BITUMINIZATION PROCESS FOR CONDITIONING RADIOACTIVE WASTES

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Abstract. *Nuclear Technology DevelopmentCenter has been carrying out a research in new technologies to immobilize radioactive wastes in different matrices, as cement, polymers and bitumen. The process consists of fixing the waste and the bituminization is an immobilization technique that uses bitumen as matrix for this proposal. It can produce for some wastes suitable waste forms with good chemical, physical and mechanical strength characteristics, avoiding the release of contaminants to the biosphere in the event of disturbances at the final disposal. Using this process it is possible to incorporate an expressive percentage of waste. Studies and experimental works on immobilization of simulated evaporator concentrate and mixed ion exchange in national bitumen with different softening point has been investigated at CDTN/CNEN. The percentage of incorporated solids in bitumen is ranged from 30 to 45%. The incorporation campaigns are performed at a bituminization pilot plant that consists of a screw-extruder of continuous flow and auxiliary equipments to maintain a sufficiently low viscosity of the bitumen during the incorporation process. The waste form obtained are evaluated according to national standards by means of thermodiferencial analysis and specific tests to evaluate the softening point, flash point, penetration, water content and homogeneity. The radionuclides release by leaching, an important parameter to evaluate how well the radionuclides are retained in the matrix and to provide information about the source term for safety assessment of waste disposal system, are also evaluated during a minimum period of one year. The results of research campaigns carried out with Brazilian bitumen to be used as matrix for the incorporation of simulated concentrate evaporator from nuclear power plants and the evaluation of the obtained products are valuable to give support to Angra 2 Nuclear Power Plant and also to the regulatory bodies in establishing the acceptance criteria for disposal.*

Keywords*: waste management, bituminization process, waste immobilization*

1. INTRODUCTION

Management of low and intermediate level radioactive wastes uses strategies that incorporate many technologies to convert waste into forms for handling, storage, transport and disposal. The treatment of these wastes has been investigated by different experts (Yim et al., 1992; IAEA, 2002) due to the importance of the safe management of radioactive waste for the protection of human health and the environment.

CDTN/CNEN (Nuclear Technology Development Center) has been carrying out a research in new technologies to immobilize radioactive wastes in different matrices, as cement, polymers and bitumen. The immobilization process consists of fixing the waste in a matrix and the bituminization is the technique that uses bitumen as matrix and can produce for some wastes suitable forms with good chemical, physical and mechanical strength characteristics, avoiding the release of contaminants to the biosphere in the event of disturbances at the final disposal.

Using this process it is possible to incorporate a significant percentage of waste and to obtain final, stable, monolithic and homogeneous waste form, suitable for subsequent steps of waste management including disposal.

In Brazil, the second nuclear power plant of 1300 MW- PWR is in operation and the radioactive wastes generated in this plant have been immobilized in bitumen. Some countries used the continuous and bath bituminization process to immobilize a wide range of wastes. The process has been investigated by different experts (IAEA, 1993; Awwal et al., 1994; Guzella et al., 2001, 2007). In the Nuclear Power Plant Goesgen in Switzerland the evaporator concentrate, the ion exchanger resins and filter cartridges from the facility have been processed with this technique since 1980 (Hoffmann, 1980).

Bitumen was chosen as solidification agent because it demonstrates some advantages such as the high volume reduction of the waste forms and good leaching, radiation and ageing resistances. Furthermore, it is possible to incorporate wastes that have very different chemical and physical properties.

In considering bitumens as matrix materials for embedding of radioactive wastes a number of physicochemical properties are important as they are related to the storage and transfer conditions of the molten bitumen, the operating conditions of the process, the compatibility with the waste, the packaging requirements and the final disposal of the waste forms. The waste forms should have adequate characteristics to avoid releasing to the biosphere in the event of disturbances in the final storage area.

CDTN/CNEN is engaged in the research and development works for treatment of low and intermediate level of radioactive wastes generated from the operation of nuclear plants and from application of radioactive materials in research, nuclear medicine and industry. An extensive research is being undertaken in order to obtain experimental data on the physico-chemical properties of the waste forms prepared with national bitumens for qualification of large scale immobilization of real radioactive wastes originated from the operation of nuclear power plants (NPP).

R&D works are concerning to evaluate the Brazilian bitumen to incorporate simulated liquid and solid radioactive wastes with concentration varying from 35 to 55 wt%. The wastes consist of simulated solutions of evaporator concentrate and simulated mixed ion exchange resins. The waste at constant flow rate are mixed with a constant flow rate of bitumen resulting in a constant flow of final product to be collected into appropriate containers. The incorporation campaigns are performed at a bituminization pilot plant that consists of a screw-extruder of continuous flow. There are also auxiliary equipments as waste feed, bitumen storage vessel, feed pumps, off-gas cleaning, and outer jackets to maintain a sufficiently low viscosity of the bitumen during the incorporation process.

The waste form obtained are evaluated according to national standards by means of thermodiferencial analysis and specific tests to evaluate the softening point, flash point, penetration, water content, and homogeneity. The radionuclide releases by leaching, an important parameter to evaluate how well the radionuclide are retained in the matrix and to provide information about the source term for safety assessment of waste disposal system, are also evaluated during a minimum period of one year, according to the standard ISO-6961 (1982).

This research is valuable to give support to Angra 2 Nuclear Power Plant and also to the regulatory bodies in establishing the acceptance criteria for the waste disposal.

2. EXPERIMENTAL PROCEEDINGS

The CDTN/CNEN pilot plant was developed in Germany at KfK Institute (Guzella, 2001) and it was designed according to the prevailing requirements for the waste forms such as homogeneity, grain size of the solids, water content, etc. The extrusion process is applicable to a wide range of wastes from nuclear power plants. Some experiments with simulated low level concentrate evaporator immobilized in national bitumen were made. They were performed in a pilot extruder and the studies on rheological properties, differential thermo analysis and leaching tests for the waste forms had been carried out.

2.1 Bitumization pilot plant

The pilot plant of continuous flow consists of a screw-extruder with evaporation capacity of 3 to 4 kg/h and production capacity of 1 kg/h. The extruder has two-rotating horizontal screws, which consist of shafts fitted with kneading, mixing and conveying sections, which alternately homogenize and convey the bitumen and the waste through the extruder until the discharge point is reached. The required heat to evaporate the free water in the waste feed and to maintain a sufficiently low viscosity of the bitumen is provided by heated oil through outer jackets located in the extruder body.

The pilot machine has five heating zones and a proper temperature profile along the length of the extruder is maintained to provide adequate evaporative capacity and to yield predetermined residual total moisture content in the product. During the evaporation, the water vapor and a small amount of oil leave the extruder, via three stream domes, and the condensate is collected to be analyzed. The conductivity, the sodium and the boron contents in the condensate show the efficiency of the process.

Adequate temperature controls throughout the bituminization process and redundant process interlocks are important aspects when operating a bituminization facility. Each stage of the screw extruder operation can be automatically operated in a panel control and the mixing process inside the extruder can be observed through the steam domes. The operational speed is usually between 200 and 250 rev./min.

The bitumen is stored in a heated tank and is continuously recirculated and all the lines of the plant are oil heated. The liquid waste is also stored in a tank and the temperature is controlled. Bitumen and simulated wastes are homogeneously dosed in the extruder by means of pumps in order to maintain the solid waste ratio constant. (Guzella and Silva, 2001).

A view of the pilot plant and the simplified flow sheet of the bituminization process are shown in Figs.1 and 2.

2 2 Experimental development work

The main properties of the bitumen, the penetration, the softening and the flash points were determined according to applicable standards (ABNT, 1998, 2000a, 2000b) at the beginning of the experimental works.

The bitumen was also analyzed by Differential Thermal Analysis (DTA) for the detection of highly exothermic compounds. The waste was simulated in order to have the same properties of the real waste generated in nuclear power plants and the evaporator concentrate solution represents the large volume of generated waste in nuclear power plants. The solid content and the specific gravity of the solution were around 25 wt% and 1, 2 g/cm^3, respectively. Table 1 presents the rheological properties of the matrix of bitumen. The contents of asphaltenes and maltenes in pure bitumen were respectively 32,5% and 67,5%, determined at Technology Research Institute (IPT) in São Paulo.

Figure 1. Bituminization pilot plant of CDTN/CNEN

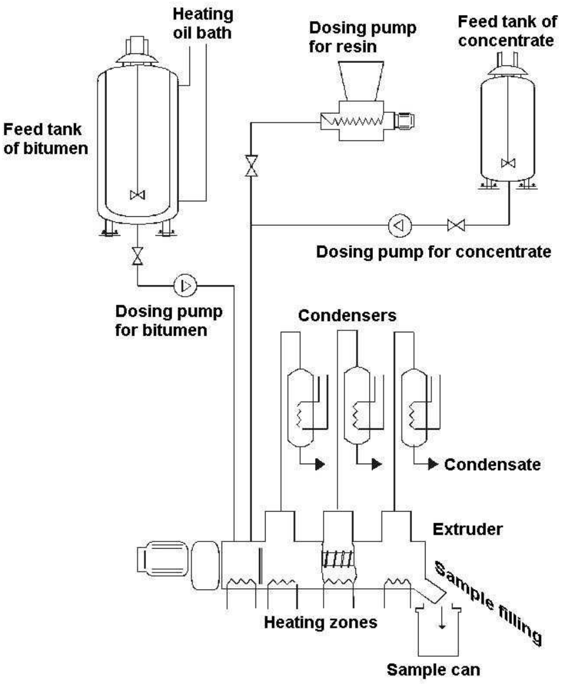

Figure 2. Simplified flow sheet of bituminization process

The solution that simulates the evaporator concentrate was investigated and Tab. 2 shows the characteristics of the simulated waste compounds. The waste solution contains boric acid, sodium chloride, ethylene diamine tetraacetic acid (EDTA), sodium sulfate and sodium phosphate. Calcium carbonate is added to the waste solution as insoluble salts.

Table1. Rheological properties of bitumen

Rheological Property	National Bitumen*
Softening Point (^oC) - (Ring and Ball)	68.3±0.5
Flash Point -(^oC) - (Cleveland)	301±2
Penetration- (1/10mm)-	10.6±1.0

* average value of 3 measurements

For studies in immobilization of evaporator concentrates many campaigns were carried out with the national bitumen. During the campaigns all operational data were registered in forms, specially developed for this purpose. The concentration of the solids incorporated in bitumen ranged from 43,1 to 51,2 wt%.

Table 2. Analytical results of the simulate evaporator concentrate solution

Parameter	Waste Solution
Boron concentration -wt (%)	3.37 ±0.34
Chloride concentration -wt (%)	0.28±0.03
Sulphate concentration -wt (%)	3.31±0.33
Total solids- wt (%)	25.7±0.1
Specific gravity- (g/cm^3)	1.21±0.12
pH	7.4±0.1

3. RESULTS AND CONCLUSIONS

The products were collected in small cans and then they were characterized. The operational data of waste incorporated in bitumen and their rheological properties and leaching resistances are shown in Tab. 3 and Tab. 4 according to the waste loading.

The softening point and the flash point were evaluated and they were higher for the waste forms than those for the pure bitumen (CNEN, 2002). The decreasing of penetration demonstrated the hardnessing of the product due to the incorporated salts and also the mechanical strength characteristic of the waste form.

Also the water content according to the standard (ABNT, 2001) was determined. Samples of waste form leaving the extruder were analyzed and the residual water content of less than 0.4 wt% is according to the results of the literature (IAEA, 1993).

Table 3. Experimental results for rheological properties of waste forms

Waste loading (wt %)	Softening point (^oC)	Flash point (^oC)	Penetration (1/10 mm)	Prod. water content wt (%)
43.1± 0.4	75.0± 1.0	327.0± 1.0	9± 1	<0.4
47.7± 0.8	79.7± 2.1	329.0± 1.0	9± 1	<0.4
51.2± 1.6	80.3±1.2	325.0± 1.0	7± 1	<0.4

Table 4. Analytical results of leaching test and release fraction of boron and sodium

Waste loading wt (%)	Average Leaching Rate (kg/m^2s) x 10^{-8}				Released Salt (%)	
	185 days (punctual)		1 year		Boron	Sodium
	B	Na	B	Na		
43.1± 0,4	4.3	4.5	2.0± 0.5	1.5± 0.4	6.0±0,6	5.0+ 0.5
47.7± 0,8	3.8	2.3	2.1± 0.4	1.3±0.5	7.0± 0,7	7.0±0.7
51.2± 1,6	2.5	2.1	3.4± 1.3	2.2± 1.1	6.0+0,6	7.0±0.7

One of the safety aspects that have considerable attention is the thermal stability of the products. Differential thermoanalysis is an excellent tool to determine the thermal stability of chemical compounds. Investigations were performed with the bitumen and waste forms. Thermograms related to one of the campaigns of immobilization and to the pure bitumen are shown on Fig. 3.

Some differential thermoanalysis curves of bitumen and waste form have shown endothermic peaks in the temperature range between 100^{o}C and 300^{o}C that indicates the presence of water or volatile organic compounds. Exothermic peaks are generally observed in the region of 400^{o}C as shown in the Fig 3. The first curve refers to the waste forms with 40 wt% waste loading and the other thermogram shows the analysis of the commercial bitumen without incorporation.

Basically bitumen is a flammable material with flash point about 300°C and the flash point of the waste form lies over 320°C. This temperature is not reached at any point in the bituminization system that is a feature that warrants the safety during the operation of the bituminization pilot plant.

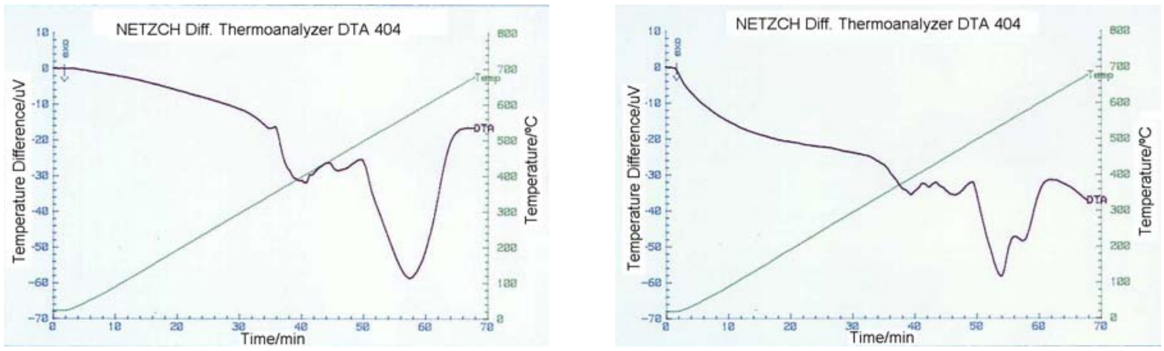

Figure 3. Thermograms of bitumen and waste form.

Leaching is an important parameter needed for the evaluation of waste forms and the results of the leaching tests should meet the acceptance criteria for disposal (CNEN, 2002). Leaching tests on bituminized waste forms are performed to evaluate on a comparative basis how well the radionuclides are retained in the matrix and to provide information about source terms for the safety assessment of waste disposal systems. In general, the leaching tests are conservative and indicate the maximum release likely to occur in a disposal environment.

The leaching tests were carried out based on ISO 6961 (ISO, 1982). Two samples of each campaign were selected to investigate leaching behaviour and they were put into 2 L polyetilene bottles containing 1.5 L of deionized water.

The samples containing a known amount of contaminant were immersed in water and changes of the water were made according to the standard method during the period of one year. The sodium and boron ions were analyzed.

The concentration of contaminant entering the solution was determined and the fractional release of contaminant released over time was calculated (Tab. 4). It also shows the average leaching rate of waste forms at several waste loadings after 185 days and one year. The leaching rate and the released fraction of boron and sodium are presented in Fig. 4 as an example for one of the campaigns. The waste forms presented approximately the same leaching rate, according to the standard acceptance criteria (CNEN, 2002).

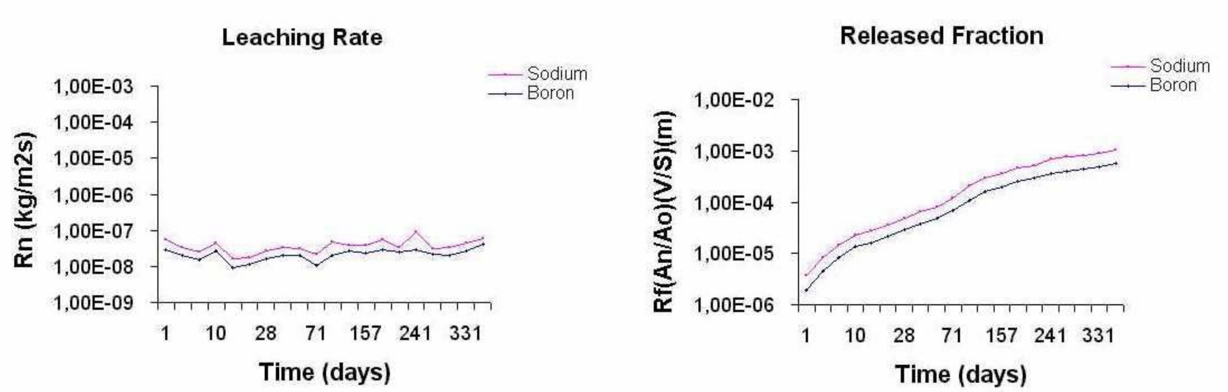

Figure 4. Leaching rate and release fraction for one immobilization campaign

The operational conditions were better for low percentage of waste incorporated and normally bituminized products resulting from extruder processes meet all the safety requirements.

Studies are being planned for the leaching resistance of waste forms using radioactive tracers and for the improvement of the waste product quality concerning to swelling. A chemical pre-treatment of the evaporator concentrate prior to incorporation or the coating of the products with a layer of pure bitumen should be investigated.

The stability of these bitumens with respect to radiations will be studied in order to define the maximum amount of waste that can be incorporated into the Brazilian bitumen matrix.

4. ACKNOWLEDGEMENTS

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