection and storage into 30 litres polyethylene bottles for decay. The time to the nuclides reach the discharge limits established by federal radiological regulations is, at least, 5 years after complete filling of the bottles. After decay, the waste is then released to the environment through controlled discharge into the sewage system.

2. ALTERNATIVES FOR TREATMENT OR CONDITIONING OF THE WASTE

In spite of the waste volume be small, its chemical composition (acid liquid form) becomes its handling, transportation and storage risky.

Keeping this reason in mind, it was performed a study to evaluate alternatives techniques for treatment or conditioning of this kind of waste, aiming at adopting safer form of storage and in this way decreasing the contamination risk. The alternatives studied were: sulphuric acid distillation, immobilization in cement or bitumen, ammonium telurate precipitation, telurate ions reduction, evaporation/crystallization, gypsum matrix and delay and decay.

2.1. Sulphuric acid distillation

Considering that the waste is composed mainly by 120 g of solid radioactive material, suspend or dissolved in one litre of 5M sulphuric acid solution, the first treatment technique was carried out through simple distillation of the waste. Water and sulphuric acid were obtained as distilled and the radioactive material as a dry product in conditions to be stored. An iodine retention system was necessary due the occurrence of iodine volatilization.

During the assays cracks and breaking occurred in the glass apparatus, caused by localized superheating. Due to these reasons stainless steel AISI 316 and 304 were assayed, aiming at substituting the glass apparatus. The results showed that stainless steel AISI 316 presented a good corrosion resistance at room temperature, but under operation conditions both of them were inadequate.

2.2. Immobilization in cement or bitumen

To use the techniques of radioactive waste immobilization under development at Nuclear Fuel Cycle Department of IPEK-CNEN/SP (cementation and bituminization), it was necessary a pH adjustment of the waste. Through this adjustment the corrosion problems were minimized and the residual iodine behaved itself like non volatile salts (NaI, NaIO₃), hindering volatilization.

On the other hand, the sodium sulphate concentration (340 g.L⁻¹) limited the amount of waste to be immobilized. This concentration was many times higher than the incorporation limit for cement matrix (3), and if bitumen was used as matrix, the hygroscopicity of the Na₂SO₄ would make the final product an unsafe form in water presence.

2.3. Ammonium telurate precipitation

Aiming at obtaining a crystalline precipitate, the waste was neutralized with ammonium hydroxide (NH₄OH), followed by ethanol addition until total crystallization. In this process, samples were analysed by γ ray spectrometry before and after the assays, in order to evaluate decontamination factor (D.F.).

The average D.F. obtained was 33, the volume reduction factor ($V_{\text{initial}}/V_{\text{final}}$) was 2.5 and the main problems occurred during the assays were:

- the precipitate adhered to the glassware wall;
- the filtration was very slow;
- the reagents used, flammable and volatile, increased the handling risks.

2.4. Telurate ions reductions

Taking into account that in the process of ¹³¹I separation by wet method, the irradiated tellurium oxide is oxidized to telurate, the waste was treated using reducing agents (Sn⁺⁺ or Fe⁺⁺), in order to obtain solid tellurium (Te⁰) as product.

(a) Sn⁺⁺ - by the addition of Sn⁺⁺ to the waste (acid medium), the telurate ions were reduced to Te⁰.

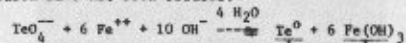


It was obtained Te⁰ as a black and fine precipitate, but with high Sn⁺⁺ consumption, probably due to the presence of molybdate ions (5).

The D.F. and the volume reduction factor were 574 and 1.5 respectively.

(b) Fe⁺⁺ - Aiming at improving the D.F. it was used Fe⁺⁺ in alkaline medium.

In these conditions iodine volatilization is avoided and Te⁰ and iron hydroxide (Fe(OH)₃) are obtained as product. Iron hydroxide is a colloid that acts as a carrier, able to carry out the telurate ions that for any reason have not been reduced.



A great volume of colloidal precipitate with high water content was obtained giving rise to an increase in the waste volume and even using iron hydroxide as carrier the D.F. was 219, lower than that obtained with Sn⁺⁺.

In short, the volume reduction factors were low or even null (case of the Fe⁺⁺), the reagents consumption was high (case of the Sn⁺⁺) and the difficulties found in the filtration process were the same of the precipitation assays.

2.5. Evaporation/crystallization

Evaporation has been used profitably as treatment technique to large volumes of low- and intermediate-level liquid waste, although it can be also recommended on small scale (6). The main attractiveness of the process is its high volume reduction factor.

Evaporator bottom is usually solidified in cement or bitumen matrices, but in the present case, solidification is not recommended due to the high content of sulphates.

On the other hand, as it is well known, the interim storage of tellurium salts as dry powder is acceptable, and so, studies about evaporation until complete crystallization of the waste salt were realized.

Preliminary screening tests showed that the technique was promising as treatment method of ¹³¹I production waste. Based on these results it was used one evaporator/crystallizer prototype (7), showed in Figure 1, to execute some tests.

2.5.1. Cold testing. Cold testing were made in order to verify tightness, experimental evaporation rate etc of the equipment. They can be divided in two phases: (a) With water: aiming at checking if the experimental evaporation rate agrees with the theoretical one (7 litres per hour) and to verify eventual leakages in the joints, this first test was done using batches of 14 litres of water.

There was no leakage in the equipment and the experimental evaporation rate achieved was 4.2 L.h⁻¹. Figure 2 shows the evaporation curve obtained.

(b) With sodium sulphate: for these tests, it was uti-

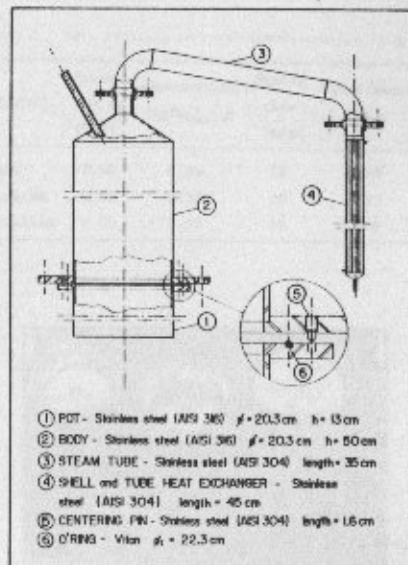


Figure 1 - Design of the evaporator/crystallizer prototype

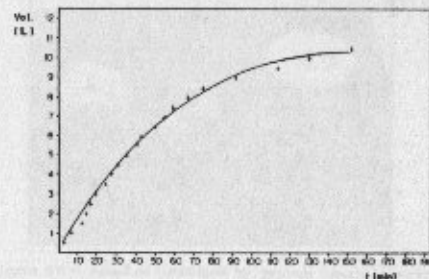


Figure 2 - Evaporation curve for water.

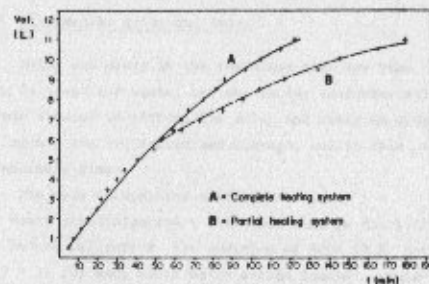


Figure 3 - Evaporation curve for sodium sulphate solution

lized a simulated waste (sodium sulphate solution with 340 g.L^{-1} concentration). One of these tests was carried out with complete heating system (7.5 kW) and the other with partial heating system (7.5 kW at the beginning and 2.5 kW after half of the volume was distilled), in order to compare the evaporation rate and volume reduction. The volume reduction factor obtained was 2 for both of them. The evaporation rate was around 5.5 L.h^{-1} for that one carried out with complete heating system and 3.7 L.h^{-1} for the test with partial heating system. The evaporation curves are shown in Figure 3.

2.5.2. Cold testing problems. The theoretical volume reduction factor was achieved and the evaporation rates were lower than the theoretical one. This result could be improved with a better insulation.

On the other hand, body - pot coupling and encrustations were the main problems found during the tests. The coupling was made difficult by any misalignment of the pot, what can lead to leakages in the process and the encrustations gave rise to three undesirable effects:

- (a) After evaporation, the pot remains adhered to the body, being necessary to apply a mechanical effort to make the body - pot uncoupling.
- (b) A thin salt layer remains adhered to the body and can contaminate the system when the uncoupling occurs.
- (c) A hard salt layer remains over the coupling flanges of the body (making difficult a perfect coupling of a new pot) and of the pot (making difficult the sealing).

Figures 4 - 9 show the evaporator/crystallizer and some encrustations occurred during the tests.

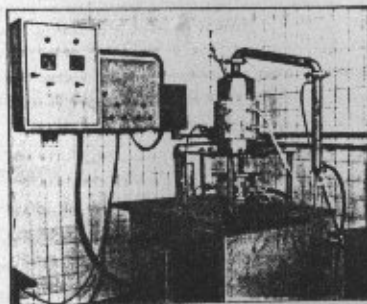


Figure 4 - General view of the equipment

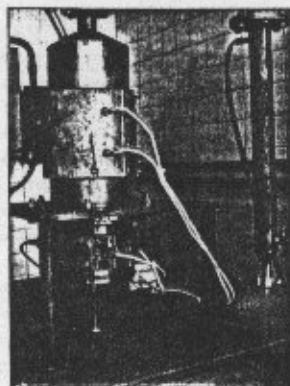


Figure 5 - Pot-body coupling

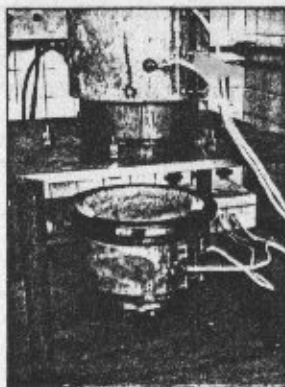


Figure 6 - Uncoupled pot after operation



Figure 7 - Concentrate waste



Figure 8 - Salt layer on the body

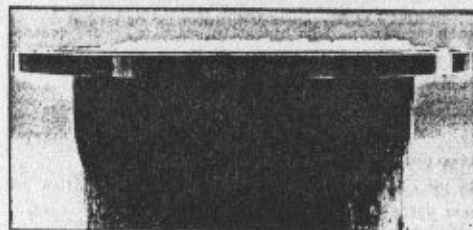
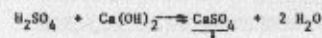


Figure 9 - Salt layer remaining over the coupling flange

2.6. Gypsum matrix

Considering that the waste has in its composition a great amount of sulphuric acid, assays were performed using calcium hydroxide (Ca(OH)_2), commercially named lime, in order to form a product that had the characteristics of a solid matrix.

The fundamental reaction of the process is



To carry out the assays, it was used a reactor provided with mixer and cooling jacket. Three different types of lime were used: light, hydrated and quicklime (utilized in civil engineering). Data referring to lime types and the process in which they were utilized are shown in Table 1.

The products of these assays were white, slightly soluble in water, have low mechanical resistance, are brittle and a loose salt crust remains in samples surface. Some samples are shown in Figure 10.

Table 1 - Data referring to waste immobilization in gypsum

Ca(OH)_2	Price per kg (US\$)	Consumption (Kg/Lwaste)	Mixing time (min)	Temperature (K)
light	0.60	0.36	10	353
hydrated	0.50	0.38	10	353
quicklime	0.05	0.98	10	363

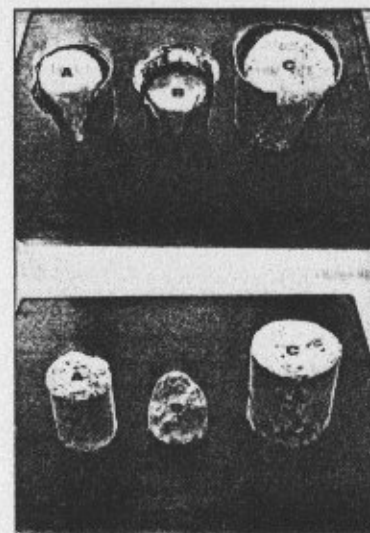


Figure 10 - Samples produced by gypsum immobilization (lime used: A - light; B - hydrated; C - quicklime)

2.7. Alternative delay and decay

Delay and decay is the technique that has been used to treat the waste, but due to its characteristics, it was studied an alternative delay and decay in order to improve the collection and storage, and in this way to minimize risks.

The main alterations carried out were:

- (a) Waste alkalization - The waste must be alkalized before collection. The addition of NaOH 10 N until pH 9 - 11 for each waste batch avoids iodine volatilization and minimizes chemical attacks. NaOH was chosen because this compound is commercially available at low cost.

(b) Bottle capacity - The capacity of the bottles to collect and to store the waste must be higher than that used till now (30 L). The use of a bottle with higher capacity decreases the total number of bottles and number of changes per year, without increase the decay or handling time. Exposures rates at 1 metre were calculated for 30 L and 180 L loaded bottles, supposing that the sources were punctual and without considering self shielding effects. Although the 180 L bottle exposure rate be higher, the accumulated dose for operation staff during one year is lower, due the number of times that the bottles are handled.

Based on the values showed in Table 2, it was chosen a 180 L bottle to collect and store the waste, in order to facilitate the waste management and minimize accumulated doses and risks in handling.

(c) Storage site - When the bottles are full, they must be stored at least for 5.3 years, permitting decay to the levels established by federal radiological regulations (8).

The site to store the bottles must be provided with a retention tray to minimize contamination in case of some leakages.

Table 2 - Comparative data between 30 L and 180 L bottles used for waste collection and storage

Bottle capacity (L)	Decay time (year)	Exposure rate $C.Kg^{-1}.h^{-1}$	** total number of bottles	Unitary price (US\$)
30	5,1	$1,1 \times 10^{-1}$	30	65,08
180	5,3	$2,1 \times 10^{-1}$	5	120,00

* Exposure rate of loaded bottles considering them as punctual sources without self shielding effects.

** Minimum number of bottles necessary to store the neutralized waste, until some of them could be released.

3. COMMENTS

Except immobilization in cement or bitumen, all the techniques are feasible, each one of course, with advantages and disadvantages. The choice of one technique can vary according to the necessities and resources of each research centre, and depending upon the selected technique, additional studies can be performed in order to improve it.

At IPEN-CNEN/SP it was established that the waste

arising from ^{131}I production must be treated by the alternative delay and decay, due to the waste volume, half life of the present nuclides and storage facility existent.

In order to describe some informations that can be useful to evaluate the techniques or to conduct further studies in this field, the alternative techniques were divided according to their similar characteristics.

(a) Ammonium tellurate precipitation and tellurate ions reduction.

Considering that the sulphate ions have the same chemical behaviour of the tellurate ions, it follows that the low volume reduction and decontamination factors are due to its presence in the waste. Therefore any procedure that decrease the sulphate ions interference will result in an increase of these factors.

Reducing agents, like hydrazine and zinc, under controlled temperature, can be also utilized to improve these factors, and borosilicate glass filters can be used to decrease the difficulties of the filtration process.

(b) Sulphuric acid distillation and Evaporation/Crystallization.

In the case of sulphuric acid distillation, studies about different types of stainless steel can be made aiming at obtaining a material with higher corrosion resistance.

Some alterations in the operation conditions (lower pressure) can be studied, since in this conditions will be achieved lower temperatures, decreasing the corrosion attacks.

The main attractiveness of this technique are the possible reutilization of the tellurium compounds and the recovering of sulphuric acid as by-product.

In the case of evaporation/crystallization, some project alterations can be made in order to decrease the encrustation difficulties and a conjoint treatment with other waste streams (with lower salt concentration) can also improve the technique.

(c) Immobilization in cement or bitumen and Gypsum matrix.

The increase in the waste volume and the short half life of the nuclides present in the waste, do not justify the immobilization in cement or bitumen, therefore this technique is not recommended.

On the other hand, the use of lime to immobilization, does not increase the waste volume and, although the gypsum does not present excellent characteristics as waste matrix, its properties are enough to make the waste a solid form for the necessary time. This fact

makes the handling, transportation and storage safer than in liquid form.

(d) Alternative delay and decay

The bottle capacity has to be selected depending on the waste volume and existent storage facility, in order to minimize the exposure rate and contamination risks. Low cost is the main attractiveness of this technique.

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REFERENCES

- 1 - PAGANO, C., Produção de iodo 131 em reatores de pesquisa, a partir de telúrio elementar. São Paulo, Instituto de Energia Atômica, 1976. (IEA-DT-007).
- 2 - INTERNATIONAL ATOMIC ENERGY AGENCY, Radioisotope production and quality control. Vienna, 1971. p.237-248 (Technical Report Series 128).
- 3 - INTERNATIONAL ATOMIC ENERGY AGENCY, Conditioning of low- and intermediate-level radioactive wastes. Vienna, 1983. p.84-119 (Technical Report Series 222).
- 4 - SAWAKUCHI, R.S. Avaliação dos resíduos no Instituto de Energia Atômica. Critérios para eliminação e estudo de técnica para seu tratamento. São Paulo, 1978. Dissertação de mestrado, Instituto de Energia Atômica. (IEA-DT-068).
- 5 - DALAQUA JR., L.; DELLAMANO, J.C. Conditioning liquid waste from I-131 production by natural Y_{90} neutron irradiation. In: INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES. Contribution of IPEN-CNEN/SP to the seminar on management options for low- and intermediate-level wastes in Latin America (IAEA). São Paulo 1987. p. 127-129 (Publicação IPEN 112).
- 6 - INTERNATIONAL ATOMIC ENERGY AGENCY. Management of radioactive wastes produced by users of radioactive material. Vienna, 1985. p.20-24 (Safety Series 70).
- 7 - GROSCHÉ FV, C.E.; DELLAMANO, J.C.; DALAQUA JR., L. Design of an evaporator/crystallizer for radioactive liquid waste treatment. In: INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES. Contribution of IPEN-CNEN/SP to the seminar on management options for low- and intermediate-level wastes in Latin

America (IAEA). São Paulo, 1987. p.70-75 (Publicação IPEN 112).

- 8 - COMISSÃO NACIONAL DE ENERGIA NUCLEAR. Gerência de rejeitos radioativos em instalações radioativas. Rio de Janeiro, Nov. 1985. (CNEN-NE-6.05.85).