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DEVELOPMENT OF A NEW PROCESS FOR RADIOACTIVE DECONTAMINATION OF PAINTED CARBON STEEL STRUCTURES BY MOLTEN SALT STRIPPING

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ABSTRACT

The main practical difficulty associated to the task of the dismantling and decommissioning of the old Nuclear Fuel Cycle facilities of the IPEN has been the large amount of radioactive waste generated in the dismantling operations. The waste is mainly in the form of contaminated carbon steel structures. In the IPEN, the presence of contamination in the equipments, structures and buildings, although restricted to low and average activity levels, constituted an important concern due, on one hand, to the great volume of radioactive wastes generated during the operations. On the other hand, it should be outstanding that the capacity of stockpiling the radioactive wastes in IPEN found been exhausted. Basically, for the dismantling operations of the units, the main radionuclides of interest, from the radioprotection point of view, are U of natural isotopic composition and the thorium-232. Some attempts were done to reduce the volume of those wastes. Nevertheless, the only decontamination available methods were chemical methods such as pickling/rinsing treatments employing acid solutions (with nitric or citric acids) and alkaline solutions (sodium hydroxide). Different concentrations of such solutions were tested. The results obtained in the employed processes were not satisfactory. Ultrasonic equipment available was also employed in an attempt to increase the efficiency of decontamination. The choice of a coating removal process for radioactive material in the form of carbon steel pieces must have into account, among other factors, that it is not necessary a high quality of finishing, since the main objective is the release of the material as iron scrap. This paper describes the development of a new method for surface decontamination by immersion in molten salt baths.

1. INTRODUCTION

During the years 70 and 80, IPEN built several facilities in pilot scale, destined to the technological domain of the several stages of the Nuclear Fuel Cycle. In the nineties, radical changes in the Brazilian nuclear policy determined the interruption of the research activities and the plant-pilot's shut-down. Elapsed more than ten years from the closing of the activities, it was evident that there would not be continuity in the R&D and that it would be necessary to find a solution for the problem. Since then, IPEN has faced the problem of the dismantling and decommissioning of their Nuclear Fuel Cycle old facilities. Those facilities had already played their roles of technological development and personnel's training, with transfer of the technology for institutions entrusted of the scale up of the units. Most of the pilot plants interrupted the activities more than ten years ago. The decommissioning strategy [1] for the Nuclear Fuel Cycle old facilities follows an approach of advancing gradually in dismantling, since the resources and technical conditions are available. Some facilities have demanded special attention, requiring preliminary operations of treatment of retained materials and/or wastes.

The closing of the program implicated, on one hand, in the reduction of the nuclear activities and, on the other hand, in new opportunities to IPEN, participating in different research programs of strategic importance to Brazil. In the last years, a change has been observed in the profile of IPEN, which was predominantly nuclear, for an extensive field of researches, mainly in the areas of new materials, alternative energies and environment. Besides the space busy for the old units constituted a valuable resource, since it could be used for other institutional priorities and national programs, there were also several concerns as, for instance, the need of constant surveillance, the possibility of deterioration of equipments and structures, the safety, and last but not least, the progressive personnel loss, for retirements and transfers for other programs.

2. PROBLEMS RELATED TO THE DECOMMISSIONING OF THE IPEN´S PILOT PLANTS

The main practical difficulty associated to the task of the dismantling and decommissioning of the old Nuclear Fuel Cycle facilities of the IPEN has been the large amount of radioactive waste generated in the dismantling operations. The waste is mainly in the form of contaminated carbon steel structures. In the IPEN, the presence of contamination in the equipments, structures and buildings, although restricted to low and average activity levels, constituted an important concern due, on one hand, to the great volume of radioactive wastes generated during the dismantling operations. On the other hand, it should be outstanding that the capacity of stockpiling the radioactive wastes in IPEN found been exhausted. Basically, for the pilot plant’s dismantling operations, the main radionuclides of interest, from the radioprotection point of view, are U of natural isotopic composition and the thorium-232.

One problem detected during the nuclear fuel cycle dismantling activities already performed in the IPEN was the difficult of treatment of contaminated painted carbon steel structures. In the IPEN’s Experimental Facilities and Pilot Plants it was very common the use of perforated carbon steel structures, as shown in the figure 1 and 2. During the dismantling and decommissioning activities, a large amount of radioactive waste was generated, mainly in the form of contaminated steel structures. This material has been characterized as low level waste but, in accordance with the CNEN’s standards, it is necessary to put all material in special drums or steel boxes. The contamination found is superficial. However, the total waste amount is in the several tons magnitude, requiring a lot of drums and work for waste conditioning. The structures present superficial contamination, as consequence of the presence of the following radionuclides: uranium of natural isotopic composition (practically, only ^{238}U and 0,7% of ^{235}U) and/or thorium compounds (^{232}Th).

The operational conditions of the fuel cycle pilot plants were deleterious to structural materials, submitting them either to a chemically aggressive environment as well as to radioactive liquids and dust that formed deposits in the structure surfaces. The chemicals employed, like acids, caused accelerated corrosion of the carbon steel. To protect the structures and to increase their useful lives, it was employed painting as a protection agent. During the facility’s operational life, several layers of paint were applied in an attempt to stop or reduce the corrosion rate, since the structures were submitted to aggressive environments.

Besides this, it was found that the most contaminated regions, in the steel structures, were the oxidized or corroded areas. The presence of several layers of paint combined with corroded regions makes the decontamination process much more difficult. In the figure 3 and 4 are shown, respectively, the carbon steel structures mainly employed in the assembling of the pilot plants of IPEN, after removal from the facilities, and the corrosion status of some structures after more than a decade since the interruption of the activities.

Figure 1: Third level of the Uranium Purification Pilot Plant, assembled with perforated steel structures.

Figure 2: The same structure shown above after tanks and piping removal.

Figure 3: Perforated carbon steel structures after dismantling.

Figure 4: Corrosion observed in some perforated carbon steel structures after more than a decade since the interruption of the activities.

Initially, in the first decommissioning activities performed in IPEN, several methods were attempted with the objective of superficial contamination removal and the consequent reduction of the contaminated waste volume, such as: decontamination by rinsing methods employing acid and alkali solutions (chemical method), combination of rinsing methods and ultrasonic device and abrasive removal (physical method). However, the results employing the above mentioned methods were not satisfactory. The combination of painting and carbon steel corrosion creates serious problems in terms of decontamination efficacy and workers exposition.

2.1. Methods Applied for Waste Volume Reducing

Some attempts were done to reduce the volume of those wastes. Nevertheless, the only decontamination available methods were chemical methods, such as pickling/rinsing treatments employing acid solutions (with nitric or citric acids) and alkaline solutions (sodium hydroxide). Different concentrations of such solutions were tested. Some tanks released in the dismantling operations were adapted and employed in the decontamination process as can be observed in the figures 5 and 6.

Figure 5: Stainless steel tank adapted for decontamination of components by pickling.

The results obtained with the employed processes were not satisfactory. Besides the generation of large effluent volumes that needed treatments by precipitation (for example, with sodium hydroxide added to U or Th acid solutions) and analysis before final disposal, the decontamination of some components it was impossible. In spite of some efficiency when applied to stainless steel components, those perforated, and several times painted, carbon steel structures were not released by this method.

Figure 6: Polypropylene tank adapted for decontamination of large steel pieces.

Ultrasonic equipment available was also employed in an attempt to increase the decontamination efficiency. It is important to mention that the ultrasonic equipment was adapted for this function. Originally, it was acquired to clean stainless steel tubes employed as cladding material of uranium dioxide fuel rods for a critical assembling (IPEN-MB 01 research reactor – Critical Facility). Therefore, the power of the equipment was not suitable for decontamination purposes. In the figures 7 to 9 it is possible to observe the ultrasonic equipment as well as the decontamination of some components. The equipment has some additional resources such as solution heating and bath agitation. The acid and alkaline solutions were again employed in the decontamination varying parameters such as concentration, temperature and time of immersion.

Figure 7: Assembling of the ultrasonic equipment.

In spite of same good results obtained with different materials, as stainless steel, even for components with complex shapes, the results were frustrating to the painted carbon steel parts. In the figure 10 are shown pictures of aluminum and stainless steel decontaminated and fully released for any proposal. The aluminum was pickled with sodium hydroxide solutions without the need of ultrasonic support. The best results with stainless steel were obtained with nitric acid solutions, temperatures between 60-70 °C, ultrasonic support and immersion period of 30-60 minutes

Figure 8: Internal view of the ultrasonic equipment and basket with contaminated parts.

Figure 9: Different solutions, concentrations, temperatures and times were tested.

Figure 10: Aluminum and stainless steel components and pieces decontaminated.

Nevertheless, the painted and perforated carbon steel could not be decontaminated satisfactorily and all the waste generated during dismantling had to be conditioned (cutting in suitable dimensions) and stored in special drums or steel boxes. The storage in drums is not suitable because it is necessary a lot of work to cut the structures in small pieces and the space is not completely fulfilled, as shown in the figure 11. The structures storage in steel boxes is much more advantageous, since it is not necessary so much cutting work for the components and the space is better occupied, as shown in the figure 12. Nevertheless, the boxes are expensive, there is a lot of free space inside them and they still need a lot of area for their storage.

Figure 11: Drums containing parts of carbon steel structures.

Figure 12: Contaminated structural parts of carbon steel stored in steel boxes (left and center) and storage of the steel boxes with radioactive waste (right).

3. DEVELOPMENT OF RADIOACTIVE DECONTAMINATION OF PAINTED CARBON STEEL STRUCTURES BY MOLTEN SALT STRIPPING

Several methods have been applied for the paint removal [2] and minimization of radioactive waste [3-5]. The choice of a coating removal process for radioactive material in the form of carbon steel pieces must have into account, among other factors, that it is not necessary a high quality of finishing, since the main objective is the release of the material as iron scrap. Different from other applications, where the main objective is to recover the component for reworking (appliances industry, for instance), the reduction of waste volume is the main driving force in our decommissioning experience, since expensive containers and space for storage are necessary. The presence of radionuclides as aerosols should be avoided since the contamination would spread out and the workers should wear special clothes, respirators and eye protection equipment, as is the case of blasting cleaning processes. Blasting also uses to generate high noise levels. Besides this, in same cases, as internal parts (tubes, for instance) and pieces with complex shapes (a lot of work is necessary), blasting is not effective.

However, molten salt stripping is an advantageous decontamination method. During this process, by-products of the reaction of the salt and the organic coating, as well as the radioactive contaminants present mainly in the corroded and oxidized areas of the metal surface, accumulate in the bath. Even when the bath is saturated with by-products, stripping will continue.

As molten salt coating removal works by combusting the coating organics, the molten salt stripping process replaces solvent strippers. The organic content of the coating or paint (hydrocarbons) will be oxidized by reaction with air and the salt bath, generating only $CO_2(g)$ and $H_2O(v)$. In spite of the small volume of spent salt generated after a relatively long period of operation (the spent salt contains metal oxides and metal salts formed by the reaction of the paint pigments with oxygen from the air and salt bath materials), the salt can be recycled.

3.1 Experimental Procedure

It was decided to explore the former experience with molten salts in the thermal decomposition of radioactive organic wastes to investigate the possibility of its application as a potential method to solve the problem of the volume of radioactive waste generated during the dismantling operations of the Nuclear Fuel Cycle Pilot Plants of the IPEN. This waste is constituted mainly by large amounts of painted carbon steel structures, superficially contaminated, in the form of structural perforated components. On one hand, the perforated components and complex shapes would require a lot of work or material (solid carbon dioxide - “dry ice”, for instance) if blasting was used. On the other hand, as the pieces are made from steel, they can be processed in relatively high temperatures without problems. As additional advantages, the piece immersion in molten salts avoids the generation of particulate material in suspension and the method can process parts with complex shapes and the intern walls of tubes. In spite of the energy requirements to melt the salt, it is possible select salt compositions of low melting point and low prices. Besides this, the salt can be reused after dissolving, filtration (to retain the radioactive oxides present in the salt solution) and recrystallizing.

In spite of the use of molten salt has already been developed for some industrial coating removal process, it has not been found references in the literature about its use for superficial radioactive decontamination. The molten salt stripping process relies on chemical oxidation of the coating by a molten salt bath. Then, the main objectives of this study were (considering the application of the method for radioactive waste treatment): development of specially formulated salt compositions that provide melting temperatures as low as possible and so effectives as possible in coating and/or corrosion products removal, besides low cost.

Initially, the system former built for treatment of radioactive organic solutions by molten salt oxidation was adapted for the first exploratory experiments of coating and contamination removal by stripping with molten salts. The system employed can be observed in the figure 13. The furnace and the reactor were assembled inside an exhaust system. The former experience of using molten salt for wastes treatment in IPEN had employed sodium carbonate

– Na_2CO_3 - that is cheap and permits the combination with halogens to form halide salts (that are retained in the bath) and release CO_2(g). The first experiments were accomplished with this salt and a nickel alloy reactor. In the figure 14, it can be observed an experiment of paint removal in the molten salt bath with sodium carbonate.

Figure 13: Molten salt stripping - exploratory system inside an exhaustion chamber.

As shown in the figure 14, the combustion of the paint creates a flame. The temperature of the bath of pure sodium carbonate was 900°C. The disadvantage of this compound is its relatively high melting temperature ~ 852°C [6]. The salt bath provides thermal inertia and effective heat transfer to avoid hot spots or temperature excursions. The molten salt also acts as a gas scrubber which retains the non-volatile reaction products (metal oxides and ashes). As the main functions of the molten salts are a heat transfer medium and catalyst to oxidize the organics in the paint, and the costs of the process and some technical difficulties are associated to higher temperatures, it is important to remove the paint in temperatures as low as possible. Then, it is necessary to look for molten salt formulations that can provide low temperature and efficient paint removal.

In the first set of experiments 42 samples were cut from contaminated structures. Each sample was characterized by measurements of its activity in terms of the counts per second. As the activity is not constant along the piece, the maximum counts per second measured was adopted. Since the kind of structure (perforated steel in L form), material (carbon steel), dimensions and coating (painted) are always the same, the main process variables were selected: salt composition; salt temperature and residence time. Four different salt compositions were selected for the tests: pure sodium carbonate; pure sodium hydroxide; the eutectic mixture of sodium carbonate (41% in mass) and sodium hydroxide (59% in mass); sodium hydroxide with addition of about 10 % in mass of sodium nitrite (oxidizing salt). Two immersion or residence times were selected: 10 and 20 minutes. Temperatures selected were 450°C and 650°C for the different salt compositions and 900°C for pure sodium carbonate. The amount of salt in the reactor was approximately 3.5 kg corresponding to about 40 cm.

Following immersion, the samples were removed from the salt bath and rinsed with water for salt removal and cooling. The rinsed items were measured again to determine their respective activities in terms of the maximum counts per second. After this step, the items were submitted to a pickling treatment with sulfuric acid (98%) diluted in water (20% in volume). In the figure 15 can be observed the monitoring of an item and the structures appearance before and after the stripping treatment by molten salt immersion.

Figure 14: Molten salt stripping - introduction (left) and removal (right) of the sample.

Figure 15: Monitoring (left), items before (above right) and after stripping (bellow right).

Considering that a possible advantage of the molten salt stripping process is the possibility of reducing the generation of secondary wastes by means of salt recycling, some preliminary tests were accomplished. The salt retains the contamination in the form of metal oxides and ashes that are insoluble. The dissolution of the salt in water followed by filtration permits the removal of those oxides. For dissolution, it is possible to use the same water employed for the rinse step. The remaining aqueous salt solution can be then concentrated in a hot-air stove or crystallizer and the salt can be reused in the process, returning to the molten salt reactor vessel. In this way, no liquid waste results from the process. The only waste generated is the small amount of material retained in the filter. The results are summarized in the Table 1. The results are presented before (only with the molten salt stripping treatment) and after the acid pickling treatment. In the figure 17 it is possible to observe the radioactive solids retained in filtration and the salt recovered by crystallization.

Figure 17: Salt solution filtration (left), radioactive waste, (center) and recovered salt (right).

Table 1: Different conditions and results for the preliminary experiments (BG= 4 counts/sec).

Sample	**Salt composition**	**Salt temperature (°C)**	**Time (minutes)**		**Counts/s**	
				Initial	**M. salt***	**Final**
1	Na_2CO_3	950	10	70	10	4
2	Na_2CO_3	950	10	40	4	4
3	Na_2CO_3	950	10	50	5	5
4	Na_2CO_3	950	20	20	5	4
5	Na_2CO_3	950	20	70	3	4
6	Na_2CO_3	950	20	70	4	4
7	NaOH + Na_2CO_3**	450	10	100	20	4
8	NaOH + Na_2CO_3**	450	10	40	20	5
9	NaOH + Na_2CO_3**	450	10	70	6	4
10	NaOH + Na_2CO_3**	450	20	120	25	5
11	NaOH + Na_2CO_3**	450	20	30	7	4
12	NaOH + Na_2CO_3**	450	20	90	6	4
13	NaOH + Na_2CO_3**	550	10	300	13	4
14	NaOH + Na_2CO_3**	550	10	300	15	15
15	NaOH + Na_2CO_3**	550	10	60	10	5
16	NaOH + Na_2CO_3**	550	20	90	20	5
17	NaOH + Na_2CO_3**	550	20	150	25	10
18	NaOH + Na_2CO_3**	550	20	80	10	7
19	NaOH + Na_2CO_3**	650	10	30	3	5
20	NaOH + Na_2CO_3**	650	10	100	7	4
21	NaOH + Na_2CO_3**	650	10	70	10	5
22	NaOH + Na_2CO_3**	650	20	250	7	5
23	NaOH + Na_2CO_3**	650	20	70	3	4
24	NaOH + Na_2CO_3**	650	20	50	4	5
25	NaOH	650	10	25	5	4
26	NaOH	650	10	90	5	5
27	NaOH	650	10	40	4	4
28	NaOH	650	20	50	5	4
29	NaOH	650	20	70	4	4
30	NaOH	650	20	80	6	5
31	NaOH	450	10	80	5	4
32	NaOH	450	10	40	5	4
33	NaOH	450	10	40	6	5
34	NaOH	450	20	80	5	4
35	NaOH	450	20	30	4	4
36	NaOH	450	20	40	6	4
37	NaOH+ $NaNO_2$***	450	10	50	14	4
38	NaOH+ $NaNO_2$***	450	10	25	5	4
39	NaOH + $NaNO_2$***	450	10	50	9	4
40	NaOH+ $NaNO_2$***	450	20	30	5	4
41	NaOH+ $NaNO_2$***	450	20	70	4	4
42	NaOH+ $NaNO_2$***	450	20	30	7	5

* Results before (only with the molten salt stripping treatment) and after the acid pickling.

** 59 wt% of NaOH and 49 wt% Na_2CO_3 *** 90 wt% of NaOH and 10 wt% of $NaNO_2$.

4. CONCLUSIONS

The treatment of radioactive wastes in the form of painted structures, made of perforated carbon steel, and presenting superficial contamination has been investigated. The superficial radioactive contamination is located mainly in the corroded regions and mixed with rust. This contamination is frequently of difficult removal due the layers of paint applied on the contaminated area. The paint applied over the contamination impedes the action of the usual acid or alkaline pickling methods.

The process selected for paint stripping was the immersion of pieces in molten salt mixtures in different temperatures and different residence times. Molten salt stripping uses simple and straightforward processing steps. The items to be stripped can be loaded into baskets or can be supported on hooks. The process allows rapid and complete painting removal with a minimum of handling. The method can be applied for parts with complex shapes. The superficial contamination of internal walls of tubes, which are not reached by blasting or abrasive methods, can be successfully treated by immersion in molten salts.

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