CHARACTERIZATION OF HYDROFRACTURE GROUTS FOR RADIONUCLIDE MIGRATION*†

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Abstract

Detailed characterization of hydrofracture grouts was performed by optical microscopy, scanning electron microscopy, x-ray diffraction, and β–γ autoradiography. Laboratory-produced samples containing simulated wastes as well as actual radioactive samples of hydrofracture grout sheets obtained by core drilling were examined in this work. X-ray-diffraction results revealed that both laboratory-produced samples and a core-drilled sample consisted primarily of calcium carbonate phases. Both sample types contained very small amounts of strontium or cesium wastes, neither of which could be detected by microscopic techniques. The core-drilled sample contained radioactive ^{90}Sr, ^{137}Cs, and ^{60}Co that could be detected by β–γ autoradiography. The autoradiograph revealed that these radionuclides were still present in the 20-year-old grout and that they had not migrated into the trapped shale fragments.

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I. Introduction

Several methods for the permanent disposal of radioactive wastes have been developed in the last 20 years.[1-5] These methods focus on the immobilization of radionuclides in borosilicace glass, Synroc, tailored ceramics, coated sol–gel—derived ceramics, or concrete and burial in suitable geologic formations. An alternative process for permanent waste disposal — termed hydrofracture — using a tailored cement grout has been successfully proved as a means of permanent disposal of radioactive liquids and sludges at the Oak Ridge National Laboratory (ORNL) (refs. 6–7). This process immobilizes and isolates the radioactive liquid and sludge waste in a cementitious grout by injecting the grout into an impermeable shale formation 200 to 300 m below the earth's surface (Fig. 1). Cost of disposing of the radioactive waste liquids and sludges by this process is about $1.50 to $2.00 per gallon.

The hydrofracture facility at ORNL consists basically of a deep encased well located in an impermeable shale formation 200 to 300 m below the surface; a series of shielded cells housing associated pumps, mixers, and piping; a control room; large external solids storage tanks; and a liquid-waste tank farm (Fig. 1). During operation, the well is slotted and hydraulically pressurized, causing a horizontal fracture within the shale and creating a seam in which to inject the grout. The liquid waste is blended with cement and other additives and pumped at about 900 L/min (150–200 gal/min) into the fractured shale, creating a thin horizontal sheet several hundred meters in diameter. The well remains pressurized for several days while the grout hardens. Numerous injections can be made into each fracture, and fractures can be created at 3- or 4-m increments, starting at the bottom of the well and extending upward to the 200-m level.

The essential feature of the shale-fracturing process is the fixation of the radionuclides in a geologic formation known to be isolated from contact with the surface environment or with subsurface aquifers. The permeability of the shale in the ORNL disposal zone is very low: the calculated rate of water movement is less than 1 cm per century. The process has additional features to provide continued containment of the radionuclides even if the isolation of the disposal formation were lost. For example, the leach rates of significant radionuclides from the set grout are quite low, approximately equal to those of borosilicate glass.[8-9] In addition, any radionuclides that might possibly be leached from the grout sheet would be retained in the disposal zone by the high ion exchange capacity of the shale. Therefore, this process offers an exceptionally favorable approach to permanent disposal of radioactive wastes.

Our objective in this characterization of hydrofracture grouts was to verify that radionuclides are fixed within the grout and do not migrate significant distances into the shale. To accomplish this, we had to identify the phases present in the grout and determine the partitioning of radionuclides within the cement phases. The grout composition could then be tailored for the development of even less leachable phases.

II. Experimental Procedure

To date we have examined two types of samples in our hydrofracture grout characterization studies. The first type consisted of samples produced in the laboratory primarily for mix development studies. Numerous samples of this type have been examined. They consist of cement, fly ash,[10-11] illite clay, attapulgite clay, and waste in the approximate proportions shown in Table I. Fly ash is added as a partial substitute

for cement to reduce the cost and to improve the retention of strontium. Attapulgite is a drilling clay that suspends the cement and absorbs water, thereby reducing the phase separation. Illite clay is added for its high capacity for cesium retention. Numerous compositions have been examined; however, they varied around the average composition shown in Table I.
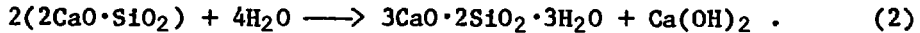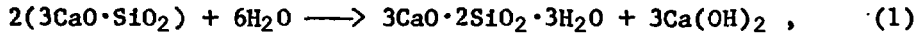
The second type of sample was core-drilled from an actual hydrofracture grout sheet injected in 1964. This sample was cured in situ for two years and cored and stored aboveground in 1966. Analytical examination identified the contained radionuclides as ^{90}Sr, ^{137}Cs, and ^{60}Co. The relative amounts of these radionuclides and the absence of fly ash identified the grout sheet as experimental injection 5. This injection occurred in May 1964 and consisted of nearly 760,000 L of grout containing about 23×10^{13} Bq (~610 Ci) of ^{90}Sr, about 5×10^{12} Bq (~145 Ci) of ^{137}Cs, and 1.8×10^{10} Bq (5 Ci) of ^{60}Co. The composition of the dry solids used in this injection was 86% cement, 8% attapulgite clay, and 6% illite clay.

Numerous analytical techniques, such as x-ray diffraction, scanning electron microscopy equipped with an energy-dispersive x-ray analysis system, optical microscopy, autoradiography, and electron microscopy, were used to characterize the hydrofracture grouts. Numerous types of samples were examined by scanning electron microscopy, including polished sections and fresh fracture surfaces.

III. Results and Discussion

Hydrofracture grouts are composed primarily of cementitious phases; therefore, it is important to understand the reactions that occur during the hydration of cement.[12-13] Portland cement is composed of four major

constituents that include tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). Minor constituents are also present as gypsum ($CaSO_4 \cdot 2H_2O$), free lime (CaO), and magnesia (MgO). Both C_3S and C_2S react with water to form a hydrated calcium silicate (CSH) and calcium hydroxide as shown in Eqs. (1) and (2):

$$2(3CaO \cdot SiO_2) + 6H_2O \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 , \quad (1)$$

$$2(2CaO \cdot SiO_2) + 4H_2O \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 . \quad (2)$$

The resulting hydrate is poorly crystallized and frequently called "tobermorite gel." Because the composition of the hydrated phase varies with age, it is often referred to as CSH. The reactions show that the considerable amount of $Ca(OH)_2$ present causes the cement paste to be highly alkaline. Tricalcium aluminate in the presence of gypsum reacts with water to form ettringite, as shown in Eq. (3):

$$3CaO \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 25H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O . \quad (3)$$
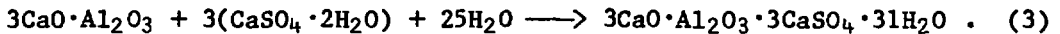
This reaction proceeds for the first 24 h or until the source of sulphur is depleted. Any further hydration of C_3A forms a low-sulfate sulphoaluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$), often referred to as monosulphate. Ettringite decomposes slowly after the first 24 h to form additional monosulphate. The final-phase C_4AF reacts with water according to Eq. (4):

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 10H_2O + 2Ca(OH)_2 \longrightarrow 6CaO \cdot Al_2O_3 \cdot Fe_2O_3 \cdot 12H_2O . \quad (4)$$
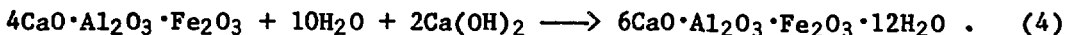
These hydration reactions occur at various rates, as shown in Fig. 2, which also shows the microstructures that develop from these reactions. The phases present in the hydrofracture grouts are certainly more complex than those present in portland cement pastes; however, the phases produced

by the hydration of portland cement must be understood to identify the more complex phase assemblage present in hardened hydrofracture grouts.

Numerous hydrofracture grouts produced in the laboratory were found by x-ray diffraction to consist primarily of calcium carbonate phases. Calcite ($CaCO_3$) was the predominant phase, with vaterite (another crystal structure of $CaCO_3$) also present. Portlandite [$Ca(OH)_2$], the primary phase formed during cement hydration, apparently reacted with CO_2 from the air to form carbonates. Other phases identified in these samples were quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$), a magnetitelike spinel (Fe_3O_4), attapulgite clay, and dicalcium silicate ($2CaO \cdot SiO_2$). The quartz, mullite, and magnetitelike spinel were from unreacted fly ash particles.

The predominance of carbonate phases in these samples was quite surprising, because the calcium-rich solutions from cement hydration were expected to react with SiO_2 present in fly ash particles to form cementitious (calcium-silicate) phases. The fly ash appears to be relatively inert and not to react with the calcium-rich solution. Other forms of highly active SiO_2 (including other types of fly ash) may need to be investigated to determine if more cementitious phases can be produced.

Scanning electron microscopy of the samples revealed very little information. Fracture surfaces examined showed that fracture occurred through the cementlike phase holding the other features together. The energy-dispersive system showed the composition of all features to be alike, all being covered with the cementlike matrix. Polished sections revealed more information because the matrix phase no longer covered all the microstructural features (Fig. 3). However, identifying individual phases within a hardened cement paste was extremely difficult. This

difficulty results from the intergrowth of the cement phases as they hydrate. After three to six months, the phases are so intergrown that no single phase material can be isolated (Fig. 2).

The core-drilled sample of hydrofracture grout was examined by optical microscopy, scanning electron microscopy, and x-ray diffraction. The x-ray diffraction results revealed that the grout consisted primarily of calcite ($CaCO_3$), vaterite ($CaCO_3$), portlandite [$Ca(OH)_2$], and Ca_2SiO_4. The absence of quartz and mullite indicates that no fly ash had been added to the grout. Grout samples prepared in the laboratory produced the same phases as those produced by actual grout sheets injected into the shale layer and cured in situ. This is an important result because information obtained from laboratory-produced samples can be used to predict what occurs in actual grout sheets.

A portion of the core-drilled sample was mounted for metallographic examination and found to contain numerous fragments of shale trapped in the grout (Fig. 4). It is important that there was no significant alteration of the grout-shale interface after nearly 20 years (2 years in situ and 18 years aboveground). Examination by scanning electron microscopy failed to reveal the strontium, cesium, or cobalt because of the very low concentration. The sensitivity of the energy-dispersive system is about 0.1%; the samples must therefore contain less than 0.1% strontium, cesium, and cobalt. Examination by ion microprobe and transmission electron microscopy also failed to reveal the radionuclides. However, the radionuclides were located by β-γ autoradiography (Fig. 5). The sample was placed on film that was sensitive to β-γ radiation and left for about 3 d; the long exposure was required because of the very small amount of activity present. The dark areas of the bright field photograph are shale fragments, and the light areas are grout. The light areas in

the autoradiograph correspond to areas of strontium, cesium, or cobalt concentrations. The autoradiograph clearly shows that the activity has remained in the grout and has not migrated into the shale after nearly 20 years. Although the grout was cured in situ for only two years, the shale fragments were trapped within the grout for the full 20 years.

A more quantitative measure of the migration of the radionuclides is desired. This is, however, the first actual proof that the radionuclides do not migrate appreciably into the shale. This result is also significant because the grout was produced nearly 20 years ago and was not optimized for radionuclide retention. Grouts produced today should be significantly improved.

IV. Conclusions

Hydrofracture grouts were characterized to verify that radionuclides do not migrate significantly from hydrofracture grout sheets into the surrounding shale. Both hydrofracture grouts produced in the laboratory and those obtained from core drilling were found by x-ray diffraction to consist of calcium carbonate phases. Specific phases, particularly the calcium silicate phases, were very difficult if not impossible to identify by microscopic techniques. Radionuclides present in extremely small quantities in the samples examined could not be identified by scanning electron microscopy, electron microprobe, or ion microprobe techniques. However, a β-γ autoradiograph clearly showed that radionuclides were fixed within the grout and did not migrate into the shale. Additional work is needed to measure the radionuclide migration quantitatively, to make better identification of the phases present, and to determine the partitioning of radionuclides within the various phases.

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Table I. Composition of Hydrofracture Grouts

| Constituent	Dry solids blend (wt %)	Final grout composition (wt %)
Portland cement	38	14
Fly ash	38	14
Illite clay	8	3
Attapulgite clay	16	6
Waste		11
Water		52

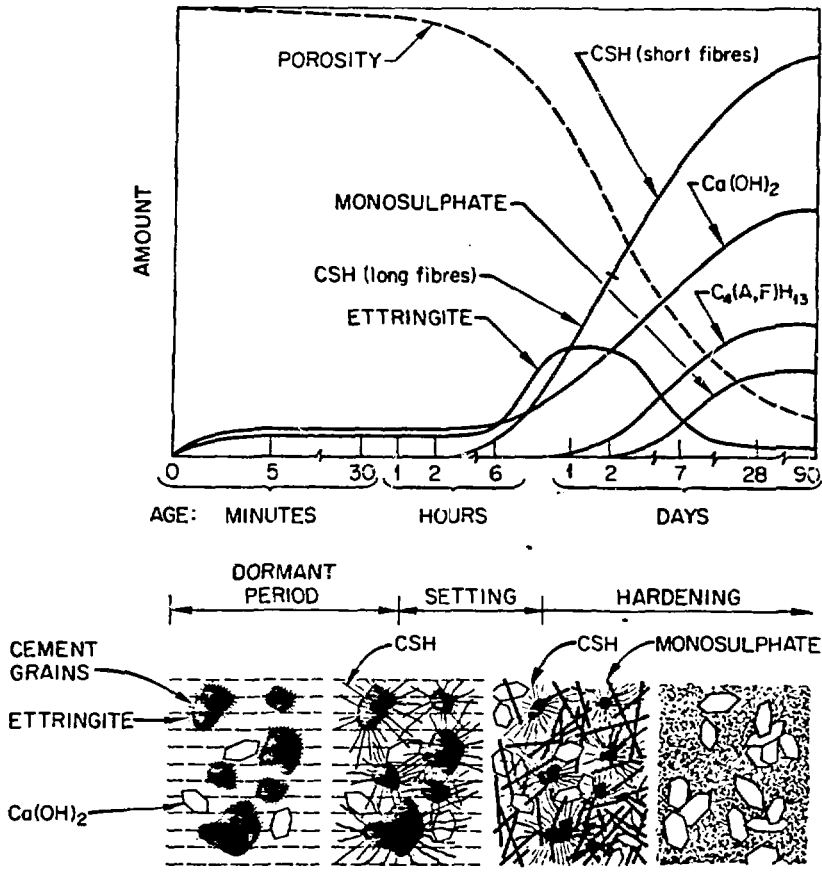**Fig. 1.** Oak Ridge National Laboratory hydrofracture facility.

Fig. 2. (*a*) Hydration of various components of portland cement at various rates. (*b*) Microstructures resulting from reactions shown in (*a*). Courtesy of I. Soroka, *Portland Cement Paste and Concrete*, Chemical Publishing Co., New York, 1982.

Fig. 3. Hydrofracture grout sample from mix development studies showing typical features such as fly ash spheres, large quartz grains, waste agglomerates, and the cementitious matrix.

Fig. 4. Core-drilled hydrofracture grout showing the grout-shale interface and numerous fragments of shale trapped in the grout.

Fig. 5. Cored grout shows no migration of radionuclides in β-γ autoradiograph. Dark areas in bright field photograph are shale fragments. Corresponding areas in the autoradiograph contain neither ^{90}Sr, ^{137}Cs, nor ^{60}Co activity.
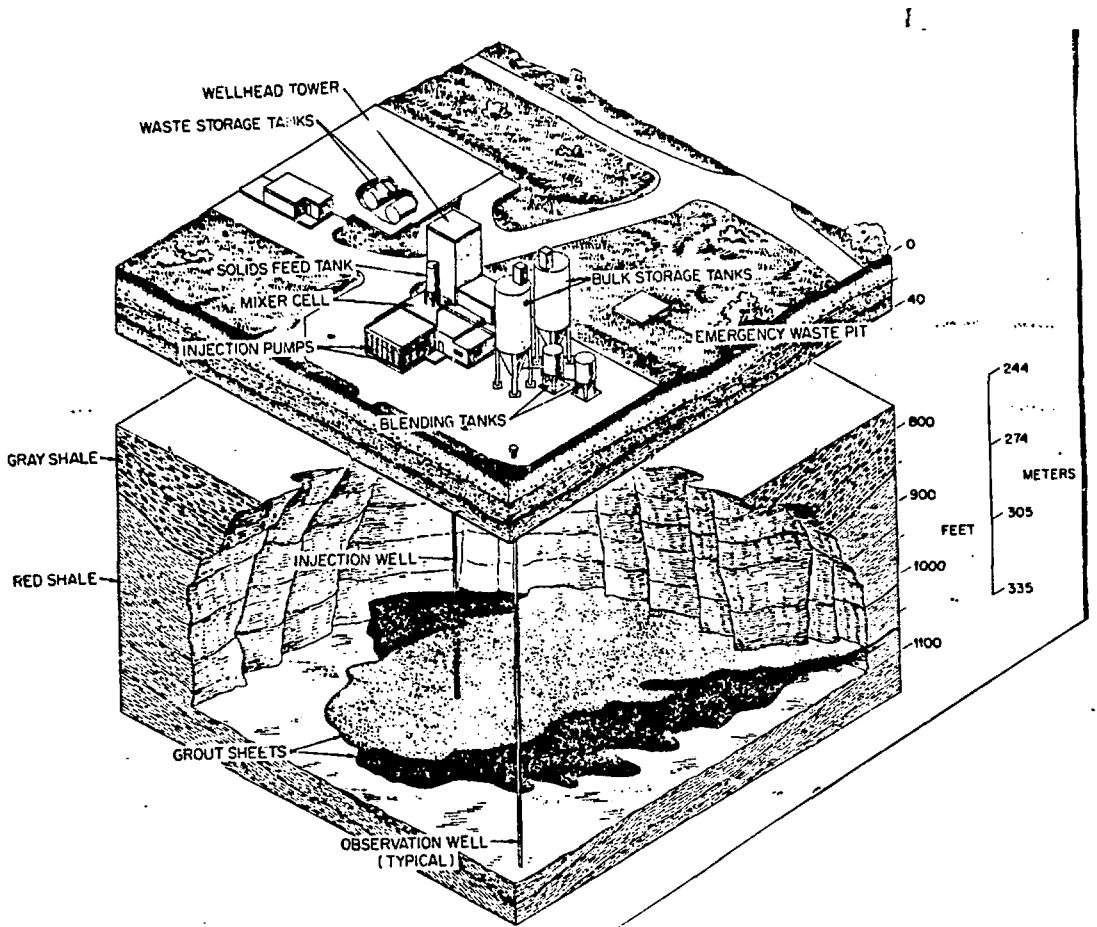
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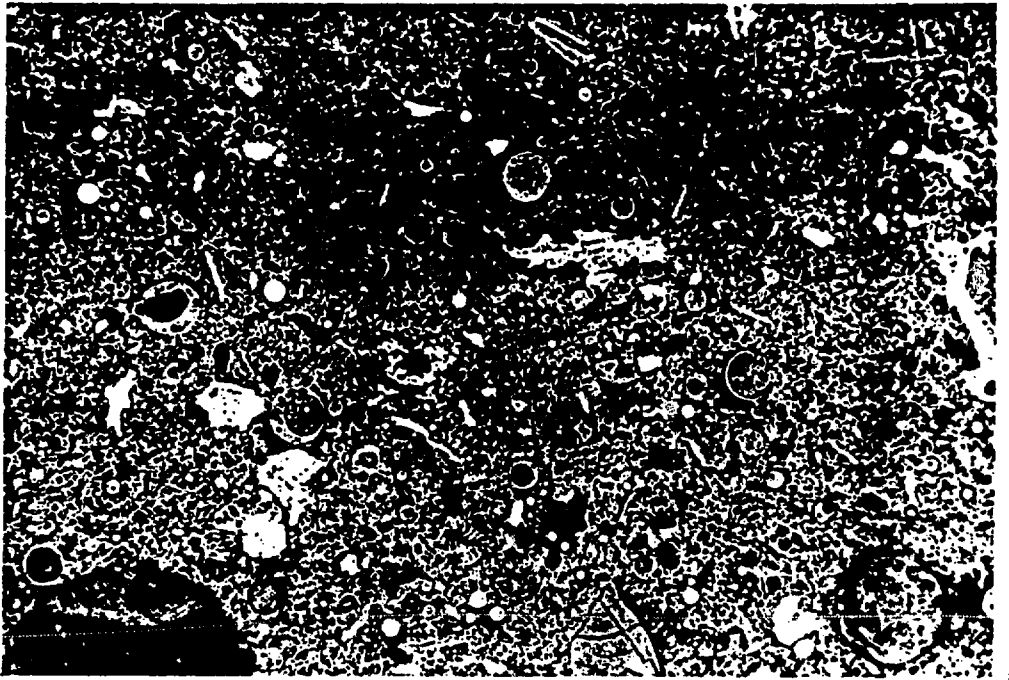
100 μm

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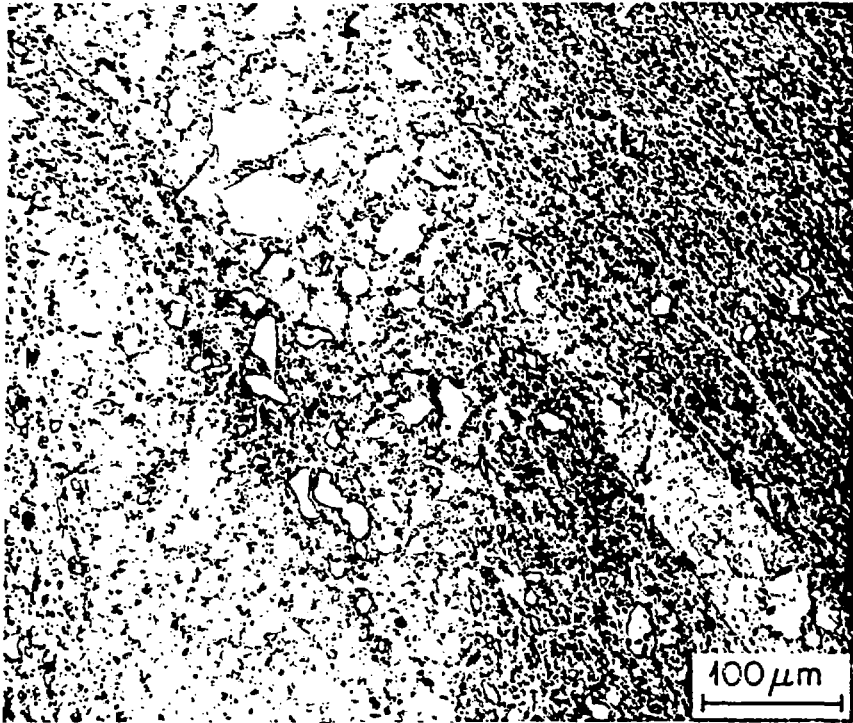
GROUT   SHALE

Fig. 4. Core-drilled hydrofracture grout showing the grout-shale
interface and numerous fragments of shale trapped in the grout.

2.5 mm

β-γ AUTORADIOGRAPH　　　　　　　BRIGHT FIELD

Fig. 5. Cored grout shows no migration of radionuclides in β-γ autoradiograph. Dark areas in bright field photograph are shale fragments. Corresponding areas in the autoradiograph contain neither ^{90}Sr, ^{137}Cs, nor ^{60}Co activity.

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