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Corps of Engineers
Waterways Experiment
Station

Structures Laboratory
3909 Halls Ferry Road
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PROJECT: Grout to Meet Physical and Chemical Requirements for
Closure of Hanford Grout Vaults

21 Jul 94

Final Report of Close-Out Activities

SUMMARY: The U.S. Army Engineer Waterways Experiment Station (WES) developed a grout based on portland cement, Class F fly ash, and bentonite clay, for the Hanford Grout Vault Program. The purpose of this grout was to fill the void between a wasteform containing 106-AN waste and the vault cover blocks. Following a successful grout development program, heat output, volume change, and compressive strength were monitored with time in simulated repository conditions and in full-depth physical models. This research indicated that the cold-cap grout could achieve and maintain adequate volume stability and other required physical properties in the internal environment of a sealed vault.

To determine if contact with 106-AN liquid waste would cause chemical deterioration of the cold-cap grout, cured specimens were immersed in simulated waste. Over a period of 21 days at 150 F, specimens increased in mass without significant changes in volume. X-ray diffraction of reacted specimens revealed crystallization of sodium aluminum silicate hydrate. Scanning electron microscopy used with X-ray fluorescence showed that clusters of this phase had formed in grout pores, increasing grout density and decreasing its effective porosity.

Physical and chemical tests collectively indicate acceptable performance of this grout as a vault-sealing component. However, the Hanford Grout Vault Program was cancelled before completion of this research. This report summarizes close-out activities for the work underway at the Waterways Experiment Station when the Program was cancelled.

Dr. Lillian Wakeley, WES, was Principal Investigator. Dr. Philip G. Malone, Mr. Brian H. Green, and MAJ Patrick T. Harrington also contributed significantly to preparation of this report. Mr. Earl McDaniel, Oak Ridge National Laboratory, was Technical Monitor for this research under U.S. Department of Energy Interagency Agreement No. DE-AI05-900R21921, "Cold-Cap Grout for Hanford Vaults."

1. Introduction

During 1993, the U.S. Army Engineer Waterways Experiment Station (WES) developed a non-radioactive grout intended for closure of Vault 102 of the Hanford Grout Vault Program. The purpose of this non-radioactive or "cold" cap grout was to fill the void in the upper 4 ft of the vault, providing a barrier between the grouted 106-AN waste and the vault cover blocks, and providing physical support for the overlying layers of the vault closure system. Following grout development, an extensive verification program was initiated involving large-scale physical modelling and chemical tests of the performance of the cold cap grout when subjected to a simulated liquid waste.

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In previous research, the WES had developed a cold cap grout for the demonstration vault of the Hanford Grout Vault Program. The report of that project, WES TR SL-92-21, (Wakeley and Ernzen, 1992) describes the vault program, and Figure 1 of that report is a drawing of a typical vault. The cold-cap grout developed during the previous program was successfully placed in the Hanford Demonstration Vault in October, 1993.

The research program described in the present report was undertaken to develop a grout to be placed at a higher vault temperature and to achieve higher strength than had been required of the cold-cap grout developed previously. Chemical compatibility between the 106-AN waste fixed in the wasteform grout to be placed in vault 102 also was a serious consideration in this research.

The U.S. Department of Energy cancelled the Hanford Grout Vault Program on October 1, 1993. At that time, the grout for vault 102 had been developed successfully to meet the new performance requirements. Physical models had been constructed and grouted at the WES, and physical and chemical performance tests were well underway. Thereafter, the WES was directed to and did initiate an orderly close-out of activities, including termination of long-term tests in progress and abbreviation or deletion of many research tasks. This report is a summary of activities completed during the orderly close-out. It presents the second successful grout formulation, and provides results of determinations of chemical and phase compositional changes of the grout when exposed to a simulated 106-AN waste.

2. Performance Requirements and Grout Development

The starting point for development of the cold-cap grout during this research was the grout designated CC20 in WES TR SL-92-21. Materials for CC20 were chosen from three groups of criteria: a) the materials had to contribute to chemical and mechanical stability in the vault environment; b) they had to enhance placement at elevated temperature; and c) they had to be available at a realistic cost without excessive shipping and with a good prognosis for continued availability over several years, so that the grout could be produced when needed for vault closure. The CC20 grout had met its performance requirements, and it was logical to base the new grout on the same materials. However, CC20 had been required to achieve compressive strength of only 400 psi, and be placeable and volumetrically stable at 105 F. Performance requirements for the new grout, outlined below, were defined to meet the greater environmental challenge posed of the interior of vault 102, namely a higher temperature and more adverse chemical conditions, both attributable to the increased radioactivity and toxicity of the 106AN waste in the wasteform grout of this vault.

For the vault 102 cold-cap grout, a series of 15 trial batches of grouts were proportioned and mixed in the laboratory at the WES, aimed toward achieving the following target properties during mixing and placement: flow time of 15 to 18 sec (CRD-C 611) for 2 hr after mixing, non-segregating, minimal bleed (CRD-C 245 and 613), placeable by pumping and freefall of 4 ft. at 140 to 150 F, and capable of flowing at least 14 ft laterally during placement at this temperature.

Target properties for the hardened grout were: compressive strength of 1100 psi at 28 days age (CRD-C 14), volume stability as indicated by shrinkage less than 0.1% and expansion of less than 0.2% (CRD-C 56)

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The formulation for grout CC34, the grout formulation recommended by the WES as a result of this research, is given in Table 1. This grout was tested extensively and meets all performance requirements. CC35, which is a slight variant of CC34, was actually used in WES physical models. Minor adjustments in mixture proportions were made during operations to complete the physical models, resulting in a 7.5% reduction in water and giving the recalculated proportions shown in Table 2. Results of tests of component materials are given in Appendix A. Appendix B lists all trial grout formulations, annotated to indicate why each trial mixture was discarded during grout development.

Two chemical admixtures were used to achieve the properties of the cold-cap grout. The naphthalene-based high-range water-reducing admixture conforms to CRD-C 87 Type F. It was essential in this mixture to achieve the flow time of 15 to 18 sec. A set-retarding admixture, CRD-C 87 Type D (hydroxylated carboxylic acid in liquid form) extended the time of setting, and caused the grout to retain its flow properties for up to 2 hr, the time allowed for mixing, transporting, and pumping at the field-placement site.

During trial batching, each grout was mixed in a 0.1-cu-ft batch using a mixer in compliance with CRD-C 210. A whisk-type mixer paddle was used for HCC21 through HCC30. For HCC31 through HCC35, a flat paddle was used on the mixer, to approximate the mixing action the grout would experience in a truck mixer during field placement. Most trial mixtures were tested for flow at 5, 15, 30, 60, 90, and 120 minutes after mixing or until flow times were unacceptably slow. Mixtures that failed some other initial criterion, such as experiencing aggregate segregation, were not tested further.

For some of the more promising mixtures, time of setting was tested according to CRD-C 614, modified by use of an automated testing apparatus. Bleeding was measured by measuring the volume of free space on top of each initially filled 3X6-in cylinder, after 24 hr. Annotations about results of these tests for trial mixtures HCC21 through HCC33 are given in Appendix B.

After 2 hr of mixing and testing for flow and segregation (visual), candidate grouts to be tested for hardened properties were cast into 3X6-in plastic cylinder molds, capped, and sealed with tape to prevent moisture loss. After 24 hr of storage at laboratory ambient conditions, cylinders were placed in water at 140 F, to simulate vault conditions. Unconfined compressive strength was tested after 7 days of elevated-temperature curing. Results of the 7-day strength tests for trial mixtures are included in the annotations in Appendix B.

Trial mixture development stopped when HCC34 was successful in meeting property requirements. A 1-cu-ft batch of this grout was prepared for additional testing prior to using it in the physical models. Flow time after 2 hr of continuous mixing was 15.6 sec. Grout mixed for this length of time experienced no bleed, when tested according to CRD-C 613. (The same grout mixed for periods of less than 1 hr experienced measurable bleeding. Results of these tests are not included in this report, and are on file at the WES.) Initial time of setting for HCC34 was 15 hr 15 min, with final time of setting at 20 hr 30 min.

Temperature rise of the grout was determined using a Q-drum apparatus, as described in WES TR SL-92-21, for two different batches of HCC34. Results are shown in Figure 1, compared to the temperature increase measured for CC-20 using the same apparatus. The desired decrease in heat output was achieved for HCC34. Tests of length change to 7-days age indicated that prism specimens

of HCC34 experienced shrinkage near the limit for this property. This was tested further with specimens cast during operations to grout the physical models, discussed in the next section.

3. Physical Models

While the HCC34 grout was being developed, a series of 3 instrumented physical models were designed and built at the WES, to be used in verification of the physical properties, heat rise, and volume stability of the cold-cap grout. One similar model had been constructed and used in analyses of the CC-20 grout. For the work supporting closure of vault 102, the WES elected to develop three such models, for improved confidence in verification. The models were designed to simulate vault conditions from just below the surface of the wasteform up to the underside of vault cover blocks, and representing the full depth to be filled by the cold-cap grout.

Models were double-walled wooden boxes, constructed as formwork, with a 6-in layer of vermiculite as insulation between the two walls and lined internally with galvanized steel. Internal model temperature was elevated to 150 F, using 3/8-in-diameter copper water lines loosely attached to each face and the floor. The internal dimensions of each model were 32 in. square and 60 in. high. Walls were reinforced externally with 2X6-in horizontal walers at 2-ft intervals. Figure 2 shows the interior of one model (with a layer of wasteform grout in the bottom), and the array of copper water pipe on the sidewalls of the model.

Simulated wasteform grout was prepared at the WES according to a formulation provided by Oak Ridge National Laboratories, using a liquid waste simulant reported by Lokken et al. (1993). A 6-in lift of this wasteform grout was placed on the floor of each model, so that the model would include an interface between wasteform and cold cap and would represent the full depth and function of the cold-cap grout. Internal temperature of each model was between 145 and 150 F when the wasteform grout was placed, and model conditions were maintained at this temperature for approximately 10 weeks between wasteform placement and placement of the first lift of cold-cap grout. Mixing and placing of the simulated wasteform grout was described in the WES progress report for April 1 through June 30, 1993.

Three separate lifts of HCC34 were placed in each model, at 10, 12, and 15 weeks after placement of the simulated wasteform. Table 3 lists proportions for a 5-cu-ft batch of this grout, which was prepared in a paddle-type grout mixer with an 8-cu-ft capacity. The first two lifts were approximately 18 in thick, and the final lift approximately 14 in. Multiple batches were required for each lift-completion event. Details of placement sequences, flow times, and other laboratory activities are on file at the WES. The HCC35 proportions were a result of purposeful omission of a small portion of the water from some of the batches, to compensate partially for the increased tendency for bleed and aggregate segregation with shorter mixing time (trial batches had been mixed for 2 hr, which was not possible during model-completion activities).

At the time of pumping and placement of each lift, specimens were cast to monitor length change and compressive strength. For the three lifts (total of nine specimens), average compressive strength at 28 days was 2000 psi. Results of tests of length change (CRD-C 56) are shown in Figure 4. Specimens cast during placement of the first lift of cold-cap grout maintained shrinkage of less than 0.1% for 40 days after casting. Specimens from the subsequent lifts exceeded this shrinkage value. However, this test method is valid for comparisons among mixtures or batches only, and does not indicate or simulate field performance.

4. Instrumentation and Monitoring of Grout Vault Models

Each model was instrumented with thermocouples imbedded in the first and second lifts of cold-cap grout, and in the head space above the third lift. Thermocouples were monitored by a computer-based data acquisition system, beginning at the time of placement of the first lift of cold-cap grout. Figures 5 through 7 show the internal temperature fluctuations in each model. In all three, the temperatures maintained in the first and second lifts were consistent, with a few exceptions attributed to times when subsequent lifts were placed. Temperatures recorded for the head space between the third lift and the model-cover panels also were consistent, slightly greater than 150 F prior to placement of the third lift and slightly less thereafter.

After the third lift was placed and reached final set, three dial gages (S1, S2, and S3 and Figure 8) were mounted on prefit invar rods to monitor deflection of the cold-cap system as indicated by changes in the distance between the upper surface of the third lift and a fixed surface above the model covers. Two additional dial gages (R1 and R2, Figure 8) were installed on prefit rods extending from the same fixed surface downward through the external walers. The lower ends of these rods were resting on a 1-in-diameter rod extending out each of two opposite sidewalls of each model at the level of the interface between the lowest lift of cold-cap grout and the underlying lift of wasteform grout. These two external gages were intended to monitor deflection from the upper surface attributable to creep of the wasteform layer or movement in the substructure of the models under the dead loads of the cold-cap. The intent was to subtract these lower deflections from the total deflection, to correct for movement beneath the cold-cap lifts. Figure 8 shows the layout of gages and rods for each model.

Figure 9 shows gage data for all gages on Model 1, and Figure 10 shows the data for the S gages corrected by subtraction of the average deflection indicated by the R gages. Figures 11 and 12 show the same for Model 2, and Figures 13 and 14 show the same for Model 3. For all three models, gage S3 indicates the greatest deflection. This gage monitored a rod closest to the center of the upper surface. During visual inspection, the upper surface of grout in each model was noted to be slightly dished in the center, possibly attributable to differential heating from the imbedded coils at the perimeter. This phenomenon was not explored, due to initiation of close-out of the project. The maximum deflection measured is about 0.02 in for the 50-in cold cap, (0.0004 in. per in), which is well within the allowable tolerance for volume change.

5. Chemical Compatibility between Cold-Cap Grout and Simulated Liquid Waste

Prior to mixing and placement of the simulated wasteform grout, the simulated liquid 106-AN waste (Lokken et al., 1993) was prepared for tests of individual components of the models. In these tests, each material such as plywood, galvanized metal sheeting, and copper tubing, used in construction of the models was immersed in the simulated liquid waste. This was done to determine if any of the model materials was likely to be oxidized rapidly during model-filling activities and cause a safety hazard. No threat of instant oxidation was revealed. Details of these tests are on file at the WES.

The simulated 106-AN waste is a highly alkaline liquid containing sodium phosphate and sodium and aluminum nitrate as major constituents. The waste interacts chemically with the cement and pozzolan used in solidification. This phase of the present project was developed to determine if the liquid waste would interact with and compromise the containment provided by the sealing grout.

The reactions of highly alkaline aqueous solutions with silicate and aluminate phases (especially glassy silicate phases) have been studied both in artificial cements formed from slag glasses (Talling and Brandstetr, 1989), and in the alteration of natural glassy sediments (Mariner and Surdam, 1970). In general, the materials formed are complex aluminosilicates containing sodium and/or calcium. These reaction products have generated some interest in that they represent crystalline chemical structures that can retain potentially hazardous and environmentally mobile nuclides such as radioactive sodium and radioactive cesium (Barney, 1975).

The goal of these experiments was to determine if direct contact with an alkaline waste would reduce the effectiveness of the grout barrier in the disposal vault. Observations made during this study may be useful in designing grout barriers that become denser and more impermeable when subjected to contact with leaking liquid wastes.

Samples of the hardened grout were prepared for these experiments by casting cylinders of 100 mm diameter by 200 mm long. The cylinders were allowed to cure in sealed molds at room temperature for 33 days. Samples from waste exposure testing were prepared by cutting disks 10 mm thick and 100 mm in diameter from the central portion of the core. Each disk was cut into six pie-shaped slices. Each slice has a mass of approximately 10 grams.

The simulated liquid waste was prepared using the formulation presented in Table 4. Reagent-grade chemicals were added to approximately 600 ml of distilled water at 40° C. The sodium phosphate and sodium citrate were dissolved in 100 ml of distilled water and added to the simulated waste solution just prior to dilution to a final volume of 1 liter. The resulting solution was clear with a faint yellow color and became cloudy if cooled to room temperature. The solution is strongly oxidizing and highly alkaline (hydroxyl ion concentration = 2.36 M).

The grout samples used in the exposure testing were dried, weighed, and placed in separate, sealed, fluorocarbon plastic jars containing 25 ml of waste simulant. The jars were maintained at a constant 60° C for test intervals of 7, 14, and 21 days. At the end of each test interval, two jars were opened and the grout specimens were analyzed. Control grout samples for comparison were maintained in distilled water. At the end of each exposure period, two samples were removed from the waste simulant, rinsed with distilled water, dried at 105° C, and weighed. The samples were prepared for X-ray fluorescence analysis (XRF) to determine the elemental composition on the surface; X-ray diffraction (XRD) analysis to identify crystalline phases present; and observation under the scanning electron microscope (SEM). The elemental analysis attachment (EDX) on the SEM was used to develop data on chemical compositions from selected sections of the surface to confirm the identification of specific phases.

The samples used for XRF analysis were rinsed with distilled water, dried, and placed directly in the sample chamber. Analysis was done using a Kevex EDX-11 X-ray Fluorescence Analyzer (Fison Instruments, Valencia, CA) operated with a standardless analytical program.

The XRD samples were prepared by scraping grout from the outer 1 or 2 mm of the sample and gently breaking up the cemented grains. The sample was sieved to collect particles that passed a 45- μ m screen. The procedure produced a sample that was enriched with products from the cement reactions, but contained few sand grains from the grout. Diffractograms were prepared from packed powder samples using nickel-filtered, copper radiation on a Phillips PW-1800 X-ray Diffractometer (Phillips Electronic Instruments Co., Mahwah, NJ).

Scanning electron microscopy was done using vacuum-dried, fractured samples. Each freshly fractured surface was coated with a 15- to 20-nm thick layer of gold and examined with an Hitachi H2500 Scanning Electron Microscope (Hitachi of America, Mountain View, CA). EDX analyses were done using a Princeton Gamma-tech Energy Dispersive X-ray Analyzer (Princeton Gamma-tech, Princeton, NJ).

The surface color of all of the grout samples exposed to the waste simulant changed from a pale brown to a pale yellowish orange or yellowish brown. Data on the changes in masses observed in the exposed specimens are presented in Table 5. The exposed specimens were hygroscopic and required care in weighing to assure accurate values were obtained. The average mass gain for exposed specimens observed at 7 days was 12.46%; at 14 days the gain was 13.83%; and at 21 days the gain was 13.97%. The control specimens changed less than 1% in mass.

The changes in chemical composition of the surface layers based on XRF analysis of the exposed samples are shown in Figure 15. The composition of the surface showed definite effects from contact with the waste simulant. Aluminum content rose nearly 10%, silicon content rose over 6%, magnesium content rose over 1.5% and phosphorus content rose almost 1%. The concentrations of calcium and iron at the surface dropped, with calcium decreasing by over 15% and iron decreasing by approximately 2.5%.

XRD patterns prepared from grout specimens that were not exposed to the waste simulant showed a broad peak indicating poorly crystalline cementing material. The samples that had been exposed to the waste simulant showed major changes in XRD patterns, indicating the formation of a sodium aluminum silicate hydrate phase (JCPDS 1981). A comparison of the pattern obtained from the file JCPDS 31-1270 and the pattern from a grout sample is given in Figure 16. Additional changes in the patterns indicate that, after exposure, magnesium silicate hydrate (M-S-H) began to form and additional calcium silicate hydrate (C-S-H) formed.

The SEM photomicrographs from control samples and from samples subjected to 7-, 14-, and 21-day exposures to waste simulant are shown in Figures 17, 18, 19, and 20, respectively. The hardened grout that had not been exposed to the waste simulant shows an open structure with fibrous and reticular networks of C-S-H (Figure 17). The glassy spherules from the silica-rich fly ash showed clean surfaces and little evidence of dissolution. After 7 days exposure (Figure 18), samples showed ball-shaped clusters of sodium aluminum silicate hydrate up to 5 μm in diameter. The composition of these clusters was confirmed by EDX. Samples prepared after 14 days exposure showed progressively more sodium aluminum silicate hydrate, both in the form of the ball-shaped clusters and distributed through the dense matrix. Samples prepared after 21 days exposure showed a very dense matrix with large amounts of sodium aluminum silicate and the glassy part of the fly ash had reacted extensively.

The results from all of the approaches used in testing the grout after exposure indicate that the grout is interacting strongly with the waste simulant and is producing a new sodium aluminum silicate phase that fills in pore spaces. The masses of the samples exposed increased by over 10% during exposure testing. The surface chemistry showed a rise in silicon and aluminum and a drop in calcium that is consistent with the surface being overgrown with sodium aluminum silicate. The XRD patterns prepared from the fine fraction of the crushed grout showed the appearance of a set of peaks that corresponds to a known sodium aluminum silicate hydrate. The SEM images showed the appearance

of prominent ball-like crystal clusters. Under examination with the EDX attachment the clusters showed the characteristic X-ray peaks for sodium, aluminum, and silicon.

In the waste-grout interaction testing reported here, evidence indicates that the highly alkaline, sodium- and aluminum-rich waste is interacting with the portland cement-based grout to form a crystalline sodium aluminum silicate hydrate and some additional C-S-H and M-S-H. The newly precipitated phases are filling in the voids in the grout and forming a dense, non-porous layer on the grout samples; and sodium and aluminum are being removed from the contacting waste simulant. During interaction with the waste, the grout acted as a chemical barrier in that it removed sodium and aluminum from the waste simulant; and the grout's ability to act as a dense, non-porous physical barrier appears to have improved over the experimental exposure period. The interaction of some alkaline wastes may not compromise the containment provided by a grout based on portland cement and a silica-rich pozzolan.

6. Decommissioning and Archiving

Monitoring of thermocouples and gages, and analysis of data from the physical models, were terminated early or deleted because of the need to terminate the project. Close-out activities included removal of 3 cores, 6-in diameter and at least 14 in long, by drilling down from the top of the upper lift and to the interface with the second lift. These cores were sealed in wax and put in indefinite storage at the WES. Smaller lengths of core, 2-in diameter, were taken from the interface between the first lift of cold-cap and the underlying simulated wasteform grout, by drilling horizontally through prelocated ports in the model walls. Visual examination of these cores prior to archiving indicated that there was minimal interaction and no bonding between the wasteform grout and the cold-cap grout in real time. These cores also are in indefinite storage. After recovery of cores of archiving, the entire model assemblies were disassembled for disposal.

7. Conclusions and Implications for Successful Grouting

- a. A cold-cap grout was developed from materials used previously in the Grout Vault Program, to achieve the properties required for mixing, placing, and long-term performance.
- b. Initial properties of the grout during mixing and pumping are strongly controlled by mixer type, mixing time, and handling procedures, as well as by component materials and proportions.
- c. Although there is potential for chemical interaction between the cold-cap grout and the simulated liquid waste, very little interaction occurred in approximately 4 months of contact between the simulated wasteform grout and the lowest lift of cold-cap grout.
- d. The most striking potential reaction indicated by tests of the cold-cap grout immersed in simulated waste liquid is formation of a sodium aluminum silicate hydrate phase. This phase fills open pores and could decrease the effective porosity of the cold-cap grout. Therefore, this chemical interaction may not represent degradation of the cold-cap grout, but could enhance its performance as a barrier to fluid migration.

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e. The grout developed here could be placed successfully if new field applications evolve with ongoing DOE programs. Although this study was not completed due to program cancellation, the results presented here support the position that carefully designed grouting technologies can be used appropriately and successfully for some waste isolation and disposal activities.

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Figure 1. Adiabatic temperature rise, Hanford cold cap grouts

Figure 2. Internal view of one model, looking from the top toward the floor (covered with wasteform grout), and showing the array of heating pipes

Figure 3. Placement of wasteform grout in physical models

Hanford Cold Cap Grout

Volume Stability of HCC-34

■ Cast 26 Aug 93 + Cast 10 Sep 93 ▲ Cast 1 Oct 93

Figure 4. Results of length-change tests of grout prisms cast during model-filling activities

Physical Model Box 1, Internal Temperatures

Figure 5. Internal temperatures, Box 1

Figure 6. Internal temperatures, Box 2

Figure 7. Internal temperatures, Box 3

Figure 8. Physical model schematic depicting dial gage locations

Figure 9. Gage data measurements for Box 1

Figure 10. Corrected for measured deflections of R1 and R2

Figure 11. Gage data measurements for Box 2

Figure 12. Corrected for measured deflections of R1 and R2

Figure 13. Gage data measurements for Box 3

Figure 14. Corrected for measured deflections of R1 and R2

Figure 15. Plot showing the variation in the surface chemistry of samples in initial condition and after 7, 14 and 21-days exposure to the simulated wastes

Figure 16. Comparison of XRD pattern from powdered grout sample after 21 days exposure (upper pattern) to the simulated waste liquid with the pattern from JPDF 31-1270, sodium aluminum silicate hydrate (lower pattern)

Figure 17. SEM photomicrograph of a fractured surface of the sealing grout specimen before exposure to the liquid waste simulant. The matrix shows a loosely consolidated structure, many of the fly ash particles show little or no reaction

Figure 18. SEM photomicrograph of a fractured surface of the sealing grout after 7-day exposure to the liquid waste simulant. Reaction products can be observed on the fly ash particles as ball-like crystal clusters

Figure 19. SEM photomicrograph of a fractured surface of the sealing grout after 14-day exposure to the liquid waste simulant. Reaction products can be observed on the fly ash particles and blended into the matrix

Figure 20. SEM photomicrograph of a fractured surface of the sealing grout after 21-day exposure to the liquid waste simulant. Reaction of the fly ash has progressed to where many of the fly ash particles are not recognizable

Table 1 HCC-34 Grout Mixture Proportions	
Materials	Saturated Surface-Dry Weight lb/ft ³
API Class H Cement	10.0
ASTM Class F Fly Ash	56.9
Fine Aggregate	33.05
Bentonite	1.5
High Range Water-Reducer	0.175
Retarder	0.5 fl oz
Water	22.0

Table 2 HCC-35 Grout Mixture Proportions	
Materials	Saturated Surface-Dry Weight lb/ft ³
API Class H Cement	10.3
ASTM Class F Fly Ash	58.4
Fine Aggregate	33.9
Bentonite	1.5
High Range Water-Reducer	0.180
Retarder	0.5 fl oz
Water	20.9

Table 3
HCC-34 Grout Proportions for 5.0-cu-ft Batches Prepared for Physical Models

Materials	Weight, lb
Class H Cement #930273	50.0
Class F Fly Ash #930226	284.5
Top Dressing Sand #930295	164.0
Bentonite #930277	7.5
PSP Powder (Lab Stock)	0.875
Placewell Retarder (Lab Stock)	2.5 fl oz
Water*	103.2
* HCC34 proportions required 111.5 lb/5 cu ft. The only change defining HCC35 is small decrease in water content.	

Table 4
Formulation of Simulated 106-AN Liquid Waste

Compound	Quantity (gm) required to make 1 liter
Al(NO ₃) ₃ • 9H ₂ O	158.0
Na ₂ SO ₄	4.40
NaCl	8.77
NaF	0.34
Ca(NO ₃) ₂ • 4H ₂ O	0.47
Na ₂ B ₄ O ₇ • 10H ₂ O	0.19
Cu(NO ₃) ₂ • 3H ₂ O	0.01
Fe(NO ₃) ₃ • 9H ₂ O	0.08
NaOH (50 mass % aqueous sol.)	188.7
NaNO ₃	2.30
NaNO ₂	52.3
Na ₂ CO ₃	40.5
HEDTA	5.29
Na ₄ EDTA	1.83
Glycolic Acid (70 Mass % aqueous sol.)	4.56
SiO ₂ (30 mass % aqueous sol.)	0.04
Na ₃ PO ₄ • 12H ₂ O	58.9
Na ₃ C ₄ H ₅ O ₇ • 2H ₂ O	8.8

Table 5
Percent Mass Gain for Grout Sample After Exposure to Simulated Waste

Sample	Exposure Time (days)	% Mass Gain	Average % Mass Gain
1	7	13.21	12.46
2	7	11.71	
3	14	14.31	13.83
4	14	13.36	
5	21	14.00	13.97
6	21	13.94	

Appendix A

Component Materials for HCC34

Chemical and Physical Properties of API Type H Cement Used in Cold-Cap Grout		
Chemical Analysis	Result	Spec Limits Type II
SiO ₂ , %	23.6	20.0 min
Al ₂ O ₃ , %	2.7	6.0 max
Fe ₂ O ₃	3.5	6.0 max
CaO, %	61.8	*
MgO, %	3.4	6.0 max
SO ₃ , %	2.5	3.0 max
Loss on ignition, %	0.9	3.0 max
Insoluble residue, %	0.24	0.75 max
Na ₂ O, %	0.07	*
K ₂ O, %	0.52	*
Alkalies-total as Na ₂ O, %	0.41	0.60 max
TiO ₂ , %	0.19	*
P ₂ O ₅ , %	0.07	*
C ₃ A, %	2	8 max
C ₃ S, %	40	*
C ₂ S, %	42	*
C ₄ AF, %	11	*
Physical Tests		
Heat of hydration, 7-day, cal/g	59	70 max
Surface area, m ² /kg (air permeability)	304	280 max
Autoclave expansion, %	0.06	0.80 max
Initial set, min. (Gillmore)	170	60 max
Final set, min. (Gillmore)	285	600 max
Air content, %	10	12 max
Compressive strength, 3-day, psi	1,700	1,000 max
Compressive strength, 7-day, psi	2,205	1,700 max
False set (final penetration), %	94	50 max
* ASTM C 150 contains no specification requirements for these chemical analysis results.		

Chemical and Physical Properties of Class F Fly Ash		
Chemical Analysis	Result	Spec Limits Class F
SiO ₂ , %	48.5	*
Al ₂ O ₃ , %	19.8	*
Fe ₂ O ₃	17.6	*
Sum, %	85.9	70.0 min
MgO, %	0.8	*
SO ₃ , %	1.1	5.0 max
Moisture content, %	0.2	3.0 max
Loss of ignition, %	3.2	6.0 max
Available alkalies (28-day), %	1.1	1.5 max
Physical Tests		
Fineness (45-μm (No. 375) sieve), % retained	24	34 max
Water requirement, %	103	105 max
Density, Mg/m ³	2.38	*
Autoclave expansion, %	0.02	0.80 max
Pozzolanic activity w/lime, psi	1,020	900 max
Pozzolanic activity w/cement (28-day), % . .	119	75 min
Laboratory cement used: Lone Star Industries, Cape Girardeau, MO		
Laboratory lime used: Chemstone		
* ASTM C 618 contains no specification requirements for results of these determinations.		

FINE AGGREGATE WORK SHEET

1. SERIAL NO. 930295	2. MEMO NO. RPP 93-15	3. DATE 3 Aug 93	4. INITIALS
5. JOB NUMBER RD3S10RS017001		6. TESTED FOR Hanford Cold-Cap Grout	
7. SOURCE ACME MATERIALS, Richland, WA			
8. PROCESSING BEFORE TEST NONE			
9. DATE RECEIVED 23 July 1994	10. SAMPLED BY B. H. Green	11. TYPE MATERIAL Top Dressing Sand	

CRD-C 108 Bulk Sp Gr: Date <u>3 Aug 93</u> Initials _____			CRD-C 108 Absorption: Date <u>3 Aug 93</u> Initial _____		
	Run 1	Run 2		Run 1	Run 2
Flask No.	30	2	SSD wt, g	224.85	308.16
a. Weight of Ag, g	500.00	500.00	O.D. wt, g	222.30	304.66
b. Wt Flask + Water, g	706.52	711.43	Moisture wt, g	2.55	3.50
c. Wt Flask + AG + Water, g	1012.05	1018.32	Absorption, %	1.134	1.135
d. Wt Displ Water (a + b - c)	194.47	193.11		Avg	1.13
Temp Water, (C)	25.6	25.6			
Sp Gr = $\frac{500}{d}$	2.571	2.589			
	Avg	2.58			

CRD-C 103 Sieve Analysis: Date: <u>3 Aug 93</u> Initials: _____			Cummulative Per Cent			
Sieve Size	Wt Ret.	% Ret.	Ret.	Pass.	Spec.	Pass/Fail
No. 4	0	0	0	100		
No. 8	0.31	0.12	0.12	99.88		
No. 16	1.69	0.64	0.76	99.24		
No. 30	13.67	5.19	5.95	94.05		
No. 50	157.8	59.96	65.91	34.09		
No. 100	81.76	31.07	96.98	3.02		
No. 200	--	()	--			
Pan	7.94	(3.02)	100.0	0		

CRD-C 104
 Fineness Modulus: _____
 Spec. F.M. _____

Chemical Analysis of Bentonite	
Material: Big Horn Gel HAN-1 SM1	Density (Mg/m ³) = 2.32
Source: Wyo-Gen, Inc. Billings, MT	Pozzolanic Activity w/ Cement (psi) = 150

Chemical Analysis by X-ray Fluorescence	
Component	Result (Mass %)
SiO ₂	77.64
Al ₂ O ₃	16.40
Fe ₂ O ₃	4.34
MgO	1.60
Na ₂ O	1.17
CaO	1.13
K ₂ O	0.37
P ₂ O ₅	0.19
TiO ₂	0.12
SO ₃	0.08
Mn ₂ O ₃	0.06
Total	103.10

Appendix B

Mixture Proportions, Flow Properties, and Performance Annotations for Developmental Grouts

**Table 4
HCC-21**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	Fine aggregate segregated out of mixture. No flow tests.
API Class H Cement	8.70	--	--	
ASTM Class F Fly Ash	45.86	--	--	
Fine Aggregate	65.99	--	--	
Bentonite	0.20	--	--	
HRWRA	0.07	--	--	
Retarder	0.3 fl. ozs.	--	--	
Water	15.00	--	--	

**Table 5
HCC-22**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	No fine aggregate segregation. 6.0% Bleed. 1,240 p.s.i. at 7 days age, elevated cure, average of three specimens.
API Class H Cement	10.00	5	10.6	
ASTM Class F Fly Ash	50.1	15	11.0	
Fine Aggregate	33.2	40	11.2	
Bentonite	0.6	60	11.2	
HRWRA	None	100	11.4	
Retarder	0.32 fl. ozs.	130	11.3	
Water	25.2	--	--	

**Table 6
HCC-23**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry, Lbs/Ft ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	3.6 % Bleed 1,146 psi at 7 days age, elevated cure, average of three specimens.
API Class H Cement	10.00	5	12.2	
ASTM Class F Fly Ash	50.1	15	12.2	
Fine Aggregate	33.2	30	12.2	
Bentonite	1.2	60	12.6	
HRWRA	None	90	12.8	
Retarder	0.32 fl. ozs.	120	13.4	
Water	24.9	--	--	

**Table 7
HCC-24**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	HRWRA added until 50 minutes age. No Bleed 2,010 psi at 7 days age, elevated cure, average of three specimens.
API Class H Cement	10.0	5	37	
ASTM Class F Fly Ash	57.4	18	21.6	
Fine Aggregate	38.1	30	22.0	
Bentonite	1.2	65	20.0	
HPWRA	0.05	90	20.0	
Retarder	0.32 fl. ozs.	120	20.6	
Water	20.0	--	--	

**Table 8
HCC-25**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface -Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	Extra HRWRA added during mixing. 1.9 % Bleed 1,555 psi at 7 days age, elevated cure, average of three specimens.
API Class H Cement	10.0	5	15.2	
ASTM Class F Fly Ash	53.7	10	13.8	
Fine Aggregate	35.6	60	13.6	
Bentonite	1.2	90	13.6	
HRWRA	0.05	120	13.6	
Retarder	0.30 fl.ozs.	--	--	
Water	22.5	--	--	

**Table 9
HCC-26**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	Extra HRWRA added during mixing. 1.8 % Bleed. 1,450 psi at 7 days age, elevated cure, average of three specimens.
API Class H Cement	10.0	5	16.6	
ASTM Class F Fly Ash	56.86	15	15.0	
Fine Aggregate	33.2	30	15.0	
Bentonite	1.4	60	15.4	
HRWRA	0.05	125	15.8	
Retarder	0.3 fl. ozs.	--	--	
Water	22.0	--	--	

**Table 10
HCC-27**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	
API Class H Cement	10.0	7	22.0	Extra HRWRA added during mixing. Plaster added to control bleeding and prevent shrinkage. No Bleed. 1,985 psi at 7 days age, elevated cure, average of three specimens. Flow test stopped at 90 minutes due to long flow times.
ASTM Class F Fly Ash	56.86	15	21.2	
Fine Aggregate	33.2	40	23.0	
Bentonite	1.4	90	23.4	
Plaster	1.0	--	--	
HRWRA	0.125	--	--	
Retarder	0.39 fl. ozs.	--	--	
Water	21.64	--	--	

**Table 11
HCC-28**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	
API Class H Cement	10.0	5	17.8	
ASTM Class F Fly Ash	56.9	15	18.2	
Fine Aggregate	32.3	30	18.4	
Bentonite	1.4	60	18.6	
Plaster	1.0	120	19.2	
HRWRA	0.15	--	--	
Retarder	0.47 fl. ozs.	--	--	
Water	22.0	--	--	

**Table 12
HCC-29**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	No Bleed Thick consistency at 2 Hours age. 1,725 psi at 7 days age, elevated cure, average of three specimens.
API Class H Cement	10.0	5	17.0	
ASTM Class F Fly Ash	55.6	20	17.6	
Fine Aggregate	32.3	30	18.8	
Bentonite	1.4	60	20.2	
Plaster	1.0	90	20.6	
HRWRA	0.125	120	22.0	
Retarder	0.47 fl. ozs.	--	--	
Water	22.5	--	--	

**Table 13
HCC-30**

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	No Bleed. 1,840 psi at 7 days age, elevated cure, average of three specimens.
API Class H Cement	10.0	5	17.2	
ASTM Class F Fly Ash	56.9	15	17.6	
Fine Aggregate	32.2	30	17.6	
Bentonite	1.4	60	17.8	
Plaster	1.0	90	18.0	
HRWRA	0.175	120	18.0	
Retarder	0.5 fl. ozs.	--	--	
Water	22.0	--	--	

Table 14
HCC-31

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	No Bleed. 1,770 psi at 7 days age, elevated cure, average of three specimens.
API Class H Cement	10.0	5	18.0	
ASTM Class F Fly Ash	49.82	15	17.8	
Fine Aggregate	40.0	35	18.2	
Bentonite	1.4	60	17.8	
Plaster	1.0	90	17.4	
HRWRA	0.175	120	17.4	
Retarder	0.5 fl. ozs.	--	--	
Water	22.0	--	--	

Table 15
HCC-32

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	No Bleed. Mixture slightly mounded in bowl after flow tests. Plaster taken out of mixture because of concerns about chemical reaction with the wasteform grout.
API Class H Cement	10.0	5	20.6	
ASTM Class F Fly Ash	48.8	15	19.6	
Fine Aggregate	40.14	30	18.8	
Bentonite	2.0	60	20.0	
HRWRA	0.175	90	21.0	
Retarder	0.5 fl ozs.	120	23.8	
Water	22.5	--	--	

Table 16
HCC-33

Mixture Proportions		Flow Properties		Comments
Materials	Saturated Surface-Dry Dry, Lbs./Ft. ³	Time after initial Mixing, Minutes	Time of Efflux, Seconds (CRD-C 611)	Thrown out. Flows too slow.
API Class H Cement	10.6	5	29	
ASTM Class F Fly Ash	56.9	15	27	
Fine Aggregate	32.2	--	--	
Bentonite	1.84	--	--	
HRWRA	0.212	--	--	
Retarder	0.5 fl. ozs.	--	--	
Water	22.0	--	--	

DATE

FILMED

10/18/94

END