PRE-TREATMENT OF ORGANIC LIQUID WASTE STREAM AT CERNAVODA NPP

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ABSTRACT

The radioactive waste management system at Cernavoda 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 ten years operation of the Cernavoda NPP a series of waste streams have been developed for waste management purpose. One of these streams is consist of radioactive organic liquid wastes: spent oils, spent solvents, liquid scintillation cocktails (LSC), flammable solids (solid-organic liquid mixture) and sludge.

Effective treatment of organic liquids waste from the initial to the final stage has been a challenge for NPP Cernavoda. All components of the organic liquid waste stream was stored in liquid form in stainless steel drums in the Solid Radioactive Waste Intermediate Storage Facility (SRWISF). This facility was originally designed for solid wastes only, the regulatory body has asked Cernavoda NPP to remove the flammable liquids from this repository as soon as possible.

As a result, at the end of 2008, Cernavoda NPP initiated the solidification of organic liquid wastes (both historical and "fresh" wastes) together with a separation of solids associated with the organic liquids. In accordance with terminology of the International Atomic Energy Agency (IAEA), this system consists of the "pretreatment" of solid and organic liquid radioactive waste.

In 2008 Mate-Fin sign a contract with Cernavoda NPP in order to treat organic liquid waste and inflamable solid waste. The quantity for the entire 4 years project was about 24 tones of organic liquid waste and inflammable waste and after 2 years Mate-Fin succesfully solidified all historical organic liquid waste.

The proposed solution to this problem is to apply proven, low cost polymers to absorb liquid compositions. The polymers may be combined to create a formula specifically designed to permanently solidify a waste stream in a simple one-step process.

Nochar polymer technology (Nochar Petrobound – N910 and Acidbound – N960) has been successfully deployed in the immobilization of organic liquids waste in Cernavoda NPP. A detailed presentation is given related to the quantities of polymer used to solidify a specific organic liquid waste, possible mixture used for a particular type of liquid, the influence of the liquid properties (ex. impurity content) on the composition (N910 versus N960) of the polymer mixture and quantity.

1. CERNAVODA NPP RADIOACTIVE WASTE STREAMS

Canadian Deuterium Uranium (CANDU ®) reactor designs were initially developed in the late 1950s and 1960s 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 unit systems are currently in operation at Cernavoda, with an additional two units expected to be brought online in the near future. The radioactive waste produced by the plants is currently stored in a purpose built interim storage facility located onsite.

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 coming from these soursec should be in the following categories (Cernavoda NPP, 2005):

- Spent resins;
- Spent filter cartridges;
- Solid waste
  - Type 1 solid waste (contact gamma dose rate < 2 mSv h^{-1});
  - Type 2 solid waste (contact gamma dose rate between 2 mSv h^{-1} and 125 mSv h^{-1})
  - Type 3 solid waste (contact gamma dose rate higher than 125 mSv h^{-1}).
- Liquid radioactive wastes
  - Aqueous liquid wastes
  - Organic liquid wastes

Generally the wastes are segregated according to source (reactor building or service building) and type of material.

Organic liquid radioactive waste consists of spent oils, spent solvents, liquid scintillation cocktails, flammable solids and sludge, which cannot be processed through the aqueos liquid radioactive waste system because of their environmental impact.

The sources of liquid organic wastes are as follows (Cernavoda NPP, 2005).

- Lubricating oil from pumps and turbines. The main pathway of contamination is contact with the reactor primary coolant. This waste contains varying amounts of tritium with activity up to about 10^8 Bq kg^1, and small quantities of radionuclides such as Nb-95, Zr-95, Cs-134 and Cs-137.
- Solvents from the decontamination area and from the laboratories and maintenance activities. Spent solvents include: white spirit, ethylene glycol, alcohol ethyl, toluene, chloroform, and acetone.
- Liquid scintillation cocktails. Liquid scintillation cocktails arise from sampling of the Moderator system, PHT systems and their auxiliary systems as well as liquid Effluent systems. They are mainly contaminated with tritium, and are segregated by tritium content.
- Radioactive sludge, from maintenance activities on the active drainage system contaminated with gamma nuclides.
- Flammable solids (solid materials, such as cloths, contaminated with oils) contaminated with gamma nuclides from maintenance activities.

Organic waste is collected at waste collection points in special canisters (one for oil and one for solvents), then placed in specially constructed 220 l stainless steel drums authorised by the CNCAN (their construction differs from the drums used for solid waste). A sample is taken for laboratory determination of the content of a suite of gamma-emitting radionuclides and the content of tritium and are agregated according to the ^3H content.

After the 200 l drums are filled, both waste types are transported to the centralised storage facility.

Flammable solids are transported to compaction room, where they are placed in 200 l drums. After filling, these drums are transported to the centralised storage facility.

2. THE NOCHAR POLYMER

Nochar® polymer technology is an example of a synthetic absorbent system. This system was identified in the optioning process for disposal technologies for this waste stream as offering an alternative waste treatment process (DOE 2001, Ohannell, 1996). Nochar® consists of a range of granulated polymer products which act to immobilize liquid materials through an absorption and inter-molecular bonding process (a mechanism of solidification rather than encapsulation).

Nochar requires no mixing or mixing equipment and it bonds the organic liquid into a soft, spongy, rubber-like material. The polymer crystals can be specifically designed to address the characteristics of mixed waste oil as they exist at any given site (Brunkow, 2002). Polymer loaded waste can be easily micro-encapsulated, far exceeding efficiencies of conventional cement and clay processes. Time of complete solidification varies between 1 hour and 48 hours, depending on the type of waste. Nochar can also be employed remotely, protecting personnel without the need for expensive robotic systems in high radiation environments.

Nochar is so stable because (Kelley, 2003):

- There is no chemical reaction; no heat build-up or heat release from waste for hydrocarbon solidification
- There is no leaching; hydrocarbons are linked and secure in the polymer
- You can blend polymers to solidify waste; polymers are hydrophobic an hydrophilic
- Polymers reduce the risk of fire
- It can immobilize LLW, ILW and HLW
- It remains solid for more than 10,000 years

3. MANAGEMENT OF THE CERNAVODA NPP LIQUID LOW LEVEL WASTE – PROJECT PERFORMED BY MATE- FIN

3.1. STEPS IN THE LIQUID WASTE MANAGEMENT

At the end of 2008, NPP Cernavoda signed a contract with MATE-FIN in order to treat organic liquid waste and inflammable solid waste. The quantity of waste for the entire four year project is about 24 tones of organic liquid and inflammable waste. Accordin to this contract, MATE-FIN initiated the tratment of the organic liquid waste stream by solidification both historical and "fresh" wastes together with a separation of solids associated with the organic liquids. Accordingly, the liquid wastes (oils, solvents and scintillation liquids) are presently being solidified using Nochar Petro Bond and Acid Bond absorbent polymer agent.

Based on the proposal of MATE-FIN specialists the management process is performed in two main steps:

- **Step 1**
    - Collection and segregation of organic liquid waste

- Treatment of organic liquid waste
- Solidification of liquids using absorbent polymer- Nochar Petro Bond and Acid Bond. The main reason was a requirement of the regulatory body not authorising the existence of inflamable liquid waste in the interim solid waste storage facility
- Separation of oil from mixed waste. Give the possibility to treat the solid part as "normal" solid waste
- Characterisation of the liquid waste. Is performed by MATE-FIN team in a laboratory located inside the rasdiological zone of the plant
- Conditioning the treated liquid waste – incineration

- **Step 2** - is performed suplementary to the first step
  - Treatment of compactable solid waste
  - Characterisation of the solid waste
  - Prepare for conditioning – shredding and packaging
  - Conditioning the treated waste together with the treated liquid waste – incineration

3.2. SOLIDIFICATION OF ORGANIC LIQUID WASTE

Solidification process performed by MATE-FIN specialists is achieved by absorbing the liquid radioactive waste into an organic polymer structure. The polymers used for this purpose is NOCHAR Petrobond® and NOCHAR Acidbond® or a mixture of them.

Solid-liquid mixtures are treated with NOCHAR Petrobond® organic polymer, the oil blend is solidified, the remaining solids (plastics and textiles or mixture) do not contain organic liquid and can be treated as "normal" solid waste. The technology developed by MATE-FIN at Cernavoda to perform the separation is based on a "sandwich" structure of solid and absorbent polymer.

4. SOLIDIFICATION AT A SMALL (LABORATORY) SCALE

5.1 EXPERIMENTAL CONDITIONS

A total of about 30 organic liquid waste streams (different type of oils, scintillation fluids, solvents) have been tested by MATE-FIN in the experimental campaign, at the end of 2008.

As it was mentioned earlier the polymers used were Nochar N910 Petrobound and N960 Acidbound. N910 is suitable for the immobilization of hydrocarbon waste streams and N960 can be used for the immobilization of acid, alkali and aqueous waste stream. These polymers can be blended in the event that a mixed hydrocarbon/aqueous waste stream is encountered. In each casea strattificated structure was realised to assure ahigher contact between the polimer and the liquid to be solidified (see figure 1).

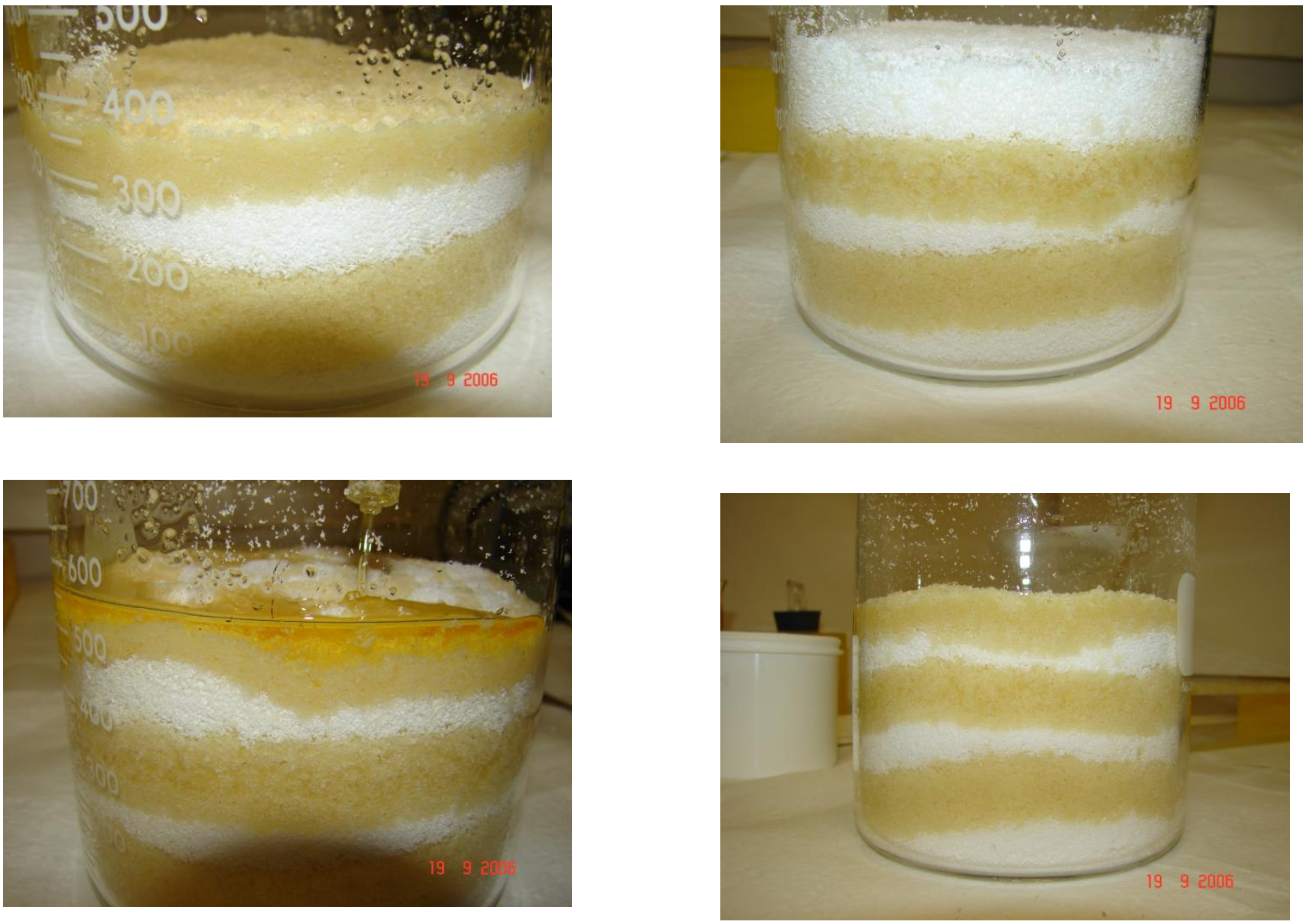

Figure 1 Solidification experiments

5.2 EXPERIMENTAL RESULTS

This section reports experimental results for a random sample of the four main waste streams tested during experimental campaign.

Test 1

- Type of waste: Pump oil
- Formula for polymers: Petrobond (95%) and Acidbond (5%); polymers are blend manually
- Bonding ratio = 1:2,5
- Time for solidification: 24 hours
- Result = good solidification

Test 2

- Type of waste: Machine oil (80%) with water (20%)
- Formula for polymers: Petrobond (84%) and Acidbond (16%); polymers are blend manually
- Bonding ratio: 1:2,2
- Time for solidification: 24 hours
- Result= good solidification

Test 3

- Type of waste : Scintillation fluid
- Formula for polymers: Petrobond (10%) and Acidbond (90%); polymers are blend manually
- Bonding ratio: 1:2
- Time for solidification: 24 hours
- Result = good solidification

Test 4

- Type of waste: Solvents
- Formula for polymers: Petrobond (10-12%) and Acidbond (90-88%); polymers are blend manually
- Bonding ratio: 1:2,1
- Time for solidification: 48 hours
- Result: good solidification

5.3 DISCUSSION

The results of the experimental campaign illustrate that Nochar N910/N960 polymer system have proved effective in the immobilization of organic liquid waste stream into a solid polymeric product, with no leaching of liquid at easy compression.

A key point arising from this experimental campaign, and thus learning for the next step the larger scale project, is the need to test for compatibility and to assess the correct organic liquid waste/ polymer ratio on a case by case basis.

5. SOLIDIFICATION AT A LARGE SCALE

On the basis of the results of this experimental campaign, MATE-FIN started the solidification of organic liquid waste from NPP Cernavoda at the beginning of 2009. During the solidification some significant differences to the experimental campaigns were observed:

1. Vacuum Pump Oil

- A safety layer at bottom of the drum of N910 (6-7 cm) and N960 (3cm) is very important. N960 must be applied to capture the tritium that can be carried by water.
- A safety layer at top of the drum (N910 and N960) have to be placed.
- Regarding the bonding ratio, it was agreed that the value of 2.5:1 (oil to polymer) as maximum ratio works well. This ratio should be maintained in all vacuum pump oil solidifications.
- The solidification at 2.5 : 1 ratio is excellent. The oil/polymer mixture dried within hours.
- The mixture is 95% - N910 and 5% - N960 and should be blended well prior to loading into the drum.
- When mixing the oil with polymer the speed of mixing is critical, make certain that it is slow, not high speed. The key point is to have liquid and polymer touch. Over mixing can damage the polymers.
- When loading the 1st layer of polymers (on top of the safety layer) is necessary to avoid to compress the polymer. During first solidifications the polymer was compressed to avoid

pooling. We noticed that the oil "pooled" at the top due to fast application of the oil through the large holes and the polymer compression slowed down the pull through of the oil.

- With the slow dripping of oil into the polymers (just as it was done in the lab experiment) little or no mixing should be required.
- It is necessary to check the 1st batch of oil from the drum to see if there is a water phase at the bottom of the oil drum. If water is present the polymer formula have to be changed to 80% - N910 and 20% - N960 for the 1st layer of polymer (this procedure should also apply to the scintillation fluid where we did notice an obvious water phase).

2. Scintillation Fluid

- The composition of this waste stream is 10% water and 90% Ultima Gold.
- Age of scint fluid: 4 months to 8 years
- From the first drum solidified, there was phasing of water and Ultima Gold in the transfer tank. The older the scint fluid is, the more likely is the appearance of bi-phase streams.
- There a re two possibilities, either stir/mix (emulsify) the entire drum of scint fluid prior to solidification, or add more N960 in the 1st layer of polymer. More N960 is required to immobilize the water.
- Safety layer must be applied in drum prior to loading the batch layer of polymer. 6-7 cm of N910 and 3 cm of N960 is optimal.
- If the 1st layer is not emulsified, it should be 75% - N910 and 25% - N960.
- Standard polymer after the 1st layer is 85% - N910 and 15% - N960. Blend the polymers well before loading into the drum.
- The maximum bonding ratio should be 2 : 1.
- Mixing will be required with this waste stream. Solidification occurs very quickly, causing a "skin" or top layer solidification. The "skin" does not allow the liquid to penetrate the polymers on its own (via gravity pull).
- Best process may be to solidify in small batches and after mixing in the final drum.
- Review of the solidification on the 2nd and 3rd days indicated a rubber-like consistency.
- Mixing must be slow, not high speed.

3. Machine Oil

- This oil is different from the vacuum pump oil. It presents high volatility with more significant water content.
- Also, issue of bi-phase, water at the bottom of the drum is likely. This must be analyzed at the time that each drum is brought in for solidification.
- First attempt of solidification was done at 2.5:1 ratio. This value was later increased to 3+ as unused polymers throughout the drum was observed. Additional oil was added.
- A full drum was loaded. For the next drums loading, the 2.5:1 ratio was applied to achieve a similar appearance as the vacuum pump oil solidification.

The solidified organic liquid was then packed into drums and allowed to cure for 24-48 hours.

The solidified organic liquid was then packed in PE bags and re-packed in 200L drums, ready for transport to incineration operator.

Between 2009 and 2010, MATE-FIN has successfully solidified all historical and "fresh" organic liquid and inflammable waste, that means about 24 tones.

In this way, MATE-FIN acted in compliance with the regulatory body requirement in order to remove all inflammable liquid waste from interim solid waste storage facility.





6. CONCLUSIONS

On the basis of the results of the experimental campaign and large scale project performed by MATE-FIN, a number of conclusions can be drawn:

- Nochar polymer systems were effective in the immobilization of organic liquid and inflammable waste from NPP Cernavoda;
- During the experimental campaign MATE-FIN established the appropriate organic liquid to polymer ratios depending on type of the waste (oil, solvents, scintillation liquid);
- During 2 years of project there were removed all inflammable liquid waste from Intermediate Waste repository from NPP Cernavoda.

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