SOLIDIFICATION TECHNOLOGY FOR ORGANIC LIQUID WASTE COMBINED WITH SOLID MATERIALS FROM CERNAVODĂ NPP, ROMANIA

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ABSTRACT

Canadian Deuterium Uranium (CANDU ®) reactor designs were initially developed in the late 1950's and 1960's by the Atomic Energy of Canada Limited (AECL) in partnership with Ontario Power Generation. CANDU ® 6 reactors are Pressurized Heavy Water Reactors (PHWRs), with an integrated containment system and are designed as either multi or single unit systems.

Two single CANDU 6 systems are currently operating at Cernavoda with an additional two units expected to be brought online in the near future.

The radioactive waste produced by the plant is currently stored in a waste interim storage facility located on-site.

The main sources of radioactive waste in a CANDU plant are:

- Primary Heat Transport (PHT) systems
- Moderator systems
- Other sources of radionuclides

The radioactive waste management system at Cernavodă Nuclear Power Plant (NPP) was designed to maintain acceptable levels of safety for workers and to protect human health and the environment from exposure to unacceptable levels of radiation.

During the operation of the Cernavodă NPP, a series of waste streams have been generated for waste treatment purposes. One important waste stream is the combination of solid materials and liquid organic waste, creating flammable solids. Flammable solids represent solid materials, such as cloth, plastic, contaminated with oil containing gamma nuclides and H-3 from maintenance activities.

This paper explores a method to solve the problem of liquid residues on solid materials by the application of absorbent materials. The existence of liquid residues on solid materials is a common problem at nuclear power stations globally. The primary issue centers on an effective method of eliminating the liquid to allow for the final acceptance and disposal of the solid waste by regulators.

INTRODUCTION

Effective treatment of flammable solids from the initial to the final stage has been a challenge for NPP Cernavodă, mainly because of tritium which is the key radionuclide for CANDU and is generated in significant quantities.

In 2008 MATE-FIN signed a four year contract with Cernavodă NPP in order to perform the characterization of organic liquid waste and burnable waste, the treatment of organic liquid waste and flammable solid waste and to condition by incineration the solidified and burnable waste. In March, 2015, a new five year services contract was signed with SN Nuclearelectrica SA. Nuclearelectrica is a Romanian state owned company engaged in the utility sector and manages the electricity generation from nuclear power plants.

MATE-FIN was founded in 1992 and was the first privately owned company in the nuclear industry in Romania. The company's shareholders come from the Bucharest-Magurele Institute of Atomic Physics, all with extensive backgrounds in the nuclear industry. MATE-FIN's services include nuclear methodologies, technologies, radiation monitoring and research. Their staff includes 70 full time employees with a high level of scientific and technical training and empirical experience in the nuclear field. A new office and laboratory is under construction immediately adjacent to the Cernavoda nuclear power plant and will open in 2016.

PROBLEM and PROPOSED SOLUTION

The problem involves the existence of organic liquids on solid materials such as textiles, plastics, etc., that result in flammable solids. This presents two primary issues: hazardous waste that poses safety problems within the plant and waste that does not meet waste disposal requirements and, thereby, cannot be sent for final disposal.

The solution proposed by MATE-FIN for flammable solids is to apply proven, low cost polymers directly to the solid materials, in order to absorb the liquid compositions. Various polymers may be combined creating one formula to capture organic and aqueous (tritium) waste streams into a permanent solidified matrix. This is a safe and simple process. Tritium is present in the waste stream primarily in the form of tritiated water. This water is organically bound in the organic waste and represents approximately two (2) percent of the total liquid composition. The solution is to eliminate the liquid phase / residue from the solid waste through solidification.

EXPERIMENTS

A series of tests were performed on several types of solids containing oil with tritium. Several different types of solid materials were selected for tests based upon the composition of the liquid waste streams. The solids included:

- Textiles; clothes, cleaning materials
- Rubber from safety gloves
- Plastic used in ventilation tents
- Mixed samples

As a contaminant, the active waste forms with high tritium content oil (3.8 10^8 Bq/kg) have been used (Figure 1). Flammable solids were then treated with a mixture of Nochar polymer N910 (applied to organic liquids) and polymer N960 (applied to aqueous liquids) Figure 2. The oil blend is solidified, resulting in a “spent” polymer (solidified organic liquid) and the remaining solids (plastics and textiles or mixture) are completely free from organic liquid and can be treated and classified as “normal” solid waste.

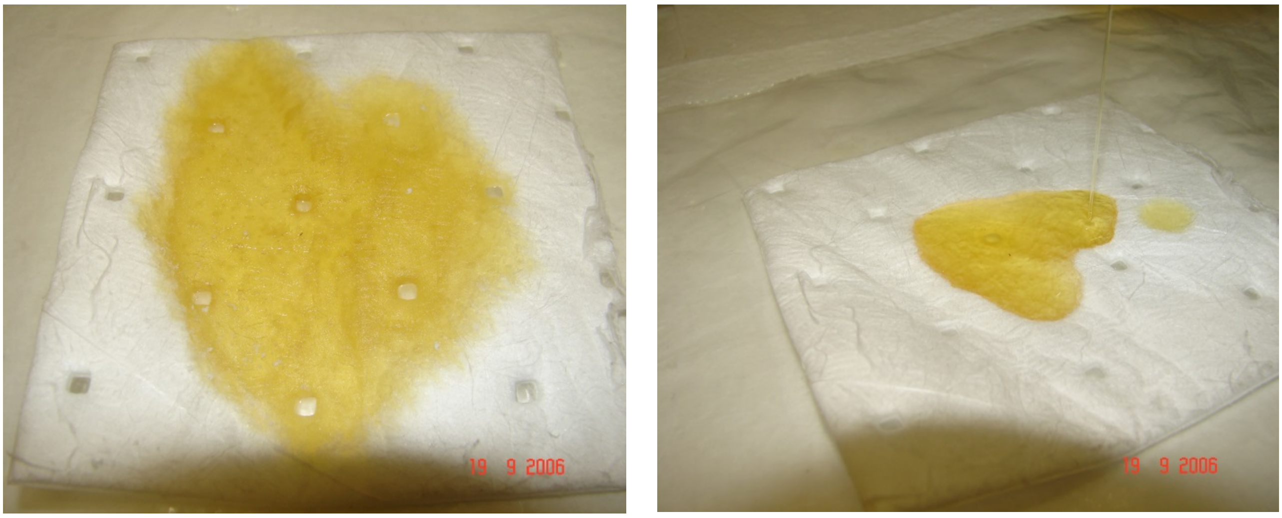

Figure 1. Contamination of a solid sample

Figure 2. Treatment of the contaminated sample

The experimental sandwich structure (layers of solid-oil mixture and polymer) were maintained for 12 days. This time period was chosen by taking into account the necessary time to absorb the liquid in the polymer matrix and by predicting a reasonable time period that is applicable in the real waste treatment process. The tritium content in the air was measured during the experimental steps to determine the amount of tritium that may have escaped from the solidification due to evaporation of HTO. Additionally, measurements were taken to comply with the necessary respiratory protection requirements.

After treatment, the polymer was separated from the solid material and the tritium content was measured in the solid materials and the spent polymer. The method to determine tritium valves was according to the following steps:

- Sample decomposition in an open microwave digestor (different type of digestion program was used for each material)
- Entrapment of the tritium in a weak acidic solution
- Distillation of the tritium content liquid
- Measurement by Liquid Scintillation Counting, using a device with 137 dpm background and 49% unquenched efficiency

The tritium content of the remaining solid was used to evaluate the performance of oil removal (or any other organic liquid) from the solid waste.

Five groups of samples were prepared:

1. Latex from safety gloves, plastic (polyethylene) used in ventilated tents, tyvek
2. Microfiber (cotton fibers wrapped in plastic)
3. Paper
4. Textile (cotton)
5. Mixed samples of 2, 3, 4.

Each group was contaminated with a real waste, high tritium content oil (3.8 10^8Bq/kg), well mixed and treated with N910 and N960 polymers. The H-3 in the oil is present in a proportion of 97% as colloidal water (HTO, DTO or very rarely asT_2O).
After treatment, the polymer and the solid were mechanically separated and the H-3 content was measured in the corresponding solid and polymer as follows:

- Sample preparation (H-3 extraction)
  - o Solid material: washed in de-ionized water in ultrasonic bath, H-3 is passed in water by an isotope exchange process
  - o Polymer: open digestion, the exhaust gas is retained in HCl solution and distillation
- In the water obtained after the washing and distillation process, the H-3 concentration was measured by LSC technique.

The results are presented in Table 1.

There is a significant amount of loss of H-3 in the process due to the evaporation of water during the treatment process. All operations are performed in a fume hood (lab scale) and ventilated tent (real scale) with high air flow rate. In the case of plastic material (latex, PET and microfiber) where the oil (and the water) is mainly localized on the surface of the material, the H-3 loss is more significant (about a factor of 20). In cotton and paper, the oil (and water) is penetrating deeper inside the material and the evaporation loss is less significant (about a factor of 10).

In the case of real waste, the assessment of the evaporation loss is more difficult. The whole separation process involves a mixture of material, a much higher quantity coming from several drums of solid-oil mixture. It is difficult to find the correlation between the original mixture, the clean solid material and the polymer. A rough assessment of the original H-3 content and treated material H-3 content ratio gives a value of 60 (Table 2). The loss of H-3 by evaporation is more significant in a ventilated tent due to the higher ventilation rate and evaporation surface.

Table 1

sample	mass sample (g)	conc H3 sample (Bq/kg)	H3 total sample (Bq)	polymer mass kg	conc H3 polymer (Bq/kg)
1	9,4	1,51E+05	1,42E+03	4,80E-01	3,66E+04
2	7,82	3,86E+05	3,02E+03	4,30E-01	4,26E+04
3	7,19	3,95E+05	2,84E+03	4,53E-01	1,14E+05
4	8,7	2,76E+05	2,40E+03	3,03E-01	9,89E+04
5	7,82	2,90E+05	2,27E+03	4,95E-01	8,68E+04

Continuation of table 1

H3 total polymer (Bq)	H3 total solid+polymer (Bq)	contaminant mass (g)	conc contaminant (Bq/kg)	H3 total contaminat (Bq)	H-3 in/out ratio
1,76E+04	**1,90E+04**	3,37	1,07E+08	**3,61E+05**	20,5
1,83E+04	**2,13E+04**	3,7	1,07E+08	**3,96E+05**	21,6
5,16E+04	**5,45E+04**	3,42	1,07E+08	**3,66E+05**	7,1
3,00E+04	**3,24E+04**	3,41	1,07E+08	**3,65E+05**	12,2
4,30E+04	**4,53E+04**	3,65	1,07E+08	**3,91E+05**	9,1

Table 2

	mass (kg)	conc H3 (Bq/kg)	H3 total	SI/SIS+P ratio
SI186	40	6,40E+08	2,56E+10	61
SIS186	**41,5**	3,63E+05	1,51E+07	
P186	60	6,74E+06	4,04E+08	

APPLICATION ON REAL RADIOACTIVE WASTE

The design and technology developed by MATE-FIN at Cernavoda to perform the liquid to solid separation is based on a “sandwich” structure of solid materials and absorbent polymers (Figure 3). All of the treatment operations are performed in a ventilated tent which permanently monitors the tritium content in the air.

Figure 3. Treatment of Real Waste

CONCLUSIONS

A key consideration for the application of this technology and process is whether the treated waste is an acceptable form for final disposal, in this case, incineration. This final form of waste has been accepted by Studsvik Nuclear AB, Sweden, where the dry solid waste and the solidified liquid waste are incinerated.

The polymer technology successfully sequesters the tritium into a dry solidified form which is safe to handle and to transport.

The solid waste is no longer in a flammable state. After treatment, the solid waste can then be packaged and transported for disposal.

REFERENCES

"The Nochar Petrobond Absorbent Polymer Tritiated Oil Solidification Demonstration at Mound", W.G. Brunkow, Chamberlain Group, D.R. Campbell, Nochar, Inc., Waste Management Conference, 2000, Tucson, Arizona

"Pre-Treatment of Organic Liquid Waste Stream at Cernavoda NPP", Gabriela Teodorov, Laszlo Toro, Adina Sandru, MATE-FIN, Dennis Kelley, Pacific Nuclear

Solutions, Dorin Dumitrescu, Cernavoda NPP, ICEM conference, 2011, Reims, France.