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TITLE: THE CEMENT SOLIDIFICATION SYSTEMS AT LANL

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THE CEMENT SOLIDIFICATION SYSTEMS AT LANL

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by

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There are two major cement solidification systems at Los Alamos National Laboratory. Both are focused primarily around treating waste from the evaporator at TA-55, the Plutonium Processing Facility. The evaporator receives the liquid waste stream from TA-55's nitric acid-based, aqueous-processing operations and concentrates the majority of the radionuclides in the evaporator bottoms solution. This is sent to the TA-55 cementation system. The evaporator distillate is sent to the TA-50 facility, where the radionuclides are precipitated and then cemented. Both systems treat TRU-level waste, and so are operated according to the criteria for WIPP-destined waste, but they differ in both cement type and mixing method. The TA-55 system uses Envirostone, a gypsum-based cement and in-drum prop mixing; the TA-50 system uses Portland cement and drum tumbling for mixing.

TA-50 SYSTEM

Operations:

The TA-50 cementation system is a fairly simple and infrequently used system. It is necessary to operate this system only 2-3 times/year to meet demands, and only ~12 drums are generated from each campaign. Each campaign is initiated by mixing the tank-accumulated evaporator distillate with caustic-based liquid wastes and NaOH to adjust the tank contents to ~pH 9. This results in the precipitation of the radionuclides in a sludge. The tank decant is processed further and then discharged to the environment. The sludge is rinsed to adjust the solids content to 20-25% and is then held for cementation.

The operation utilizes a DOT 17-C, 55-gal drum as the waste container. The drum is first preloaded with the following constituents: 1) 282 lb Portland cement, 2) 3 gal vermiculite and, 3) 2.5 gal sodium silicate. The sludge volume needed per drum is 23 gal. This volume is assured by draining the sludge first into a 23-gal transfer tank. The sludge is then transferred to the drum through a discharge hose, using a PVC bag sleeve wrapped around the hose to prevent splashing. Due to the low radiological content of the sludge (~2 curies/drum), this operation takes place without glovebox containment. The operators, though, do wear respirators while the drum is being filled, and a negative pressure differential is maintained between the room and tumbling chamber. After the transfer, sealant is applied to the lid gasket, and the drum lid is secured in place. A modified radiator stopcock assembly is installed in the lid bung hole to allow drum venting after tumbling.

The tumbling apparatus mixes two drums at a time. The drums are secured within collars located at opposite ends of a shaft which is rotated to tumble the drums end to end. The drums are mixed for 20 minutes at ~25 rpm. After mixing, each drum is vented through the stopcock fitted with a HEPA filter. The stopcock is then replaced with the carbon composite filter, and the drum package is sent to storage.

TA-50 Problems:
The TA-50 cementation system has experienced only minor problems. During attempts to maximize waste loading, some drums did show surface moisture or a surface too irregular for good radiographic inspection, but the current recipe has been shown to consistently produce a proper set. Because of this, the drums are not routinely inspected to verify set condition. A set-condition verification plan using radiography, though, is being discussed with the WIPP-WAC Committee at this time.

A problem was identified in 9 drums stored uncovered in the outside environment. These drums were found to have developed pinhole-sized corrosion holes through the drum walls at the cement surface. No internal liquid was present, but was previously indicated by crystalline formations found on the cement surface and exuding from the pinholes. A survey of drums stored inside found no other such corrosion, and it was surmised that rainwater, gaining entrance though the carbon filters, had been responsible. So, LANL has also learned the importance of protecting drums with carbon filters from the environment.

TA-55 SYSTEM

Operations:
LANL's cementation system at TA-55 was designed to meet a much more demanding schedule and waste stream versatility. Although the system's primary waste stream is nitric acid-based evaporator bottoms, it is called upon to immobilize a wide variety of other wastes from TA-55 in the form of particulates and water-immiscible organic liquids. The system's design and operation allows for all of these other wastes to be cemented in the same drum with evaporator bottoms. The immobilization agent is Envirostone cement, a gypsum-based product containing ~20% polymerization agent to increase resistance to leaching. It was chosen due to its ability to solidify both acidic and water-immiscible organic wastes in a WIPP-acceptable waste form. The drum package consists of a DOT 17-C, 55-gal drum, lined by 1/16-inch thick lead shielding, 2 PVC bags for glovebox attachment and an inner rigid PE liner. The higher radionuclide content of this waste necessitates this operation takes place within glovebox containment.

The cement fixation glovebox consists of two sections: the mixing section and the pretreatment section. The pretreatment section contains a glass column into which the liquid wastes are vacuum-transferred and pretreated before being discharged to the drum. Here the organic waste is mixed with emulsifier, and acidic waste is coarse-adjusted to ~pH 2 using NaOH solution. The majority of the pH adjustment is done in the column to minimize fuming in the open glovebox, which obscures viewing and increases corrosion of the mixer motors. The mixing section of the glovebox contains mixing stations for two 55-gal waste drums. Each mixing station is outfitted with a 3 1/2-horsepower electric mixer, equipped with two marine props. The mixers serve to provide stirring both during the in-drum pH adjustment and addition of the cement powder to the drum.

After the coarse-adjusted acidic waste is discharged to the drum, the pH is fine-tuned with NaOH to ~4. The pH is monitored by a portable sensor suspended from an extension tube into the solution in the drum. After final pH adjustment and removal of the pH sensor, any available water-immiscible organic waste is emulsified in the glass column and discharged to the drum. Cement powder addition is then started. The cement is transferred from an outside bulk silo, through a series of screw feeders into the glovebox and directed to the drum by a flexible hose. Particulate wastes are added to the drum as the cement is being added to be suspended in the paste. After the prescribed amount of cement has been added, mixing is continued. Mixing was originally continued only until a homogeneous mixture was achieved, but has since been extended to loss of vortex. The next day the drum is inspected for absence of free liquid and particulate and for an adequate set and, if acceptable, is removed from the glovebox, sealed and sent to storage.

<u>Free Liquid Problem:</u>
Since the start-up of this system 2 1/2 years ago, all drums have set hard and dry and were closed with all confidence that they were WIPP-destined. What was discovered ~1 1/2 years ago, though, has resulted in a loss of WIPP certification for this system. A large percentage of drums were found to be generating free liquid after drum closure. The liquid did not behave like bleed water that can appear during the first few days of the curing of cements and is thereafter reabsorbed. This liquid did not appear until 8 to 44 weeks after the drums were produced, and no reabsorption has been observed. Volumes greater than 15 liters have been seen, with a few drums actually overflowing through the lid carbon filter. The liquid was found to be low-level radiologically, ~4 orders of magnitude lower in curie content than the original TRU waste. The cement surface in all drums was found to have remained hard.

To investigate the problem, several small-scale studies with evaporator bottom waste were conducted. Increasing the cement added to equal volumes of waste liquid was found to delay the liquid appearance and reduce the total volume generated, but not prevent it. Liquid appeared after no more than 25 weeks. Volumes close to 20% of the original waste liquid were observed, with liquid generation continuing for up to 40 weeks. In these studies, the mixing time was similar to that originally used in the full-scale system, only long enough to wet the cement powder and achieve a homogeneous paste. A subsequent study demonstrated that a significant benefit could be achieved by extending the mixing time to loss of vortex. Extended-mix samples have still not generated liquid 50 weeks after mixing. Extended mixing to loss of vortex was incorporated into the full-scale system ~6 months ago. Likewise, none of these drums have generated liquid. At the same age, ~25% of the short-mixed drums with the same cement ratio had generated liquid. This trend looks encouraging, and, in fact, extended mixing may have solved the liquid generation problem. On the other hand, it may have only delayed it. More time will be needed to determine this.

Ever if extended mixing does prove to have suppressed liquid generation, it is important the responsible mechanism is understood. The mechanism does appear to be radiation-dependent. Gamma irradiation has recently been found to produce liquid in short-mixed, simulated waste samples cemented with Envirostone. No unirradiated, simulated-waste sample has ever been found to generate liquid. Gamma irradiation has also indicated the phenomenon is not related to the Envirostone polymer. Liquid was likewise generated from a simulated waste sample cemented with Plaster of Paris (Envirostone without polymer). The mechanism may be related to radiolysis of the interstitial water in the cemented waste, with the resulting H2 gas providing the driving force. Future studies will investigate this further by trying to correlate H2 gas generation with that of the liquid. Characterization comparisons on short and extended mixes are being set up to identify differences that may effect resistance to the driving force. It is known extended mixes have greater compressive strength, but SEM, porosimetry and other techniques will be used to search for other differences. These differences may be valuable in developing an operating window necessary to suppress liquid generation.

The full significance of this phenomenon is yet to be determined. It may be restricted only to inadequately-mixed, Envirostone-cemented waste forms. On the other hand, Portland formulations, or any porous waste form containing interstitial water, may be susceptible. At this time, only limited information has been obtained at LANL on how other cements respond. A simulated waste sample cemented with Portland has not generated liquid after an accumulated exposure to ~10 megarads of gamma irradiation. Gamma-irradiated, short-mixed samples have generated liquid at ~3 megarads. In addition, a survey of drums produced by the TA-50 Portland operation has detected no liquid. Further studies are planned to investigate Portland formulations, as well as, other cements.

In conclusion, LANL, of course, welcomes assistance in any form in solving this free liquid problem. No other similar occurrence outside LANL has yet been uncovered to provide insight, but it is not unreasonable that other sites may also have this problem and not be aware of it. LANL would not be aware of this problem if a drum had not overflowed through the carbon filter. A survey of other cemented waste streams, especially Envirostone-based ones, should be seriously considered to investigate this further.

THE CEMENT SOLIDIFICATION SYSTEMS AT LANL

WORKSHOP ON RADIOACTIVE, HAZARDOUS, AND/OR MIXED WASTE SLUDGE MANAGEMENT

December 4, 1990

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LANL CEMENT SOLIDIFICATION SYSTEMS

- Plutonium Facility wastes sent to evaporator
- Evaporator bottoms to TA-55 Cement System:
  - Uses Envirostone Cement
  - In-drum Prop Mixing
- Evaporator distillate to TA-50 Cement System:
  - Uses Portland Cement
  - Mixing by Drum Tumbling

TA-50 CEMENTATION SYSTEM

- Simple design and low throughput
- Drum preloaded with Portland, vermiculite and sodium silicate
- 23 gallon sludge per drum at 20-25% solids
- Low radioactivity requires no glovebox
- Stopcock assembly used to relieve pressure
- Two drums tumbled simultaneously

TA-50 CEMENTATION SYSTEM PROBLEMS

- Exceeding maximum waste loading caused:
  - Minor moisture
  - Irregular surface impeding future radiography
- Rainwater through carbon filters

TA-55 CEMENTATION SYSTEM

- High throughput & flexibility
- Combines particulate and organic waste with evaporator bottoms
- Glovebox containment
- Envirostone cement compatible with acid and organic wastes
- Drum assembly includes lead shielding and rigid liner

TA-55 GLOVEBOX DESIGN

- Pretreatment section:
  - Organic emulsification
  - Coarse pH adjustment
- Mixing section:
  - Two mixing stations
  - Mixers used for pH adjustment and cement addition

TA-55 CEMENTATION SYSTEM

- pH fine-tuned in drum
- Cement powder from silo through screw feeders to drum
- Particulate added to cement paste
- Inspection for liquid and particulate before drum closure

TA-55 FREE LIQUID PROBLEM

- Low-level liquid appears after 8-44 weeks
- Higher cement/liquid ratio delays and reduces liquid
- Extended mixing suppresses liquid to date
- Radiation-dependent mechanism
- Radiolysis on pore water
- Characterization studies planned
- Susceptibility of other cements needs to be investigated

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