

TECHNICAL ADVANCES IN THE USE OF CEMENT FOR EFFECTIVE  
SOLIDIFICATION OF LOW LEVEL RADIOACTIVE WASTE

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ABSTRACT

Conventional techniques for solidifying low-level radioactive wastes with cement do not ensure waste product integrity and the most efficient utilization of container volume. Prior industry studies failed to specify test sample conditioning required to simulate the thermal effects of full scale cement solidification. An innovative chemical and process research program by Chem-Nuclear Systems, Inc. has resulted in improved formulations and testing procedures custom designed for the nuclear industry. These advances have already provided process control methods accurately predicting successful waste treatment even at record high volume efficiencies. New evidence has been described for leach resistant polymer structures formed during and after cement hardening.

BACKGROUND

Immobilizing low-level radioactive waste in cement has been an attractive disposal method since cement is relatively inexpensive and readily available. However, the chemistry of cement is complex, and even today is not clearly defined by the cement industry. Strengths and cure times of cement are based on the use of reasonably clean water with near neutral pH and relatively low ionic content. A cement mix made with water containing boric acid would cure so slowly that no practical strength would be developed. Unfortunately, boric concentrates were one of the first waste streams generated by the nuclear industry which required solidification. Initial attempts to treat this waste with cement produced unsatisfactory results, and corrective actions were not developed. Instead, solidification with new media gained favor, including urea formaldehyde and other organic polymers. A second waste form resisting satisfactory cement solidification has been ion-exchange resin beads in various stages of chemical depletion. When solidified with cement, the resultant products swelled and crumbled, especially when exposed to water or moist atmosphere. Other wastes such as oils, cleaning fluids, and decontamination liquids have been difficult to solidify with cement, forming products of questionable integrity. With this background of technical difficulties, can cement now offer solutions to current waste disposal problems, given today's regulatory and environmental constraints? The answer is yes, but a clear understanding of each situation and its associated chemistry is mandatory.

TECHNICAL GOALS

Chem-Nuclear's research efforts concerning cement solidification intensified after 1979 and were directed toward the following objectives:

1. Develop reliable and predictable processes for solidifying waste with cement using the largest containers consistent with safety and economy.
2. Determine maximum waste loading efficiencies in conjunction with improved product integrity.

3. Conduct leach tests and evaluate additives improving nuclide retention and long-term product durability.

This paper highlights the results of research efforts, and describes some **key advances** in cement formulae and processing technology.

TEST SAMPLE CONDITIONING

The hydration of cement is an exothermic reaction, which for typical Portland cements may release as much as 135 calories for each gram fully hydrated. The test solidification of 100 ml of typical waste liquid, which could be accomplished using as much as 250 gms of cement according to some published formulas, has then a potential release of reaction energy exceeding 33,000 calories. Since the curing of small test samples is difficult to control adiabatically, cure proceeds more slowly with no significant heat generation. However, when this sample formula is scaled-up to economical handling and shipping sizes, typically 200 cubic feet, the actual mixture may require 15,000 lbs. of cement mixed with 110 cubic feet of waste. This mass could rapidly generate hazardous internal temperatures, and solidify to a final product of poor integrity. Therefore, the successful scale-up formula must be verified with a sealed lab sample oven-heated to simulate the average high temperature expected during the full-scale solidification. Temperature control, along with appropriate formulation, has shown that for the above lab formula only 125 gms of cement or less are required for a firm and dry solidification.

CONVENTIONAL ADDITIVES

The speed of cement hydration, affecting set and cure, is substantially controlled by pH and the chemical nature of the waste itself. For certain waste mixtures adjusted to a pH of 11.5 or greater, the heat of hydration may be released too quickly, but for borated liquids with pH controlled to 10.5 or less, set and cure may be delayed for days or weeks. The use of calcium hydroxide as an additive for cement solidifications introduces a desirable buffering effect and produces a controllable relationship with pH, cure time, and heat release. In addition, it has been shown that pre-treating ion-exchange resin beads with sodium hydroxide instead of lime promotes subsequent bead swelling and weaker, less water-resistant matrices.

The suggested use of massive excesses of cement to prevent these shortcomings is only partially effective. In fact, it seriously increases product weight and lowers waste loading efficiency. Test on full-scale billets of ion-exchange resin beads solidified using cement and lime not only verify firm, uniform solids, but indicate little change in product dimensions or integrity even after months of exposure to water. The amount of original resin bead slurry in these tests represented up to 80% of the total solidified volume.

The inherently high pH generated by BWR sulfate concentrates after cement and lime addition can cause rapid curing and non-uniformity. The controlled use of a well known inhibitor such as boric acid effectively retards the set so that the time of cement addition is less critical and the resultant product is more uniform. Cement industry publications also document that calcium chloride, when used in limited amounts, is known to accelerate cure and minimize bleed liquid.<sup>2</sup> Our testing confirms this effect for solidifying boric acid concentrates, but later formulas produced better results without using undesirable chloride additives.

#### PROCESSING FLEXIBILITY

Chem-Nuclear has determined that the separate addition of lime and cement is preferred to achieve improved solidification reactions. An example is the controlled addition of lime to boric acid waste for form insoluble borate structures. Since lime adds no particular structural strength to the matrix, loadings in excess of the molar requirements by the boron analysis should be avoided to ensure maximum waste loading efficiency. An important consideration for certain laboratory test mixtures containing lime, especially those containing resin beads, is allowing ample time for reactions to proceed to near completion before cement addition. The limited solubility of lime compared to sodium hydroxide demands adequate mixing time, since delayed calcium exchange reactions occurring after cement has partially set will seriously weaken or degrade the matrix. The separate addition of lime and cement necessitates overall flexibility in the mechanical processing equipment and limits the usefulness of "fixed formula" cements. These findings confirm Portland I cement as the prime solidification media being readily available, cost effective, and of consistent quality regardless of supplier.

#### NEW CHEMISTRY

Our research program determined that no single formula is useful for the treatment of all waste forms if product integrity, waste loading, and leachability characteristics are to be considered. Studies indicate that with the timely introduction of certain proprietary additives, the boric acid in PWR waste is converted to inorganic, mineral-like, polymer structures. This effect does not substantially increase product strength, which already exceeds the suggested standards, but it has increased waste to additive volume ratios by 13% and allowed waste loadings up to 80% of the total matrix volume. Other advantages of this unique chemistry are decreasing the amount of cement required, which reduces the exothermic heating, lowers product density to less than 90 pounds per cubic foot, and provides positive control of free liquid by causing faster initial set. Incidentally, current technical publications describe the cement chemistry in definite polymeric terms. The December issue of *Science* 82 cites Martin Marietta Company study which states that through calcium silicate formation during the hardening process, cement particles link by themselves and form long polymer chains.<sup>3</sup>

An additive much ignored in current cement technology is silica. The Romans discovered that adding to cement certain volcanic deposits from Pozzuoli, in Italy, not only produced high quality concrete, but also made it virtually impervious to water.<sup>4</sup> This was because the type of silica in the additive gradually combined with lime to form compounds insoluble in water. These Roman cement structures made 2,000 year ago, some even formed underwater, are in better condition today than many products poured in the past 30 years. A recognized leader in the stabilizing treatment of fly ash sludges has determined that lime similarly reacts with individual sludge components to form various stable hydrates of calcium aluminosilicates. It should be noted that these desirable silicate reaction products are derivatives of calcium and should not be confused with processes involving soluble sodium or potassium silicates, which are added to cement as solids or water solutions to accomplish a type of waste solidification. It would be expected that these soluble reagents would be less likely to form durable, water insoluble materials still retaining the sodium or potassium ions. Chem-Nuclear is researching modern silica-type additives, with the expectation of improving both waste volume efficiency and product durability.

#### LEACHABILITY

The leachability of solidified radioactive waste is current regulatory concern, and test performance criteria for waste forms have been proposed in 10 CFR 61. Chem-Nuclear is actively and independently pursuing improved leachability control. Our early test results for solidified simulated PWR waste containing 10% boric acid showed that release of Co-60 and Ce-144 was not detectable, Sr-85 released only slowly, but Cs-137 readily migrated to the leachant. This information is consistent with data reported<sup>5</sup> for silicate cement formulas where it is indicated that divalent and trivalent nuclide ions form insoluble, crosslinked silicate mineral structures. Certain clays and powdered natural zeolites are reported to be effective additives for reducing cesium leachability. Chem-Nuclear has developed new proprietary formulas for boric acid waste that form insoluble inorganic polymers interspersed throughout the cement structure which should retard cesium extraction by leach water. This technology, in conjunction with new silica-type additives, shows promise for effective leach control, and testing of polymer and silica-modified formulations are in progress. During initial testing, a water soluble dye was dissolved in boric acid solution and samples were solidified using several cement formulas currently known. After proper curing, the different test blocks were immersed in water, and the dye began to be extracted immediately from all test blocks except the one representing the new polymer cement formula. The dye in the polymer cement could not be removed even after the sample was crushed and redispersed in the water.

There remains considerable disagreement as to the manner in which leach tests should be performed and in the interpretation of test results concerning actual waste monoliths buried in a specific location. The choice of nuclide test tracers, their concentration, and the chemical form in which they are introduced need standardization so that results from different laboratories can be compared. Chem-Nuclear has recently completed leach studies on a full-size 50 gallon cement test block formulated with 20 gallons of lubricating oil which represented waste material. The original objective was to determine the rate of oil released under the condition of total immersion in tap water. The test results demonstrated not only that oil release was slow, but that release stopped altogether after 7 months. Oil ceased to be released when the inherent

chemistry of the cement system completed formation of an impervious polymer layer of calcium silicate over the entire surface of the monolith. Oil released from the immersed billet rose to the leach water surface and was removed weekly. For the first 6 weeks the block was in a horizontal position, and literally lost about 0.35 gm of oil per day square feet of exposed surface. The mass was then placed in an upright position and the leach water was changed. Over the next 12 weeks, oil continued to be released at a linear rate of about 0.23 gm per day per square feet of exposed surface. Oil release slowed gradually thereafter, and almost no measurable amount was seen between 6 and 7 months, at which point only about 1.4% of the original oil charged had been leached. After removal of the block from the leach water, the reason for the lack of additional oil release was apparent. A smooth, white mineral coating approximately one hundredth (0.01) of an inch in thickness was firmly deposited over the entire surface of the solid. From the known amount of total oil released, it was calculated that leaching occurred only through the first six one-hundredth (0.06) of an inch of the matrix. Test chips chiseled from the block confirmed this figure, as unleached oil droplets were still embedded at only one-tenth (0.10) of an inch from the exposed outer surface.

There are several significant conclusions that may be drawn from the above test concerning the leachability of cement and appropriate test procedures.

1. The leaching mechanisms described infer that sample size and dimension directly affect the percentage amount of waste material extracted. A typically small cylindrical lab sample tested in similar fashion would have suggested that a much greater fraction of waste would have been leached from a full-scale billet than was actually found.
2. The leachability of a waste matrix is not necessarily predicted by extrapolation from a test period of short duration, especially if the solidification matrix contains properly formulated cement that may form an impervious barrier during contact with water.
3. The ability of a waste matrix to "seal itself" during contact with aqueous leachants shows that properly formulated cement is superior to other solidification media. While this effect has not yet been proven with other waste types, the formation of insoluble barriers of calcium silicate is consistent with published reports from independent companies and research laboratories. Also, there is reason to believe that a "sealed" block, if subsequently fractured even after a period of years, would immediately begin re-sealing at the broken surfaces when again in contact with water. This potential assurance of long-term, positive control of leachability cannot be ignored.

#### SUMMARY

Research in cement technology is being conducted in only a handful of laboratories worldwide and is almost exclusively being conducted on structural and flexibility improvements for the construction industry. The goal in radwaste solidification should be long-term integrity of the product and

economy of process, transportation, and disposal. Our findings can be summarized as follows:

1. Leachability studies should include tests on large, "real world" waste volumes.
- NOTE: By ASME standards, concrete does not develop full strength for thirty (30) days; leach tests, therefore, should not commence until the mix has fully cured, preferably by heat-conditioning to temperatures reached during full-scale solidifications.
2. Properly formulated cement products can seal themselves. Studies of duration less than one year may have little validity since mineral coatings may take longer to form on the monolith surface.
  3.  $^{85}\text{Sr}$  and  $^{137}\text{Cs}$  should be "mechanically" secured in the waste matrix made impervious to water as it is difficult, if not impractical, to fix them chemically.
  4. The use of soluble sodium or potassium additives should be avoided.
  5. Resin bead swelling in cement when in contact with water can be avoided economically with the proper choice of additives.
  6. Solidification volume efficiencies of 80% (or more) can be achieved.
  7. New polymer/silica cement formulas show promise in their ability to seal themselves even underwater and/or mechanically bind nuclides.
  8. The mechanical processing system must be flexible in design to ensure proper mixing and addition sequences required for various waste forms.

The benefit of ongoing cement research is indicated by the recent certifications of a new chemical process for solidifying borate concentrates where 100% of the usable container volume is filled with waste. This process is now available for commercial operations.

Urea-formaldehyde and the Dow binder are both polymers that have been used for waste solidification, but whose solid properties differ widely. There are similar quality discrepancies in the solidification capability of various cements, and only proved reliable formulas should be considered. Is cement a good answer? Yes, the path is now clear for this most cost efficient and previously misunderstood media.

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3. American Association for the Advancement of Science, Science 82, December, 1982, Washington, D.C. p.53.

4. Iler, Ralph K. The Chemistry of Silica, John Wiley & Sons, Inc., Somerset, N.J., 1979, p.438
5. Granlund, Roger W. and Hayes, John E. "Solidification of Low-Level Radioactive Waste Using a Cement Silicate Process".