TWENTY-FIVE YEARS OF RADIOACTIVE WASTE CEMENTATION AT LOS ALAMOS NATIONAL LABORATORY (LANL)

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ABSTRACT

At the LANL TA-55 Plutonium Facility, cement fixation has been used for 25 years to dispose of TRU-radioactive[a] wastes generated by its plutonium processing activities at Technical Area 55 (TA-55). As regulations and standards propagated, particularly those associated with the Waste Isolation Pilot Plant (WIPP)[1] and the Resource Conservation and Recovery Act (RCRA)[2] , the cementation process was upgraded to meet ever more stringent requirements. In addition, improvements were made to the process equipment and raw materials to increase throughput and waste loading and reduce labor intensity. This presentation will discuss the evolution of cementation operations from 1980 to 2005.

INTRODUCTION

From 1980 to 1988, cementation operations at TA-55 were conducted using makeshift equipment and borrowed glovebox space. The Portland cement powder used as the stabilization media was loaded into 1-gal containers at a remote location and transferred to the cement glovebox through a conveyor system and hand-to-hand through the glovebox lines. The primary TRU waste stream to which Envirostone™ was applied was evaporator bottoms generated from nitric acid-based plutonium processing at TA-55. This waste liquid was composed of high concentrations of nitric acid and a large number of nitrate salts near their saturation level,[3] including several that would later be regulated by the EPA under RCRA as hazardous materials.[2] The primary waste stream was acidic evaporator bottoms. This waste was pretreated with NaOH to a pH of 13 to precipitate the metal and Pu hydroxides. The hydroxides were filtered and the filter cakes were mixed with Portland cement and water by hand-kneading inside plastic bags. After cementation the bags were placed in a 1-gal container and transferred by the same hand-to-hand/conveyor method to a remote glovebox location where they were loaded into the 55-gal shipping drum.

Process Modifications

The original equipment and process by which liquid waste was cemented was obviously extremely labor intensive. The system was modified in 1981 to decrease physical demands by using electric or pneumatic mixing in 1-gal cans. Additional relief came with elimination of the filtration step and the cementation of the unfiltered precipitate. Transport of the cement powder and cemented waste containers to and from the cement glovebox remained unchanged. Each drum was loaded with 35 one-gallon cans of cemented waste.

Envirostone™ Gypsum Cement

In 1983 LANL investigated a product manufactured by United States Gypsum Company called Envirostone™[b] Gypsum Cement. Envirostone™ was a finely ground, nonflammable powder composed of calcium sulfate hemihydrate, water-soluble melamine formaldehyde resin and a small amount of ammonium chloride that served as a cross-linking agent to facilitate resin curing.[4] Several characteristics of Envirostone™ appeared favorable for cementation operations. First, Envirostone™ hardened at a lower pH of 4. This resulted in less NaOH for pH adjustment and greater waste loading in the mixing container. Second, unlike Portland cement, Envirostone™ was compatible with non-polar organic liquids, such as waste oils, when used in conjunction with Envirostone™ Emulsifier.[5,10] The only apparent drawback to the conversion to Envirostone™ was a its relatively short shelf-life of 6 months[5] and a cost of approximately 10 times that of Portland Type I/II Cement.[6]

Large-Scale Cementation System

In 1988 a significant improvement was made to cement operations by installing a glovebox system dedicated to waste cementation operations. The cementation was performed directly in the 55-gal drum attached to the glovebox.[7,8] The cement powder was delivered to the drum via a bulk storage and screw-feeder delivery system.[9] The mechanized cement delivery system and the in-drum mixing greatly reduced manpower requirements, as well as the time required to produce a cement drum. Due to better utilization of the drum volume, waste loading per drum was increased by 70%. The combination of increased waste loading and faster production resulted in an increase in throughput of 240%.

Envirostone Deficiencies

The 55-gal system operated successfully under both the WIPP and RCRA requirements. However, in 1989 the Envirostone™ waste forms were discovered to be experiencing a delayed free-liquid phenomenon[11,12,13] This resulted in loss of WIPP certification for the TA-55 solidification process and a major effort to remove the free liquid from the drums.[13,14] The free-liquid generation occurred from 7 to 44 weeks after cementation and resulted in the generation of up to 15 liters of liquid from the 55-gallon waste drum.[15] This phenomenon was ultimately traced to internal pressurization by the radiolytic hydrogen breakdown of interstitial water that pushed the water to the surface.[16-20] In 1992 it was also found that the Envirostone™ waste form could not meet the RCRA limit for chromium.[3] The relatively high porosity of the Envirostone™ waste form contributed to these occurrences.[21,22]

Portland Cement

To address the deficiencies of Envirostone™ waste forms, LANL workers investigated the relative performance of Portland-based cemented waste forms. It was shown Portland waste forms did not generate free liquid under ^{60}Co irradiation equivalent to 10^7 rads.[11] On the other hand, the Envirostone™ samples generated free liquid after $2.5X10^6$ rads. Portland waste forms also were shown to exhibit at least an order of magnitude greater resistance to chromium leaching in the Toxicity Characteristic Leaching Procedure (TCLP) and easily passed the EPA chromium standard for non-mixed waste.[2] Based on these results, the cementation operation was converted to the use of Portland cement in 1996. The expected decline in waste loading due to the additional pH adjustment was not significant due to the lower amount of Portland cement required to achieve an adequate stabilization.[11] The loss of the ability to cement the various non-polar organic wastes was rendered inconsequential when the EPA determined that cementation would no longer be allowed for the stabilization of such wastes. The Portland process has continued to successfully meet the current WIPP and RCRA waste form requirements to the present time.

CONCLUSION

As the standards by which waste forms have become more stringent, the waste stabilization field has had to remain flexible and innovative. As at any production facility, LANL took efforts to improve efficiency by changes in both equipment and materials. Thus, the large-scale cementation system was developed and the use of Envirostone™ was started. Mechanically, the cementation equipment has held up surprisingly well over its 17-year life span and still offers reliable service. LANL came full circle with respect to its stabilization media, returning to Portland cement to meet waste form standards after utilizing Envirostone™ for its potential production benefits. As waste form standards continue to tighten, there is every expectation that Portland cement will continue to produce acceptable waste forms. If further improvements are required of the Portland waste form, a wide variety of industry additives are available to enhance performance.

FOOTNOTES

[a] TRU waste is any waste that contains alpha-emitting radionuclides of atomic weight greater than 92 with a half-life exceeding 20 years and a specific activity of greater than 100nci/g.

[b] Envirostone™ is a registered trademark of United States Gypsum Company, Chicago, Illinois.

[c] Portland additives are available to reduce porosity (fly ash), counteract undesired set accelerations or delays, reduce the water content, and improve compressive strength.

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