OVERVIEW OF THE APPLICATIONS OF CEMENT-BASED IMMOBILIZATION TECHNOLOGIES DEVELOPED AT U.S. DOE FACILITIES

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ABSTRACT

This paper briefly reviews seven cement-based waste form development programs at six of the U.S. Department of Energy (DOE) sites. These sites have developed a variety of processes that range from producing 25-mm-(1-in.-) diam pellets in a glove box to producing 240-m-(800-ft-) diam grout sheets within the bedding planes of a deep shale formation. These successful applications of cement-based waste forms to the many radioactive waste streams from nuclear facilities bear witness to the flexibility and reliability of this class of immobilization materials.

The U.S. DOE sites and their programs are:

1. Oak Ridge National Laboratory (ORNL), Hydrofracture Grout;
2. Hanford, Transportable Grout Facility (TGF);
3. Savannah River Plant (SRP), Nitrate Saltcrete;
4. EG&G Idaho, Process Experimental Pilot Plant (PREPP);
5. Mound Laboratory (ML), Waste Pelletization Process;
6. ORNL, FUETAP Concretes, and
7. Rocky Flats Plant (RFP), Inert Carrier Concrete Process (ICCP).

The major issues regarding the application of cement-based waste forms to radioactive waste management problems are also presented. These issues are (1) leachability, (2) radiation stability, (3) thermal stability, (4) phase complexity of the matrix, and (5) effects of the waste stream composition. A cursory review of current research in each of these areas is included along with a discussion of future trends in cement-based waste form developments and applications.

INTRODUCTION

Cement-based materials are the most widely used hosts for radioactive low-level waste (LLW) streams, for the following reasons: (1) the materials are low cost; (2) the processes run at low temperature, use standard "off-the-shelf" equipment, and adapt easily to hot cell applications with remote operation and contact maintenance; (3) these waste forms are highly resistant to chemical, thermal, and radiation degradation; and (4) high waste loadings are achieved with a minimum waste volume increase when the waste host formulas are tailored to the specific waste streams. Therefore, the major U.S. Department of Energy (DOE) research and production sites use cement-based waste forms to immobilize their LLW liquids, sludges and solids in mixtures with blends of cements, fly ashes, clays, and other components, whenever they are required to contain or fix large quantities of wastes (>1 million gal).

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5. Mound Laboratory (ML), Waste Pelletization Process;
6. ORNL, FUETAP Concretes; and
7. Rocky Flats Plant (RFP), Inert Carrier Concrete Process.

PROGRAM DESCRIPTIONS

A brief summary of these major DOE waste management programs, which use cement-based waste forms, is presented in this section.

Oak Ridge National Laboratory (ORNL) Hydrofracture Grout

The hydrofracture process[1] has been used at ORNL for the permanent disposal of pumpable LLW liquids and slurries that are generated in this laboratory's diverse research, pilot-scale demonstration, reactor operation, and isotope production facilities. In this process (Fig. 1), the fluid wastes are mixed with a blend of Portland cement, ASTM class F fly ash, and natural clay minerals to form a pumpable grout slurry that is then injected into an impermeable shale formation at a depth of 200 to 300m (700 to 1000 ft). This fluid grout is forced between the bedding planes of the Conasauga shale where it solidifies in thin grout sheets.

Oak Ridge National Laboratory (ORNL) has used this process for nearly 20 years. This method was developed from 1959 to 1965, and the first facility operated from 1966 to 1979. This first

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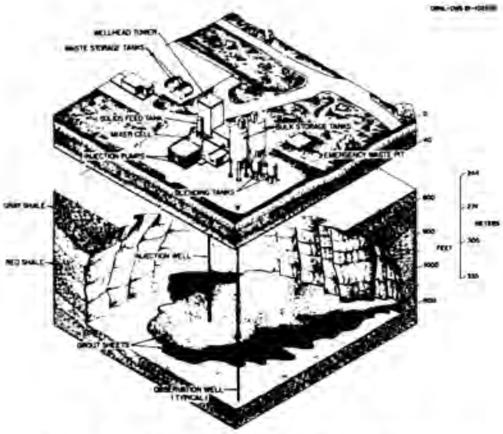

Fig. 1. ORNL hydrofracture process.

hydrofracture facility disposed of more than 8 million L (2 million gal) of waste grout and more than 600,000 Ci of activity. A second hydrofracture facility[2,3] was built to accommodate the 40-year backlog of waste sludges that were hydraulically mined from underground concrete storage tanks. The second facility (Fig. 2) began operation in June 1982 and has already disposed of over 10 million L (2.8 million gal) of grout slurries and 800,000 Ci of waste activity in the first 19 months of its operation.

Fig. 2. Second ORNL hydrofracture facility.

The development of grouts for the hydrofracture process has formed the technological basis for many applications of bulk in situ solidification processes. Furthermore, the 20-year operational history of this ORNL disposal technique has established:

1. the reliability and/or the recoverability of such large-scale grouting systems from process upsets,
2. proven costs of materials, operation, and capital equipment that are lower than most current waste disposal technologies,
3. the flexibility of grouting systems to accommodate a broad spectrum of waste chemistries with a few simple dry-solids blends, and
4. nearly two decades of environmental exposure showing no significant interaction between the host rock and waste form.

This ORNL bulk slurry-grouting technology is currently being transferred and adapted to the waste-management needs of the Hanford Grout Program (HGP), the Weldon Spring Formerly Utilized Site Remedial Action Program (FUSRAP), and the National Lead of Ohio (NLO) Fernald site.

Hanford Transportable Grout Facility Program

The Hanford Transportable Grout Facility (TGF) program is managed by Rockwell Hanford Operations, with technical assistance from Battelle Pacific Northwest Laboratory (PNL) and grouting technology transfer from ORNL. Grouting disposal operations are planned to begin in 1986.[4] Future Purex operations at Hanford will produce liquid wastes requiring storage and tank space that will be freed by disposing of current wastes which are to be immobilized by grouting in near-surface vaults (Fig. 3). Also, this figure shows a future option of sluicing some of the backlogged wastes that are in existing single-wall storage tanks and immobilizing those that are determined to be LLW in a pumpable grout slurry.

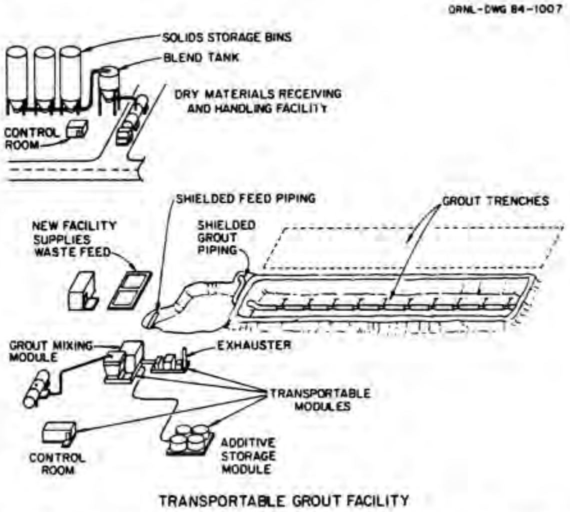

Fig. 3. Rockwell Hanford transportable grout facility.

The shallow land burial siting and grout facility development projects are currently under way by these three organizations, and a 1986 startup is planned. The waste streams currently under study for immobilization in the Hanford Grout Program are (1) Hanford Facility Waste (HFW, decontamination and resin regeneration solutions), (2) double-shell tank salt slurries, and (3) neutralized cladding-removal wastes. The candidacy of these and other waste streams for the near-suface disposal vaults is dependent on the resolution of their classifications as low-level, transuranic (TRU), or high-level waste (HLW). Also, the jurisdictional boundaries among the DOE sites, the state of Washington, the Environmental Protection Agency (EPA), and the Nuclear Regulatory Commission (NRC) are being redefined, and the issues regarding the status of these wastes as mixed radioactive and hazardous chemical wastes are just beginning to be addressed.

Savannah River Plant Nitrate Saltstone

During the 25-year operating history of the Savannah River Plant (SRP), process wastes have accumulated and have been stored in double-wall steel tanks. SRP intends to remove these wastes, separate the radioactive components, and send the resulting high-level defense wastes to the Waste Isolation Pilot Plant (WIPP) in New Mexico. This high-level defense waste will be immobilized in borosilicate glass prior to shipment (Fig. 4). However, the bulk of the SRP waste is a salt cake of predominately sodium nitrate and nitrite, which is rendered an extremely low-level radioactive waste by this SRP partitioning process. Therefore, the principal environmental hazard from this waste stream is the nitrate anion, which forms very soluble salts.

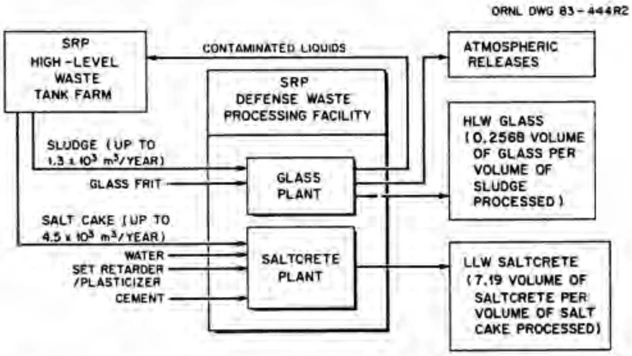

Fig. 4. Savannah River Plant waste treatment plans.

Since 1979, the Savannah River Laboratory (SRL) has been developing a process to safely dispose of the SRP nitrate/nitrite salt waste. This process will mix these salt slurries with a specially formulated cement-based blend to form a pumpable salt, cement-based slurry that will be solidified in shallow trenches and capped. The subsequent impermeable monolitn will prevent the percolation of water, support the water-diverting cap, and form an effective diffusion barrier to the leaching of the soluble nitrate salts. The goal is to meet the federal drinking water standards for nitrate in the nearest ground water at the upper aquifer's exit from the disposal site boundary.

EG&G Idaho Process Experimental Pilot Plant (PREPP)

Since 1970, TRU-contaminated wastes have been placed in interim storage at the Idaho National Engineering Laboratory (INEL), and about 2800 m3 (100,000 ft3) of waste is received each year. The final destination of these TRU-waste packages is the WIPP deep geological repository for defense wastes in New Mexico. Because of the waste package degradation during storage and the regulatory changes in the transportation and WIPP acceptance criteria during this operational period, many of the currently stored packages will be repackaged after their retrieval from the interim storage facilities.

Those packages determined unsuitable for transport to the WIPP facility will first be sent to the Process Experimental Pilot Plant (PREPP) (Fig. 5). All of the unsuitable packages and their waste will be shredded and incinerated to produce a mixture of metals, glass, ceramics, calcined sludges, and ash.[5] This incinerated mix will be screened to separate the fine and coarse fractions. The coarse fraction will be placed in 208-L drums. The fine fraction will be mixed with cement[6] and other additives to form fluid grouts[7] that will be poured over the coarse debris in the drums. The grout will then flow into the interstices encapsulating and fixing both the PREPP coarse and fine wastes into durable monoliths.[8] After a minimum curing time, the cement-based waste form will be transferred to an intermediate storage area, where it will remain for 5 to 10 years before being shipped to the WIPP facility for permanent disposal.

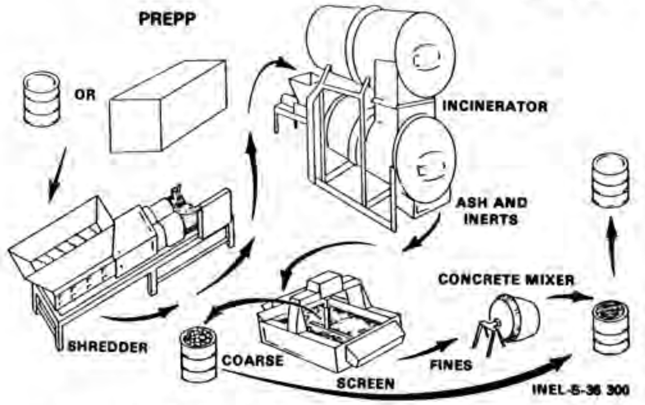

Fig. 5. Process Experimental Pilot Plant (PREPP) flow diagram.

Mound Laboratory (ML) Waste Pelletization Process Demonstration

Mound Laboratory (ML) developed a TRU waste immobilization method for the ML cyclone-incinerator ash, sludges, salt residues, and contaminated soil.[9] The Materials Research Laboratory (MRL) at the Pennsylvania State University[10] had shown that strong, dense, and impermeable cement-based waste forms could be formed with radioactive wastes at moderate temperatures and pressures [150 to 250°C and 177 to 344 MPa (25,000 to 50,000 psi)]. Subsequently, ML developed and demonstrated a process that pressed 1-in.-diam pellets of waste and Portland cement at 177 MPa (25,000 psi).[11,12] This process was demonstrated with "hot" materials in 1982, and the leaching and radiolysis characteristics were studied and documented. Since 1982, no further development has been done, and there are no current applications of this technology in the United States. However, the Federal Republic of Germany (FRG) has developed and tested a disposal scenario that pelletizes the low- and medium-level (LLW and MLW) radioactive wastes from sites throughout the FRG and transports these pellets to a central disposal site, like Gorleben.[13,14] Figure 6 shows this scenario, which uses remote, cost-effective bulk processing and handling technologies to produce and transport the pelletized waste forms to the disposal site, where these pellets are encapsulated in a clean grout paste that is used to form a large monolith [75,000 m^3 (2.69×10^6 ft^3)] in salt caverns at 1000 m below sea level in a salt dome.

ORNL HLW Concretes Formed Under Elevated — Temperature and Pressure

Oak Ridge National Laboratory developed cement-based waste hosts[15-17] that were formed under elevated temperatures and pressures (FUETAP). FUETAP concretes were shown to be effective hosts for high-level radioactive defense waste and may even be considered for commercial HLW applications. The tailored formulas developed at ORNL were prepared from common Portland cements, fly ashes, sands, and clays, with wastes like calcines, frits, and sludges. Figure 7 shows that these concretes are produced by an accelerated cure under mild

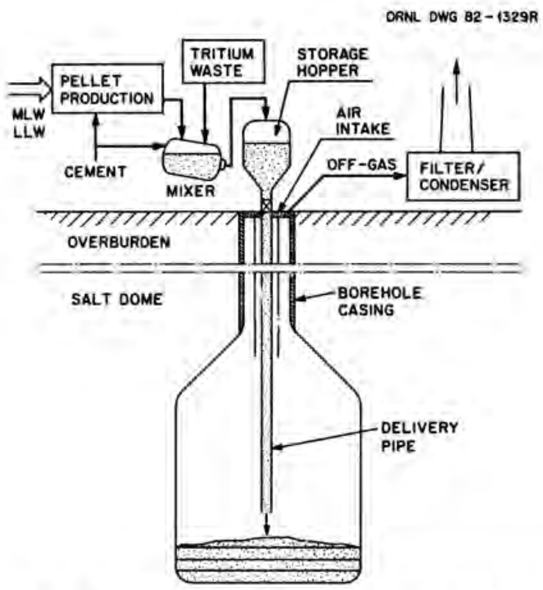

Fig. 6. F.R.G. in situ bulk solidification in salt caverns.

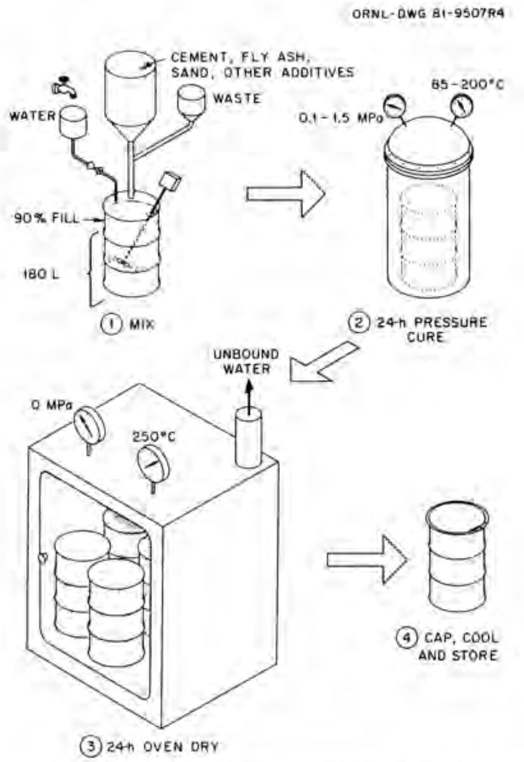

Fig. 7. Generalized FUETAP flowsheet for SRP waste.

autoclave conditions (85 to 200°C, 0.1 to 1.5 MPa) for up to 24 h. The solids are subsequently dewatered at 250°C for 24 h to remove the unbound pore water.

The resulting products were strong (unconfined compressive strengths of 40 to 60 MPa), leach resistant [plutonium leaches at a rate of 10-12 g/(cm^2·d)], and radiolytically stable, monolithic waste forms (total gas G-value of 0.005 molecule/100 eV). This study concluded that these dewatered, autoclaved, cement-based waste hosts were suited for the disposal of HLW.

Since 1981, no further development studies have been conducted at ORNL, and the DOE defense community has no plans to continue this work. However, a 1984 study by GA Technologies chose FUETAP as a potential process to stabilize High-Temperature Gas Reactor (HTGR) fuel pellets. This study reaffirmed the cost-effectiveness[18] of using cement-based waste forms and is the basis for a continuing development program. This ORNL process will be used by GA to perform a demonstration with unirradiated HTGR fuel pellets and perhaps irradiated fuel from the Fort St. Vrain reactor.

Rocky Flats Plant (RFP) Inert Carrier Concrete Process (ICCP)

The Rocky Flats Plant (RFP), together with Quadrex, Inc., has taken a novel approach with some of the TRU waste streams that are difficult to process with standard processing equipment. Some preliminary ORNL studies[19] had shown that it was difficult to process some of the TRU sludges and scavenger precipitates resulting from the RFP operations. Heavy loadings of dispersion aids and super plasticizers are required in the cement-based formulas in order to reduce the water demand of these wastes. This minimizes the volume increase upon immobilization and reduces the subsequent shipping costs to the WIPP facility. Using conventional processing equipment, this resulted in a product with a 40 wt % waste loading with a 20 vol % increase in the waste stream to the final product.

In order to improve the mixability of these sludges with the cement-based fixation blends, Quadrex, Inc., in conjunction with the RFP staff,[20] has developed a processing technique (Fig. 8) that fluidizes both the waste and cement-based components with an inert volatile halocarbon carrier, such as Freon TF. These two fluidized mixtures are metered and blended, and then the volatile inert carrier is removed. This results in good mixing without adding excess water, thus minimizing the final volume of waste to be transported.

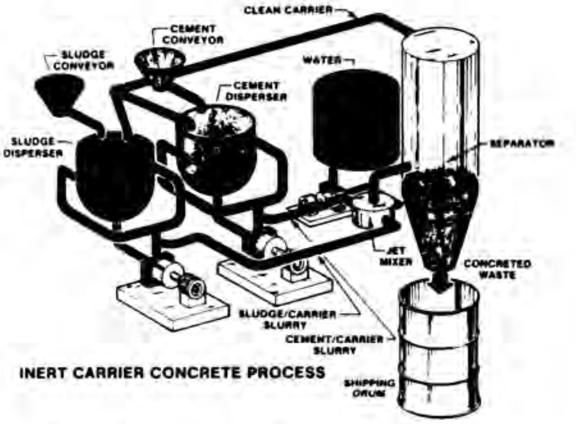

Fig. 8. Inert carrier concrete process.

This approach showed that it is possible to achieve a 40/40/20 ratio of waste-solids/cement/water with no net increase in waste form volume over the dried waste-solids. But, as the added equipment investment, operating complexity, and material costs offset the improved mix homogeneity and lower shipping costs, the RFP has developed an immobilization process using conventional mixes and processing equipment.

DISCUSSION OF MAJOR ISSUES IN USING CEMENT-BASED RADIOACTIVE WASTE FORMS

The common issues in all of these diverse examples of the applications of cement-based immobilization processes and waste forms to radio-active waste management are:

1. leachability,
2. radiation stability,
3. thermal stability,
4. phase complexity of the matrix, and
5. effects of waste-stream composition.

Much of the effort associated with these development programs has been to establish realistic performance criteria and realistic testing protocols to evaluate and compare the performance of these cement-based waste forms among themselves and with other waste forms, like glass, asphalt, polymers, gypsum, and high-temperature ceramics. While the engineering of the cement-based processes is an extrapolation of experience, the performance characterization of these complex, multiphase solids becomes involved. The following discussions summarize the experience of the United States in evaluating the performance of cement-based waste forms in regard to these issues.

Leachability

While cost is usually the final deciding factor, leachability is usually the first concern raised in comparisons of waste forms, even though most pathways analyses ignore the waste forms in their anaylses, and the disposal regulations give no credit for more "durable" waste forms. Nevertheless, most figure-of-merit selection schemes give a large weight factor to leach rates, even on the shorter-lived nuclides, like ^{137}Cs and ^{90}Sr. However, it is very difficult to justify such concerns about leaching of these nuclides in the case of a well-sited repository with a benign hydrology. Then, the leach rates only play a significant role in the analyses of transportation accidents and in early (<300 to 500 years) intrusion-by-man scenarios.

There is a large volume of leach data for various waste forms, such as cement, gypsum, asphalt, grout, polyurethane resins, borosilicate glasses, monazite, and perovskite. Because the measured leach rates are so sensitive to the choice of leach-testing protocol, there is considerable disagreement as to how to interpret and compare the measured leach rates. Nevertheless, we can summarize some general trends in the nuclide leaching behavior of cement-based grouts.

Ordinary Portland cements (OPCs) have very little intrinsic ion exchange capacity for cesium,[21,22] but readily available, inexpensive additives can reduce the cesium leach rate by orders of magnitude (Fig. 9).

The mechanisms controlling strontium leachabilities are more complex and involve the participation by strontium in the hydrosilica formation reactions. The strontium leach rates decrease with the age of the specimen[23] and decrease with a reduction of the excess calcium in the formulation. This is why silica-rich pozzolans, such as fly ash and fumed silica, are successful in reducing strontium leach rates in grout formulas.

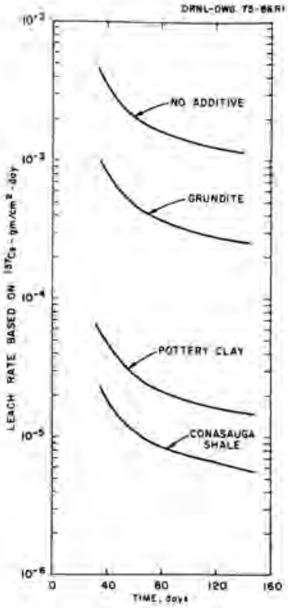

Fig. 9. Leach rates of ^{137}Cs from grouts with various mix additives.

Therefore, the leach rates of grouts can be "engineered" with additives to result in leach rates comparable to the reference borosilicate glass in nearly all of the current standard leach tests, such as the modified-IAEA, ANS 16.1, and the MCC-1. In many cases, the grouts can be shown to be superior to this reference material in long-term tests of a year or more. The effective diffusivities [see Eq. (1)] for cesium and strontium from hydrofracture grouts are on the order of 10^{-8} to 10^{-10} cm^2/s and 10^{-9} to 10^{-12} cm^2/s, respectively. The resulting leach rates are on the order of 10^{-7} to 10^{-8}g/(cm^2·d) or less.

$$F(V/S) = 2[D_e t/\pi]^{1/2} \qquad (1)$$

where

F = fraction leached,
V = sample volume (cm^3),
S = sample surface area (cm^2),
De = effective diffusion coefficient,
t = time (s),
π = 3.14.

The leach rates of uranium, plutonium, and other transuranics are generally so low that it is difficult to measure their leach rates reliably. For example, the leach rates of plutonium are reported to be less than 10^{-11} to 10^{-13}g/(cm^2·d), reflecting the laboratory's detection limits.[21,22] The effective diffusivities for plutonium are estimated to be 10^{-15} to 10^{-19} cm^2/s. Based on both costs and leach rates, cement-based waste forms are the principal choice for TRU wastes.[24,25]

Radiation Stability

Concretes have been used for years in reactor shielding and have been shown to be durable in intense fluxes of radiation. Cementitious materials can even be used to make reactor vessels. Therefore, the concern over radiation stability does not involve the mechanical integrity of the waste-host material but, rather, the radiolytic gases generated by the interaction of the waste form's pore water with the alpha, beta, and gamma radiation. Because the radiolysis products of the pore water are hydrogen and oxygen, there is a concern that an explosive mixture could form in the package. Another concern is that the pressure in the package could become sufficient to breach the waste package prematurely.

The FUETAP studies[13] at ORNL showed that removing the excess, unbound pore water reduced the total gas generation rate from 0.01 to 0.005 molecule/100 eV. Figure 10 estimates the gas pressurization for undewatered and dewatered FUETAP concretes in a 208-L drum filled to 90% capacity. These data show that in the first 1000 years of accelerated dose, less than 1 atm of pressure was formed in the drum. In the dewatered case, pressurization was negligible.

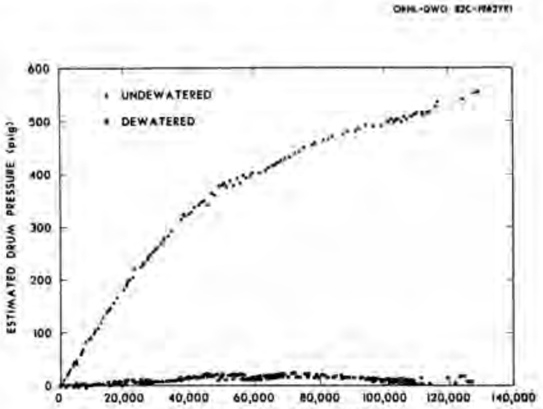

Fig. 10. Comparison of gas generation rates of SRP FUETAP concrete before and after dewatering.

Again, there is a great deal of difficulty in comparing the measurements from different laboratories, because the gas generation rates are sensitive to the specimen geometry, the radiation spectrum, the excess volume of the test apparatus, the water content of the formulas, and the chemistry of the immobilized wastes. For example, a high-nitrate waste will reduce the gas generation rate by a factor of 5 to 20 lower than a mix with water, and these generation rates with alpha radiation are 5 to 10 times higher than those with gamma radiation.

Thermal Stability

The two major concerns with regard to the thermal stability of cement-based grouts are, first, the thermally driven decrepitation from long-term (100 to 1000 years) elevated temperatures due to the decay heat of HLW and, second, the thermal expansion and gasification during a transportation fire. The first concern involves the thermal acceleration of the complex cement-matrix reactions and the differentiation of the amorphous hydrosilicate phases. The resulting crystalline phases are determined by their thermodynamic stabilities and kinetics of formation at the repository's prevailing temperatures and pressures. This concern is only relevant to cement-based waste forms that contain HLW or are codisposed with HLW in a deep geological repository. In the second case, with LLW, ILW, and TRU wastes, no significant intrinsic heat is generated in the wastes, and most of their disposal scenarios involve only the risk from the heat of a transportation accident with a short-term fire [800 to 900°C (1470 to 1650°F) for 30 min].

In general, a moderate increase in temperature to 85 to 115°C (185 to 238°F)[8,13] accelerates the cementation reactions and improves the retention of both cesium and strontium nuclides by the cement-based waste hosts. The strength increases, and the porosity decreases. Since the boiling point of the pore water is 119 to 121°C (246 to 250°F), the package must be designed to withstand or vent the steam pressure that will result from higher temperatures. Another option to avoid both thermal and radiolytic pressurization is to remove the pore water before closing the package, as in the case of FUETAP waste forms. Because removing the excess water stops the cement hydration reactions, the waste form must have reached a reasonable degree of maturity (cure) before being exposed to temperatures sufficient to dry it out.

Concretes can withstand temperatures up to 250°C (480°F) for periods of 2.5 years or more. A study by the Portland Cement Association (PCA)[26] on construction concrete showed a decrease in initial compressive strength that continued throughout the thermal exposure. However, FUETAP concretes which were cured under mild autoclave conditions [85 to 200°C (185 to 392°F)] and dewatered at 250°C (482°F) showed only a small decrease in strength (10%) in the first months but no change afterwards.[13] The FUETAP waste form did not have coarse aggregate or rebars that interact chemically and mechanically with the binding matrix, which were the principal factors in determining the strength of construction concretes. Long-term exposure data are insufficient for these materials at these temperatures.

With regard to transportation testing, the Federal Republic of Germany (FRG) has described an extensive series of fire tests[27] on cement-based waste forms containing sludges with nitrate salts, shredded paper, metal, and ion exchange resin beads. The 200-L drums were exposed to 800 to 900°C (1472 to 1652°F) for 70 to 120 min. The results showed no catastrophic failures. Only the first 2 to 3 cm (0.75 to 1.2 in.) of the monoliths saw temperatures over 110°C (230°F). Sufficient venting through the failed drum lid gasket allowed the steam to escape without rupturing the drum or breaking the ring clamp holding the lid. There was no evidence that any of the contents of the drum were dispersed during these fire tests. Also, there was no evidence that these waste forms had expanded at a rate greater than the carbon steel drums. Therefore, there were no apparent stresses on the drum.

Phase Complexity of the Matrix

The principal concern with regard to the complexity of cement-based waste hosts depends on the ability to predict the mechanism of immobilization and which phases are responsible for sequestering the particular nuclides. Some believe that without this knowledge, the prediction of longevity in a specific geochemical setting cannot be expressed in thermodynamic terms and cannot be modeled. Nevertheless, the record of performance of ancient grouts shows that thermodynamically stabile phases are not necessary for sequestering nuclides and heavy metals for millenia.

Figure 11 shows the evolution of principal phases during the course of the serial and parallel reactions that occur during curing of cement paste.[28]

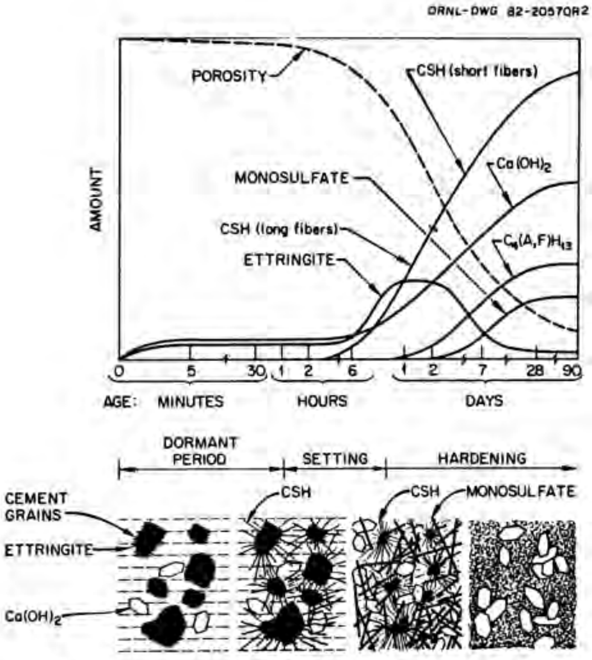

Fig. 11. Course of cement paste reactions.

When the finely dispersed, complex waste sludges are blended with the grout slurries, these cement phases form a binding with a micron-range texture. Therefore, it is very difficult to use microscopic methods to resolve these phases and detect the trace chemical concentrations of the nuclides that may be adsorbed, chemisorbed, or coprecipitated.[13,29]

Nevertheless, the evidence is very strong that elements can be fixed for millennia in grouts[30,31] in a variety of geochemical settings. Ancient grouts from Cyprus and Greece, which are 3500 to 2300 years old, have held their trace metal fingerprints, allowing their constituents to be traced to nearby pits from which they had been mined in antiquity. Furthermore, these ancient grouts still are composed largely of undifferentiated, amorphous hydrosilicates, even after thousands of years. Thus, the in situ performance of these ancient grouts demonstrates that thermodynamic arguments are not as important as many perceive, because these metastable amorphous hydrosilicates have been extremely effective in sequestering a wide range of elements.

Effects of Waste Stream Composition

Waste streams are generally widely fluctuating, complex mixes of elements whose concentrations may vary by one or two orders of magnitude between lots. Since many of these waste constituents have the capacity to interfere with the cement chemistry by accelerating or retarding the various reactions shown in Fig. 11, there has been much negative experience with cement-based waste forms where an inexperienced operator had a "flash" set or no set at all. However, many studies have shown that "forgiving" formulas can be found that tolerate the real waste streams from the DOE sites. Cement-based waste forms should not be applied without determining in advance these interactions between the cementitious components of the dry-solids blends and the constituents of the waste streams. Having done this correctly, cement-based immobilization processes are extremely reliable.

Figure 12 indicates the formation reaction rates of the cementitious phases from a plot of their collective heat-generation rate [J/(g·h)] and time (h). This collective heat release rate results from the changing sums of the serial and parallel reactions of the cement paste and the pozzolanic additives in the grout-waste slurry. The results of studies with isothermal conduction calorimetry[32] show that the maximum heat evolution rate and the reciprocal of its time of occurrence is a sensitive index of the retardation and acceleration effects of the waste streams.

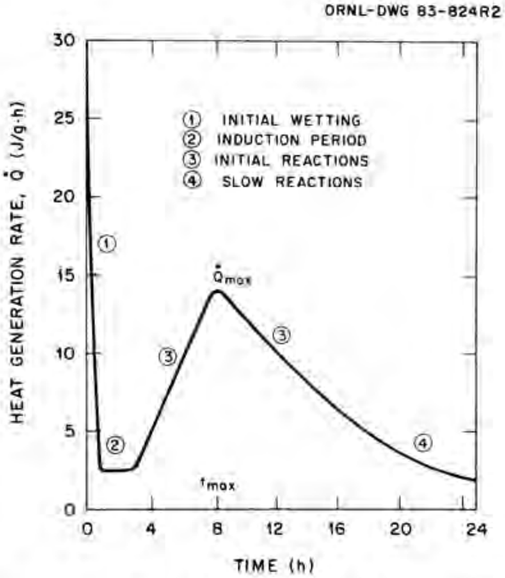

Fig. 12. The relation between heat generation rates in cement paste and time.

For example, the ranking of common waste stream cations and anions that are set accelerators and retarders is shown below:

Cations:

$1/2\ Ca^{2+} > 1/2\ Ni^{2+} > 1/2\ Ba^{2+},\ 1/2\ Mg^{2+}$

$> 1/3\ Fe^{3+},\ 1/2\ Cr^{2+} > 1/2\ Co^{2+} > 1/3\ La^{3+}$

$>> NH^{4+},\ K^{+} > Li^{+} > Cs^{+} > Na^{+}$

<------Acceleration

Retardation ------->

$1/2\ Cu^{2+} > 1/2\ Zn^{2+} > 1/2\ Pb^{2+}$

Anions:

$OH^{-} > Cl^{-} > Br^{-} > NO^{3-} > SO_4^{2-} >> CH_3CO_2^{-}$

<-------Acceleration

Also, many set retarders like fluoride, borate, and complexing organics, such as hydroxycarboxylic acids, citric acid, tartaric acid, benzoic acid, phenol, ethylenediaminetetraacetic acid (EDTA), are commonly found in many waste streams from nuclear facilities. Even the nitrate anion, which is a mild accelerator at low concentrations, can be a set retarder at high concentrations (>1 M).

Therefore, it is impossible to predict a priori, on the basis of chemical analyses of waste streams, how such complex mixtures of accelerators and retarders will effect the set times of particular cement-based blends. Furthermore, these chemical analyses are on 250- to 500-mL samples from 200,000-L (50,000-gal) tanks that are poorly mixed and stratified. The interactions of the waste stream constituents and the cement-based blend components must be determined beforehand with the expected range of waste stream fluctuations.

Cement types and additives can be found to mitigate and offset the combined effects of these waste stream accelerators and retarders. Formulas can be found that are tolerant to the orders of magnitude variation in waste stream constituents. For example, the new ORNL hydrofracture facility has disposed of over 10 million L (2.8 million gal) with only two dry-solids blends, for high- and low-ionic strength waste streams. These wastes represent the 40-year history of the laboratory's pilot-scale testing of the major processing technologies for the various nuclear fuel cycles. These two formulas have successfully immobilized a great spectrum of waste streams and tolerated their variations. Therefore, an appropriate development program can assure processable formulas that are tolerant to these waste stream interactions.

CONCLUSIONS

These studies have shown the broad spectrum of wastes to which cement-based immobilization processes have been shown to be applicable. They include: (1) ion-exchange media, (2) evaporator bottoms, (3) filter media, (4) sludges, (5) slags, (6) incinerator ash, (7) calcines, (8) shredded metals, (9) shredded paper, (10) contaminated oils, and (11) biodigester underflows. Also, cement-based grout slurries have been demonstrated to be compatible with a wide variety of processing technologies, in both batch and large-scale continuous fixation plants.

This paper also briefly described the key issues associated with the application of cement-based hosts to the immobilization of radioactive waste. Although these issues were not completely resolved within the limitations of these discussions, the bases for their resolution were indicated in all cases. Extensive research efforts continue in each of these areas.

In addition, the economics of these cement-based immobilizations favor further development. For example, the total cost of treatment and final disposal via the ORNL hydrofracture process is from $1.00 to $1.50/gal, which is cheaper than current shallow land burial while achieving lower public risk. Therefore, developing such large in situ solidification technologies has a great economic incentive.

Significant future developments will emphasize formulating specific phases that are known to effectively sequester specific troublesome nuclides. Also, additives will be used that maintain the redox potential in the hosts such that nuclides like technetium and neptunium are held in immobile oxidation states.

Another key development area will be the application of these cost-effective, cement-based waste management technologies to hazardous chemical wastes. Preliminary studies at ORNL show that the hydrofracture is applicable to (1) stack-scrubber solids, (2) pickling liquor sludges, (3) fly ash, and (4) oils contaminated with polychlorinated biphenyls (PCBs), polynuclear aromatics (PNA), and pesticides.[33,34] The laboratory's studies are currently addressing the issues of permitting and delisting these waste forms as nonhazardous wastes under the current EPA regulations by virtue of their geochemical stability and nonleachability. Also, economic studies show that regional treatment and disposal facilities for hazardous industrial wastes using large-scale in situ disposal technologies are less expensive and safer than current technologies.[35] The use of cement-based waste hosts is rapidly expanding in scope.

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