Prospects on Immobilization of Liquid Organic Radwastes with the Use of High Technology Polymers – 14065

Yury Pokhitonov *, Valery Romanovsky **, Dennis Kelley ***
* V.G. Khlopin Radium Institute
** Khlopin Radium Institute
*** Pacific Nuclear Solutions

ABSTRACT

Liquid organic radioactive wastes are generated from nuclear fuel cycle facilities and nuclear research centers and from certain uses of radioisotopes in medicine and from research and development in other fields.

The problem of liquid organic radioactive waste immobilization deserves special attention for a number of reasons. Compared to other radioactive wastes, the volume of organic wastes generated is rather small; nevertheless they require a waste management strategy for safe handling, processing and final disposal.

The paper constitutes a survey of literature data depicting methods applied for the management of liquid organic radioactive wastes and the prospects polymer materials usage for the solidification of radwaste with different compositions.

The data on experience of Nochar polymers usage are presented. The main merit of the Nochar polymers is that they provides possibilities to perform the process of waste immobilization directly in containers and the possibilities for urgent localization of radioactive wastes in case of emergency.

This paper describes the technique for liquid organic radioactive waste processing that includes the solidification of LRW by means of the addition of polymers and thermal destruction of solidified solutions in closed vessel.

An important advantage of the alleged technique is the significant volume reduction of the solidified waste moved to the repository.

INTRODUCTION

Liquid organic radioactive wastes are generated from nuclear fuel cycle facilities and nuclear research centers and from certain uses of radioisotopes in medicine and from research and development in other fields.

The most typical liquid organic wastes include: lubricating and hydraulic fluids from reactor operation, solvents and/diluents from fuel reprocessing, scintillation fluids from analytical laboratories, dry cleaning solvents, and miscellaneous organic solvents from decontamination and decommissioning activities.

Radioactive oil wastes produced in nuclear power stations consist of lubricating oils from primary heat transferpumps, hydraulic fluids from fueling machines and turbine oils. These are normally low level wastes (LLWs) containing only relatively small quantities of different radionuclides, such as ^{137}Cs, ^{134}Cs, ^{58}Co, ^{60}Co and ^{65}Zn.

Because the main source of contamination is contact with the reactor primary coolant, these wastes contain varying amounts of water depending on reactor type.

At the same time the removal of tritium from pressurized heavy water reactors (PHWR), heat transport system heavy water can produce an unusual intermediate level tritiated oil waste through contamination of vacuum pump oil by gaseous tritium.

The second, rather large source liquid organic radioactive wastes are tributyl phosphate (TBP) the most commonly used organic extractant in spent fuel reprocessing. During solvent extraction the TBP is diluted, usually with a light saturated, hydrocarbon, as a rule a mixture of paraffins. Although TBP and its diluent are relatively stable during use, they are subject to degradation by hydrolysis and radiolysis. After repeated recycle the solvent is deemed unsuitable for further use and constitutes an intermediate level waste (ILW).

Other sources of liquid organic wastes should be noted and include a variety of organic decontamination liquids from miscellaneous operations, historical usage and / or scintillation liquids.

Scintillation liquids are used in radiochemical analysis (measuring ^{3}H and ^{14}C and less widely for ^{125}I, ^{32}P and ^{35}S) and consist of a three-component mixture of a solute, a solvent, and the sample under investigation.

One of the options for the management of organic radioactive wastes is to store them indefinitely above-ground in an engineered warehouse type facility. This can present a number of problems, both environmental and economic. In this case institutional control is required, and at the same time stored organic wastes may deteriorate and evolve radiolytic gases and presenting a fire hazard.

The most effective liquid organic waste management strategy should be include optionsn for different wastes. The selection the most effective process requires a systematic analysis of whether it is better to store the waste or to treat the waste for disposal.

The main merit of the Nochar polymers is that they provide 1) the option to perform the process of waste immobilization directly in containers and 2) possibilities for urgent localization of radioactive wastes in case of emergency.

This paper describes the technique for liquid organic radioactive waste processing and provides data on experience of Nochar polymers usage. An important advantage of the alleged technique is the significant volume reduction of the solidified waste moved to the repository.

RESULTS OF EXPERIMENTS AND DISCUSSION

No one technique of liquid organic wastes treatment appears to have an overriding advantage in comparison to the other one [1-2].

The incineration is attractive because organic wastes are easily combustible, and high volume reduction factors can be achieved. Where possible, incineration provides very high volume reduction, particularly if the liquid can be fed directly to the incinerator. Depending on the activity of the ash residue, it may be simply packaged for storage and/or disposal or a further immobilization step may be required.

Nevertheless, at the same time incineration alone is not necessarily a satisfactory treatment for organic wastes as further immobilization of the ash may be required depending on its activity level and radionuclide inventory.

The equipment is sophisticated, particularly for off-gas systems which can include afterburners, heat exchangers, cold air injection, filter candles, bag houses, scrubbers and HEPA filters. This means that adoption of this process requires a substantial capital outlay, and operating and maintenance costs are likely to be high.

Even though the technology is well developed, problems still arise with improper burning, component corrosion and off-gas filtration, suggesting that further design improvements are required to enable the technique to attain its full potential. Any decision on whether or not organic radioactive waste incineration should be adopted is likely to depend on the individual economics of each waste storage/disposal scenario.

On the other hand if the costs of waste storage or disposal are sufficiently high to make volume reduction attractive, incineration may be the preferred option despite its generally high cost.

Among the other options it is necessary to note cementation, wet oxidation, and absorption process [1, 2, 3 - 5].

Portland cement alone is not very effective for solidification of any organic liquid wastes. Typically, only about 12 vol. % oil waste from nuclear power plants (NPPs) can be incorporated into cement and still have a waste form that is dry and has reasonable compressive strength. However, significant increases in waste loadings can be obtained by the uses of suitable wetting agents. Mixtures of cement and emulsifying agents improve solidification of organic liquid wastes, particularly if the waste is multiphased, i.e. oil/water/solvent.

Laboratory studies on the cementation of organic liquid waste have been undertaken at Brookhaven National Laboratory [3], and some commercial versions of the process are known [6]. The processes differ from one another in the ingredients used and the order in which they are mixed. This process A cementation process was used at power plant to solidify 9500 L of contaminated turbine oil/penetrating oil/water mixture [4].

The special cement mixtures have been formulated, based on components including: fly ash, bentonite clay, calcium chloride (to accelerate set), and silicate additives to reduce the leachability of organics.

Direct immobilization of TBP and/or odorless kerosene in cement has been cursorily investigated at Harwell [2]. Using cements prepared at 9:1 or 3:1 ratios of blast furnace slag to Portland cement, loadings of TBP / kerosene of ~ 6 wt. percentage could be achieved before TBP/ kerosene began to weep from solidified cement blocks. The loading could be increased to 14 wt. % by the use of emulsifying agents to homogenize the organic and water phases. The compressive strengths of the cement blocks were reduced as the loading of TBP / kerosene or the water concentration increased.

A similar treatment was used at Hanford to solidify about 400 L of pump oils, spirits and TBP / dodecane solvents [5].

The composition for solidification is by weight: organic liquid waste 20 %, emulsifier 4 %, cement 68 %, phosphate additive 8 %. (The phosphate additive is claimed to decrease the amount of cement required for solidification and also to accelerate the set of the mixture and provide better compressive strength of the waste form.)

Absorption is probably the simplest process that can be adopted to convert liquids to a solid form and is practiced extensively in many areas. Many absorbents are available, varying from very simple materials such as sawdust to complex alkyl styrene polymers.
However, the most important drawback of adsorbents is the increase in volume of the final solid waste form that could be as high as 300%.

Absorption and cementation technologies may be use together for treatment of organic liquid wastes [3]. In this approach the organic liquid waste, instead of being emulsified, is absorbed to produce a dry solid, which may then be incorporated into cement. Waste forms produced in this way could contain up to 56 vol. % organic waste. The usual procedure is to saturate the absorbent with the organic liquid then mix this with cement and sufficient water to hydrate the cement.

The limitation of the approach is the requirement to convert liquid into the dry solid state prior to the addition of a binder.

It should also be emphasized that neither processes discussed above can be considered as universal, notably, it is impossible to use single-type equipment for processing of various tapes of liquid organic radioactive waste. The problem of the organic waste solidification can be solved by means of polymers capable to form the insoluble and chemically stable products.
The earliest studies of the polymers application for incorporating LRW were published 30 - 40 years ago [7]. However polymers were not widely used for solidification of LLW during in the past.

Polyvinyl chloride (PVC) was used as an immobilization agent for the spent solvent (TBP /10 vol. % kerosene) at the reprocessing plant (WAK) in the Federal Republic of Germany, from 1971 to 1980 [8].

A technique for immobilization of TBP (20 %) in kerosene in modified polybutadiene rubber of molecular weight 8000 to 9000 and a cross linking agent has also been developed [9]. The components combine and solidify to form a three dimensional matrix in which the TBP and kerosene are trapped at a molecular level.

The cause of depressed attention to polymer materials is appearance and successful introduction in industrial scale another technological processes - cementation and incineration.

In addition, organic materials are inferior to cement with respect to chemical and radiation stability.

Only 10 years ago, it seemed that the polymers would remain just a chapter in history and the prospects for the application of polymers was limited.

Nevertheless, today it's safe to say that the situation is slowly changing, particularly due to the market appearance of the high-tech polymers manufactured by Nochar Company. The, unique properties of these polymers have gradually raised the demand in various countries [10-16].

The principal advantages of waste immobilization within a polymer matrix are as follows:

1. Possibilities to perform the process of waste immobilization directly in containers, and the possibilities for urgent localization of radioactive wastes in case of emergency at various establishments of nuclear and chemical branches.

2. Specially designed equipment or supplementary energy supply are usually not required.

3. The reduction of the number of unit operations as compared with conventional processing methods.

4. The availability of a large range of solution composition with varying properties and processing parameters.

The experimental results obtained have shown that Nochar polymers have a versatile affect and are capable to solidify aqueous solutions of various acidities and specific activities; organic liquids (solvents and extractants); and suspensions and smudges of different compositions.

In addition, the final goal of any waste management is the maximum possible reduction in volume of the materials to be stored in special conditions, with simultaneous minimization of their liberation into environment.

For this goal achieving the complex technology that includes the preliminary solidification of solutions (including organic liquids and mixtures of aqueous and organic solutions) followed by thermal destruction of solidified polymer composition could be used.

As an alternative to the incineration process to reduce the waste volume we used the high temperature closed vessel treatment (carbonization) of the solid organic waste.

The solidification process is performed repeatedly (after the solidified waste is either held in the air at room temperature or dried at the temperature of 20-150^{o}C).

At this stage reducing the volume of solid waste (compared to the initial volume) is obtained by removing the most volatile organic components of the mixture during the evaporation process and reuse of polymers the next portion of liquid organic waste solidification.

If apart from organic liquids the liquid waste contains an aqueous phase, a combination of various polymer materials is used to solidify the whole mass of the liquid waste, without additional stages associated with the mix separation and the liquid phase removal.

After several portions of the solutions are solidified and the compound is held in the atmosphere of air (or under vacuum at the room or elevated temperature) the closed vessel thermal destruction procedure is performed. The ash remainder mass after the process is completed does not exceed 5-15% of the liquid waste mass.

The sequence of individual operations is shown in Fig. 1.

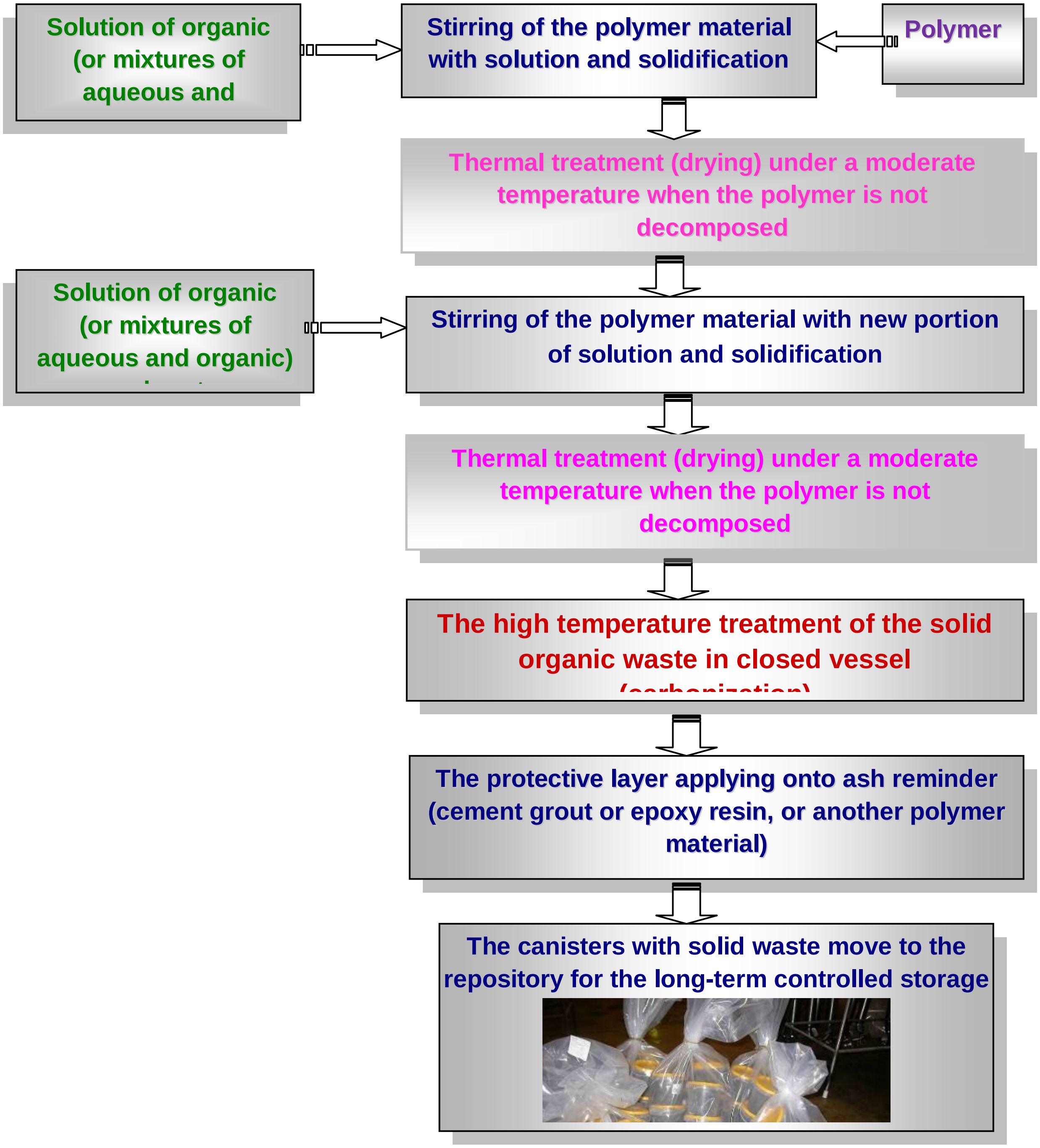

Fig. 1. The sequence of operations when using complex technology of liquid organic waste solidification into the polymer matrix and subsequent thermal degradation of solid waste.

The final stage of the process assumes the surface coating of the compound or the carbonization ash reminder with the protective layer that provides the higher water resistance of the solidified waste and, hence, prevents the radionuclide leaching. The waste prepared according to the described procedure is put into canisters and moved to the repository.

The both the carbonization processes, the thermal treatment in a closed volume and the incineration, are bulky.

On the other hand, if the waste storage costs inclusive of the repository cost are big enough, the waste volume reduction procedure by means of carbonization might appear economically sound, regardless of the high equipment cost.

It should be noted that in the process of liquid organic radioactive waste (LORW) treatment all the procedures specified above could be involved; however separate stages might be eliminated depending upon the composition, specific activity, and the radionuclide speciation of the processed waste.

CONCLUSIONS

Criteria that might be applied in the selection of treatment processes for organic radioactive wastes could include the economics of the process and of waste storage and the desirability of volume reduction. The influence of any or all of these criteria on treatment selection is likely to be case specific to a particular waste producer, or disposal facility operator, and to an individual country.

The necessary condition for the successful sharing of the experience in the application of polymers is the technical and economical assessment of different options available for the LRW solidification. The assessment process could help to visualize the economic effect from the implementation of the proposed technology gained from the reduction of the waste volume transferred to the repository.

It is worth to mention that besides the atomic industry applications the polymers could find their use at various enterprises for localizing toxic waste, namely, heavy-metal containing sludge of the sewage treatment plants, galvanic sludge, etc., severely hazardous when accumulated in the environment.

REFERENCES

1. Willis A.S.D., Haigh C.P., Martin, W., Williams, J.E., "The Design, Development, Construction and Commissioning of a Waste Solidification Plant", Radioactive Waste Management (Proc. BNES Conf. London, 1984), British Nuclear Energy Society, London (1984) 153–160.

2. Options Treatment and Conditioning of Radioactive Organic Liquids. International Atomic Energy Agency. IAEA-TECDOC-656, Vienna (1992).

3. Clark D. E., Colombo P., Neilson R. M. Jr. Solidification of Oils and Organic Liquids, Rep. BNL-51612, Brookhaven Natl Lab., Upton, NY (1982).

4. Jones D., Remark J., D'Muhala T. F., Ward R. C. Solidification of Oil at the James A. Fitzpatrick Nuclear Power Station, NUS Process Service Corp. and Nuclear Technology Corp., Rockville, MD (Nov. 1985)

5. Greenhalgh W. O. Immobilization of Organic Liquid Wastes, Rep. HEDL-SA-3377-FP, Hanford Engineering Development Lab. Richmond, WA (1985).

6. Bowerman B., Kempf C. R., Mackenzie D. R., Siskind B., Pieiulo P. An Analysis of Low-Level Waste: Review of Hazardous Waste Regulations and Identification of Radioactive Mixed Wastes, Brookhaven Natl Lab., Upton, NY (1985).

7. Management of Low and Intermediate Level Radioactive Wastes with Polymers. International Atomic Energy Agency. Technical report series No 289. Vienna (1988).

8. Steag Kernenergie GmbH, Einbettung von Reaktorbetriebsabfallen in Kunststoff, Europ. Appl. Res. Rep. 1 4 (1979) 993-1083. NUKEM-FuE 81074, Final Report BMFT-Working Programme 1982, Nuklear-Chemie und -Metallurgie GmbH, Hanau 1982.

9. Meldrum I. G., Fisher R. G., Plomer A. J. Oil solidifying additives for oil spills. Arctic Marine Oil Pollution Technology, Proc. Sem. Edmonton, 1981.

10. Ake, T.N., et al., "The Nochar Petrobond Absorbent Polymer Tritiated Oil Solidification Demonstration at Mound", WM'00 (Proc. Int. Conf. Tucson, 2000), WM Symposia, Inc., Tucson, AZ (2000) (CD-ROM).

11. Deployment of Nochar Petrobond Technology to Solidify TRU Oil at Rocky Flats. Rocky Flats, Colorado, Environmental Technology Site, PRO-1582-POP/PQP, United States Department of Energy, Office of Environmental Management, October 23, 2001.

12. Kelley D., Campbell D. 'Proven Technologies for the Treatment of Complex Radioactive Liquid Waste Streams; U.S. Department of Energy and International Case Studies', 29th International Symposium on the Scientific Basis for Nuclear Waste Management MRS 2005.

13. Dennis Kelley, Dennis Cambell, Yuri Pokhitonov, et al. "Innovative Technology for Liquid Radwaste Treatment for Use in Newly Designed Applications", 10th International Conference on Environmental Remediation and Radioactive Waste Management, ICEM '05, 4–8 September, 2005, Glasgow, Scotland, UK.

14. Bao Liangin, Lin Meiqiong, Dennis Kelley, "China's Scientific Investigation for Liquid Waste Treatment Solutions", 15th Pacific Basin Nuclear Conference, 15–20 October, 2006, Sydney, Australia.

15. Yury Pokhitonov, Vladislav Kamachev, Dennis Kelley. U.S. Department of Energy's Initiatives for Proliferation Prevention in Russia: Results of Radioactive Liquid Waste Treatment Project, Year 1. International Conference «Waste Management-2010, Phoenix, AZ, USA, March 7-11, 2010.

16. Yury Pokhitonov, Dennis Kelley. The Polymers for LRW Soilidification: a Lost Chapter in the History of Engineering or a Step Forward? International Conference Waste Management-2013, Phoenix, AZ, USA, February 24-28, 2013.