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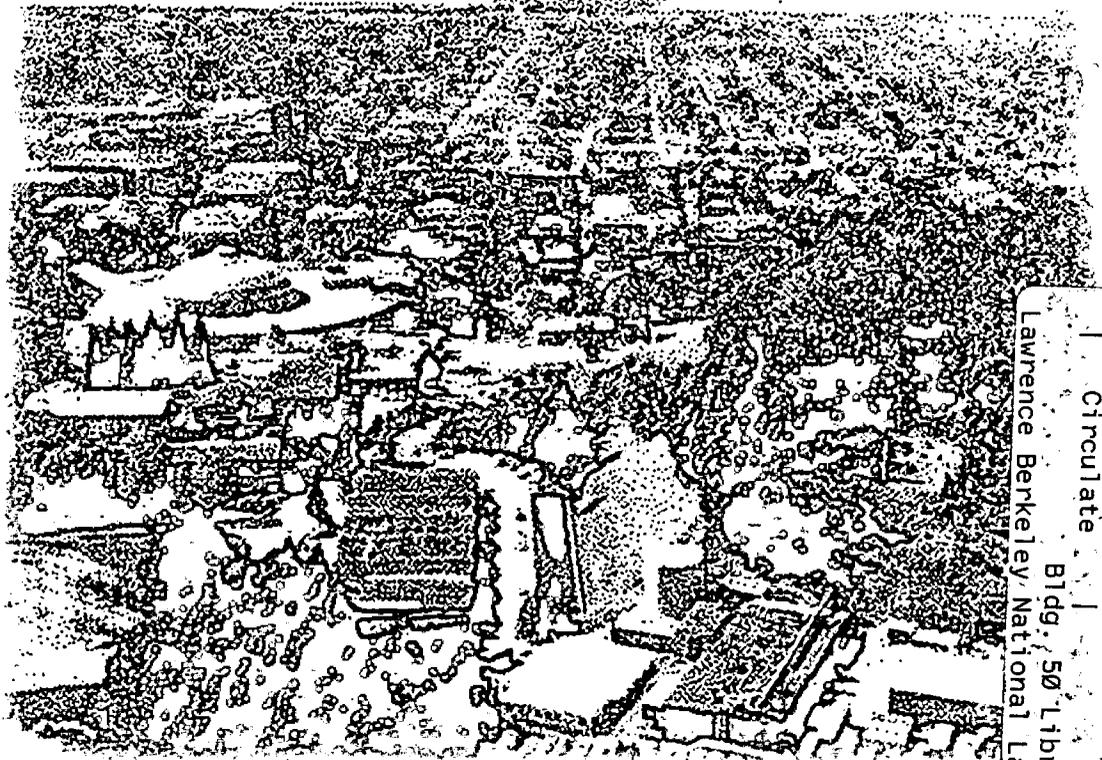
Effect of Dilution and Contaminants on Sand Grouted with Colloidal Silica

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EFFECT OF DILUTION AND CONTAMINANTS ON SAND GROUTED WITH COLLOIDAL SILICA

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ABSTRACT: Colloidal silica is a low-viscosity chemical grout. Samples of grouted sand were made by pouring sand into liquid grout in molds, with the grout diluted to concentrations ranging from 27 down to 5 wt. % silica. The unconfined compressive strength of the grouted sand, measured after 7 days, was proportional to the silica concentration, up to a maximum of 400 kPa. The hydraulic conductivity of the grouted sand decreased with increasing silica concentration in a nearly log-linear manner down to a minimum of 2×10^{-9} cm/sec, and was below 1×10^{-7} cm/sec for grouts as low as 7.4% silica. Inclusion of 5% volumetric saturation of organics (PCE, CCl₄, or aniline) in the samples had little effect on the strength or hydraulic conductivity. Samples were immersed in test liquids (organics, water saturated with organics, and plain water control) for up to one year. All samples increased in strength during immersion except for those immersed in aniline; samples immersed in water saturated with aniline were also weaker than control samples.

KEYWORDS: Chemical grout, colloidal silica, contaminants, hydraulic conductivity, permeability, grouted sand, compressive strength, immersion, aging.

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INTRODUCTION

The development of *in-situ* barrier contaminant containment technology is impelled by the need to prevent release of contaminants from buried sources and the need to contain existing contaminant plumes. Containment can be a practical alternative to other options, such as excavation and disposal of contaminated soils or pumping and treating. One particular advantage of barrier containment is that it minimizes exposure of workers or the public to contaminants. Additionally, the existence of an in-situ barrier permits application of more intensive remediation technologies, such as soil washing or alcohol flooding, without the risk of spreading the mobilized contaminants beyond the contained region. Finally, it is the only technology currently capable of providing horizontal barriers (bottoms) in containment systems.

Formation of subsurface barriers by injection is known as Viscous Liquid Barrier (VLB) technology. Low-viscosity liquids are injected through multiple injection points in the subsurface. The intersecting plumes merge to completely surround, and isolate, the contaminant source and/or plume. Once in place, they gel or cure to form a nearly impermeable barrier. In applying this technology, it is important to match the grout to the waste and to the soil conditions, and to control the gel time and the emplacement of the fluid to form the barrier (Persoff *et al.*, 1994; Moridis *et al.*, 1995).

Colloidal Silica

The formation of VLBs by injection of colloidal silica was recently demonstrated at Brookhaven National Laboratory (Moridis 1998). Colloidal Silica (CS) is a stable aqueous suspension (colloid) of silica microparticles. The particles are approximately uniform in size, and CS is available with particle sizes from 2 to 100 nm. The colloid is stabilized by an electrical charge on each particle, either by raising the pH or by isomorphous substitution of alumina for silica on the particle surface. Without such stabilization, the colloid would gel, and controlled gelling is accomplished by destabilizing the colloid. Each

negatively charged particle is surrounded by a double layer of ions. Adding an electrolyte compresses the double layer and allows the particles to approach each other closely enough to form interparticle siloxane bonds. Gel time is controlled by adjusting the pH and/or ionic strength of the grout.

The principal advantages of CS over other injectable grouts are its low viscosity and non-toxicity. Unlike microfine cements, the particles cannot be filtered out by the soil. Detailed discussions of CS properties and its use in VLB technology can be found in Persoff *et al.* (1994) and Moridis *et al.* (1995, 1996). The increase in viscosity of the CS following injection is due to a controlled gelation process induced by the presence of a neutralizing agent or a concentrated salt solution, either one of which is added immediately prior to injection at ambient temperatures. The CS has a tendency to interact with the geologic matrix, and therefore special formulations or techniques are required to minimize or eliminate the impact of such interactions.

Although sodium silicate (water-glass) grout is chemically similar to CS, sodium silicate grout exhibits syneresis (i.e., shrinkage of the gel with expulsion of water), while CS does not exhibit this property (Yonekura and Kaga, 1992). Also, sodium silicate is typically delivered at 38% solids with a viscosity of 200 centipoise (cP), and must be diluted to reduce its viscosity before it can be used for grouting, while colloidal silica is delivered at solids content as high as 50% by weight with much lower viscosity, typically 5 to 8 cP. Gelled-in-place CS was first studied for the petroleum industry (Jurinak and Summers, 1991, Seright 1993) and later for soil stabilization (Yonekura *et al.* 1992, 1993,) and most recently for protecting groundwater quality (Noll, 1992, Persoff *et al.*, 1994, 1995, Moridis *et al.*, 1995). Noll (1992) investigated the use of colloidal silica diluted so that its solids content was reduced from 30% (a typical nominal value for material as delivered) to values as low as 5%. The more dilute colloids could still be made to gel, although more slowly, and the resulting gel was weaker.

Objectives of the Study

Because the proposed application of colloidal silica grout involves emplacing it in the subsurface by permeation, jet grouting, or soil mixing, where its role as a barrier will be to resist flow of contaminants, the effects of these contaminants on the properties of the soil-grout mixture are of particular interest. The purpose of this work was to determine whether barriers formed by injecting colloidal silica could meet regulatory requirements for low permeability, and withstand the effects of contaminants.

TEST PROGRAM

This work comprised four Experiments. In Experiments 1a and 1b, samples of grouted sand or soil were prepared with a range of CS dilutions. Hydraulic conductivity and unconfined compressive strength were measured by ASTM methods D-5084 and C-39, respectively. In Experiment 2, the same properties were measured on samples of grouted sand that incorporated 5% volumetric saturation of NAPLs, simulating application in a contaminant plume. In Experiment 3, samples, prepared without any contaminants, were immersed in several contaminant liquids and tested after 1 month, 3 months, and 1 year.

Experiment 4 was later added when modifications in the test methods necessitated by the presence of NAPLs in Experiments 2 and 3 were found to have affected the results. In Experiment 4, samples were tested using both the original and modified methods, to confirm that in Experiments 2 and 3 strength was underestimated and hydraulic conductivity was overestimated. Despite the existence of these known systematic errors, the inclusion of control samples in Experiments 2 and 3 permits conclusions to be drawn from these data.

MATERIALS

The CS used in this work was DuPont Ludox SM. Pertinent properties of the CS are summarized in Table 1. Brines were made from distilled water and reagent NaCl. Dilution of the CS retards the gelling; to compensate for this effect and have similar gel times for all formulas, the pH of diluted CS was reduced by titration with concentrated HCl.

The two soils used were Lapis Lustre Monterey #0-30 silica sand, and Trevino sandy loam. Lapis Lustre Monterey #0-30 sand (RMC Lonestar, San Ramon, CA) was used for all Experiments except 1b. This is a silica sand with $d_{10} = 0.35$ mm and $d_{50} = 0.49$ mm. Trevino sandy loam from Beaumont, TX was selected for Experiment 1b to represent a potential application site. Pertinent properties of this soil are summarized in Table 2.

Three reagent-grade NAPLs were used in Experiments 2 and 3: C_2Cl_4 (perchloroethylene, PCE), CCl_4 (carbon tetrachloride), and $C_6H_5NH_2$ (aniline). Water saturated with each of these NAPLs, and with an equimolar mixture of all three, was prepared by stirring distilled water with an excess of NAPL and then decanting.

METHODS

In Experiments 1a and 1b, the grout formula was varied while the soil-grout ratio (R_{SG}) was held constant. The grout formulas covered a range of dilutions of the CS, from full strength (27.0 wt % after brine addition) down to 4.9 wt %. The appropriate brine addition was determined from gel-time tests and the R_{SG} was selected to simulate permeation grouting of Monterey sand or in-situ soil mixing of Trevino soil.

Gel-time Tests to Select Brine Concentration

The gel time of colloidal silica is controlled by the concentration of silica, the concentration of added brine (expressed as the final molarity of NaCl after mixing with the

colloid), and the pH. Some soils, and contaminants, also affect the gel time of CS through chemical interaction (Persoff *et al.*, 1994). Gelling of grout samples was assessed visually, according to the gel-state descriptions modified from Sydansk (1990) and summarized in **Table 3**. Grout formulas were designed to increase in viscosity (state 2) in 2 hr and gel solid (state 9) in 4 hr. These gel times were achieved by adding NaCl and, for the more dilute formulas, titration with HCl. Grouts with 19.7% silica or more reached the gel-time target without pH adjustment; to avoid using high concentrations of NaCl with the more dilute formulas, the grout was titrated to approximately neutral pH.

Gel time jar tests were used to determine the pH and NaCl concentrations to be used in the grout formulas for each dilution of CS. Twenty mL of colloidal silica was delivered by syringe into a 60-mL glass jar. Four mL of brine was slowly added to the jar by syringe while swirling the mixture by hand. The mixture was then allowed to stand unagitated between readings (continuous agitation of the grout delays gelling and weakens the gel). In tests to determine the effect of soil on gelation, 20 g of soil was also added to the 24 mL of grout. In tests to determine the effect of contaminants, all three liquids (CS, dilution water, and brine) were pre-saturated with pure NAPL before conducting the gel time test.

Sample-Preparation Method to Maximize Sample Reproducibility.

Permeability testing of grouted sands is very sensitive to the method of sample preparation (Malone et al 1986). To most accurately represent field conditions, one can inject the grout into the ground, forming a bulb, excavate the bulb, and core or carve out a cylindrical sample for testing. Such a sample is subject to many variables which are difficult to control, including the techniques of injection and sample recovery, the permeability and heterogeneity of the soil, and how completely the grout fills the pore space. Injecting grout into laboratory sandpacks eliminates soil heterogeneity and encourages uniform penetration of grout by confining its flow to one direction, but does

not guarantee that the filling of pore space by grout will be the same in all samples. This second method sacrifices representation of field conditions without maximizing sample reproducibility. Systematic determination of the effects of controlled variables (grout dilution and immersion in contaminants) upon properties of the grouted samples (strength and permeability) requires that samples be prepared as reproducibly as possible. The method of sample preparation was therefore chosen to maximize reproducibility. This was achieved by mixing the grout and soil in a cylinder mold as described below. In samples prepared this way, grout effectively completely fills the pore space. Excellent reproducibility of samples is shown in the results. The permeability measured represents the minimum achievable with a perfect injection (and thus may not represent actual field conditions) and the properties depend solely on the grout. While a field injection is not simulated, the grout and soil chemistry are accurately represented.

Soil-Grout Ratio (R_{SG}) for Sample Preparation.

The different textures of the two soils required that different R_{SG} , representing different methods of emplacement, be used for Experiments 1a and 1b. For each experiment the composition of the CS grout was varied (principally by diluting the Ludox SM with water), while R_{SG} was maintained constant. Two criteria were used to select the R_{SG} : (1) the prepared sample must be a stable suspension before the liquid CS is fully gelled; (2) the suspension, while not necessarily Newtonian, must be sufficiently fluid enough to permit emplacement.

Experiment 1a: Uncontaminated Monterey Sand Grouted With Five CS Dilutions.

For Experiment 1a, the first criterion dictated that samples must contain sand grains packed as densely as dry sand, with the grout filling the voids between the grains. The R_{SG} , determined by trial, was 340 g : 78 mL. Assuming a grain density of 2.65 g/cm³ for

silica sand, a porosity of $(78/(78+(340/2.65))) \times 100 = 38 \%$ of the sample volume (completely filled with CS) is calculated. This R_{SG} was also used for Experiments 2, 3, and 4.

The liquid grout was prepared as follows: The CS was first diluted from its as-received silica concentration of 29.5 wt % with distilled water. For grouts that required pH adjustment as shown in Table 3, the pH was pre-titrated with concentrated HCl to approximately 8.5. NaCl brine was then added to the diluted colloid with constant swirling, and final pH adjustment followed immediately. The pH was adjusted in two stages so that gelling began as soon as possible after brine addition.

Samples made for Experiment 1a were prepared by pouring sand into liquid grout, which then gelled with full saturation of the pore space assured. The sand and grout were mixed to fill each 50 mm diameter x 100 mm long (2 x 4 inch) cylinder mold. The bottoms of the plastic cylinder molds were removed and replaced by caulked-on lids for easy removal of the samples from the molds for testing. To prepare each sample, the liquid grout was poured into the mold, and the pre-weighed sand was poured slowly into the liquid under continuous gentle agitation to settle the sand. Table 4 summarizes the composition of the samples.

Experiment 1b. Uncontaminated Trevino Soil Grouted With Five CS Dilutions.

Trevino silt loam has too much fines to permit permeation even by CS, and also accelerates CS gelling. Samples for Experiment 1b therefore were made to simulate the results of in-situ soil mixing or jet grouting. Samples were prepared by combining the liquid grout and the soil in a Hobart mixer, using same dilutions of CS as in Experiment 1a. The R_{SG} was selected to give a consistency that was sufficiently fluid to be spooned into the molds without trapping air bubbles, and yet sufficiently "thick" to maintain the soil particles in a uniform suspension rather than settling to the bottom. With a ratio of 1200 g

soil to 1400 mL grout, a grout containing 19.7 wt. % silica formed a stable suspension after 2 minutes of mixing and remained workable sufficiently long to permit preparation of four samples. This ratio of soil to grout was maintained for all samples in Experiment 1b. More dilute grouts were mixed until onset of gelling produced the desired consistency. Then the grout and soil were poured into the molds and each sample was vibrated on a shaking table for 1 min. to eliminate air bubbles. Samples were finally covered with plastic caps and stored in a fog room at 100% relative humidity and temperature $21 \pm 1^\circ\text{C}$ for 7 days until tested. The quantities of the various liquid ingredients (making up 1400 mL) are summarized in Table 5.

Experiment 2: Monterey Sand, With and Without NAPL Contamination, Grouted With Two CS Dilutions.

The data of Wilkins *et al.* (1995) suggest that in NAPL-contaminated unsaturated sandy soil, residual saturation of water and NAPL are typically 10 and 5 %, respectively. Sand was prepared for Experiment 2 by first adding sufficient water, and then sufficient NAPL, to produce these saturations in the sand. No liquid drained from the sand. Samples for Experiment 2 were then prepared as for Experiment 1a. The dilution water in the grout was reduced to compensate for the water pre-added to the sand to yield samples with 7.4 and 19.7 wt. % silica. Samples were made with the three NAPLs, and, as a control, samples were also prepared with 10% water saturation and no NAPL.

Experiment 3: Uncontaminated Monterey Sand Grouted With Two Dilutions of CS, Immersed in Contaminants.

Samples were prepared as for Experiment 1a, and then several samples made with each grout formula were immersed in each of nine test liquids: (a) the three NAPLs used in Experiment 2, (b) water saturated with each of the three NAPLs (i.e., water with the maximum contaminant concentration), (c) water saturated with an equimolar mixture of the

three NAPLs, (d) HCl diluted to pH 3, and (e) distilled water. The CS, being basic, raised the pH of the dilution liquid during immersion. The pH of the distilled water increased to 10, while frequent monitoring and titration of the dilute HCl was necessary to maintain the pH between 2.5 and 3.

TEST METHODS

Age of Samples When Tested

Experiments 1a, 1b, 2, and 4 did not require long-term immersion. In these experiments strength was measured after curing samples in their molds in a fog room at 7 days. Because of the limited number of cells available for hydraulic conductivity measurement, not all tests could be run at the same time, so the curing time for these samples ranged between 8 and 15 days at 100% relative humidity and temperature $21\pm 1^\circ\text{C}$. In experiment 3, which involved long term immersion and strength testing only, samples were cured at 100% relative humidity and $21\pm 1^\circ\text{C}$ for 10 days and then immersed in test liquids at room temperature for times ranging from 30 to 390 days. After removal from immersion samples were maintained at 100% relative humidity and $21\pm 1^\circ\text{C}$ for one day until tested.

Measurement of Unconfined Compressive Strength.

Unconfined compressive strength was measured according to ASTM C-39-86, using a loading rate of 3.7 N/s (50 lb/min.). In this test, flat and parallel sample ends are assured by capping the ends. In Experiment 1, the samples were capped with Cylcap sulfur mortar, according to ASTM C-617-72. To avoid exposing personnel to NAPLs during the capping and testing, different capping and testing procedures were used for Experiments 2 and 3. Hydrostone, a gypsum plaster, was used so that the capping could

be done in a hood without exposing the samples to heat. After capping, the samples were enclosed in zip-lock plastic bags and tested in the bags.

Measurement Of Hydraulic Conductivity.

Hydraulic conductivity was measured in a flexible wall permeameter by ASTM D-5084, at a net confining pressure of 207 kPa (30 psi). In this method the sample in a triaxial cell is confined in a latex membrane, to eliminate wall flow errors. For testing contaminated samples, as in Experiment 2, the latex membrane must be protected from contacting NAPL, which could weaken the membrane (Daniel *et al.*, 1984; Acar *et al.*, 1985). Several authors have placed inert (generally Teflon®) membranes between the sample and the latex membrane to protect the latter (Daniel *et al.*, 1984; Foreman and Daniel 1986; Uppot and Stephenson, 1989; Daniel and Trautwein, 1994). In our experiments we wrapped 0.076-mm (0.003-inch) -thick Teflon® tape (Boart Longyear, Salt Lake City, UT), around the sample with a 10 mm overlap, which was held in place with vacuum grease. The Teflon® tape was 100 mm wide; this is longer than the sample, so the tape extended over the porous stones and onto the endcaps. The latex membrane was then placed over the Teflon® tape, and measurement then proceeded as for uncontaminated samples. We found that identical samples, measured with and without Teflon® tape under the latex membrane, gave different values of hydraulic conductivity, which we attribute to the existence of a small parallel flow path formed at the overlap of the Teflon® tape. This problem is discussed further below.

RESULTS AND DISCUSSION

Effects of Soil and of Contaminants on CS Gel Time

A typical set of gel time curves for CS grout is shown in **Figure 1**. In these tests, the gelling of CS, diluted to 27 wt. % silica, with no soil, Monterey sand, and Trevino soil

was monitored. The Trevino soil accelerated the gelling of CS. This may be attributed to two properties of the soil reported in Table 2. First, the pH of the soil is 8.2, so the soil addition reduced the pH of the grout, which accelerates the gelling of Ludox SM (Noll *et al.*, 1992). Second, with 16.3 meq/100 g cation exchange capacity and 1920 ppm calcium content, the soil contains much exchangeable Ca. When the soil is added to grout which is 0.1 M in NaCl, some of the exchangeable Ca is released to the grout, which accelerates its gelation. This effect has been observed for a similar type of CS with Hanford (Washington) sand (Persoff *et al.*, 1994).

Before preparing samples for Experiment 2, gel time tests were conducted in which the brine and the colloid were pre-saturated with NAPLs. Results of these tests are shown in **Figure 2**, which shows that aniline, alone among the NAPLs tested, accelerated gelling. The mechanism is not known, but the aniline, being polar, is much more soluble than the other NAPLs.

Effect of CS Dilution on Strength of Grouted Sand (Experiment 1).

The compressive strength and hydraulic conductivity of Monterey sand and Trevino soil grouted with CS are shown in **Figures 3 and 4**, respectively. In these Figures, the mean and standard deviation of 5 strength measurements, and duplicate measurements of hydraulic conductivity, are shown. In **Figure 3**, the line fitting the strength data is a least squares fit, not forced through the origin.

Figure 3 shows that as the silica content of the grout was reduced by dilution, the unconfined compressive strength of the sample decreased and the hydraulic conductivity increased. The Monterey sand itself is not cohesive, and any unconfined compressive strength results from the cementing effect of the grout, which increases linearly with the amount of silica in the grout.

In the case of Trevino soil, the samples with 7.4 % silica were barely strong enough to test. **Figure 4** shows that increasing the silica content beyond this value increased the unconfined compressive strength, and the increase in strength per unit increase in silica content was close to that observed for Monterey sand.

Samples in Experiment 1 were tested at 7 days. However, Monterey sand grouted with CS continued to gain strength during one year; for example, **Figure 7** shows that after 7 days the strength of samples made with 19.7 wt. % silica was 350 kPa, and this increased to 490 kPa after 30 days immersion in water, 543 kPa after 99 days, and 690 kPa after 349 days. We have not investigated the long term strength increase of sand grouted with full strength CS, but **Figure 3** suggests that it would be greater in proportion to the silica content, i.e., approximately 950 kPa at one year. These values are in general agreement with the long-term strengths reported by Yonekura and Miwa (1993). They found that the strength of sand grouted with (presumably undiluted) colloidal silica was independent of gel time in the range 10 sec - 1 hr, and continued to increase during 1000 days of aging. Tested at 100 days, the strength was 655 kPa (95 psi), and the ultimate strength was more than twice that value.

Consolidation of Experiment 1 Samples.

The samples consolidated to some degree during the hydraulic conductivity measurement due to the 207 kPa (30 psi) confining pressure. The volume of each sample was measured both before and after the hydraulic conductivity measurement. After measurement, the sample was then oven-dried and weighed. From the volume and dry mass data, and assuming a density value of 2650 kg/m^3 for both the sand and the colloidal silica particles, the dry density and the porosity before and after consolidation were calculated. These calculated porosities are shown in **Figures 5 and 6**. **Figure 5** shows that the dry density (and porosity) of the Monterey sand samples changed very little due to the 207 kPa (30 psi) confining pressure applied during hydraulic conductivity

measurements. The sand grains were packed sufficiently densely to constitute a skeleton that resisted deformation by the confining pressure. By contrast, the Trevino grouted samples contained much less soil (only 1200 g per 1400 mL of grout), and the sample strength was lower (**Figure 2**), allowing significant consolidation to occur (**Figure 6**). After consolidation, the sample density increased and its porosity decreased, resulting in low hydraulic conductivity.

Effect of Dilution on Hydraulic Conductivity (Experiment 1)

The hydraulic conductivity of the grouted samples is the principal property of interest. A value of 10^{-7} cm/sec is generally accepted as the requirement for barrier material. The data in **Figures 3** and **4** show that this criterion is met by all the samples made with a silica content exceeding 7.4 wt. %. (In the case of the Trevino soil, the hydraulic conductivity was measured after consolidation.) A silica concentration of 7.4 wt. % represents therefore the maximum feasible dilution of Ludox SM for use as a barrier material.

Figure 3 also shows a strong effect of the silica concentration on the permeability of the grouted Monterey sand samples. There was no consolidation for these samples. The sand grains themselves are effectively impermeable and the measured hydraulic conductivity can be understood to represent the hydraulic conductivity of the gelled Ludox SM itself, multiplied by a factor of approximately 0.38, representing the volume fraction of the sample occupied by gelled grout.

The relationship between silica concentration and hydraulic conductivity can be explained, at least qualitatively, by considering the structure of the gelled CS. The gelled CS has a high water content, and constitutes a second, microporous medium that fills the macropores of the sand. Iler (1979) describes gelled CS as consisting of a network of particle chains. Within the CS, the space between the gelled chains of silica particles

constitutes a network of micropores through which water can flow. The size of these micropores depends upon the silica concentration: at 27.0 wt % silica the grout is $(100 - 27.0/2.65) = 90\%$ water by volume, and at 7.4 wt % it is 97% water. Considered as a porous medium, the grout with 7.4 wt % silica therefore has only 8 % more pore space than grout with 27.0 wt % silica, but its hydraulic conductivity is 30 times as great. Flow resistance results from viscous drag on water as it flows through a tangle of chains of gelled particles. The low value of hydraulic conductivity results from a highly divided flow path with many small pores. Decreasing the silica concentration by a factor of $(27.0/7.4)=3.67$ increases the space between chains. This space between chains may be considered as a measure of the effective radius of micropores. For purposes of this discussion, pores may be approximated as parallel tubes in which laminar flow of water is described by the Hagen-Poiseuille equation (Vennard and Street 1975). For fixed pressure gradient and viscosity, the flow through each tube is proportional to the fourth power of the radius. Flux, or Darcy velocity, is thus proportional to the square of the radius. While the geometry of the system is not defined well enough to permit actual calculation of the change in permeability, reducing the concentration of silica particles has the effect of increasing the separation between chains of silica particles. This is similar in effect to increasing the pore diameter, which can account for the observed increase in permeability.

Effect of Inclusion of, and Immersion in, NAPLs on Strength and Hydraulic Conductivity. (Experiments 2 and 3)

The results of measurements on Experiment 2 and 3 samples are shown in **Tables 6 and 7**. To determine the effects of contaminants, results must be compared with results for uncontaminated samples. However, because of modifications in the test methods used for Experiments 2 and 3 (i.e., use of zip-lock plastic bags and Hydrostone caps), these comparisons cannot be made with samples from Experiment 1a, but must be made with

uncontaminated samples tested as controls in Experiments 2 and 3. We first discuss the results of Experiments 2 and 3, and then the effects of the test-method modifications.

When preparing samples for Experiment 2, sufficient NAPL to saturate 5% of the pore space was added to the sand before the sand was poured into the liquid grout. **Table 6** shows that inclusion of NAPL did not adversely affect the hydraulic conductivity of the samples except for those prepared with CCl_4 , for which the hydraulic conductivity was greater than that of the water control at both 7.4 and 19.7 wt % silica. All samples made with 19.7 wt % silica, including those containing CCl_4 , still met the barrier standard of 10^{-7} cm/sec.

Aniline was the only compound that adversely affected the strength of samples. This was observed both when aniline was included in the sample (**Table 6**) and when uncontaminated samples were immersed in aniline. **Figure 7** shows that samples gained strength during the immersion, except for samples immersed in aniline and water saturated with aniline. In that sense, immersion in aniline weakened the samples. **Table 6** shows that PCE may have increased the strength of the samples, and CCl_4 increased the hydraulic conductivity.

Effects of Test-Method Modifications for Contaminated Samples (Experiments 2 and 3)

Because the samples in Experiments 2 and 3 were contaminated by inclusion of, or immersion in, toxic solvents, the methods for measuring strength and hydraulic conductivity were modified to minimize worker exposure during testing and to prevent damage to latex membranes. For strength measurement, the hot Cylcap was replaced by room-temperature Hydrostone and the samples were tested in zip-lock plastic bags; for hydraulic conductivity, the sample was wrapped with Teflon tape under the latex membrane. We refer to these as modified methods. Some grout formulas that were tested by standard methods in Experiment 1 were also tested by modified methods in Experiment

2. Matched data in **Table 7** show that the samples of Experiments 1 and 2, identical in composition but differing in the test method, gave different results. This suggested that the modifications (introduced because of NAPL contamination) had the effect of increasing the measured hydraulic conductivity and decreasing the measured strength. To confirm this, in Experiment 4, duplicate samples were prepared at the same time without contamination, and tested by both methods. The results of these tests are summarized in **Table 7**.

The data in **Table 7** show that the modified test method for strength (i.e., replacing the Cylcap sample cap with Hydrostone) caused an underestimation of strength, but only for the stronger samples (those made with 19.7 and 27.0 % silica). This is reasonable because the requirement for the capping compound is that it not fail before the sample. Similarly, (although here the small number of samples makes the conclusion less certain) the use of Teflon® tape caused an overestimation of the hydraulic conductivity. In light of these results, we caution that the results of Experiments 2 and 3 can be interpreted only to determine the effects of inclusion or immersion in contaminants *relative to the water control*.

Several authors (Daniel *et al.*, 1984; Foreman and Daniel 1986; Uppot and Stephenson, 1989; Daniel and Trautwein, 1994) have used of Teflon® tape to protect latex membranes, but our results show that this may cause errors. Hydraulic conductivity was greater when measured with Teflon® tape under the latex membrane ("modified method" in **Table 7**) than when measured without the tape. Comparing the hydraulic conductivity of two samples measured in Experiment 4 and shown in the last line of **Table 7**, it appears that the use of Teflon® tape had the effect of increasing the measured hydraulic conductivity by 3.4×10^{-8} or 3.0×10^{-8} cm/sec. The suspected cause of this error is the triangular gap formed at the overlap of the 0.076-mm-thick Teflon® tape. This gap, if not completely closed by the 207 kPa confining pressure, could transmit flow in parallel with the sample. To estimate the size of the gap responsible for such an error, note that for a sample 51 mm in diameter, under a unit hydraulic gradient, hydraulic conductivity of $3.0 \times$

10^{-8} cm/sec transmits 6.1×10^{-13} m³/sec. From the Hagen-Poiseuille equation (Vennard and Street 1975), this is the flow rate that would be carried by a tube of diameter 0.04 mm under unit hydraulic gradient. This is close enough to the thickness of the Teflon® tape to suggest that the gap is not completely closed even by 207 kPa confining pressure, and is responsible for overestimating hydraulic conductivity.

An error in hydraulic conductivity measurement caused by a parallel flow path is additive, not multiplicative. For such an error to be significant, the flow through the gap must be comparable in size to the flow through the sample. As a result, gap-flow errors can be neglected if the sample transmissivity (i.e., the product of the sample cross-sectional area and permeability) is large compared to flow through the gap under unit hydraulic gradient. Previous investigators appear to have been justified in neglecting such errors. For example, Daniel *et al.* (1984) found that measurements with and without a 0.13-mm-thick Teflon® tape showed only minor differences in measured hydraulic conductivity. Sample diameters and hydraulic conductivities were not reported in that work, but typical values may be 71 mm and 10^{-7} cm/sec. Such a sample would transmit 4.0×10^{-12} m³/sec under unit hydraulic gradient. This is large enough to swamp the gap-flow estimated here, and justify neglecting the error. However, Teflon®-wrap errors as observed here are not necessarily negligible for all samples, especially those with extremely low permeabilities. Using larger sample diameters also reduces the relative error when measuring such samples.

CONCLUSIONS

1. The unconfined compressive strength of sand grouted with Ludox SM is proportional to the concentration of colloidal silica particles, up to a maximum of approximately 400 kPa (60 psi).

2. The hydraulic conductivity of sand grouted with Ludox SM decreases with increasing concentration of colloidal silica particles, down to a minimum of 6.0×10^{-7} cm/sec at 27.0 % by weight. For silica particle concentration greater than 7.4 % by weight, the hydraulic conductivity is less than 1.0×10^{-7} cm/sec; that is, it meets the generally accepted criterion for a barrier material. In this range, the log of hydraulic conductivity decreases approximately linearly with increasing concentration of colloidal silica particles. These values of hydraulic conductivity were measured on samples prepared so as to ensure 100% filling of pore space, and therefore represent the lower limit of permeability achievable with perfect grouting.

3. Monterey sand provided a skeleton to prevent consolidation of grout under confining pressure. Under these conditions, the measured hydraulic conductivity is therefore a function of the grout, and variation of hydraulic conductivity with silica content can be explained on the basis of flow through a network of gelled silica chains.

4. Trevino soil samples were weaker than Monterey sand samples because the soil-grout ratio was lower. In hydraulic conductivity testing under 30 psi confining pressure, these samples consolidated and thereby achieved low hydraulic conductivity. As with Monterey sand, for silica particle concentration greater than 7.4 % by weight, the hydraulic conductivity is less than 1.0×10^{-7} cm/sec; that is, it meets the generally accepted criterion for a barrier material.

5. Trevino soil samples were very weak at low concentration of colloidal silica particles; but above 11 % silica the strength increased linearly with increasing concentration of colloidal silica particles, up to a maximum of approximately 275 kPa (40 psi). Above 11 % silica by weight, the increase in strength per unit of concentration was similar to that observed in Monterey sand samples.

6. Samples immersed in water continued to gain strength for one year. However, samples Immersed for up to one year in aniline, or in water saturated with aniline, did not gain strength. Immersion for up to one year in the other test liquids (PCE, CCl₄, water saturated with these NAPLs, water saturated with the mixture of 3 NAPLs, and HCl diluted to pH 3) had no significant effect, i.e., they also gained strength during one year of immersion.

7. The use of a 0.076-mm thick Teflon® wrap between the sample and the latex membrane during measurement of hydraulic conductivity caused additional flow equivalent to an increase in hydraulic conductivity of 3×10^{-8} cm/sec for a 5.1-cm diameter sample.

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APPENDIX I: REFERENCES

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Table 1 — Typical Properties of Ludox SM Colloidal Silica^a

density (kg/m ³)	1210
SiO ₂ (weight %)	29.5
pH	10.0
viscosity @ 25 C (mPa-s)	5.7
surface area (m ² /g)	350

^a reported by manufacturer (DuPont Specialty Chemicals)

Table 2 — Properties of Trevino sandy loam^a

cation exchange capacity (meq/100 g)	16.3
pH	8.2
elemental composition (ppm)	
Na	117
K	548
Mg	571
Ca	1920
size fractions (%)	
sand	52
silt	42
clay	6

^a reported by A&L Eastern Agricultural Laboratories, Richmond, VA.

Table 3 — Jar-Test Gel State Codes

1	No detectable gel formed. The gel appears to have the same viscosity (fluidity) as the original polymer solution and no gel is visually detectable.
2	Highly flowing gel. The gel appears to be only slightly more viscous than the initial polymer solution.
3	Flowing gel. Most of the obviously detectable gel flows to the bottle cap upon inversion.
4	Moderately flowing gel. A small portion (about 5 to 15%) of the gel does not readily flow to the bottle cap upon inversion—usually characterized as a "tonguing" gel (i.e., after hanging out of the bottle, gel can be made to flow back into the bottle by slowly righting it
5	Barely flowing gel. The gel slowly flows to the bottle cap and/or a significant portion (> 15%) of the gel does not flow upon inversion.
6	Highly deformable nonflowing gel. The gel does not flow to the bottle cap upon inversion (gel flows to just short of reaching the bottle cap).
7	Moderately deformable nonflowing gel. The gel flows about halfway down the bottle upon inversion.
8	Slightly deformable nonflowing gel. Only the gel surface deforms slightly upon inversion.
9	Rigid gel. There is no gel-surface deformation upon inversion.
10	Ringing rigid gel. A tuning-fork-like mechanical vibration can be felt or a tone can be heard after the bottle is tapped.
11	Rigid gel no longer ringing. No tone or vibration can be felt or heard, because natural frequency of the gel has increased.

Table 4. Formulae for Experiment 1a Samples (340 g Sand and 78 mL Grout Per Sample).

Volume Colloid per Sample (mL) (1)	Silica Concentration After Dilution (wt %) (2)	Added Brine NaCl Concentration (M) (3)	Volume Brine per Sample (mL) (4)	Final NaCl Concentration (M) (5)	Volume Distilled H ₂ O (mL) (6)	Final pH (7)
13	4.9	1.8	13	0.3	52	6.95
20	7.4 ^a	1.2	13	0.2	46	6.95
26	9.8	1.2	13	0.2	39	6.48
52	19.7 ^a	0.6	26	0.2	0	10 (not adjusted)
71.5	27.0	1.2	6.5	0.1	0	10 (not adjusted)

^a these formulae also tested in Experiments 2 and 3

Table 5. Formulae for Experiment 1b samples (1200 g Trevino soil per batch)

% silica (1)	Volume CS (mL) (2)	Volume H ₂ O (mL) (3)	Vd. 1M NaCl (mL) (4)	Final [NaCl] (5)	Vol conc. HCl (mL) (6)	Final pH (7)	Mixing time (8)
4.9	234	746	420	0.3 M	4.1 mL	6.50	3.0 h
7.4	350	770	280	0.2 M	5.5 mL	6.83	3.0 h
9.8	466	654	280	0.2 M	7.4 mL	6.89	1.8 h
19.7	934	326	140	0.1 M	none	~10.0	2 min.
27.7	1316	0	84	0.06 M	none	~ 10.0	8 min.

Table 6. Compressive Strength and Hydraulic Conductivity of Samples of Monterey Sand, Contaminated with NAPLs and Grouted with Two Dilutions of CS (Experiment 2).

Percent Silica (1)	Contaminant			Unconfined Compressive Strength (kPa)		Hydraulic Conductivity (cm/sec)	
	compound (2)	density ^a (kg/m ³) (3)	solubility in water ^b (M) (4)	Mean of 5 tests (5)	Std. dev (6)	Mean of 2 tests (7)	Difference between 2 tests (8)
7.4	PCE	1623	0.00091	149.9	8.1	3.30E-07	1.00E-07
	CCl ₄	1594	0.0063	129.3	9.0	7.95E-07	3.10E-07
	aniline	1022	0.39	129.7	10.7	2.80E-07	1.00E-07
	water	998	--	128.0	9.0	2.55E-07	1.50E-07
19.7	PCE	1623	0.00091	273.9	15.4	1.35E-08	1.00E-09
	CCl ₄	1594	0.0063	296.3	21.7	4.25E-08	2.10E-08
	aniline	1022	0.39	236.4	20.8	1.33E-08	7.50E-09
	water	998	--	295.9	36.0	2.40E-08	1.60E-08

^aWeast *et al.* 1965

^bSchwartzbach *et al.* 1993

Table 7. Comparison of values measured with modified and unmodified test methods.

Property	%	ASTM	Experiment 1			Experiment 2			Experiment 4			Experiment 4		
			Not Modified			Modified			Not Modified			Modified		
(1)	Silica (2)	(3)	n (4)	Mean (5)	σ^{**} (6)	n (7)	Mean (8)	σ^{**} (9)	n* (10)	Mean (11)	σ^{**} (12)	n (13)	Mean (14)	σ^{**} (15)
Unconfined compressive strength (kPa)	7.4	C-39	5	123.9	7.2	5	128.0	9.0						
	19.7	C-39	5	349.6	26.4	5	295.9	36.0						
	27.0	C-39	5	416.5	35.1				4	416.1	18.6	3	367.5	9.7
Hydraulic conductivity (cm/sec)	7.4	D-5084	2	4.95E-08	1.7E-08	2	2.55E-07	1.5E-07						
	19.7	D-5084	2	6.65E-09	7.0E-10	2	2.40E-08	1.6E-08						
	27.0	D-5084	2	1.9E-9	0.4E-9				1	5.0E-9		1	3.9E-8 ^a	

^a after this measurement, the sample was remeasured using the unmodified method, and hydraulic conductivity was 9E-9 cm/sec.

**standard deviation, or difference between 2 measurements

FIGURE CAPTIONS

Figure 1. Gelling rate of colloidal silica grouts, diluted to 27 wt. % silica, with and without soil. pH 10 and 0.2 M NaCl were used for this test. Samples with soil contained 10 g soil to 24 mL grout.

Figure 2. Gelling rate of colloidal silica grouts diluted to 19.7 wt. % silica and saturated, respectively, with PCE, CCl₄, or aniline, or containing no NAPL (control). pH 10 and 0.3 M NaCl concentration were used for this test.

Figure 3. Compressive strength and hydraulic conductivity of samples of Monterey sand grouted with various dilutions of Ludox SM. Curing time for strength samples was 7 days; and for hydraulic conductivity ranged between 8 and 15 days.

Figure 4. Compressive strength and hydraulic conductivity of samples of Trevino soil grouted with various dilutions of Ludox SM. Curing time for strength samples was 7 days; and for hydraulic conductivity ranged between 8 and 15 days.

Figure 5. Porosity of Monterey sand samples, calculated from density measurements before and after consolidation at 207 kPa (30 psi), and assuming proportions as shown in Table 4. Curing time for samples ranged between 8 and 15 days.

Figure 6. Porosity of Trevino soil samples, calculated from density measurements before and after consolidation at 207 kPa (30 psi) and assuming proportions as shown in Table 5. Curing time for samples ranged between 8 and 15 days.

Figure 7. Compressive strength of Monterey sand grouted with two dilutions of Ludox SM, after immersion for up to one year in various liquids. In each graph, the lower set of curves show data for 7.4 wt % silica, while the upper set of curves are for 19.7 wt % silica. Data for zero immersion time are taken from Figure 3. All other samples were immersed after 10 days curing. (a) water, pure chlorinated organics and water saturated with chlorinated organics. (b) water, pure aniline and water saturated with aniline, (c) water, HCl diluted to pH3, and water saturated with an equimolar mixture of three organics.

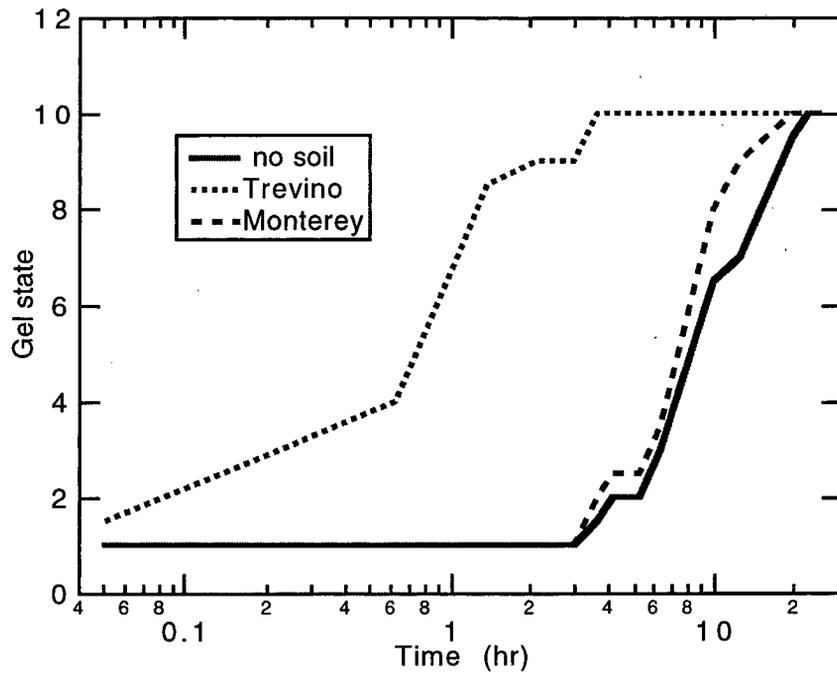


Figure 1.

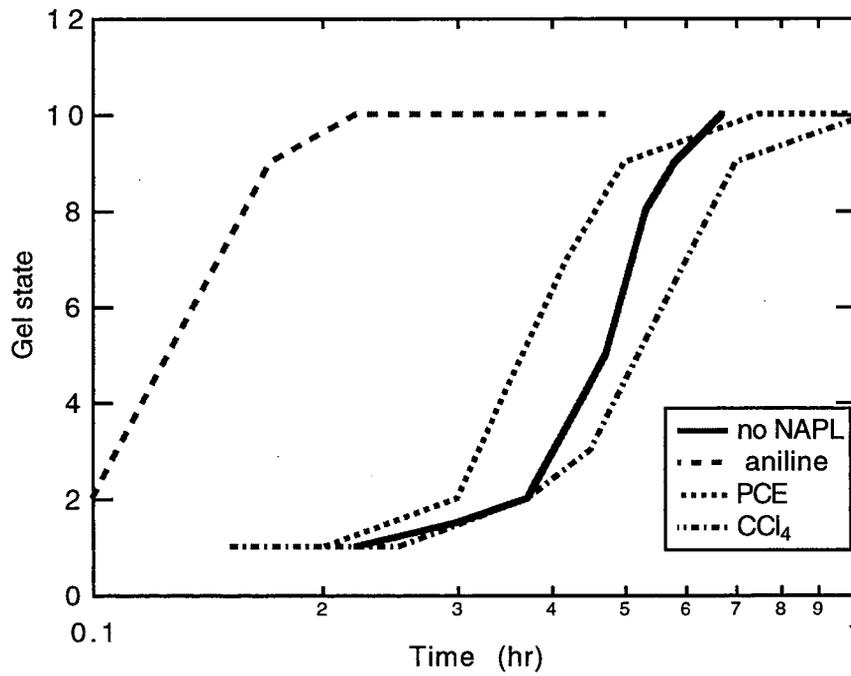


Figure 2.

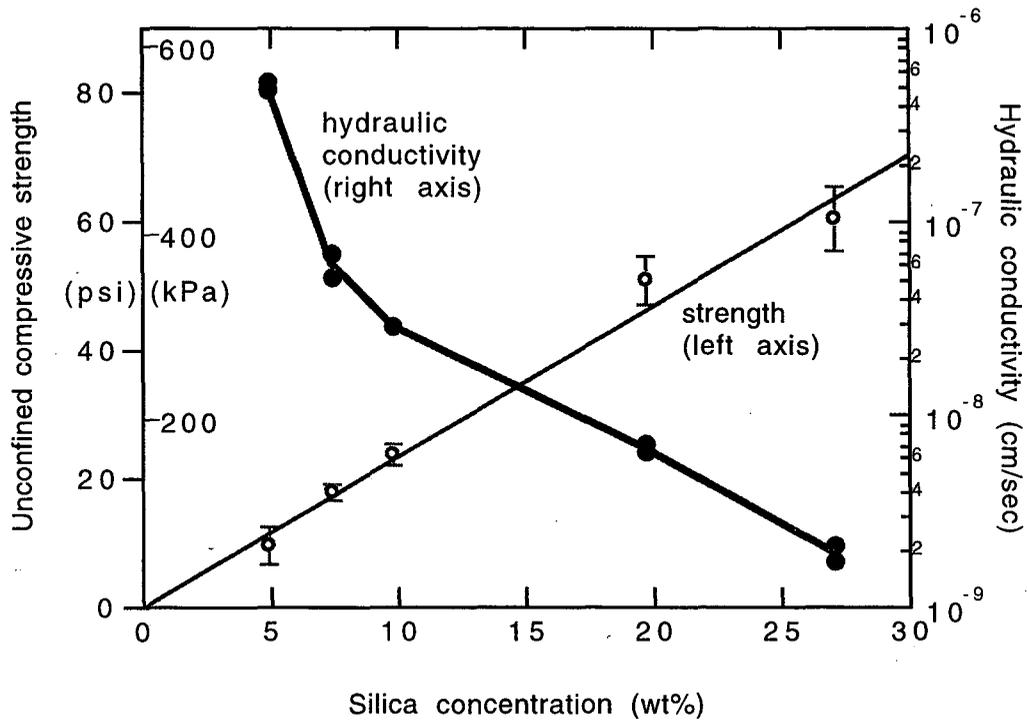


Figure 3.

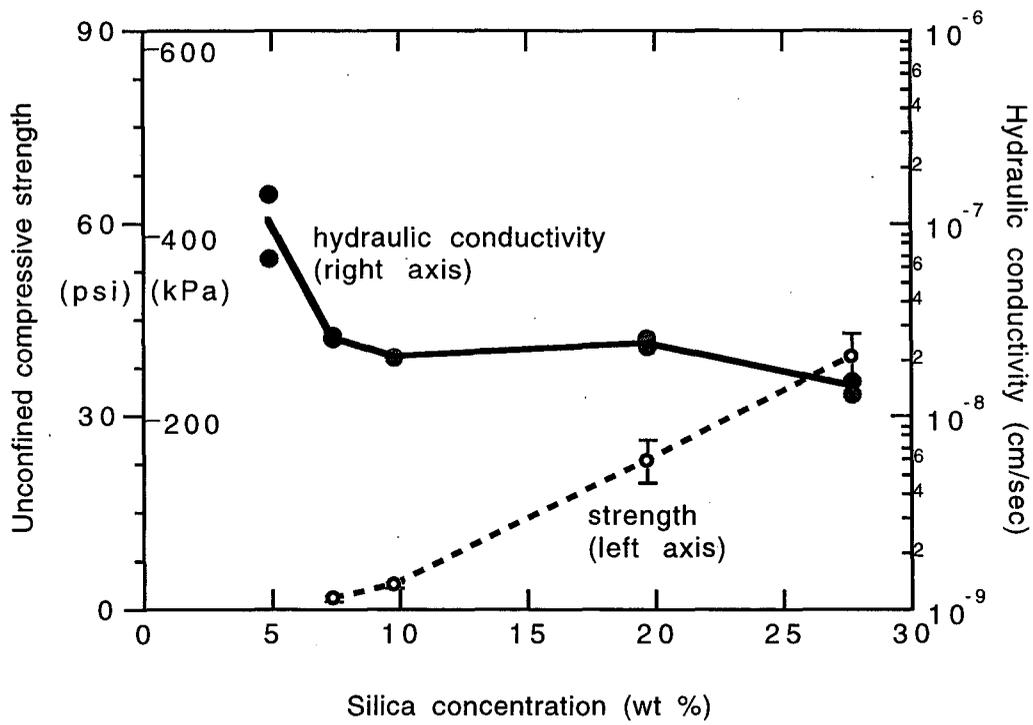


Figure 4.

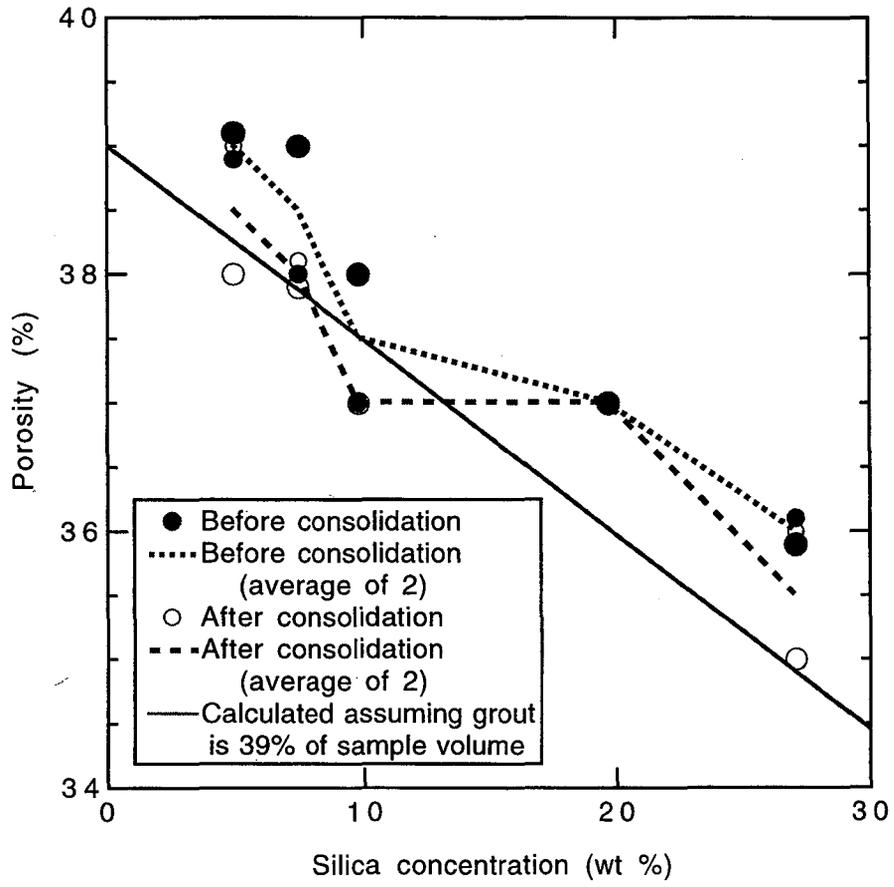


Figure 5.

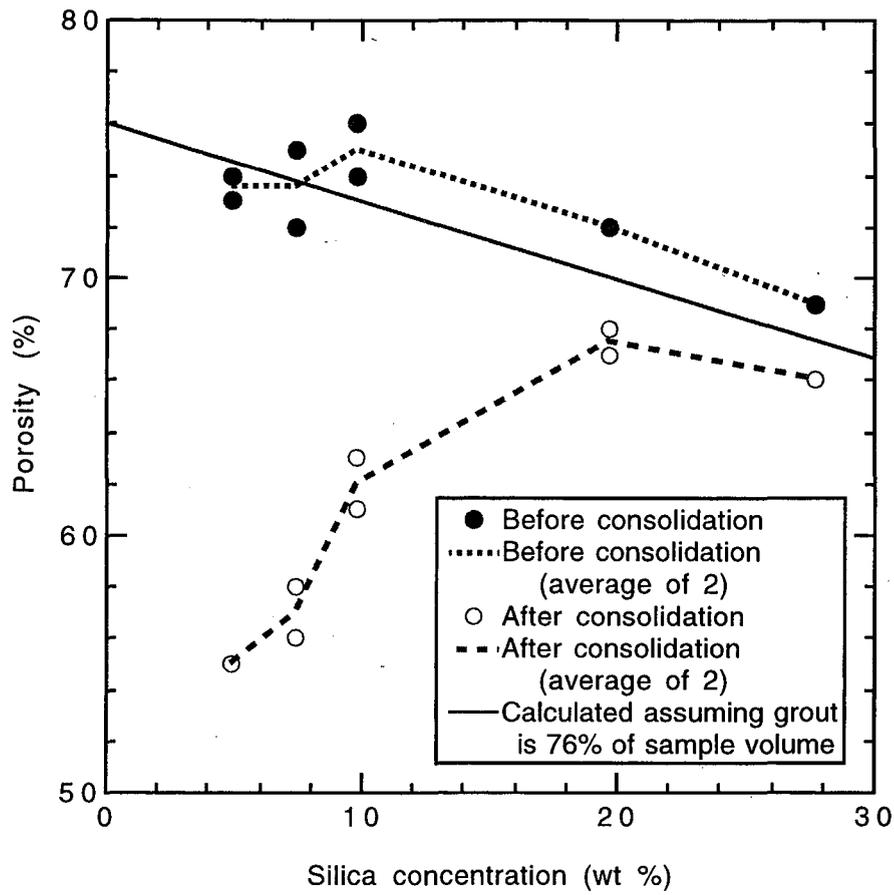


Figure 6.

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