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# GROUT FOR CLOSURE OF WASTE-DISPOSAL VAULTS AT THE U.S. DOE HANFORD SITE

Lillian D. Wakeley*
Earl W. McDaniel
James J. Ernzen*

Chemical Technology Division
Oak Ridge National Laboratory†
Oak Ridge, Tennessee 37831

*U. S. Army Engineer Waterways Experiment Station, Vicksburg, MS 29180-6199.

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# GROUT FOR CLOSURE OF WASTE-DISPOSAL VAULTS AT THE US DOE HANFORD SITE

by

Lillian D. Wakeley*, Earl W. McDaniel**, Jeff Voogd†, and James J. Ernzen‡

## ABSTRACT

For permanent disposal of radioactive wastes from reprocessing, the US Department of Energy (DOE) has chosen to grout wastes in concrete vaults within a subsurface multiple-barrier system. The subject of this research is the non-radioactive, or "cold cap" grout, which fills the upper 120 cm of these vaults, and provides support for overlying barriers. Because of the heat evolved by the wasteform, this void-filling grout must perform at temperatures higher than those of usual large-volume grouting operations. It must have: low potential for thermal expansion and heat retention; a low modulus to withstand thermal and mechanical stresses without cracking; strength adequate to support overlying barrier-system components; and minimal potential for shrinkage. In addition, it must be pumpable, self-levelling, and non-segregating. Materials for formulation included a large percentage of Class F fly ash, and coarsely ground oil-well cement. Grout development included chemical and physical characterization, and physical and thermal modelling.

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*Chief, Engineering Sciences Branch, Concrete Technology Division, Structures Laboratory, US Army Waterways Experiment Station, Vicksburg, Mississippi 39180-6199.

**Manager, Hanford Grout Program, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6044.

†Grout Technology Program Manager, Westinghouse Hanford Corporation, Richland, Washington 99352.

‡Assistant Chief, Concrete Technology Division, Structures Laboratory, US Army Waterways Experiment Station, Vicksburg, Mississippi 39180-6199.

## BACKGROUND

The Hanford Grout Vault Program was developed to reduce the need for temporary storage capacity for soluble radioactive waste and provide permanent disposal of defense low-level wastes at the Department of Energy facility at Hanford WA. These wastes include chemically toxic and radioactive salts created during more than 40 years of processing nuclear weapons materials. The wastes have been dewatered to varying extents and stored in "temporary" underground steel tanks. For permanent disposal, the waste is removed from its temporary tank by being reslurried with water, mixed with the dry-blended components of the wasteform grout, and then pumped into underground concrete vaults. Being solidified in wasteform grout makes the radioactive waste components less soluble and less likely to be leached or otherwise transported into the biosphere (1). The cold cap grout is then placed on top of the wasteform grout in layers filling the vault to the underside of its cover blocks, to form a load-bearing barrier between the covering layers and the hazardous materials contained below them. The vault measures 15.2 m x 38.1 m x 10.4 m and is filled to a height of 9.2 m with wasteform grout and later covered with 1.2 m of cold cap grout (2). Figure 1 shows a section view of the first concrete vault at Hanford which is filled with wasteform grout. WES developed the cold cap grout for this vault.

## PERFORMANCE REQUIREMENTS FOR COLD CAP GROUT

The plastic flow specification required that the cold-cap grout be essentially self levelling in that it needed to travel 14.3 m horizontally following a 1.2 m vertical drop without segregating. This requirement stemmed from the location of existing ports in the vault cover blocks. No bleeding was allowed since free water migrating to the surface of the cold cap after casting could bring radioactive material with it and contaminate the cap material. Placement operations also dictated that the grout would probably be batched at a concrete plant 45 minutes away, trucked to the site, and then pumped into the vault. For this reason, all fresh grout properties had to be maintained for a minimum of two hours.

The grout was required to attain an unconfined compressive strength of 0.067 MPa at 28 days. Volume stability was a critical parameter in maintaining the integrity of the cap so grout shrinkage was limited to a value of 0.1% in the lower lifts and 0.01% in the top lift and no expansion was permitted. The grout had to be geochemically stable when in contact with the wasteform grout at temperatures estimated to reach 70 °C and contribute as little heat as possible to the vault itself. The current vault temperature had stabilized at 45 °C and assuming that the maximum grout placement temperature would not exceed 38 °C, a maximum temperature rise of 50 °C was chosen as a requirement to avoid overheating the mixture.

## MATERIAL SELECTION

Based upon the above specifications, materials were chosen which would, when properly proportioned, give the highest probability of success. API Class H oil well cement was chosen because of its coarsely ground particle size and reduced rate of heat evolution would be helpful in reducing cracking due to thermal strains. The low alumina content of the cement was also expected to provide excellent resistance to sulfates which are present in the liquid waste (3). A low-calcium ASTM Class F fly ash was chosen to supply the pozzolanic reaction needed to fill up the microstructure with secondary hydration products thereby improving leach resistance. A Class F ash was specifically chosen for its demonstrated ability to provide added resistance to sulfate attack and its slow heat generation (4,5,6). Fly ash also had a positive effect on workability. The chemical and physical characteristics of the fly ash are shown in Table 1.

Also to reduce heat evolution, a natural, well rounded sand from a source near the Hanford site was proportioned in the grout. The coarse fractions above the #8 size were sieved out to reduce segregation in the mixture and improve flow properties. Approximately 2.5 kg of sodium bentonite clay was used per cubic meter of grout to aid in pumpability, reduce segregation, and eliminate bleeding. To produce as durable a product as possible, the ratio of water to cementitious materials was held at 0.40. This necessitated the use of both a high-range water-reducing admixture and a set retarder to obtain the required flow properties for the two hour time period needed between mixing and pumping.

## EXPERIMENTAL PROCEDURES

The experimental testing program was accomplished in three phases: 1) plastic properties testing, 2) hardened properties testing and, 3) full-depth physical model.

### Plastic Properties Testing

The cold cap grout will be pumped into a 1.2 m cavity above the wasteform grout which is currently generating sufficient heat to maintain the vault temperature at 45 °C. It was desirable to proportion the mixture with a minimum cement content and still meet the plastic and hardened grout properties specified. For this reason fly ash replacement values of 67 to 80 % were used. The ratio of cementitious materials to sand (C+FA/S) was varied between 1:1 and 2:1 initially since it was unclear at the outset how the aggregate content would affect the volume stability of the grout at the elevated vault temperature. Initial mixtures were proportioned in 0.1 cubic foot batches in a laboratory bench-top mixer meeting the requirements of ASTM C 305 and were tested for flow, segregation, bleeding, and compressive strength. Grout flow was tested using the flow cone procedure in ASTM C 939 at intervals of 15, 30, 60, 90, and 120 minutes after starting mixing. From WES experience with grouting operations, a flow time of 15 to 18 seconds, measured according to ASTM C 939, was chosen to meet the flow requirments. After two hours of mixing, bleeding was measured in a 500 ml graduated cylinder according to ASTM C 940. Compressive strength was measured on both 76 mm x 152 mm cylinders and 50 mm cubes according to ASTM C 39/109 at 7, 14, and 28 days. Mixture segregation was checked by physical inspection prior to each flow test. At the completion of Phase I, two mixtures with 285 $kg/m^3$ of cement and one mixture with 178 $kg/m^3$ of cement were selected to continue to Phase II. Table 2 shows the mixture proportions for three mixtures which were chosen to proceed with hardened properties testing.

## Hardened Properties Testing

The three mixtures shown in Table 2 were then proportioned in larger batch sizes and specimens cast and tested for time of set, volume stability, chemical interaction with simulated wasteform grout, compressive strength, and semiadiabatic temperature rise. The volume stability measurements were made on 25- x 25- x 285-mm prisms which were cured and stored in environmental conditions of 45 °C and 100 % relative humidity to simulate conditions inside the vault. Since the exact relative humidity inside the vault was not known, companion prisms from each mixture were cast and stored at 38 °C and 40 % relative humidity to present a worst case scenario. All mixing was done at 23 °C for two hours whereupon the molds were filled and immediately placed in the elevated temperature chamber. The specimens were removed at 24 hours, demolded, and returned to the chamber. Measurements were taken daily till 7 days, weekly till 28 days, then monthly till 180 days, and currently are measured at 90 day intervals. Figures 2 and 3 plot the volume stability versus time for the three mixtures at each temperature and relative humidity.

Initial temperature rise measurements were obtained by measuring the heat loss from a 152- x 305-mm cylinder in a calibrated calorimeter and then calculating the temperature rise this mixture would exhibit inside the vault assuming the vault would respond like an adiabatic environment at 45 °C. This commercial semiadiabatic device[1] was used to screen candidate mixtures to determine which would undergo full-scale adiabatic testing. Figure 4 shows the adiabatic temperature rise calculated by the CIMS system for the three candidate mixtures.

Since the grout would be placed in was at 45 °C environment, an adiabatic temperature rise limit of 50 °C was placed on the cold cap mixture to ensure it did not overheat in the vault. The data shown in Figure 3 indicates that mixtures 1 and 2 exhibited peak temperature rise figures greater than 50 °C with mixture 2 with its higher sand content being slightly cooler. Mixture 3 recorded a calculated adiabatic heat rise of 41 °C. For this reason, mixtures 2 and 3 were chosen to perform full adiabatic temperature rise tests. A 0.40 $m^3$ sample was mixed in a rotary drum mixer for two hours and placed in a environmentally controlled room where the temperature of the room was matched to the heat generation of the sample. Figure 5 shows the adiabatic temperature rise measured on mixtures 2 and 3. Mixture 2 exceeded the 50 °C limit almost immediately and the test was terminated after two days. The termperature of mixture 3 rose more slowly and stayed below the 50 °C limit. Based upon these data and data generated from the

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[1]"Computer Interactive Maturity System (CIMS)" by Digital Site Systems Inc.

volume stability measurements, the decision was made to use mixture 3 in the next phase of the test program.

## PHYSICAL MODEL TEST

The final phase of the research was to construct and cast a large scale physical model of the cold cap which incorporated measuring all of the grout properties tested separately in the previous phases. The concept was to simulate on an engineering scale the environmental conditions in the vault and the mixing and placement operations as they might occur on the site. The model was insulated and heated at 45 °C to simulate the vault environment and was instrumented for strain, temperature, and volume change. Model dimensions were chosen to reflect the actual depth being placed in the vault, to eliminate the edge effects inherent in small specimens and give realistic temperature and strain profiles and volume changes. Long-term data from this model were intended to validate the measurements made on previously cast laboratory specimens and provide more complete data for thermal modelling efforts to follow.

### Mixing/Placement

The base of the cube was filled with a 152-mm lift of surrogate wasteform grout and then followed by three 41-mm lifts of cold cap grout placed one to four weeks apart. The cap was cast in separate lifts since this is how the vault will be filled to reduce the possibility of continuous crack propagation. One quarter of the cube was instrumented with 18 Carlson strain meters to measure changes in both thermal strain and temperature as each lift was added to the cube. Six gages were placed in each lift with one at the cube centerline and the remaining gages placed in a rectangular pattern to measure changes in the material as the grout approaches the corner of the model. Each cold cap lift also was instrumented at the cube centerline with five thermocouples plus one in the wasteform grout to record a continuous profile of temperature data.

Each lift of cap grout was batched in a computer-controlled batch plant and mixed for two hours in a pug mill prior to being placed in the cube by concrete bucket. Flow and segregation were measured at 30-minute intervals and strength cylinders were cast and tested at 7, 14, and 28 days. The average 28-day compressive strength of the grout mixture placed in the physical model was 10 MPa. None of the lifts exhibited any surface bleeding.

Strain and Temperature Measurements

Each grout lift was batched at approximately 27 °C and was placed into the cube at 45 °C. The highest temperature attained by any of the three lifts was 61 °C which amounts to a 41 °C rise in the grout itself. Figure 6 plots the grout strain versus time at the centerline of the each lift at the center of the cube. The maximum strain recorded in the first lift was over 2000 microstrains which is well above the strain limit expected for cementitious grout. Visual inspection of the surface revealed several cracks but it was unclear whether they were due to thermal effects or drying shrinkage around the instrumentation. Of note here is the fact that prevention of cracking was not a performance requirement. The second lift of cold cap grout was placed six days later and this lift was moist cured by ponding a thin layer of water on the surface each day. This water was depleted each day by a combination of absorption and evaporation but it served to keep the surface from drying out and no cracking was observed during the 30 days in between lifts 2 and 3. The maximum strain measured at the cube centerline in the second lift was 1550 microstrains. This is also many times the strain limit typically associated with hardened grout yet this lift showed no visible signs of cracking.

We postulate that the cracking observed in the first lift was due to drying shrinkage and that the elastic modulus of the grout may low enough in the early ages that the material can accomodate these large strains without damage prior to final set.

Volume Stability Measurements

After the final lift was placed the top of the cube, five dial gages were attached to a fixed support simulating the vault cover blocks above the grout surface. The actual volume stability of the grout surface was measured to validate the data obtained from the laboratory prism specimens. Figure 7 shows the deflection of the surface with respect to the cover blocks through 40 days age. The average deflection is 0.076 mm. When divided by the 1.2 m depth of the cold cap grout, the shrinkage of the cold cap is calculated to be 0.006 %. This value meets the performance requirements.

## SUMMARY AND CONCLUSIONS

A non-radioactive sanded cold cap grout was developed to serve as a void filler between the waste grout and the underside of the cover blocks in the first Hanford Grout Vault. Using a small amount of Class H oil well cement, a large amount of ASTM Class F fly ash, a natural sand, and bentonite clay, a grout was developed which met a demanding set of plastic and hardened physical properties. The choice of a large amount of pozzolan in the form of Class F fly ash was instrumental in achieving the performance requirments needed for the cold cap grout in this waste vault.

ACKNOWLEDGEMENT

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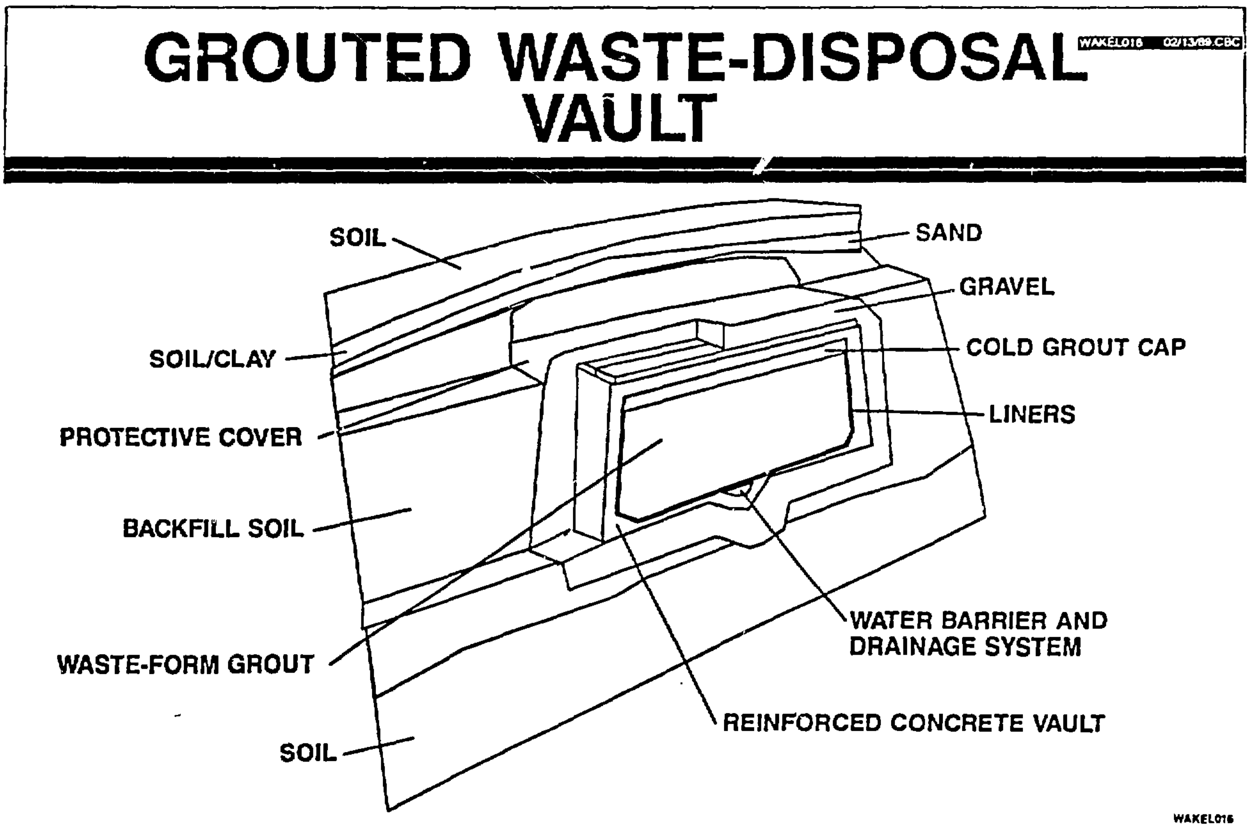


FIGURE 1. GROUTED WASTE-DISPOSAL VAULT

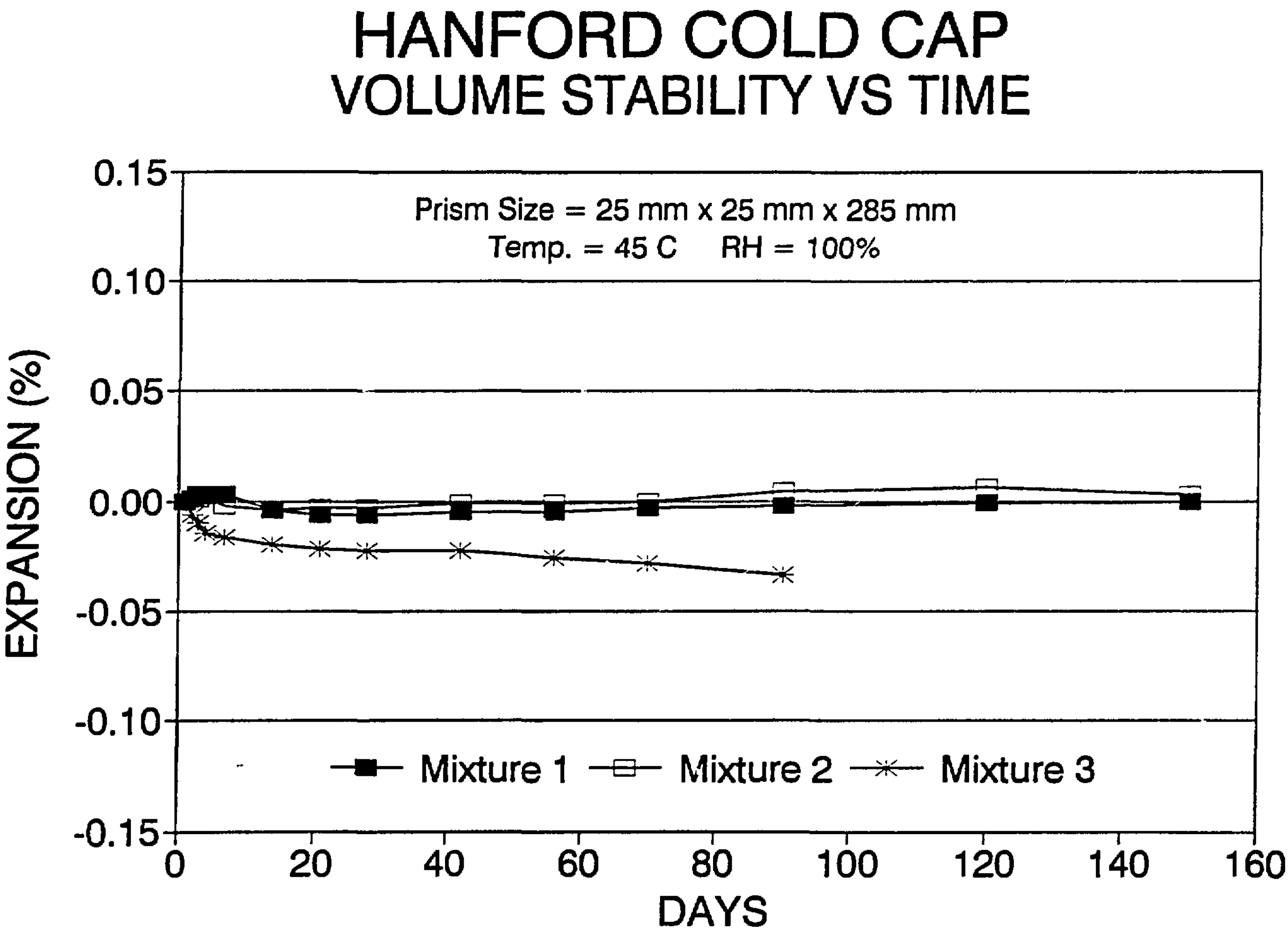


FIGURE 2. HANFORD COLD CAP VOLUME STABILITY VS TIME

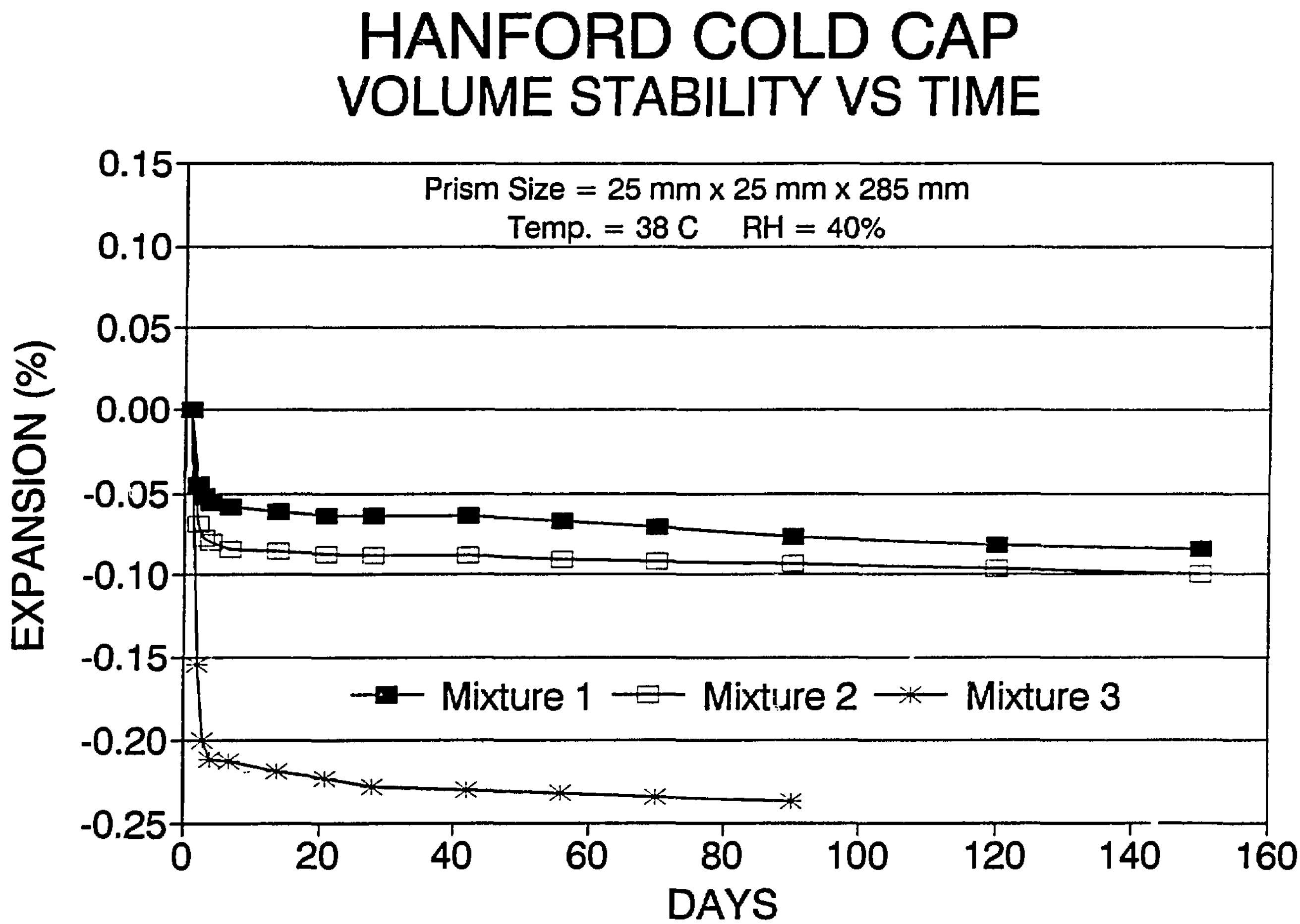


FIGURE 3. HANFORD COLD CAP VOLUME STABILITY VS TIME

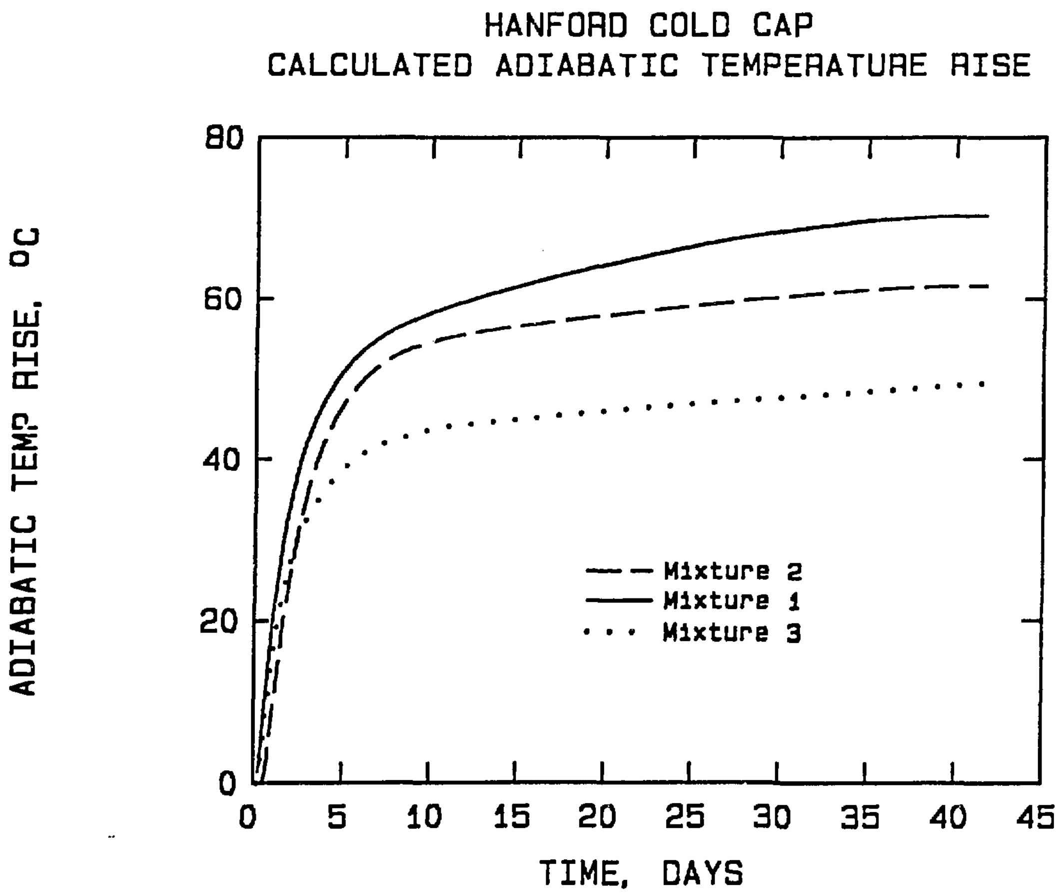


FIGURE 4. HANFORD COLD CAP CALCULATED ADIABATIC TEMPERATURE RISE

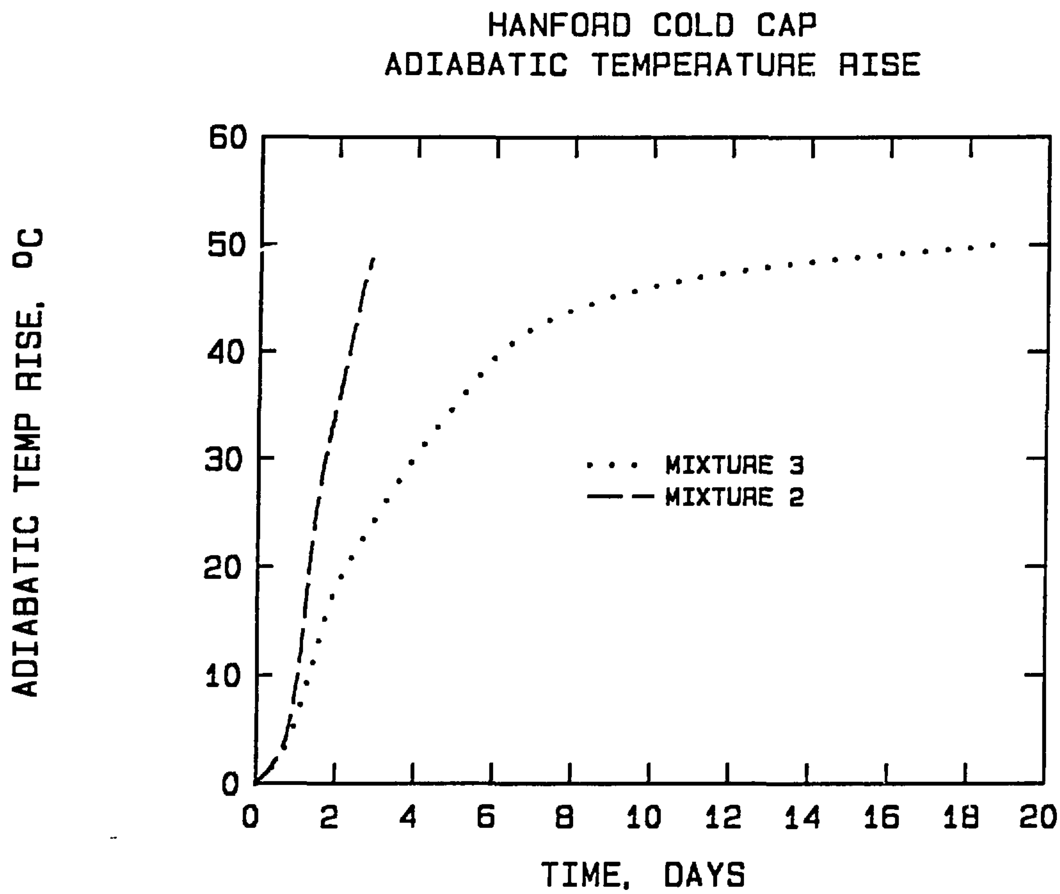


FIGURE 5. HANFORD COLD CAP ADIABATIC TEMPERATURE RISE

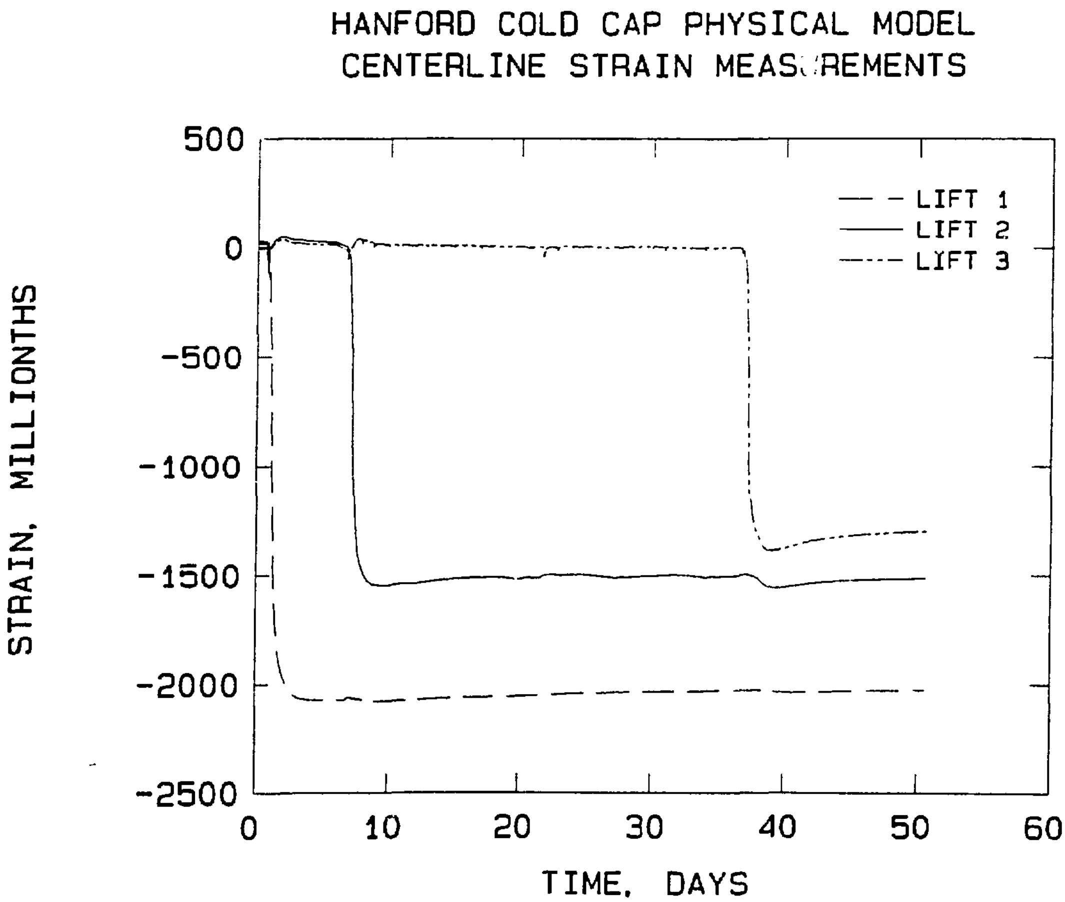


FIGURE 6. HANFORD COLD CAP PHYSICAL MODEL
CENTERLINE STRAIN MEASUREMENTS

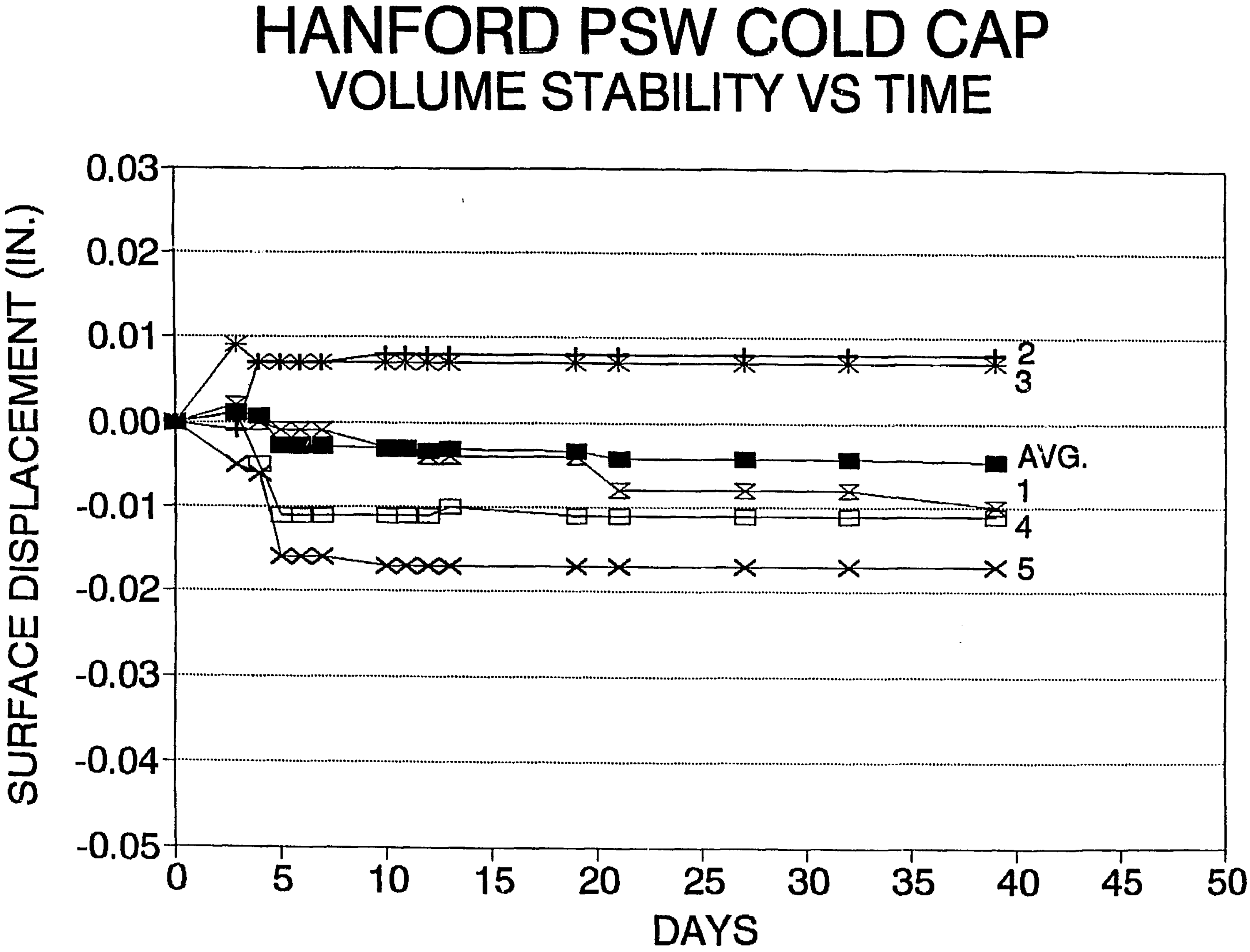


FIGURE 7. HANFORD PSW COLD CAP VOLUME STABILITY VS TIME

TABLE 1

## HANFORD COLD CAP
## Chemical and Physical Properties of Fly Ash

| Chemical Analysis | Results |
|---|---|
| $SiO_2$, % | 48.5 |
| $Al_2O_3$, % | 19.8 |
| $Fe_2O_3$, % | 17.6 |
| Sum, % | 85.9 |
| MgO, % | 0.8 |
| $SO_3$, % | 1.1 |
| Moisture content, % | 0.2 |
| Loss on ignition, % | 3.2 |
| Available alkalies (28-day), % | 1.1 |

| Physical Tests | Results |
|---|---|
| Fineness (45-micrometre), % retained | 24 |
| Water requirement, % | 103 |
| Density, $Mg/m^3$ | 2.38 |
| Autoclave expansion, % | 0.02 |
| Pozzolanic activity w/lime, psi | 1,020 |
| Pozzolanic activity w/cement (28-day), % | 119 |

TABLE 2

## HANFORD COLD CAP CANDIDATE MIXTURE COMPOSITIONS

| MATERIAL | Kg/m$^3$ | | |
|---|---|---|---|
| | MIXTURE 1 | MIXTURE 2 | MIXTURE 3 |
| CLASS H CEMENT | 285 | 285 | 178 |
| CLASS F FLY ASH | 691 | 584 | 661 |
| NATURAL SAND | 475 | 749 | 781 |
| BENTONITE CLAY | 23 | 23 | 23 |
| WATER | 386 | 340 | 335 |
| HRWR | 2.60 | 2.8 | 2.7 |
| RETARDER | 144 ml | 144 ml | 80 ml |
| WATER/CEMENT RATIO | 0.40 | 0.39 | 0.40 |