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DEVELOPMENT PROGRAMS IN THE UNITED STATES OF AMERICA FOR THE APPLICATION OF CEMENT-BASED GROUTS IN RADIOACTIVE WASTE MANAGEMENT

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L.R. Dole and T.H. Row*

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.) diameter pellets in a glove box to producing 240 m (800 ft.) diameter 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 materials.

This paper also discusses the major issues regarding the application of cement-based waste forms to radioactive waste management problems. 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 area is given.

This paper also discusses future trends in cement-based waste form development and applications.

Introduction

Cement-based materials are the most widely used hosts for radioactive low-level and Intermediate-level wastes (LLW and ILW), for the following reasons: (1) the materials are low cost; (2) the processes occur at low temperature, use standard "off-the-shelf" equipment, and are easily adapted to hot cell application with remote operation and contact maintenance; (3) these waste forms are highly resistant to chemical, thermal, and radiation effects; and (4) high waste loadings with a minimum of waste volume increases can be achieved, when the waste host formulas are tailored to the specific waste streams.

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Therefore, the major U.S. Department of Energy (DOE) sites use cement-based waste forms to immobilize their LLW and ILW waste 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.

The DOE sites and their programs are:

1) Oak Ridge National Laboratory (ORNL), Hydrofracture Grout,
2) Hanford, Hanford Grout Program (HGP),
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 .

Program Descriptions

The following are brief summaries of these major DOE waste management programs which use cement-based waste forms:

1. Oak Ridge National Laboratory (ORNL) Hydrofracture Grout.

The Hydrofracture Process [1] has been used at ORNL for the permanent disposal of pumpable low-level (LLW) and intermediate-level (ILW) waste liquids and slurries which have been generated in this Laboratory's diverse research pilot-scale demonstrations, reactor operations, 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 which is then injected into an impermeable shale formation at a depth of 200-300 m (700-1,000 ft.). This fluid grout is forced between the bedding planes of the Conasauga shale where it solidifies in thin grout sheets.

ORNL hydrofracture is a large-scale batch process in which 600,000-800,000 L (150,000-200,000 gal) of waste solution or slurry is injected semicontinuously in 18 h of operation spread over 2-3 d. ORNL has used this process for nearly 20 years. This process was developed from 1959 to 1965, and the first facility operated from 1966 to 1979. This first hydrofracture facility disposed of more than 8 million liters (2 million gal) of waste grout and more than 600,000 Ci of activity. A second hydrofracture facility [2,3] was

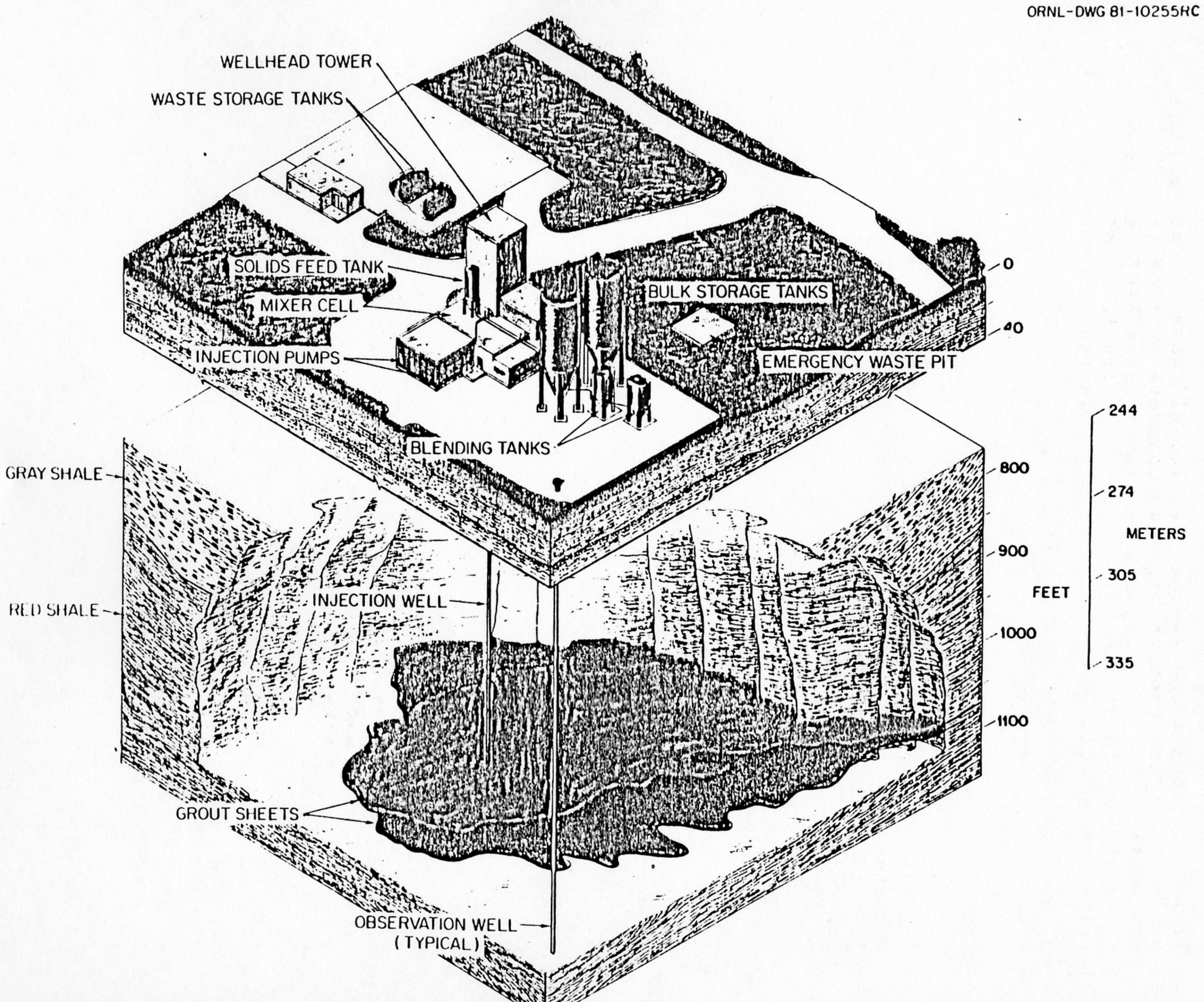

Fig. 1. ORNL Hydrofracture Process.

built to accommodate the 40-year backlog of waste sludges which 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 liters (2.8 million gal.) of grout slurries and 800,000 Ci of waste activity in the first 19 months of its operation.

ORNL has worked off its backlog of past wastes and is processing only wastes from current operations. At the present level of Laboratory activity and with improved liquid-waste management techniques, ORNL needs to do only 1-2 hydrofracture campaigns every 1-2 years.

The development of grouts for the hydrofracture process has formed the technology 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 below 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 show that there has been no measurable migration of radionuclides or significant interaction between the host rock and waste form.

This ORNL grouting technology is currently being transferred and adapted to the the waste management needs of the Hanford Grout Program (HGP), the Weldon Spring Formerly Utilized Site Remedial Action Program (FUSRAP), and the NLO Fernald site. The ORNL grouting group also supports the development of on-site grouting facilities at the Oak Ridge Gaseous Diffusion Plant (ORGDP) and the Y-12 Production Facility (Y-12). ORNL has also conducted studies to support waste management programs at the Savannah River Plant (SRP), Rocky Flats Plant (RFP), EG&G Idaho, West Valley Nuclear Fuel Services (NSF), and the NLO Fernald site.

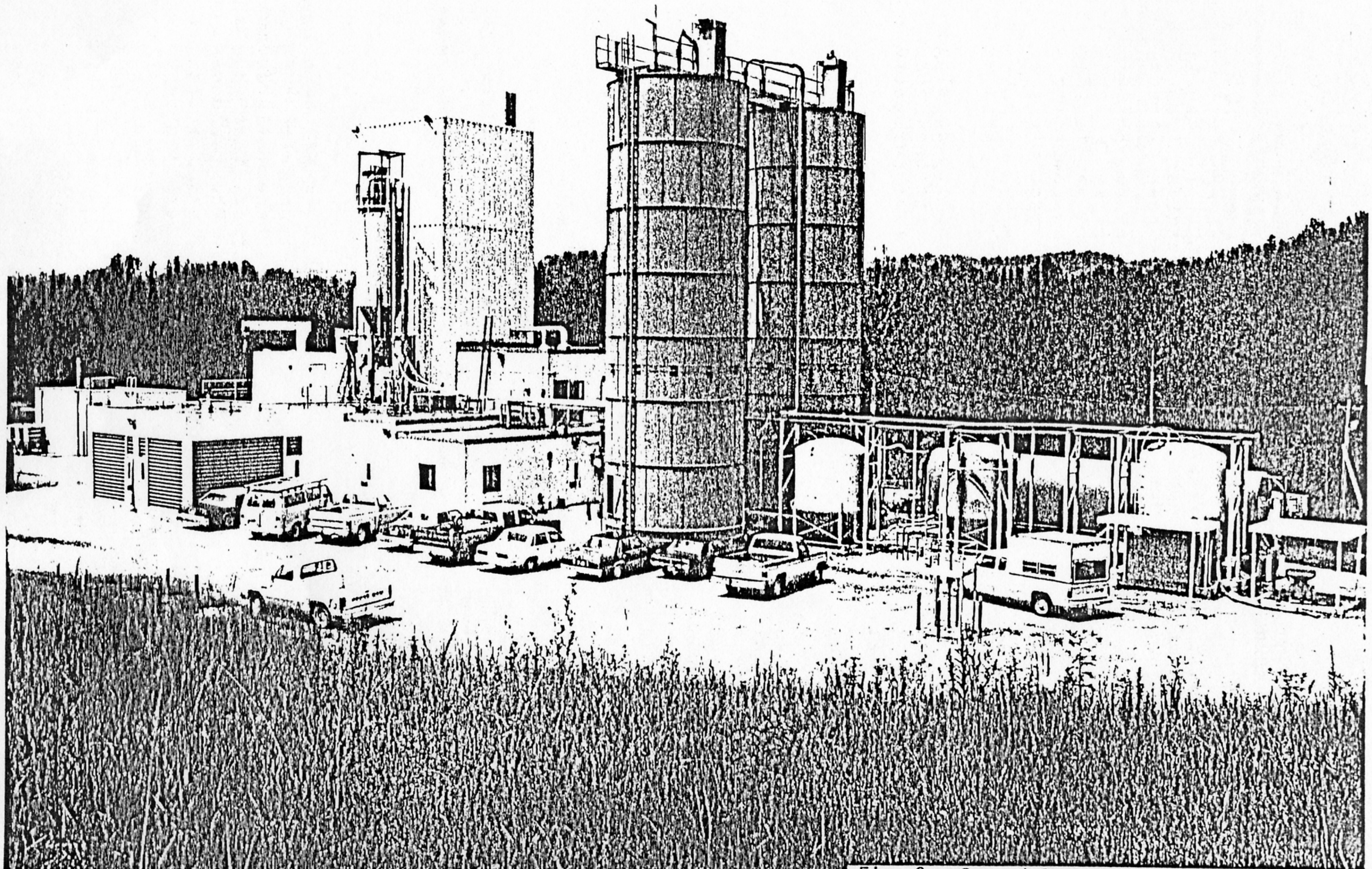

Fig. 2. Second ORNL Hydrofracture Facility

2. Hanford Grout Program.

The Hanford Grout Program (HGP) 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 which are in existing single-wall storage tanks and immobilizing those that are determined to be LLW in a pumpable grout slurry.

The shallow land burial siting and grout facility development projects are currently underway at these three organizations, and the 1986 start-up date is obtainable. The waste streams currently under study for immobilization in the Hanford Grout Program are the (1) Hanford Facility Wastes (decontamination solutions and mop water), (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 are dependent on the resolution of their classifications as low-level, transuranic (TRU), or high-level waste. Also, the jurisdictional boundaries among the DOE sites, the States, the Environmental Protection Agency (EPA), and the Nuclear Regulatory Commission (NRC) are being redefined, and the issues regarding the status of these wastes as co-contaminated radioactive and hazardous chemical wastes are just beginning to be addressed.

3. Savannah River Plant Nitrate Saltcrete.

Process wastes have accumulated over the 25-year operating history of the Savannah River Plant (SRP) and have been stored in double-wall steel tanks. SRP intends to remove these wastes and 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 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 waste by this SRP partitioning process.

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 saltcrete that will be solidified in shallow trenches and capped. The subsequent impermeable monolith will prevent the percolation of water, support the cap, and form an effective diffusion barrier to the leaching of these soluble salts. The goal is that the federal drinking water standards for nitrate are met at the aquifer's exit from the disposal site boundary.

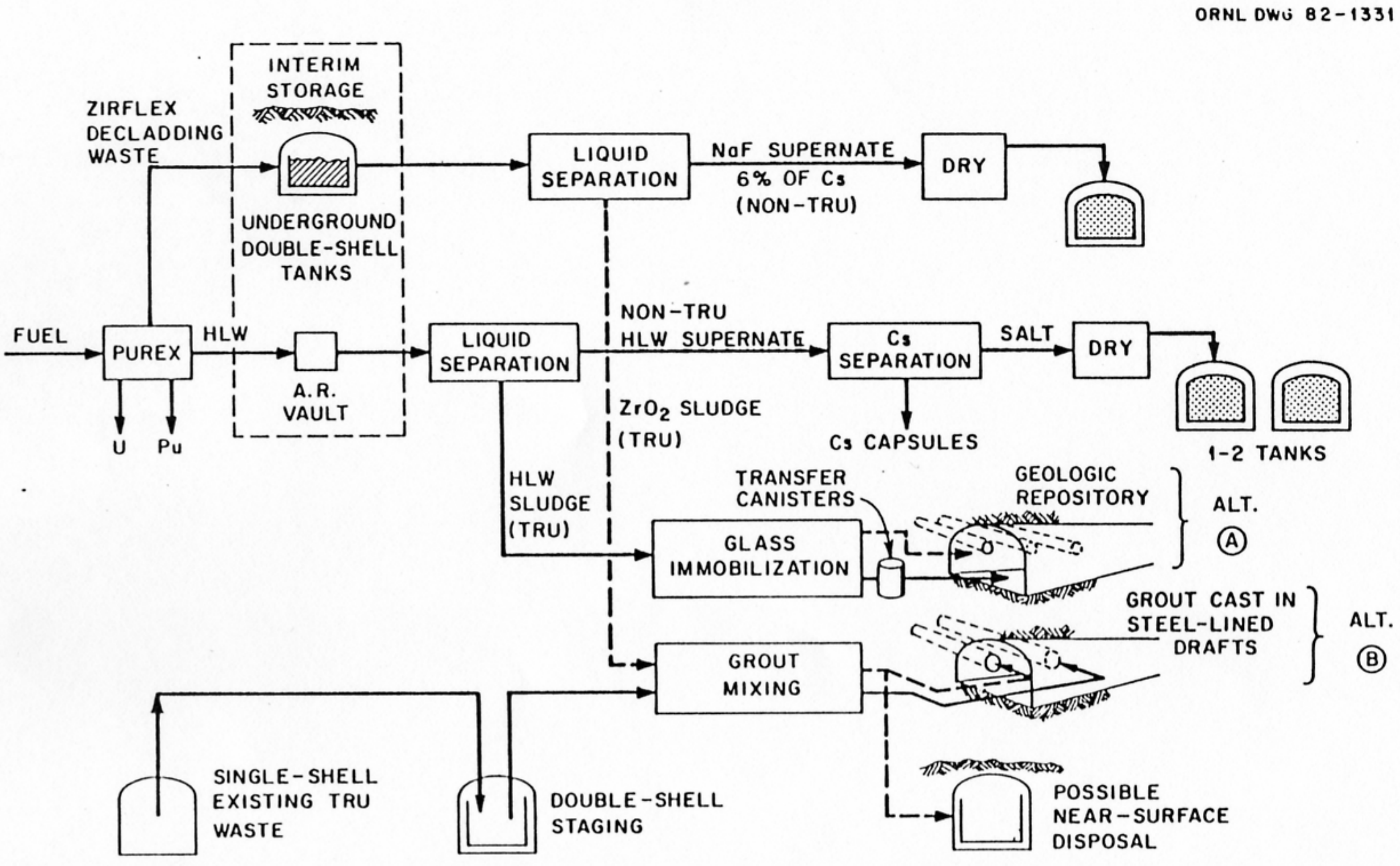

Fig. 3. Hanford Grout Program.

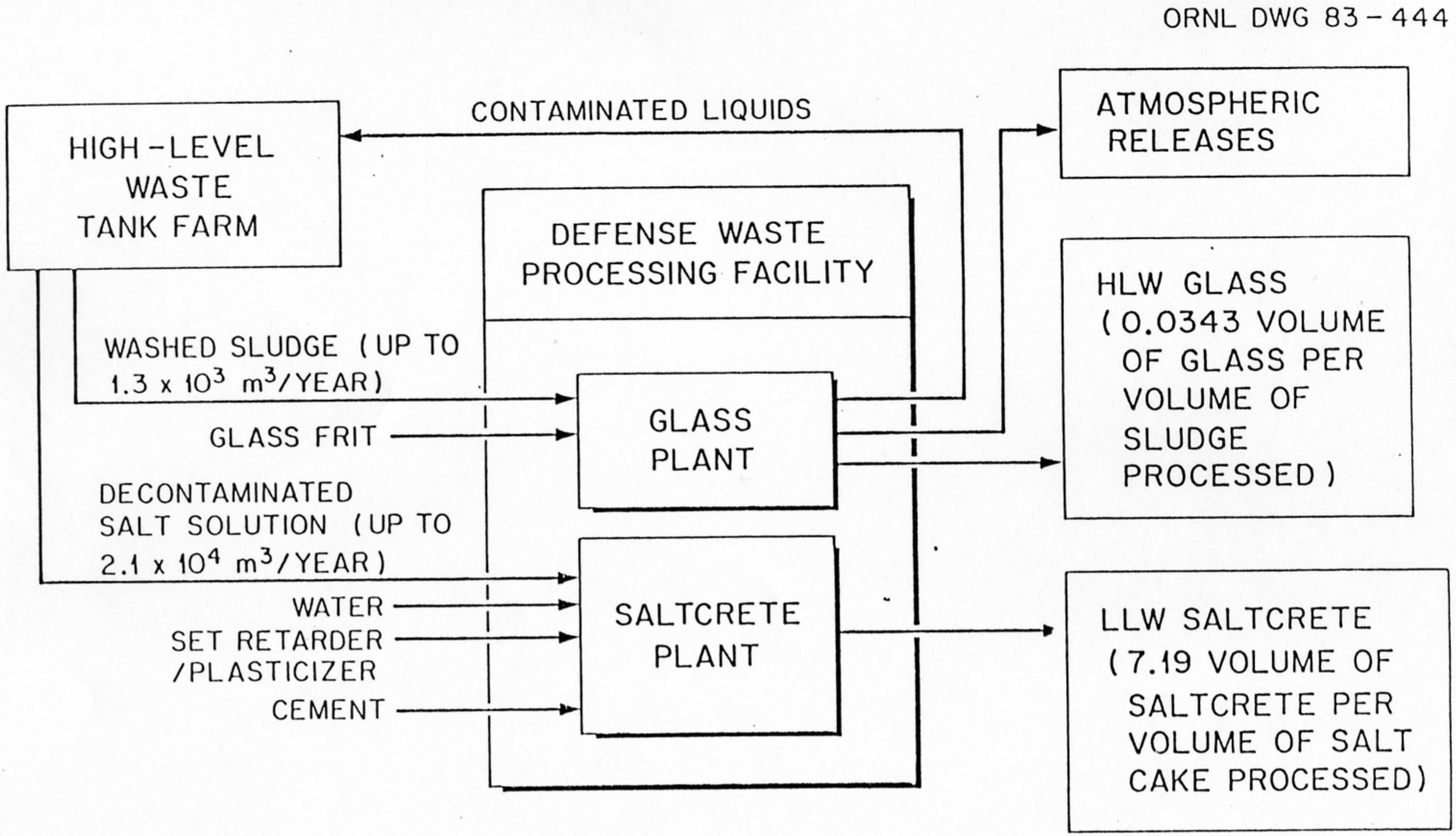

Fig. 4. Savannah River Plant Waste Treatment Plans.

4. 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 2,800 m^3 (100,000 ft^3) 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 into 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 5-10 years before being shipped to the WIPP facility for permanent disposal.

5. 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 high pressures [150-250° C and 177-344 MPa (25,000-50,000 psi)]. Subsequently, ML developed and demonstrated a process that pressed 1 in. diameter 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.

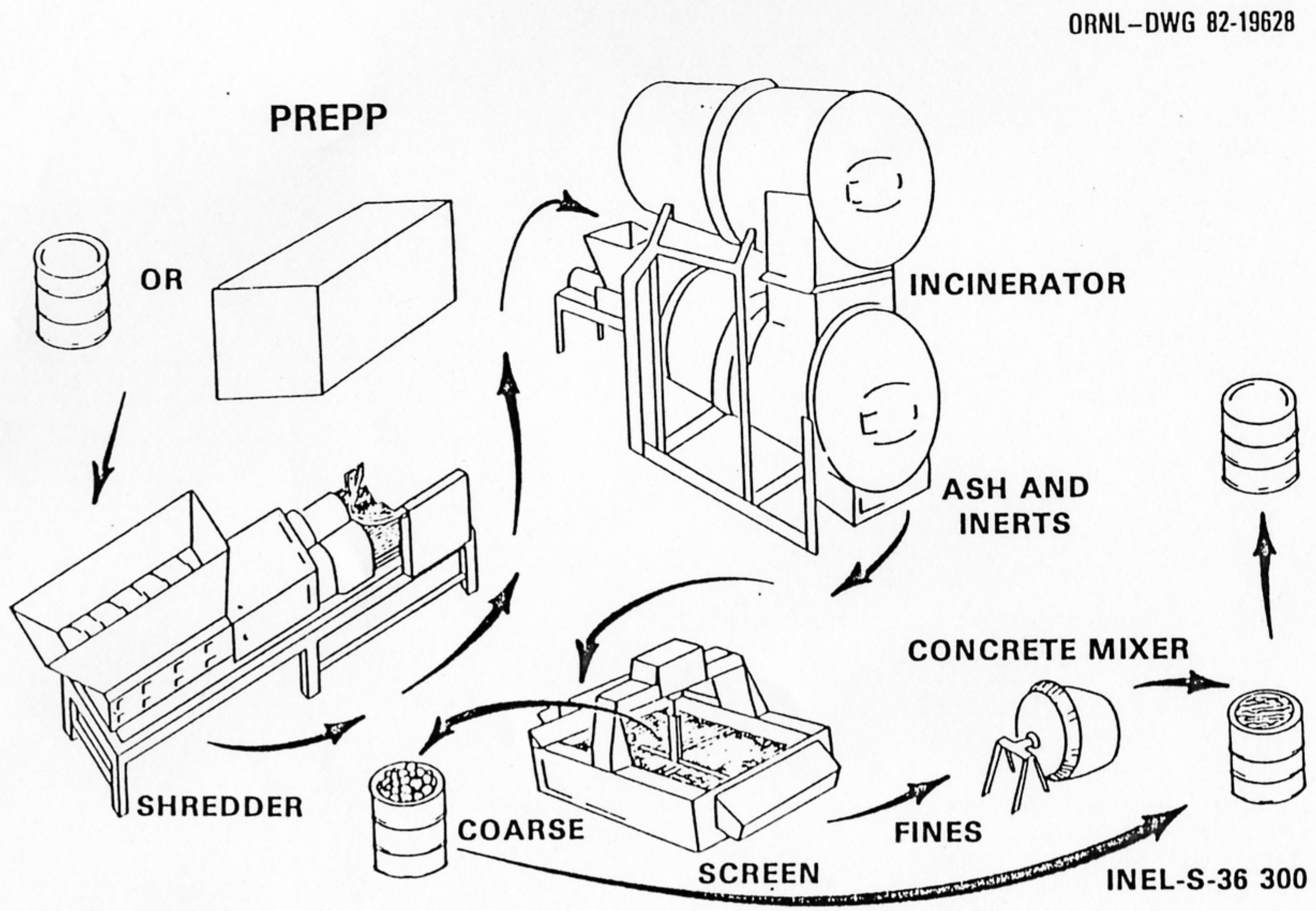

Fig. 5. Process Experimental Pilot Plant (PREPP) Flow Diagram.

6. ORNL HLW Concretes Formed Under Elevated Temperature and Pressure.

ORNL developed cement-based waste hosts [13,14] 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, sand, and clays with wastes like calcines, frits, and sludges. Figure 6 shows that these concretes are produced by an accelerated cure under mild autoclave conditions (85-200° C, 0.1-1.5 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 40-60 MPa), leach resistant [plutonium leaches at a rate of 10 pg/($cm^2 \cdot d$)], and radiolytically stable, monolithic waste forms (total gas G-values 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 [15] of using cement-based waste forms and is the basis for a continuing development program. GA will use this ORNL process to perform a demonstration with unirradiated HTGR fuel pellets, and perhaps irradiated fuel from the Fort St. Vrain reactor.

7. 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 [16] 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.

In order to improve the mixability of these sludges with the cement-based fixation blends, Quadrex, Inc., has a processing technique (Fig. 7) that fluidizes both the waste and cement-based components with an inert volatile halocarbon carrier. These two fluidized mixtures are metered and blended, and then the volatile

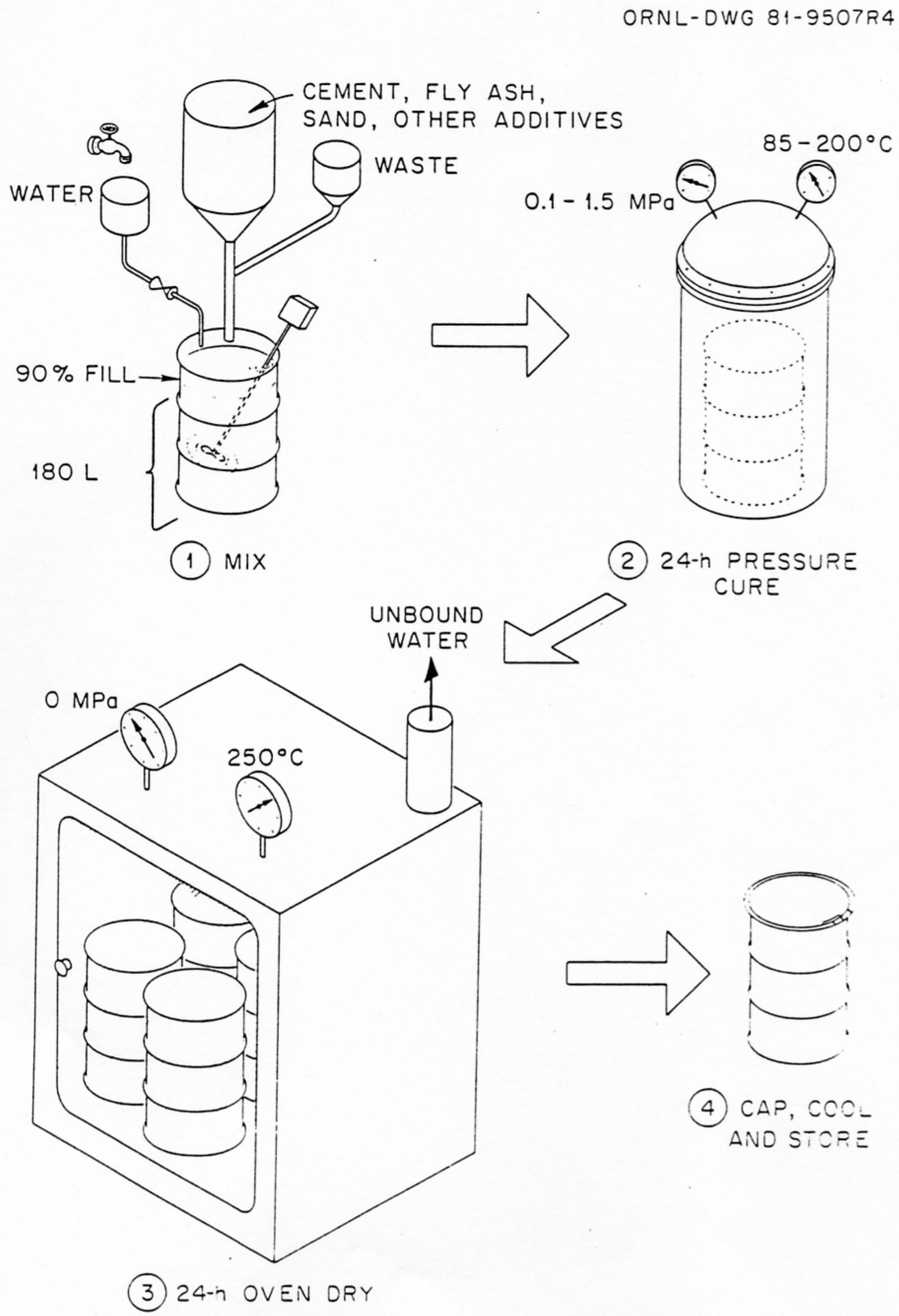

Fig. 6. Generalized FUETAP Flowsheet for SRP Waste.

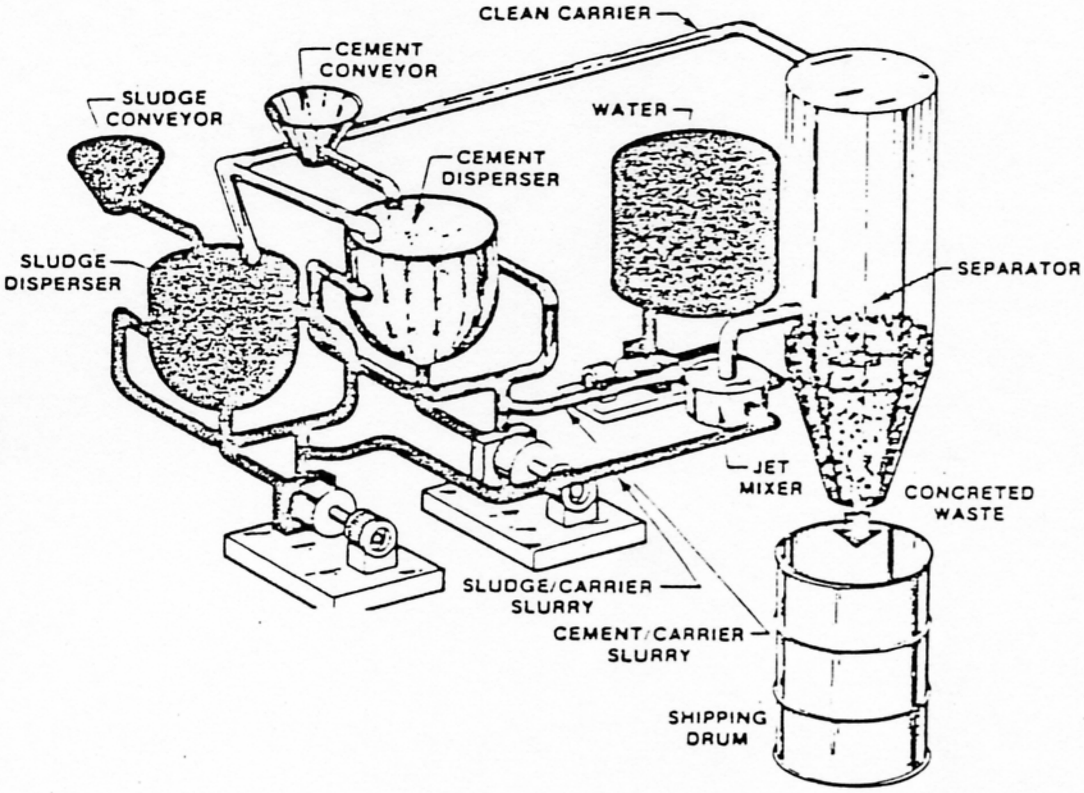

Fig. 7. Inert Carrier Concrete Process.

inert carrier is removed. This results in good mixing without adding excess water, thus minimizing the the final volume of waste to be transported.

Since this study is still in progress, not enough data are available to determine if the added equipment investment, operating complexity, and material costs will be offset by the improved mix homogeneity and lower shipping costs.

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 radioactive 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 a relatively simple extrapolation of experience, the performance characterization of these complex, multiphase solids becomes an involved task. The following discussions summarize the United States' experience in evaluating the performance of cement-based waste forms in regard to these issues.

1. 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 source-terms and the disposal regulations give little or 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 Cs-137 and Sr-90. 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 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, perovskite, and so on. Because the measured leach rates are so sensitive to the choice of leach-testing protocol, there is a large amount of 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 (OPC) have very little intrinsic ion exchange capacity for Cs [17,18], but readily-available, inexpensive additives can reduce the Cs-leach rate by orders of magnitude (Fig. 8).

The mechanisms controlling Sr-leachabilities are more complex and involve a participation in the hydrosilica formation reactions. The Sr-leach rates decrease with the specimen's age [19] and decrease with a reduction of the excess Ca in the formulation. This is why silica-rich pozzolans, such as fly ash and fumed silica, are successful in reducing Sr-leach rates in grout formulas.

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 superior to this reference material in long-term tests of a year or more. The effective diffusivities for Cs and Sr from hydrofracture grouts are on the order of 10^{-11} 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.

The leach rates of U, Pu, and other transuranics are generally so low that it difficult to measure their leach rates reliably. For example, the leach rates of Pu are reported to be less than 10^{-11} to 10^{-13} g/(cm^2·d), reflecting the laboratory's detection limits [20,21]. The effective diffusivities for Pu 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.

2. 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

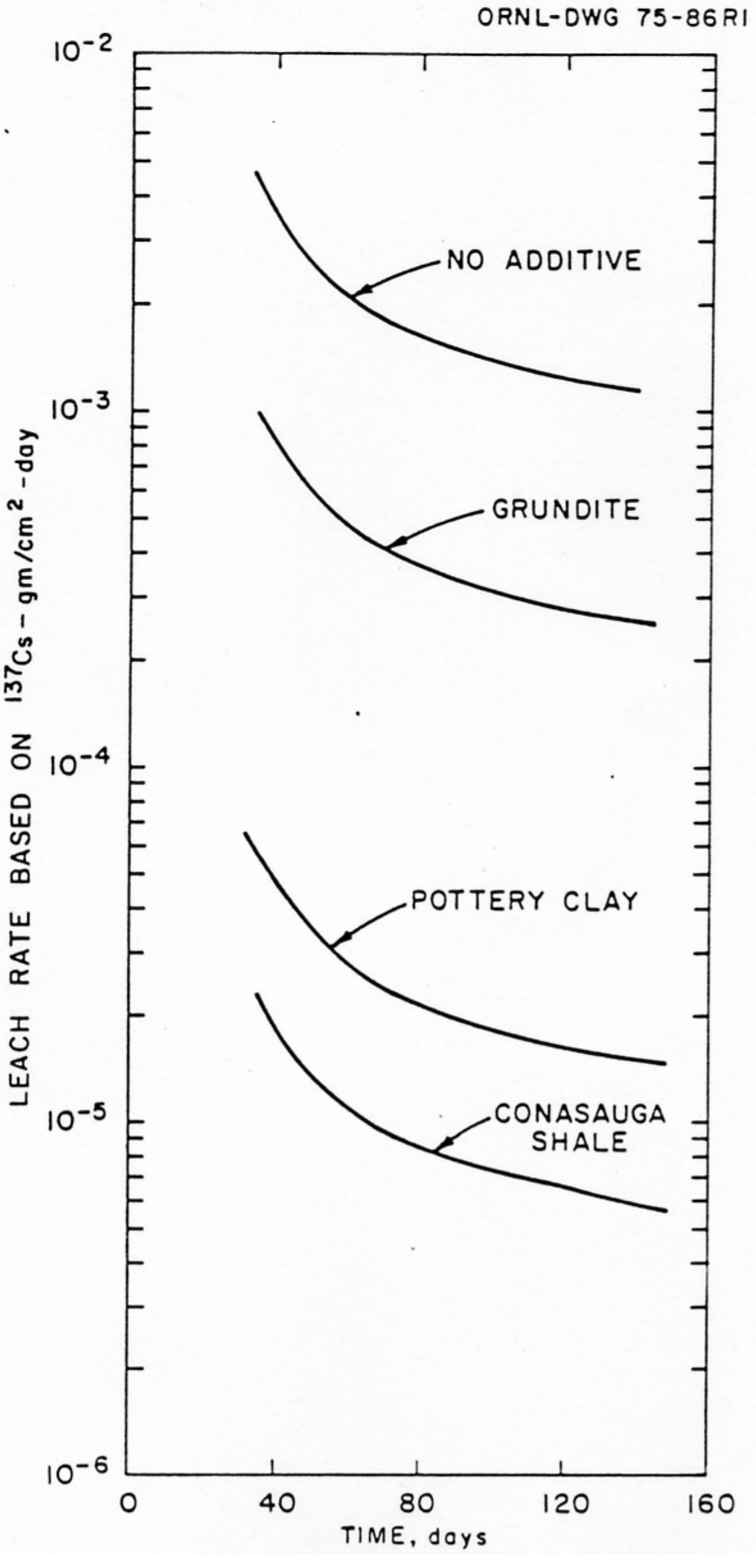

Fig. 8. Leach Rates of ^{137}Cs from Grouts with Various Mix Additives.

explosive mixture could form in the package. Also, there is a concern that the pressure in the package could become sufficient to breach the waste package prematurely.

The ORNL FUETAP studies [13] showed that removing the excess, unbound pore water reduced the total gas generation rate from 0.01 to 0.005 molec./100 eV. Figure 9 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 1,000 y of accelerated dose there was less than 1 atmosphere of pressure formed in the drum. In the dewatered case, there was negligible pressurization.

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 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 5-20 lower than a mix with water, and measurements of gas-generation rates with alpha radiation is 5-10 times higher than those with gamma radiation.

3. 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 elevated temperatures (100-1,000 y) due to the decay heat of HLW and second the thermal expansion and gasification during a transportation fire. The first 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. Tnis concern is only relevant to cement-based waste forms which contain HLW or are co-disposed with HLW in a deep geological repository. In the second case with LLW, ILW, and TRU wastes, there is no significant intrinsic heat generation 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 [800-900° C (1470-1650° F) for 30 min].

In general, a moderate increase in temperature to 85-115° C (185-238° F) accelerates the cementation reactions and improves the cement-based waste hosts retention of both Cs and Sr nuclides. The strength increases and the porosity decreases. Since the boiling point of the pore water is 119-121° C (246-250° 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

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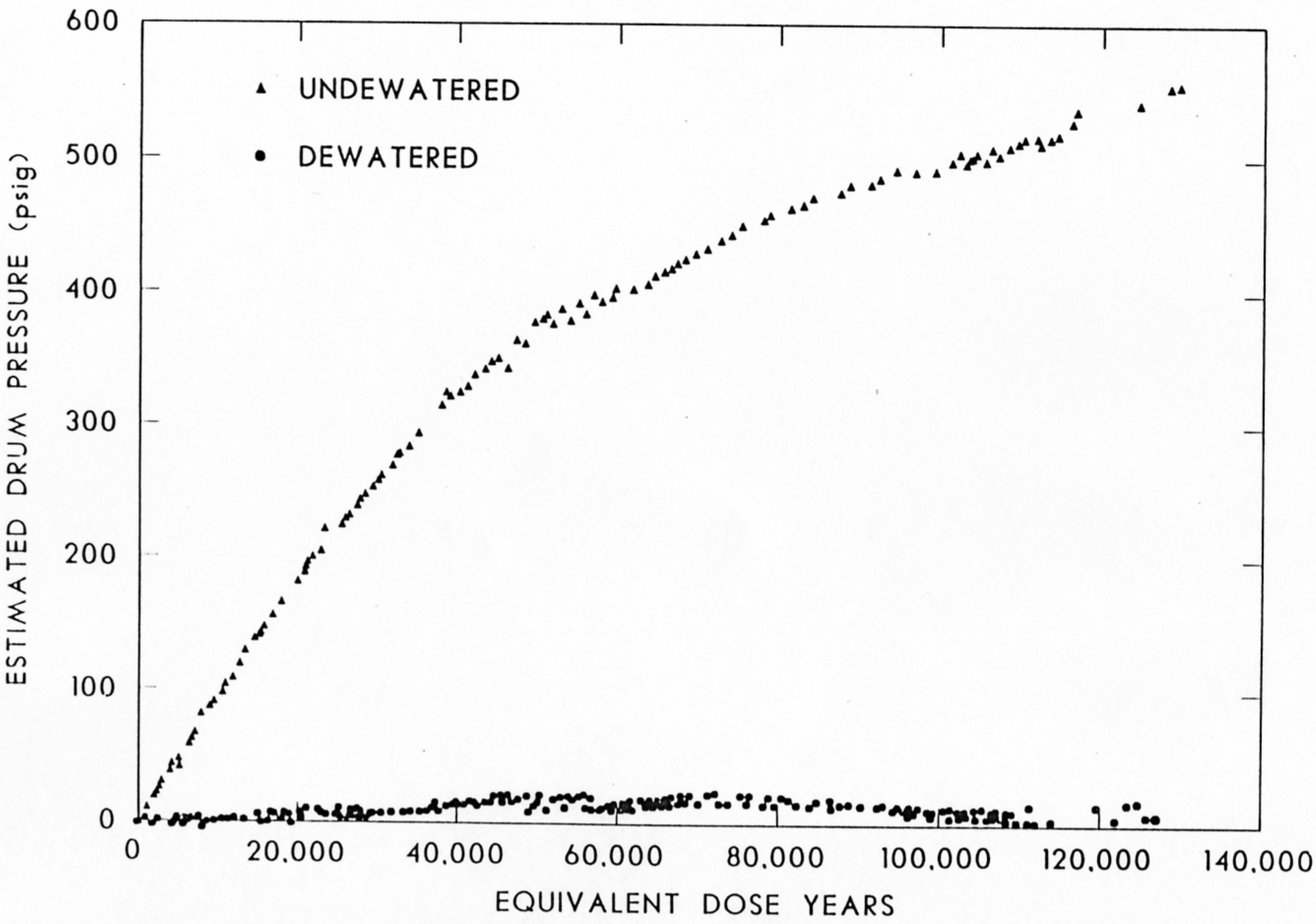

Fig. 9. Comparison of Gas Generation Rates of SRP FUETAP Concrete Before and After Dewatering.

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 long periods of at least 2.5 y or more. A study by the Portland Cement Association (PCA) [22] 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 [85-200° C (185-392° 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 were the principal factors in determining the strength of construction concretes. There are insufficient data on the long term exposure of these materials at these temperatures.

With regard to transportation testing, the Federal Republic of Germany (FRG) has described an extensive series of fire tests [23] on cement-based waste forms containing sludge with nitrate salts, shredded paper, metal, and ion exchange resin beads. The 200-L drums were exposed to 800-900° C (1472-1652° F) for 70-120 min. The results showed that there were no catastrophic failures. Only the first 2-3 cm (0.75-1.2 in.) of the monoliths saw temperatures over 110° C (230° F). There was sufficient venting through the failed drum lid gasket to allow the steam to escape without rupturing the drum or breaking the ring-clamp holding the lid. There was no evidence that any of the drums' contents 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 stress on the drum.

4. Phase Complexity of the Matrix.

The principal concern with regard to the complexity of cement-based waste hosts turns on the ability to predict the mechanism of immobilization and to predict which phases are responsible for sequestering the particular nuclides. Without this knowledge, the prediction of longevity in a specific geochemical setting cannot be put in thermodynamic terms and cannot be modeled. Figure 10 shows the course of the serial and parallel reactions that occur during curing of cement paste [24].

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

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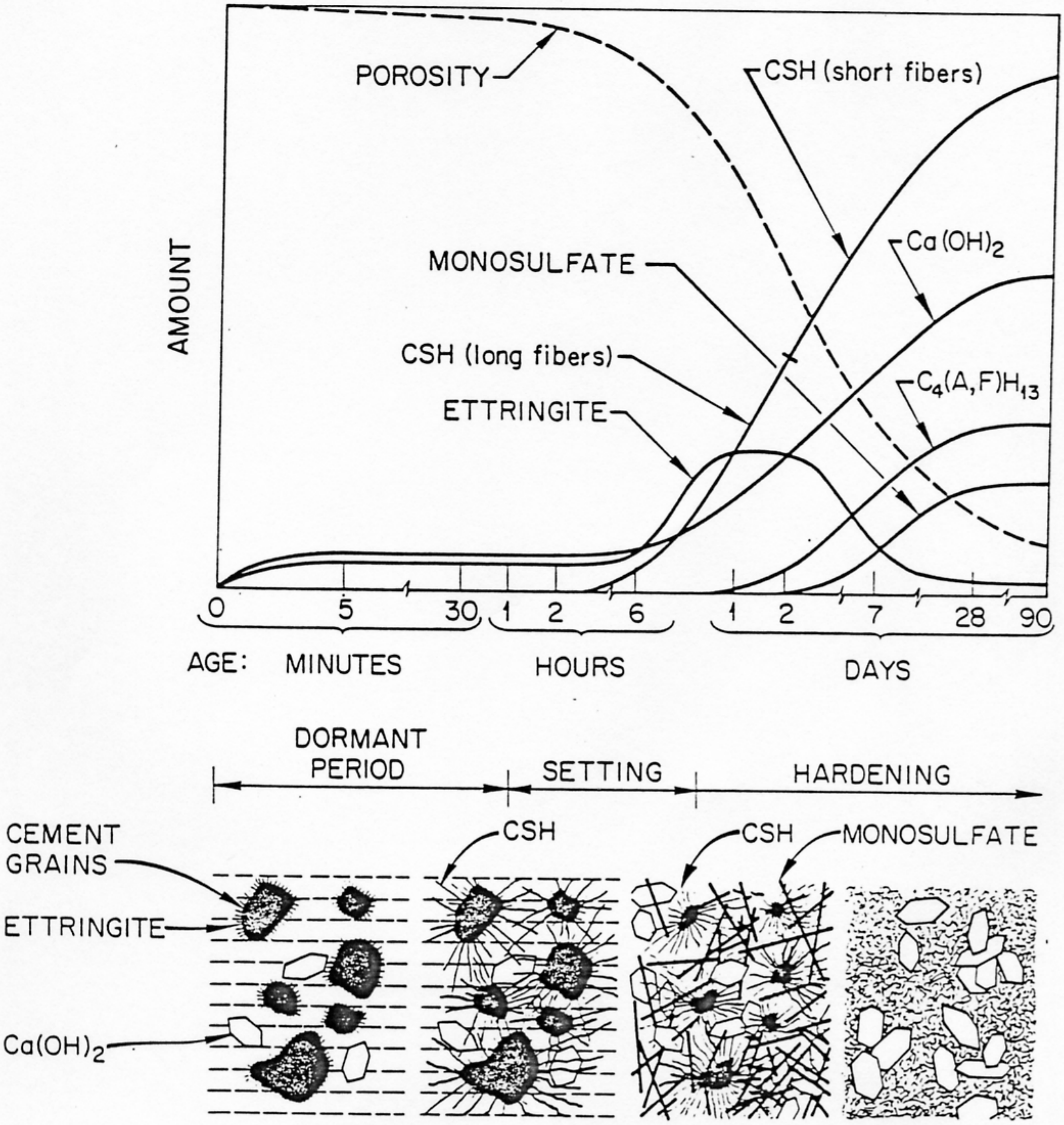

DRAWING FROM PORTLAND CEMENT PASTE AND CONCRETE
by I. Soroka

Fig. 10. Course of Cement Paste Reactions.

to resolve these phases and detect the trace chemical concentrations of the nuclides that may be adsorbed, chemisorbed, or co-precipitated [25, 13]. Nevertheless, the evidence is very strong that elements can be fixed for millennia in grouts [26, 27] in a variety of geochemical settings. Ancient grouts from Cyprus and Greece, which are 3,000-8,000 years old, have held their trace metal finger prints allowing their constituents to be traced to nearby pits from which they had been mined in antiquity. Furthermore, these ancient grouts still consist in a large part of undifferentiated, amorphous hydrosilicates even after thousands of years. So, thermodynamic arguments are not so important in the face of this evidence that these amorphous hydrosilicates are extremely effective a sequestering a wide range of elements.

5. Effects of Waste Stream Composition.

Waste streams are generally widely fluctuating, complex mixes of elements, whose concentrations my vary by one or two orders of magnitude between lots. Furthermore, many of these waste constituents have the capacity to interfere with the cement chemistry by accelerating or retarding the various reactions shown in Figure 10. This explains much of the negative experience with cement-based waste forms where an inexperienced operator had a "flash" set or no set at all. Cement-based waste forms should not be applied without determining in advance these interactions between the cementitious components of the blends and the constituents of the waste streams. Figure 11 presents the relationship between the 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 show that the maximum heat evolution rate and the reciprocal of its time of occurrence is a sensitive indices of the waste streams retardation and acceleration effects.

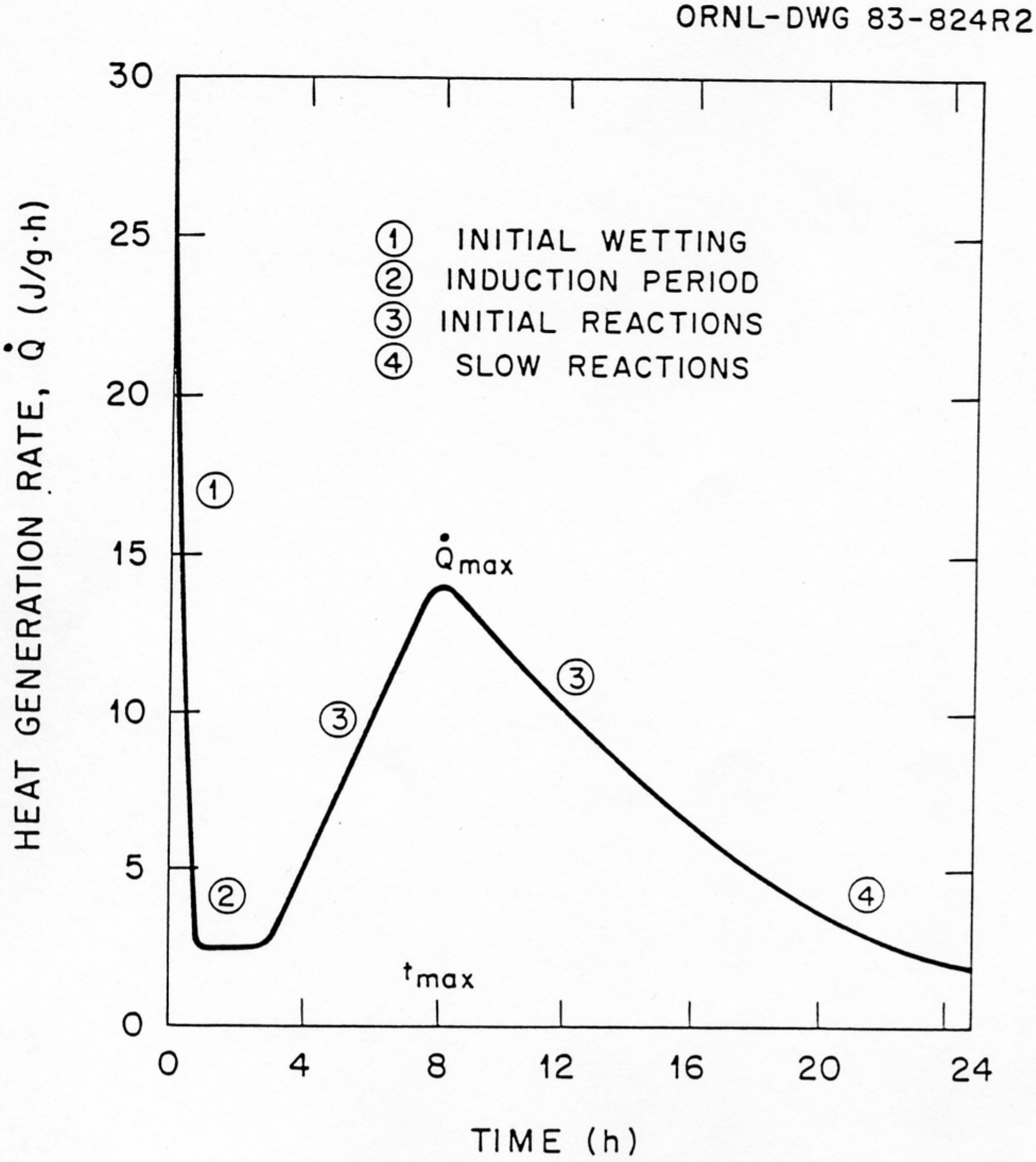

Fig. 11. The Relation Between Heat Generation Rates in Cement Paste and Time.

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

Cations;

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

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

$>> NH_4^+, K^+ > Li^+ > Cs^+ >$

Na^+

<------Acceleration |

| Retardation ------->

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

Anions;

$OH^- > Cl^- > Br^- > NO_3^- > SO_4^{2-} >> CH_3CO_2^-$

<-------Acceleration |

There are also many set retarders like fluoride, borate, and complexing organics, such as hydroxycarboxylic acids, citric acid, tartaric acid, benzoic acid, phenol, ethylene diamine tetraacetic acid (EDTA), etc., that 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 250-500 mL samples from 200,000 L (50,000 gal.) tanks that are poorly mixed and stratified. It is required that 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 liters (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, 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. These issues were not completely resolved within the limitations of these discussions, but the in all cases the bases for their resolution was indicated. A large body of research in each of these areas continues.

As always, the economics of these cement-based immobilization processes are compelling. For example, the total cost of treatment and final disposal via the ORNL hydrofracture process is between $1.00-1.50/gal, which is cheaper than current shallow land burial and is lower in public risk. So, there is a great economic driving force to develop such large in situ solidification technologies.

The significant future developments will be in the direction of formulations that form 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 Tc and Np 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 (PCB), polynuclear aromatics (PNA), and pesticides [29, 30]. 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 these cement-based waste forms' geochemical stability and non-leachability. 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 [31]. The use of cement-based waste hosts is rapidly expanding in scope.

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