THE IMMOBILIZATION OF ORGANIC LIQUID WASTES

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ABSTRACT

This report describes a portland cement immobilization process for the disposal treatment of radioactive organic liquid wastes which would be generated in a FFTF fuels reprocessing line. An incineration system already on-hand was determined to be too costly to operate for the 100 to 400 gallons per year organic liquid. Organic test liquids were dispersed into an aqueous phosphate liquid using an emulsifier. A total of 109 gallons of potential and radioactive aqueous immiscible organic liquid wastes from Hanford 300 Area operations were solidified with portland cement and disposed of as solid waste during a 3 month test program with in-drum mixers. Waste packing efficiencies varied from 32 to 40% and included pump oils, mineral spirits, and TBP-NPH type solvents.

INTRODUCTION

The immobilization of organic liquid wastes to be generated by the proposed BRET-FMEF (Breeder Reprocessing Engineering Test--Fuels and Materials Examination Facility) operations is described in this report. A liquid/solid incinerator system was originally procured by Westinghouse Hanford Company for this purpose. It was expected that volumes up to 6500 gallons of organic liquid waste per year would be generated. The incinerator equipment is shown in Fig. 1. The original scope of the FMEF included the cleanup and examination of fuel assemblies. The mission of FMEF was changed and fuel examination was eliminated reducing the anticipated yearly generation rate of organic liquid wastes to 1000 gallons or less.

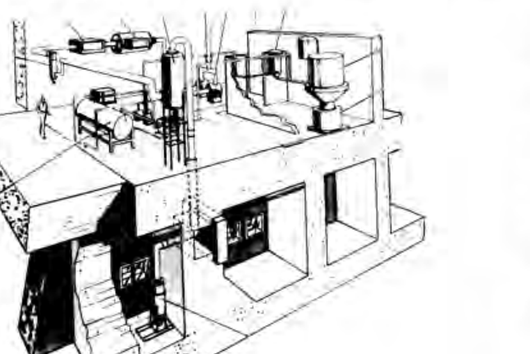

Fig. 1. Liquid/Solid Incinerator.

The BRET design included the installation of the liquid/solid incinerator equipment for treatment of the organic liquid wastes. However, design changes included the installation of a solvent recycle system designed to reduce the generation of organic liquid wastes to about 100 gallons per year. Installation of the incinerator system including exhaust handling and cleanup was estimated to cost about $420,000. The treatment of only 100 gallons of liquid waste didn't justify the installation of the incinerator system plus $100,000 per year to operate it ($1000 per gallon). It is not economically practical, even including the disposal of Hanford 300 Area organic liquid wastes (100 to 400 gallons per year).

Other optional methods of treating the organic liquid wastes were considered including (1) the physical sorption of the liquids and (2) the immobilization of the liquid with portland cement. Absorbed liquids were considered poor waste forms because the waste liquid is readily displaced by other liquid that might inadvertently come in contact with the material. Also, waste packing efficiencies are poor (<33 vol.%), and it is difficult to be certain that all liquid is absorbed. However, immobilization of liquids into a portland cement physically fixes the liquid within the solid and the solid resists displacement of waste components by ground water or other liquids. The cement immobilization option is the basis of the study included in this report. Waste packing efficiencies are better (approximately 35 to 40 vol.%) and "free liquid" if any, is readily apparent from a visual examination of the top product surface. The small volume of waste liquids to be treated would require minimal cement mixing equipment (≤$25,000) and expense costs for cementation are estimated to be ≤$10/gallon and facility space required for the cement equipment would be about 190 ft^2. Originally 290 ft^2 was allotted for the incinerator and the offgas handling system.

Description of the Organic Liquid Wastes

The organic liquid wastes anticipated under BRET operations were primarily residues of TBP (Tributyl Phosphate) used to extract the plutonium from the reprocessing feed, and dodecane or NPH (normal paraffin hydrocarbon) used as a diluent. The TBP is a viscous and oily liquid. Dodecane is a straight chain paraffin hydrocarbon similar to kerosene and handles like a very light oil. Both TBP and dodecane are mutually miscible but immiscible in water. The water immiscibility is the characteristic that makes the disposal of organic waste liquids difficult.

Exposure to radiation destroys the extraction properties of TBP. The formation of DBP and MBP (dibutyl phosphate and monobutyl phosphate) are radiation effects, both exhibiting reduced extraction properties. Radiation has no marked affect on the dodecane diluent.

Therefore, spent 30% TBP-dodecane can be treated in fractional distillation unit to recover the dodecane diluent and undegraded TBP. The degraded TBP must be disposed of and replaced.

The generation of other organic liquid wastes can also result from BRET operations. There are various vacuum pumps, recirculation pumps, etc. These pumps and other machinery require lubricant oils which periodically have to be replaced and disposed of. The heavier oils are also immiscible in water and are part of the organic liquid waste disposal problem. In this report 30% TBP-dodecane and Duo Seal vacuum pump oil are the organic liquids for which cement processing and treatment have been studied.

<u>Use of Emulsifiers</u>

Portland cement is a hydraulic setting cement requiring water to induce hardening of the cement-liquid mixture. Therefore, in order to immobilize water immiscible liquids in portland cement some means of dispersing the liquids in water is required. The easiest way of doing this is to add an emulsifier to the organic liquid so that it is miscible in water. The emulsifiers or dispersants tested for use with the TBP-dodecane solvent and Duo Seal vacuum pump oil include glycerine, Maysol 776, Turco 6007 additive, Tergitol NP-10, Kleen Kut 6222 cutting oil, and Union 76 No. 10 water soluble cutting oil. The latter emuslifier, the Union 76 No. 10 oil appeared to exhibit the best overall dispersion characteristics.

Laboratory emulsion studies using the Union No. 10 oil for TBP-dodecane showed that 20 vol.% emulsifier was required for true theoretical emulsification (non-separable single phase). However, limited dispersion allowed incorporation with cement to occur at lower ratios. The effect of the addition of emulsifier versus the compression strength of cement was tested. The results of the test are shown in Fig. 2. The ratio of No. 10 emulsifier oil to 30% TBP-dodecane should be kept between 15 and 17 weight % for the maximum strength cement product.

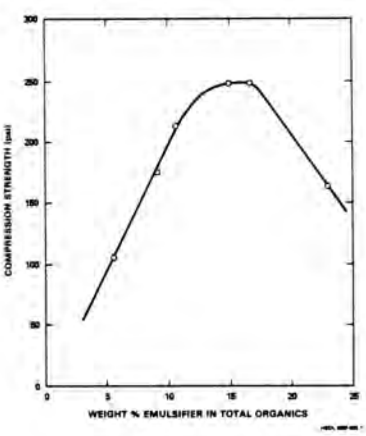

Fig. 2. The Effect of Emulsifier Content on the Cement Strength.

<u>Cement Mixing Equipment</u>

A Kitchen Aid heavy duty mixer Model K5SS with a 5 quart stainless steel bowl shown in Fig. 3 was used for mixing small test batches of cement. The small batches were used for making standard 3-inch diameter by 6-inch high cylindrical samples. The cement mixes were used to define the compositional phase diagrams shown later on. The Kitchen Aid mixer made uniform water-organic emulsions and subsequently smooth cement mixes.

Fig. 3. Lab Scale Cement Immobilization Tests.

Sears and Roebuck utility batch concrete mixer Model No. 838-95001 with a 4.0 cubic ft. capacity and an average 2.5 cubic ft. delivery capacity was used for larger test batches. This mixer allowed the testing of 30 gallon drum batch quantities of non-radioactive cement test batches weighing approximately 450 lbs.

For radioactive work, the cement and component materials were placed in a 30 gallon drum, the drum sealed, and the drum was fixed to a Model 201-VS Morse 500 lb capacity drum roller shown in Fig. 4.

Fig. 4. Drum Roller Cementation Equipment.

The mix included cement, waste oil, emulsifier, aqueous liquid, and sometimes a cement additive. Excellent mechanical mixing was required to make good cement and was generally achieved if substantial void space was left in the drum allowing material movement. However, if the drum was filled to near capacity, mixing was difficult and additional mixing was often required.

The waste packing efficiency related to the fill volume is important in maintaining economy, so the drum roller device was replaced later on by a Morse end-over-end drum rotator mixer. The end-over mixer exhibits better overall mixing properties allowing higher waste packing efficiencies. The end-over drum mixer is shown in Fig. 5.

Fig. 5. The End-Over Drum Mixer.

Cement Compositions and Mixing Diagrams

The maximum cement composition recommended for the fixation of waste oil is given below:

Component	Weight Percent
Waste Oil or Solvent	20% (40 vol.%)
Emulsifier	4%
Cement	68%
Aqueous Phosphate Additive	8%
	100%

This composition is based on cement phase diagrams of several different types of portland cement and can be used with any of the cements tested. The phase diagrams were developed to allow real time adjustments in cement compositions by operators immobilizing either TBP-dodecane solvent or pump oil wastes. Figs. 6-8 are phase diagrams of Type I-II, and III portland cements and emulsifiers with the TBP-dodecane and pump oil. These diagrams show the range of cement compositions that can be considered. Cement mixes with less liquid than the minimum liquid boundary mix are probably too dry to mix properly. The mixes with more liquid than the maximum liquid boundary mix will exhibit free liquid following set (oil, water, or both).

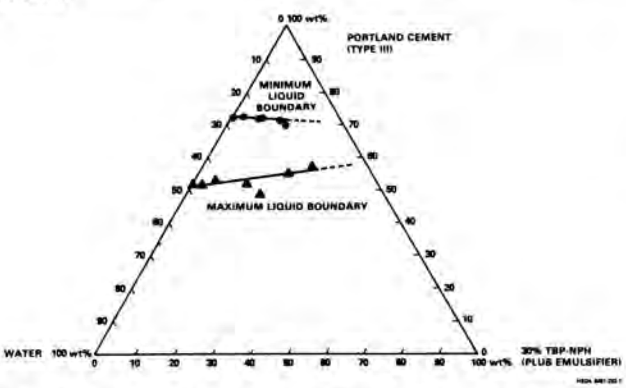

Fig. 6. Solidification of BRET Organic Liquid Wastes In Cement.

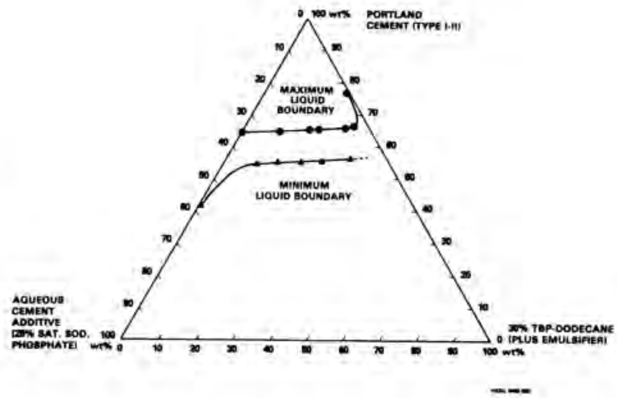

Fig. 7. Cement Immobilization of TBP-Dodecane Liquid Wastes Using a Phosphate Additive.

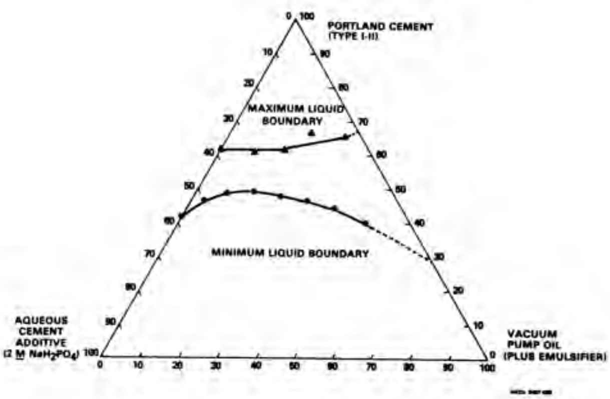

Fig. 8. The Immobilization of Vacuum Pump Oil in Portland Cement.

The phase diagrams do not reflect or exhibit any mechanical strength characteristics. At high waste contents the solid lines become dashed denoting an area of dubious product characteristics. Mix compositions in the area enclosed by dashed lines would yield a soft product and would not be recommended unless a 28-day compressive strength of 50 psi could be achieved. This value was suggested by Phillips[1] as the minimum strength value to define a waste product as a monolithic solid by 10 CFR-61 regulations. Presently, the U.S. Department of Energy does not have any strength requirements for solidified waste. However, the 50 psi minimum value was used for these studies to define a monolithic solid.

Use of Phosphates as a Cement Additive

Figure 9 shows the phase diagram for cement solidification of neutralized phosphoric acid. The figure shows a very different downward direction of the curve as opposed to the generally horizontal direction of the curves in the other phase diagrams.

This is a very good indication that phosphate species can be used as an additive to decrease the amount of cement that is required for solidification. That indeed is the result when adding phosphate

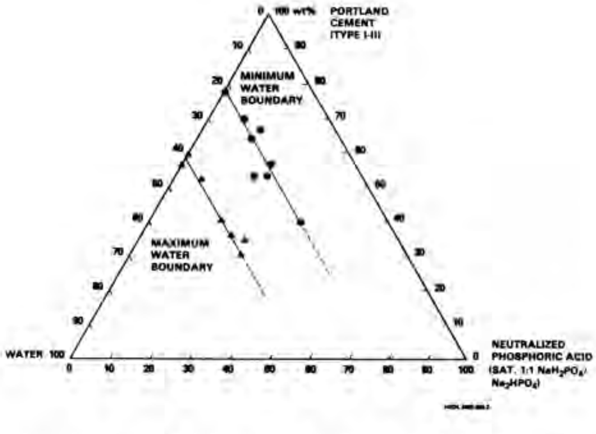

Fig. 9. Cement Solidification of Neutralized BRET Electropolish Liquid Waste (Phosphoric Acid).

species to mixes containing liquid wastes. It exhibits the affect of accelerating the set and also reducing the ratio of cement required for solidification. Phosphoric acid residues arise as another BRET liquid waste generated by the Decon Cell electro-polishing activities. The electro-polish liquid is expected to be grossly contaminated and will require immobilization. It appears there could be advantages in combining a portion of the phosphates liquid wastes with those of organic liquids. Organic liquid wastes act as set retardants and they make the cement slurries more fluid requiring more portland cement powder. The phosphate species on the other hand act as set accelerators and they make cement/slurry/fluidity decrease. The addition of phosphates to the organic liquid cementing process improves it through faster setting and higher waste packing efficiencies.

The Optimum Amount of Phosphate Additive in Cement Mixes

The optimum amount of phosphate to add to a portland cement mix was found to be about 2 wt.% liquid additive in the case where an exactly neutral (1:1 ratio Na_2HPO_4 to NaH_2PO_4) 25% sat. sodium phosphate liquid was being used as the additive. Figure 10 shows the result of a plot of cement compressive strength versus the amount of phosphate added. The 2 wt.% additive liquid turns out to be very close to 0.5 wt.% dry phosphate salt basis or 5 grams dry phosphates per kilogram cement mix.

The Optimum Phosphate Specie

The tribasic phosphate is generally regarded as a set retardant. However the other phosphate species exhibited cement acceleration characteristics sometimes causing a rapid preliminary cement set.

This is helpful for improved solidification of the organic liquids, organics typically act as set retardants. However, selection of the optimum phosphate specie is needed to both accelerate the set, and also provide better compression strength. Figure 11 shows the variation of compressive strengths of the various phosphate species at the same concentration level. The monobasic basic specie NaH_2PO_4 appears to be the best phosphate specie to use.

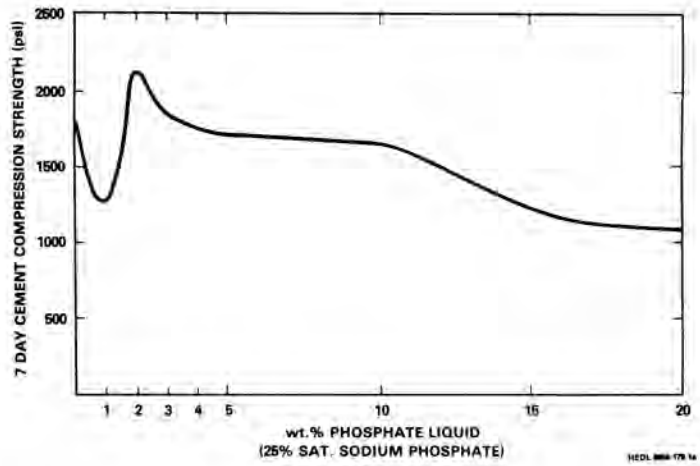

Fig. 10. The Effect of Phosphate Addition on Cement Compression Strength.

Confirmation of the Immobilization Process

The immobilization process was tested by cementing organic liquid waste generated in Westinghouse Hanford Company 300 Area operations into solid waste packaged in 30 and 55 gallon drums. The test demonstrated that the portland cement immobilization method could readily be used to treat and dispose of the anticipated 100 gallons per year radioactive organic liquid waste to be generated by BRET operations. The test commenced on May 8, 1984 with the immobilization of 14 gallons of vacuum pump oil in portland cement using water soluble #10 oil as an emulsifier. This type of activity continued intermittently concluding with the solidification of 9.6 gallons of oil on August 14, 1984.

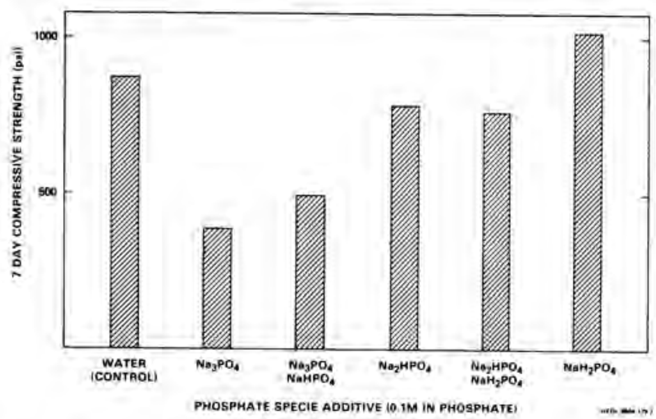

Fig. 11. Cement Strength Versus Phosphate Species.

A total of 109 gallons of organic oil or solvent waste was solidified during that three month test period. All waste residues were solidifed into monolithic solids acceptable for disposal. Most of the organic liquid wastes immobilized were pump oil, some mineral spirits and TBP-NPH extraction solvent containing uranyl nitrate. All of the waste liquids were either radioactive or potentially contaminated and were disposed of as radioactive waste. Solidifications were carried out with Type I-II, Type III, and Pozzolan type portland cements using the drum roller mixing equipment shown in Fig. 4. Obviously; there would be no problems in treating 100 to 400 gallons of organic liquid wastes per year, since this rate was easily demosntrated on a part time basis. Realistically 10,000 gallons per year could be treated and disposed of by solidifying two or more 55 gallon size drums per day.

Product Quality

The quality of an immobilized solvent or oil product is of interest. Cement immobilization can be carried out in a way that fixes the oil and contains it within the product solid. The phase diagrams shown in previous sections define mixing parameters and possible compositions, but they do not infer anything about the quality of the product. Physical and chemical tests on the product are required to define the product quality characteristics. Phillips[1] of Hittman uses a minimum of 50 psi compressive strength to define the physical strength of a cement-waste monolithic solid when qualifying it under Code of Federal Regulations 10 CFR-61 requirements. In this report, the 50 psi compressive strength value will also be used as a minimum strength characteristic to define a "free standing monolithic solid."

A drum of cemented solvent waste was prepared in a 55 gallon drum and later was sectioned to examine the inner cement solids. All of the inner cement set-up and formed a light strength cement product. A quarter section of the drum with cemented waste is shown in Fig. 12.

Fig. 12. A Quarter Section of Cement Immobilized Organic Liquid Waste.

A portion of one of the quarter sections was also cut up into smaller cube sections for testing as shown in Fig. 13. The scope and funding of the program was such that it was not possible to test the product against 10 CFR-61 requirements. However, a compression test of a 6-inch cube section air cured 7 days exhibited 111 psi compression strength. A section was also immersed in water with no apparent detrimental effect. The density of the cement was 1.75 g/cc and waste solvent loading was 35 vol.%.

Cement - Solvent waste mixes containing up to 35 vol.% organic liquids can be solidified directly with

Fig. 13. A Six-Inch Cube Cement Section for Compression Strength Testing.

just cement, emulsifier, waste, and water (no set-accelerator). Figure 14 shows a 30 gallon drum of cement solids that was made up with two 5-gallon cans of 30% TBP-dodecane extractant solvent. The product exhibited a 28-day compression strength of 250 psi, a density of 1.75 g/cc, and the product was flame resistant as shown in Figs. 15 and 16. The product was also immersed in water 1 week with no apparent detrimental effects.

Fig. 14. Cement Solidified TBP-Dodecane Solvent Waste.

Cement - Solvent waste mixes containing up to 45 vol.% organic liquids can be solidified by the use of additives such as monosodium hydrogen phosphate solutions. A composition for 40% is shown, higher compositions are soft and might not meet 10 CFR-61 requirements.

SUMMARY

The following conclusions were made from this study:

1. Solvent waste up to 35 volume percent can be incorporated into cement solids with the use of emulsifiers only.

2. Solvent waste up to 45 volume percent can be incorporated into cement solids with the use of phosphate or other appropriate cement-set additives

in addition to emulsifiers. However, cement products containing greater than 40% might not pass 10 CFR-61 requirements.

3. The cemented solvent waste products improve the fire safety consideration; most cemented products are flame resistant and won't burn without an outside source of heat or flame.

4. The volume of radioactive organic liquid wastes generated in the Hanford 300 and 400 Areas from normal operations can be fixed in cement and disposed of in a practical way with minimal capital equipment cost.

5. Electro-polishing waste liquids (phosphoric acid residues) can also be incorporated into cement for disposal and can be used to accelerate the cement fixation of organic wastes.

6. Use of the incinerator to dispose of a few hundred gallons of organic liquid waste is impractical from a cost standpoint. The cement method appears much more practical.

Fig. 15. Cement Solidified Solvent Product with 35% TBP-NPH Burns when Burner is Applied.

Fig. 16. Cement Solidified Solvent Product with 35% TBP-NPH Quits Burning as Soon as Burner is Removed.

REFERENCES

1. J. W. PHILLIPS, "Qualification of Waste Forms to Meet the Requirements of 10 CFR-61," Waste Management '84, Tucson, Arizona; Volume 2, p. 183, (March 11-15, 1985).