

CONTAINMENT OF RADIOACTIVE WASTES  
USING IMPROVED CEMENTITIOUS BINDERS

J.E. Carlson

Chem-Nuclear Systems, Inc.  
Barnwell Low-Level Waste Disposal Facility  
Barnwell, South Carolina 29812

SUMMARY

Continuing research to improve the solidification of radioactive waste using Portland cement has produced waste forms with markedly lower leach rates for Cesium-137, as well as for other nuclides tested, such as Strontium-85. This has been accomplished primarily by utilizing mineral materials replacing part of the cement, to combine in-situ with lime formed as a by-product during hydration reactions. It has now been demonstrated that these pozzolanic reactions within the pores of the matrix will even prevent the rapid leaching of concentrated nitrate solutions that have been solidified with these same cement admixtures.

INTRODUCTION

The use of Portland cement to solidify low-level radioactive waste materials has been established as the preferred method at many nuclear power plants throughout the world. Chem-Nuclear has pioneered in developing this application for more than a decade. General cement usage for waste solidification began in 1981 to assure compliance with more stringent requirements regarding the volume of free liquid associated with solidified waste products. The South Carolina Department of Health and Environmental Control license for the Barnwell Site (1) specified that drainable liquid could not exceed one gallon, or one-half of one percent of container volume, whichever was less.

While it was demonstrated that cement was an excellent medium for producing dry waste forms, it was quickly apparent that existing concrete technology at that time did not address troublesome chemical reactions encountered with certain waste streams, notably the set inhibiting effect of boric acid solutions and post-expansion of solidified resin bead slurries. It was also discovered that high concentrations of Portland cement (relative to water) that were common for construction work produced undesirably high exotherms in the compact geometry of a 200 cubic foot waste liner. It was with this background of problems that separate formulas were developed, designed to efficiently process each individual waste form according to its particular chemistry. This approach has resulted in over 50 formulas that are fully approved for solidifying Class B and Class C wastes in accordance with the requirements of 10 CFR Part 61.56(b) and the Branch Technical Position (BTP) paper (2).

BACKGROUND

Most Chem-Nuclear solidification formulas contain proprietary additives that are not described in published concrete handbooks, and some represent unique compositions. U.S. Patent 4,620,947, issued November 4, 1986, and assigned to Chem-Nuclear (3), describes the chemical interaction of magnesium oxide to improve the solidification and waste

loading efficiency (initial volume of waste to final solidified volume) of hot boric acid solutions. Continued research in this area has resulted in successful solidification of more highly concentrated borate liquids, even exceeding 50 percent solids. For the past five years, Chem-Nuclear has used proprietary additives to process radioactively contaminated lubricating oils at 40 percent waste volume efficiency in forms that meet certification requirements as necessary. Ongoing research has demonstrated more recently that additional additives that interact with oil facilitate waste loading up to 60 percent without loss of mechanical strength.

IMPROVING THE WASTE BINDING PROPERTIES OF CEMENT

The initial adoption of the 10 CFR 61 NRC BTP paper in 1983 focused quantitative attention on the leachability of solidified waste forms. The establishment of a 6.0 minimum leach index (negative log of diffusivity) for any contained radionuclide also provided a meaningful basis for comparison of various solidification formulas and media. Other parts of the regulation relate to maintaining compressive strength above 50 psi after various exposure conditions. There has been relatively little difficulty meeting these latter criteria with cement formulas. However, initial testing of solidified waste forms for leachability in deionized water, per ANS 16.1 (4), indicated that some formulas were marginally acceptable as concerned leach index. It was recognized at this point that general improvement (reduction) of product permeability would impact on almost all solidified waste forms, except where specific additives exerted predominant control of leaching.

Control of permeability in the concrete industry was for many years accomplished by using low water-to-cement ratios (W/C). The following graph (Fig. 1) (5) illustrates that low permeability is achieved in this fashion, but the corresponding waste loading efficiencies (below 66 percent) are usually prohibitive from weight, cost, exotherm development, and burial volume considerations. Even with lower W/C ratios, cured cement is severely attacked by

solutions containing as little as 0.2 percent (weight) sulfate (6). One principal chemical reason for rapid penetration of water into cured cement is the normal presence of hexagonal crystals of by-product lime, amounting to about 20 percent of the hardened matrix (7). Not only does the lime contribute little to product strength, but it is water-soluble, especially under acidic conditions. This further increases matrix porosity as the lime is removed, and continued leaching is assured.

Current research (8) reports show that it is possible to sharply reduce cement permeability by causing the internal reaction of by-product lime with certain mineral additives. This occurs even when the additives directly replace part of the

Cement, so that the water-to-cement ratios are actually higher, and faster leach rates would be expected. However, a secondary reaction of lime with exposed mineral surfaces within the cement pores themselves results in such significant blockage that the final permeability is improved up to a reported three orders of magnitude. Finely divided amorphous silica minerals are the preferred additives for obtaining in-situ reactions with calcium hydroxide. Silica fume, fly ash, blast furnace slag, rice husk ash, and even ground glass have been reported to demonstrate such pozzolanic activity. The following graph (Fig. 2), developed by Chem-Nuclear, shows that cement admixtures containing mineral additives are likewise three orders of magnitude more leach resistant than with

### COEFFICIENT OF PERMEABILITY VS WATER/CEMENT RATIO ( MATURE PORTLAND CEMENT PASTES )

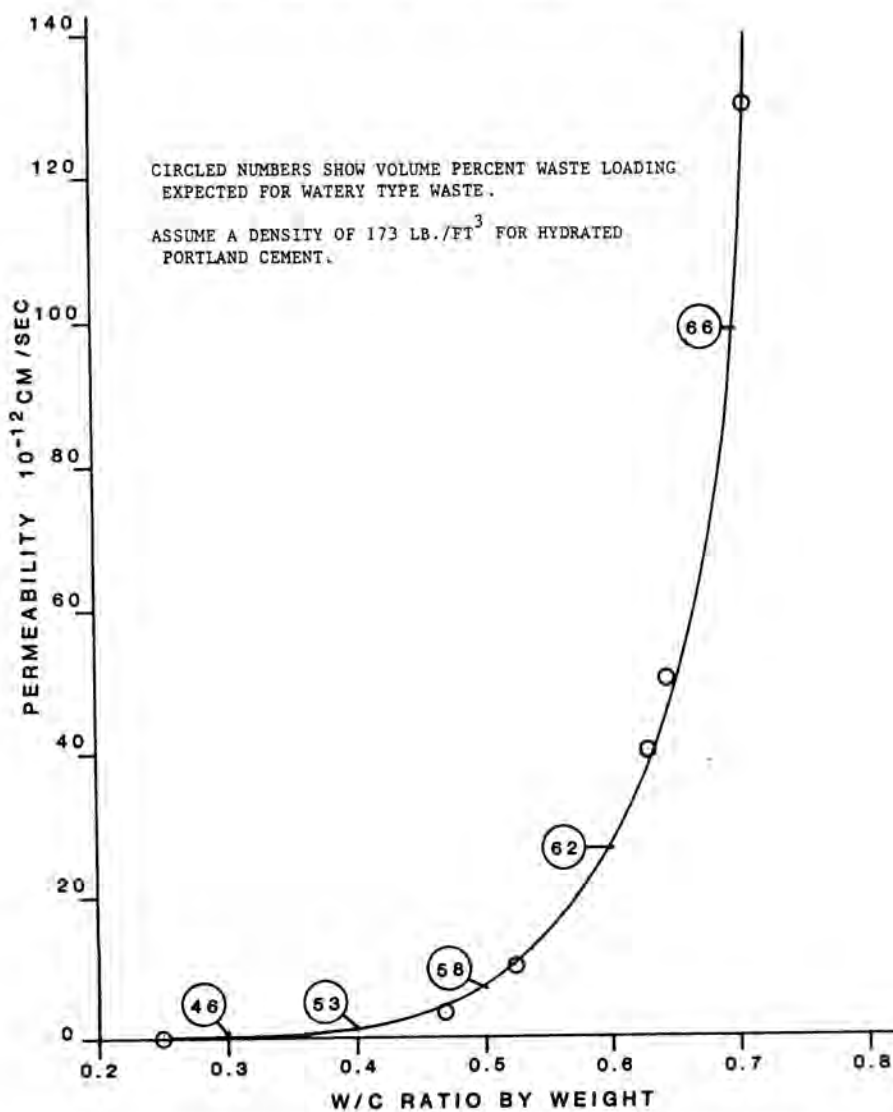


Fig. 1. Coefficient of Permeability vs. Water/Cement Ratio (Mature Portland Cement Pastes).

Portland cement alone. The individual test billets were in the form of tapered cylinders with exposed surface areas of 220 cm<sup>2</sup>, and each was spiked with 55 microcuries of Cesium-137. All other test details are as specified in the ANS-16.1 procedure, except that measurements continued beyond 90 days to demonstrate longer term leaching effects.

In regard to prolonged testing of solidified waste forms, there is an additional chemical mechanism for cement products only that leads to improved leach resistance. This is the gradual exterior deposition of crystalline mineral coatings presumed to be calcium silicate hydrates. It may be argued that the crystals might not form under conditions of continuous leaching by moving water; but intermittent leaching that promotes crystal deposition may be a more likely scenario. In any event, later leach index values above 9.0 were recorded for mineral-modified Portland cement. By comparison, no deposited crystals or later leach improvement was observed for a magnesium oxide "cement" containing the same mineral additives but without any calcium compounds in the formula. Previous observation of a mineral coating was documented by Chem-Nuclear in 1982. It was found that a water-immersed drum-size cylinder of cement-solidified lubricating oil stopped releasing the oil after several months due to surface mineral deposition.

#### SOLIDIFICATION OF CONCENTRATED NITRATE SOLUTIONS

In some waste handling situations, a known radioactive hazard is further complicated by the

presence of chemical components that are listed under EPA disposal regulations. These "mixed waste" compositions then require processing that takes into consideration the respective individual radiological and RERCA regulations. The release of certain dissolved metals, organic pesticides, and even a common anion such as nitrate, is now controlled by EPA regulations.

The EPA specifications for release of chemical materials from monolithic structures are not expressed as leach index numbers that would relate to measurements for radionuclides. Furthermore, the test involves pH adjustment of leachate with acetic acid, which increases the solubility of certain heavy metals. Nitrate release during the test is limited to 45 ppm, and meeting the regulation for such a soluble component requires a solidified waste form that is nearly impervious. Studies by Chem-Nuclear have shown that satisfactory nitrate retention is accomplished with practical cement admixtures even for wastes approaching 50 percent salt concentration.

The graphical information in Fig. 3 illustrates an application of recent improvements in the control of radionuclide leachability as applied to concentrated chemical wastes. It is clear that there is an optimum replacement of cement with mineral additive to achieve the tightest possible matrix. The nitrate study confirms that the internal sealing of cement pores does occur for appropriate admixtures, even when the wet paste is nearly saturated with soluble salts. It is estimated that the formulas demonstrating the least

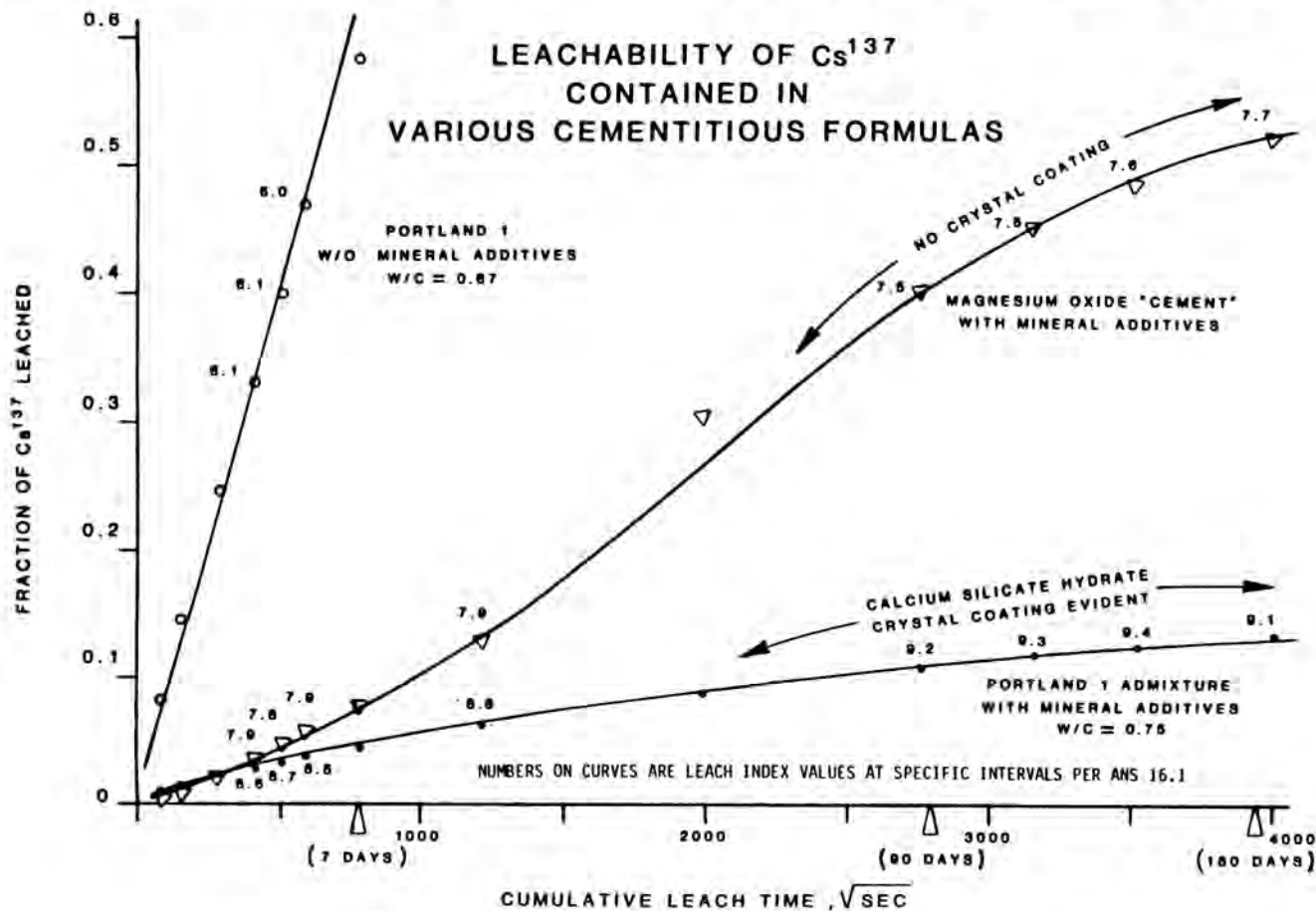


Fig. 2. Leachability of Cs<sup>137</sup> contained in Various Cementitious Formulas.

**CEMENT SOLIDIFICATION  
OF  
NITRATE SOLUTIONS  
( 90% SODIUM FORM )**

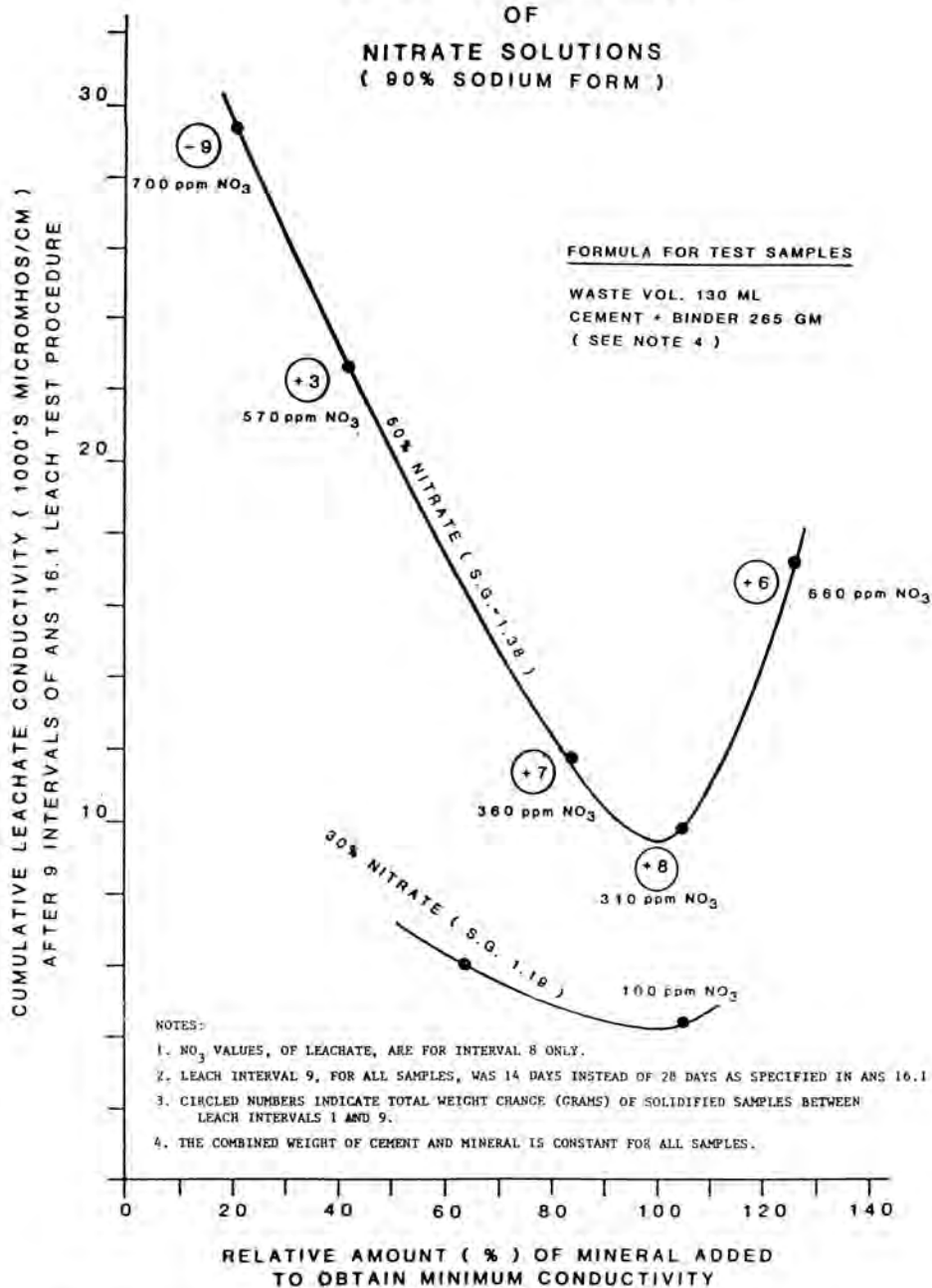


Fig. 3. Cement Solidification of Nitrate Solutions (90% Sodium Form).

cumulative conductivity have equivalent leach index values of 9.0 or more with respect to nitrate, and would pass the EPA requirements. Weight change measurements of the test pieces after damp drying also confirms which formulations are most leach-resistant.

An important point to be emphasized from the curve in Fig. 3 is the somewhat narrow range over which mineral addition promotes minimum leaching. It follows that the reactivity of the cement and mineral must be reasonably controlled, and the preparation of test samples must reflect at least the degree of cure anticipated after the buried container no longer affords protection for the solidified mass. All solidified nitrate samples

developed crystalline coatings after leach intervals became prolonged, but these would not be expected to form and reduce leaching under the conditions of the EPA toxicity tests.

The results of the current study in the "mixed waste" area cannot be automatically extended to soluble waste combinations containing different chemical materials. Apparently, nitrates do not interfere with normal cementitious reactions, but this is not true for other salts such as borates and sulfates. Progress made thus far, however, will allow Chem-Nuclear to address the disposition of new waste combinations by appropriate application of our developed technologies.

## REFERENCES

1. South Carolina Department of Health and Environmental Control.
2. U.S. NUCLEAR REGULATORY COMMISSION, Low-Level Waste Licensing Branch, Technical Position on Waste Form, 1983.
3. J.E. CARLSON, "Solidification of Aqueous Radioactive Waste Using Insoluble Compounds of Magnesium Oxide," U.S. Patent 4,620,947 (Nov. 4, 1986).
4. "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes," ANS 16.1, American Nuclear Society Draft Standard, April 1981.
5. "Guide to the Selection and Use of Hydraulic Cements," Committee Report, ACI 225R-85, Title 82-85, ACI JOURNAL, Figure 6.6, p. 917, November-December 1985.
6. *Ibid.*, Table 6.5, p. 918.
7. P.K. MEHTA, "Pozzolanic and Cementitious Byproducts as Mineral Admixtures for Concrete--A Critical Review," in Fly Ash, Silica Fume, Slag and Other By-Products in Concrete, V.M. Malhotra, Ed., Vol. 1, p. 5, American Concrete Institute, Detroit, Michigan (1983).
8. B.K. MARSH, R.L. DAY, D.G. BONNER, "Pore Structure Characteristics Affecting the Permeability of Cement Past Containing Fly Ash," Cement and Concrete Journal, 15:6 (Nov., 1985), 1027-1037.
9. Federal Register (FR) vol. 45, #98, 5/19/80.