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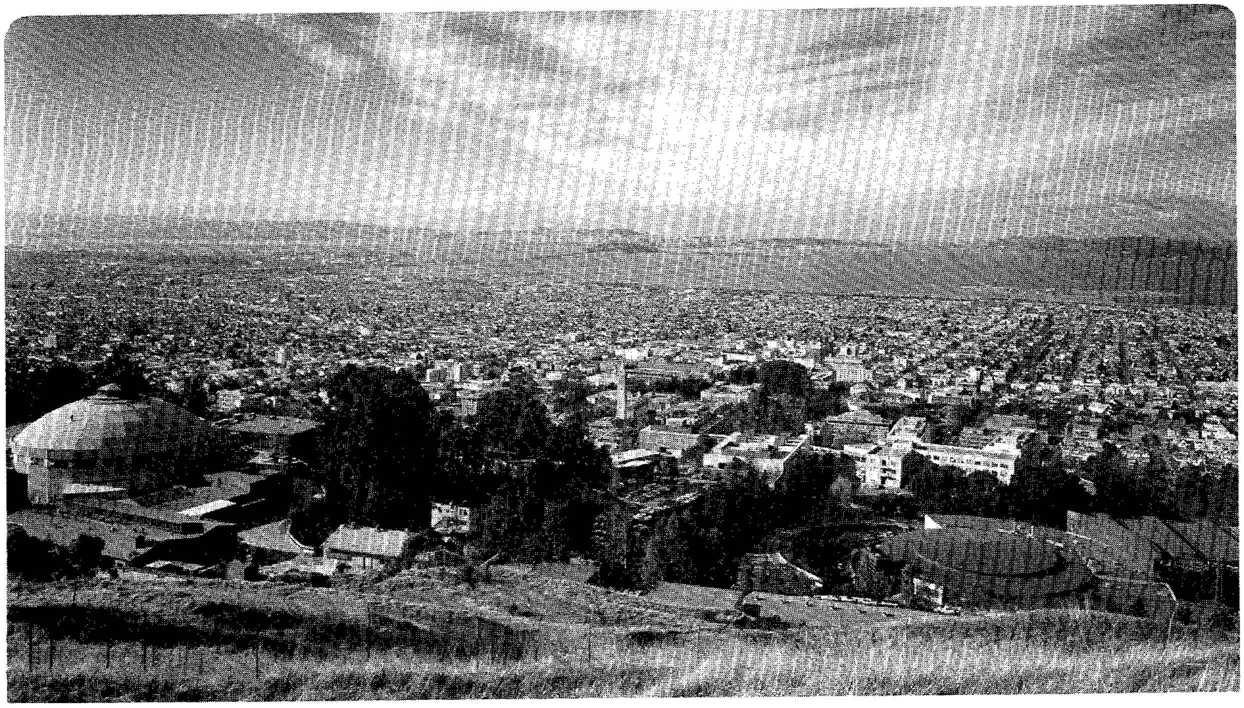

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NEW BARRIER FLUIDS FOR SUBSURFACE CONTAINMENT OF CONTAMINANTS

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ABSTRACT

In some situations, containment of contaminants in the subsurface may be preferable to removal or treatment in situ. In these cases, it may be possible to form barriers by injecting fluids (grouts) that set in place and reduce the formation permeability. This paper reports laboratory work to develop two types of fluids for this application: colloidal silica (CS) and polysiloxane (PSX). Falling-head permeameter tests of grouted Hanford sand, lasting 50 days, showed hydraulic conductivities of order 10^{-7} cm/sec for these two materials. Low initial viscosity of the grout is necessary to permit injection without causing fracturing or surface uplift. Experiments with crosslinked polysiloxanes showed that they could be diluted to achieve adequately low viscosity without losing their ability to cure.

Control of the gel time is important for grout emplacement. Gel time of CS grouts increased with increasing pH (above 6.5) and with decreasing ionic strength. Salt solutions were added to the colloid to increase the ionic strength and control gel time. When injected into Hanford sand, the CS grout gelled much more quickly than the same formula without sand. This effect results from salinity that is present in pore water and from multi-valent ions that are desorbed from clays and ion-exchanged for mono-valent ions in the grout. Ion-exchange experiments showed that most of the multi-valent ions could be removed by flushing the sand with 15 PV of 4% NaCl, and sand treated in this manner did not accelerate the gelling of the grout.

When grout is injected into unsaturated soil it slumps, leaving the soil only partially saturated and achieving less permeability reduction upon gelling. Multiple injections of CS grout in 1-D sand columns demonstrated that by accumulating the residual gelled grout saturations from several injections, low permeability can be achieved.

INTRODUCTION

The development of effective in situ containment technologies is necessitated by a) the need to control and/or suppress the release of contaminants from buried sources, b) the need to prevent the spread of existing plumes, and c) the inability to effectively remove contaminants from the subsurface. Contaminants from buried wastes or from contaminated soils in the vadose zone can be mobilized and migrate toward previously uncontaminated regions of the aquifer. Underground storage facilities for hazardous wastes may be subject to leakage and/or leaching. Contaminants cling tenaciously to subsurface materials (especially clays), and traditional physical extraction methods are slow and often ineffective. Excavation of contaminated soils and disposal in protected facilities is expensive and often impractical. Containment on-site and control of the groundwater flow pattern can limit the off-site threat, and may supply a long-term solution. In areas where complete control is necessary, impermeable barriers are preferable to sorption barriers. Moreover, a variety of barrier-fluid technologies must be developed for different soil and waste-type conditions.

Despite the obvious need, containment technologies have been largely limited to expensive "brute-force" approaches involving trenching, and cut-off and slurry walls. The effectiveness of these methods is limited. This investigation is intended to address a knowledge gap in this area, and provide powerful and more economical containment methods with broad applicability in a large variety of sites. Moreover, these can be applied without excavation in areas afflicted by a wide range of contaminant problems (ranging from immiscible organic contaminants to solutes to heavy metals to mixed wastes) on both a temporary and a permanent basis.

FLUIDS INVESTIGATED

Three types of barrier fluids with desirable properties were selected for investigation. The first type are organic polymers belonging to the PolyButene (PB) family. These materials are liquids with a very strong temperature dependence of viscosity, practically solidifying at ambient aquifer temperatures. Emplacement requires heating the subsurface prior to injection. Natural cooling after the cessation of injection is expected to create a chemically inert "monolith" or "cage", thus entrapping and completely isolating the contaminated region. Obtaining regulatory approval for injection should be no problem, as PBs are FDA-approved for food contact (21 CFR Section 177.1430).

The second type is Colloidal Silica (CS), which is a silicon-based chemical grout. It poses no health hazard, is unaffected by filtration, is chemically and biologically inert, has excellent durability characteristics, and is injected isothermally. Its containment performance is controlled by the gel time, which depends on pH, temperature, the chemistry of the injected suspension, and chemistry and mineralogy of the aquifer porous medium. This material has been previously investigated in the oil industry for the sealing of "thief zones" in petroleum reservoirs.

The third type of barrier fluids belongs to the PolySiloXane (PSX) family, which are crosslinked polymers similar to RTV rubbers. PSXs are mixtures of two fluids, are chemically and biologically inert silicon-based polymers, are unaffected by the aquifer or waste chemistry, and their containment performance depends on temperature and the ratio of the two constituents. PSX have been used as materials for medical implants, as well as carriers for a variety of medicines injected into the human body, and a wealth of information is available on their non-toxicity.

FORMATION OF BARRIERS BY SOIL PERMEATION

For this investigation, we assumed that the barrier fluid(s) would be injected, at pressures below lithostatic, so as not to fracture the formation or cause surface uplift. Fluid would be injected into the porous formation through vertical or horizontal wells, and would permeate the formation to form "plumes," geometrical regions in which the pore space is saturated to some degree, up to full saturation, with the barrier fluid. The fluid would then congeal, gel, or set in place. The permeability of the plume would be near zero. Several intersecting plumes would be emplaced to form a vertical or horizontal barrier in situ.

Other modes of emplacement are possible, including hydraulic fracturing, in which fluid is injected at a sufficient pressure to fracture the formation. In this case, the surface may be uplifted as well. Because hydraulic fracturing for grout emplacement would not be feasible under tanks which are in danger of rupturing, this investigation was confined to fluids sufficiently inviscid to be injected by permeation without fracturing. The criterion for grout viscosity was initial viscosity less than 200 cP, with gel time (or viscosity increase) occurring between 12 and 24 hr to allow time for injection.

METHOD OF PERMEABILITY REDUCTION SCREENING

For all three types of materials, the first screening test was to determine whether grouted sand had sufficiently low permeability. Permeability testing of grouted sands is very sensitive to the method of sample preparation and testing (1). The method of preparation can determine how completely the grout saturates the pores in the sample, and the method of testing can determine whether errors such as wall flow (bypassing the sample) or evaporation losses (misinterpreted as flow through the sample) are significant. Methods of sample preparation include:

1) Pour liquid into permeameter mold, then pack in sand. This method achieves a high degree of pore space saturation; measured permeability will be low.
2) Pack sand in permeameter mold, inject grout. The pore saturation may be less than 100%, but macroscopic sweep efficiency will be good.
3) Inject grout into soil, form a bulb, core the bulb and put the sample in a permeameter. This test method best simulates field performance, but it may be difficult to obtain reproducible results, and the sample is more difficult to test than a sample formed in a mold.

We used a variation of method (2). A sandpack was prepared in a glass or Lucite cylinder, and grout was placed on top of the sand and allowed to drain into the sandpack by gravity. Oklahoma #1 (OK-1) sand, 98% silica, was used for these experiments because soil from the Hanford reservation, the eventual intended demonstration site, had not yet been received. Particle size analyses of OK-1 and Hanford sands are shown in Fig. 1.

Several sandpacks were prepared in modified 250-mL glass graduated cylinders. First a 1/8-inch diameter hole was drilled in the wall at the bottom of the cylinder to allow air to be displaced and liquids to drain out. A 100-mesh stainless steel screen was cut to fit and cemented into the cylinder at the 30 mL mark with silicone caulk. Five mL of dry coarse sand was poured onto the screen to prevent loss of the finer OK-1 sand that followed. Then dry OK-1 sand was poured in slowly while tapping the side of the cylinder, up to the 110 mL mark. From the mass and bulk volume of sand added, and the sand grain density, these sandpacks were estimated to have 36% porosity.

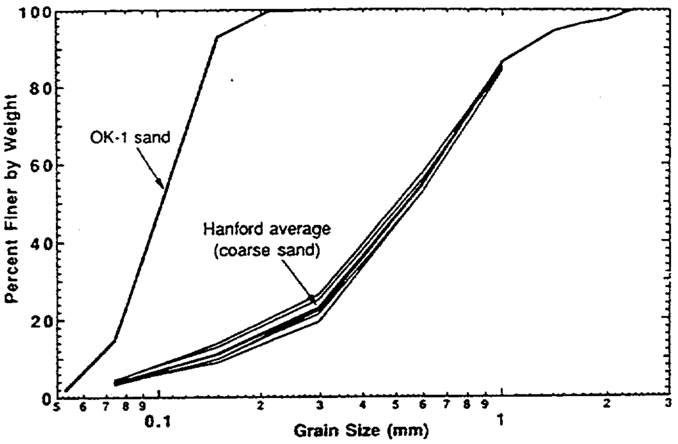

Fig. 1. Particle size analyses of sands used in this study.

The permeability of a representative sandpack was measured by standing it in a large beaker filled with water and saturating it from below. After the sandpack was fully saturated, the water levels inside and outside the graduated cylinder were monitored as their difference decayed exponentially; hydraulic conductivity was calculated from the rate of decay and the geometry of the system. Several observations were made to ensure that the head difference decayed exponentially over time. Hydraulic conductivity measured in this manner was found to be 1.7×10^{-2} cm/sec, which is close to the value later obtained for Hanford sand, despite the difference in median grain size.

Candidate barrier fluids were placed on top of the sandpack and allowed to drain in by gravity. When the sandpack was fully saturated with barrier fluid, excess fluid was allowed to drain through until none remained above the sandpack; or (if the fluid gelled before all the liquid flowed through), excess material was removed to expose the top of the grouted sand. Then water was placed on the grouted sand column and the water level was monitored to determine the rate of flow under a hydraulic gradient of approximately 1 foot of head per foot of length..

In this paper we report data from investigations of two of the classes of materials investigated, colloidal silica and polysiloxanes. Work on application of polybutenes is reported elsewhere (2).

GELLING MATERIALS (COLLOIDAL SILICA - CS)

We concentrated on chemical grouts because they can penetrate soil pores more easily than particulate grouts. Silica-based grouts, which block pore space with aqueous silica gel formed in situ, were chosen for investigation because of their low toxicity. Yonekura and Kaga (3) found that colloidal silica grouts were superior to sodium silicate grouts because the former lose less SiO_2 by leaching than the latter and are not affected by syneresis (shrinkage of the gel with expulsion of water). For this reason, we have focused on colloidal silica (CS) grouts.

The theory of gelling of colloidal silica is discussed by Iler (4). Essentially, the negatively charged colloidal particles are surrounded by an electrical double layer of cations. When the ionic strength of the colloid is increased, the double layer is compressed, allowing the particles to approach more closely and form Si-O-Si bonds between particles. Networks of particle chains form a gel. Gel time data are reported by Bennet et al (5) and by Noll et al (6). We measured gel time curves for several commercially available colloidal silicas. Two different materials, designated CS-A and CS-B, were selected for this work on the basis of availability, cost, and observed properties of the gels. Potassium, sodium, and calcium chlorides were all evaluated as salts to induce gelling; NaCl was used for most of this work, again for reasons of economy. Complete data are shown in elsewhere (2); in this paper we show only representative data.

Control of CS Gel Time in Absence of Sand (Jar Gel-Time Tests)

Control of gel time is necessary to control grout placement. Previous studies of grout emplacement (7) have dealt with the formation of grouted bulbs in saturated sands. Under these conditions, grout displaces the native water radially outward from the point of injection, but flow of groundwater or differential density will displace the grout bulb or distort its shape. Karol (7) therefore recommends a short grout gel time to prevent grout from mixing with groundwater or being displaced after injection. In studies in which freshly mixed grout was injected for longer than the gel time, it was found that as the first grout injected gelled, newly injected grout would break through the shell of gelling grout and start a new bulb on the periphery of the earlier injected grout. This results in the formation of knobby or irregular grout bulbs.

We monitored gel times for CS using the qualitative test of Sydansk (8), modified slightly. Essentially, 11 stages of gellation are distinguished visually, ranging from no change in viscosity (1) through barely flowing gel (5) to rigid gel (9), ringing rigid gel (10), and rigid gel no longer ringing (11).

For gel-time jar tests, 20 mL of colloid were placed in a 60 mL screw-capped vial. Then 4 mL of salt solution was slowly added from a syringe or pipette while the contents of the vial were continuously mixed by swirling. The slow addition of the salt solution and mixing during addition are important to avoid locally high salt concentrations, especially when the salinity of the added salt solution is high (e.g. 100 g/L). Locally high concentration of salt results in instant flocculation rather than slow gelling After the addition of the salt solution, the vial was mixed thoroughly by shaking. Then the gel state was visually assessed at intervals. In some experiments pH was adjusted by titration with 12N HCl before salt addition, and then measured again after mixing. Typical results of gel time tests with pH held constant are shown in Fig. 2. Data for other pH values are presented elsewhere (2). Results of tests over the range of pH values are summarized in Fig. 3. These data are consistent with those of Noll et al. (6), who also found that as pH decreases below 6, gel times increase. Note that these gel times were measured in the absence of soil; the effects of soil on gel time are discussed below.

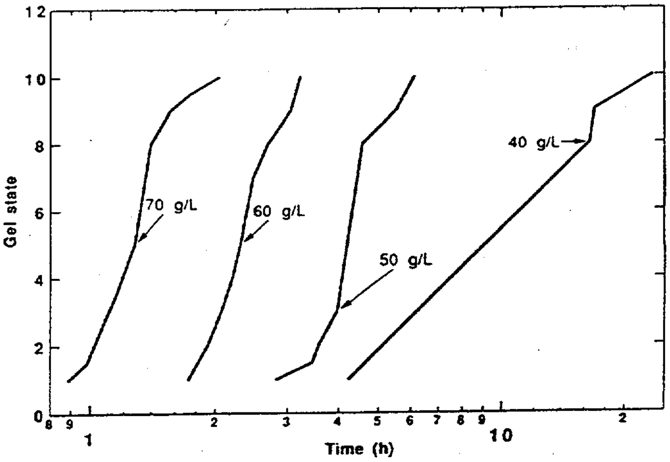

Fig. 2. Gel-time jar test of CS-B with varying concentrations of added NaCl, pH adjusted to 8.9 (the natural buffered pH of Hanford sand). The vertical axis is a visual assessment of gel state, modified from Sydansk (8).

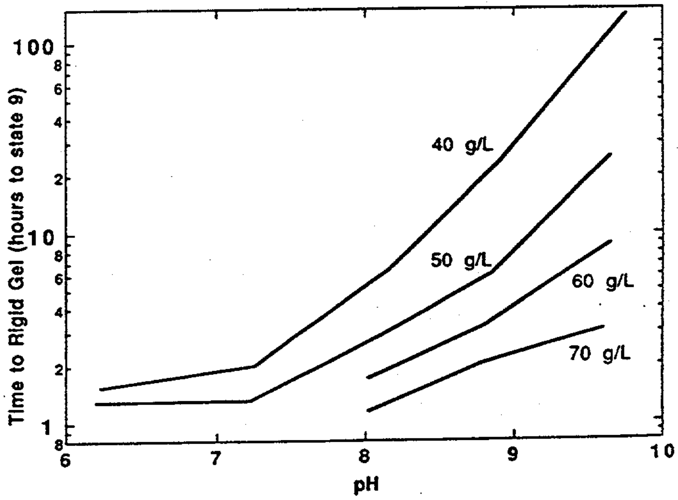

Fig. 3. Time to rigid gel (state 9) of CS-B with varying concentrations of added NaCl and varying pH.

Permeability Reduction by CS Grout with Complete Liquid Saturation

Colloidal silica grout was tested in two sandpacks. One was initially dry (#C1), and the other was saturated with distilled water and drained by applying 1 psi air pressure on top of the sand (#C2). A mixture of 50 mL CS-A and 10 mL of 90 g/L KCl solution was poured onto each sandpack. From jar gel-time tests, this grout increases in viscosity in 11 min and gels rigid in 15 min. The grout penetrated the sand. In sandpack #C1 (initially dry) , about 2 mL drained from the bottom of the sand before gelling prevented further flow. In sandpack #C2 (drained) about 10 mL of liquid drained from the sand. This liquid was turbid, but did not gel until the next day. This indicates that it was a mixture of grout and displaced pore water.

In both sandpacks, gelling occurred before the grout liquid level had reached the top of the sand. To conduct the water permeability test, the glass cylinder was cut at the level of the top of the sand, and the top part of the cylinder was removed. The cured colloidal silica remained as a cylinder; it was removed and the glass tube was reassembled and epoxied together. A solution of 15 g/L KCl (i.e., the same salinity as the grout, or "design concentration") was placed on top of the grouted sand. There was no flow through the grouted sand in either test, but after 1 week the test was discontinued because the epoxy seal started to leak. This test indicated that colloidal silica can be an effective grouting agent if the pores can be saturated. Achieving a high degree of pore saturation is discussed below.

Additional permeability tests were done on sand columns that were grouted in the course of experiments to control the gel time of colloidal silica in Hanford soil. The method of preparation of these tests is described in a later section. Essentially, the sandpack was preflushed with a salt solution and then saturated with grout; viscosity of the grout was monitored until gelling was complete. Then the sandpack was placed in a vertical position with a head of water over it. Decline of water level during the first 50 days of testing indicates hydraulic conductivity of 3×10^{-7} and 4×10^{-7} cm/sec for two tests, but the actual hydraulic conductivities may be even lower as the aforementioned values may include water loss due to evaporation.

In the course of the analysis of the way CS works, it became evident that an effective sealing is possible in the unsaturated zone (on which our work focuses) if the pore space is completely filled by the CS suspension. However, due to unavoidable gravity effects, a saturation redistribution will occur, resulting in partial drainage of the CS suspension from the pores and replacement by air. This reduces the effectiveness of the CS as a barrier fluid, and results (after gellation) in the emergence of a new porous medium with a porosity reduced by at least the residual saturation. Microscopic investigations confirmed this expectation. The "new" porous medium is less permeable than the original, but still permeable. The problem is addressed by multiple CS injections, a process discussed in detail in a later section.

Effects of Soil on Gelling of CS

In the course of multiple-injection tests reported below, we observed that when grout was injected into sand (Hanford sand or OK-1 sand), the grout gelled more rapidly than the same grout gelled in a vial with no added sand or soil. This observation prompted us to conduct additional gel-time jar tests in which we added 10 g of soil or sand to the vial. These tests showed that addition of sand or soil accelerated the gelling of CS, and that increasing the amount of sand increased the acceleration. When the CS, even with no added salt solution, was poured into a column of Hanford sand, gellation was almost immediate. This indicated that when the colloidal silica contacted the sand, its ionic strength increased sharply. Two mechanisms might explain this: either pore water present in the Hanford sand contained sufficient ionic strength to cause rapid gellation, or that multi-valent ions adsorbed on the sand, (most likely on clay particles) were exchanged for mono-valent Na ions in the colloid, causing rapid gellation. Multi-valent ions cause more rapid gelling than equivalent mono-valent ions. It was also possible that both mechanisms were at work. Exhaustively washing the sand with distilled water reduced but did not entirely eliminate the acceleration in jar tests.

To clarify the effects of soil and soil-water chemistry on the gelling of CS grouts, we analyzed the soil and pore water, and conducted column ion-exchange and pore water displacement experiments. The water content of the Hanford sand (coarse fraction) was found by weighing, drying, and reweighing to be 5.04 ± 0.27 weight %, which corresponds to approximately 21% saturation. At this saturation, the mobility of the water is too low to permit a sample to be extracted by centrifugation. To extract a sample, we added distilled water to the sand, mixed it, and extracted a sample of the diluted pore water for analysis. The results of this analysis, corrected for dilution, are shown in Table I.

TABLE I

Major Ion Distribution in Pore Water (3 samples)

	A	B	C
filtered	0.45 μm	0.22 μm	0.22 μm
	mg/L	mg/L	mg/L
Al^{+++}	189.0	4.2	ND
Ca^{++}	273.0	205.8	210.0
Fe (total)	336.0	2.1	ND
K^{+}	109.2	77.7	79.8
Mg^{++}	86.1	27.3	27.3
Mn^{+++}	4.2	ND	ND
Na^{+}	378.0	357.0	378.0
Si (total)	714.0	174.3	174.3
Sr^{++}	1.2	0.8	0.8
Cl^{-}	NA	152.9	146.0
NO_3^{-}	NA	36.8	39.7
$SO_4^{=}$	NA	361.2	350.7

Note: HCO_3^{-} was not measured

NA = not analyzed

ND = not detected

We prepared two columns of Hanford sand and flushed one with distilled water and the other with a solution of NaCl. Analyses of major multivalent cations in the effluents are shown in Fig. 4 for both the distilled water flush and the NaCl flush. The data in Fig. 4 show that multivalent cations are removed from Hanford sand much more effectively by flushing with a 4% NaCl solution than by flushing with distilled water. When flushed with distilled water, all multivalent ions rapidly approached the lower detection limit, except for Ca and Mg, which are replenished by dissolution of solid-phase minerals (principally carbonates) in the Hanford sand. When flushed with 4% NaCl, the effluent contains large

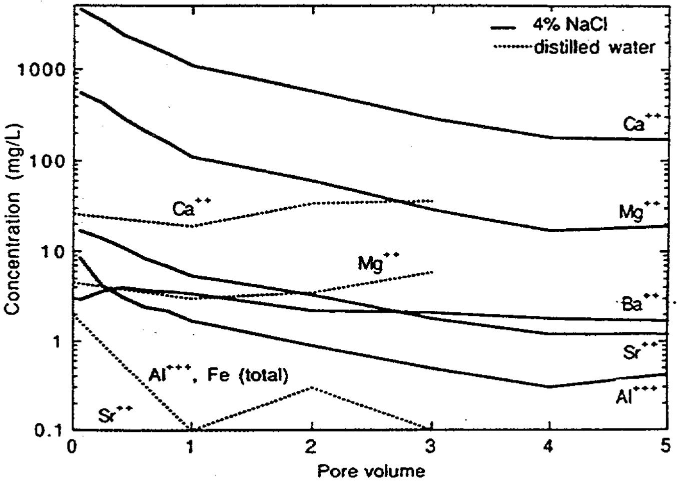

Fig. 4. Major ions in the effluent, Hanford sand flushed with distilled water or with 4% NaCl.

concentrations of desorbed Ca, Mg, Ba, and Sr, which are exchanged for Na in the flush water. Flushing with NaCl can remove the adsorbed Ca and Mg from clays, but cannot reduce the Ca and Mg concentrations in the effluent to zero, because of dissolution of minerals. To determine whether the remaining Ca and Mg concentrations were low enough to permit gel time control in Hanford sand, we conducted tests to measure the gel time in the sand, and compare it to jar gel-time tests in vials.

Control of CS Gel Time in Hanford Sand (Column Gel-Time Tests)

Jar gel-time tests with added sand had shown that the sand-grout ratio was important, and because jar tests could not achieve the same sand-grout ratio that would exist in-situ, we conducted a series of column gel-time tests using sand from the Hanford reservation. Also, the sand-flushing tests had shown that the multivalent cations which were believed to be responsible for premature gellation could be removed (or at least reduced) by preflushing with 4% NaCl. Therefore we conducted experiments to determine whether such preflushing could be effective in preventing premature gellation of colloidal silica grouts injected into Hanford sand. Lucite tubes were packed with Hanford sand and pretreated in one of three ways: a) no preflush, b) preflush with 10 PV distilled water to displace native pore water, and c) preflush with 15 PV of 4% NaCl solution, followed by 5 PV of salt solution at the design concentration (i.e., same concentration as the grout). After pretreatment, the sand columns were saturated with grout, and tubes filled with water were connected at each end. The end tubes were made of flexible tygon tubing so they could be raised or lowered, thus creating a hydraulic disequilibrium condition. At intervals, falling head permeameter tests were done by creating a hydraulic disequilibrium and measuring the rate of its decay (quicker return = more permeable). The smallest hydraulic conductivity that can be measured by this method was estimated as 3×10^{-7} cm/sec. The change in hydraulic conductivity (equivalent to increase in viscosity of the gelling grout) was monitored as a means of monitoring the gelling of the grout in situ. Such a test would detect any possible effects of interaction of the grout with the porous medium (physical as well as chemical), and accurately reproduce the solid-liquid ratios. The results of all these tests showed that when the Hanford sand was not preflushed, or preflushed with distilled water only, the grout gelled even before the entire 25-cm length of sand column was saturated, but when the sand was preflushed with 4% NaCl, the grout was able to penetrate completely through the sand column, so that permeability measurements could be made to monitor the gelling of the grout in situ. A typical test result is shown in Fig. 5. The results of the two jar tests show the reproducibility of the jar test technique, with no added sand or soil. The permeability of the sandpack decreased at the same time as the grout gelled. In this test, the hydraulic conductivity fell to the lower measurable limit by 2.9 hr. This shows that the grout gelled at the same rate in the sand column as it did in the jar test, and means that preflushing with 4% NaCl was effective in eliminating the gel-accelerating effects of the sand, Without such preflushing, gelling was so rapid that the tests could not even be conducted. Results of other sand-column gel tests are presented elsewhere (2); in all cases gel time in preflushed sand columns was between 50 and 100% of gel time in jar tests (i.e., gel tests in which the effects of sand are absent). Since control of gel time is important in controlling the emplacement of grout plumes, preflushing will be a necessary part of emplacement of CS grouts. It is noteworthy that the time elapsed between the preflush and grout injection can be important; Jurinak and Summers (9) were forced to wait a day between the two in an oil-field application (their well P-1) and the injected colloid gelled prematurely. Mineral dissolution during the waiting period appears to have been the cause.

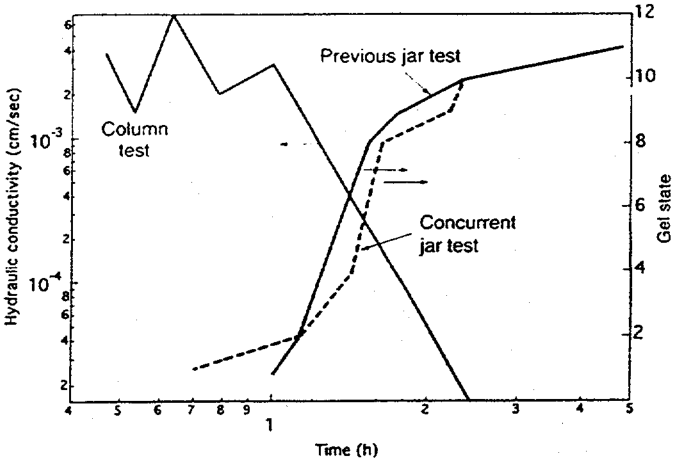

Fig. 5. Comparison of gel-time column test and jar test, CS-B and 70 g/L NaCl. Hanford sand was pretreated by flushing with 15 PV of 4% NaCl followed by 5 PV of 11.7 g/L NaCl.

Multiple Injections of CS

An intended site for application of this technology is the unsaturated soil beneath existing tanks, approximately 50 m above the water table. When aqueous grout is injected into unsaturated soil, the grout slumps, that is, drains downward under the influence of gravity. The grouted soil volume may be saturated with grout immediately after injection, but under drainage, the grout saturation will decrease to field capacity. This may result in an incomplete sealing of the grouted region, i.e. a non-zero permeability. We injected CS grout into preflushed unsaturated Hanford sand to observe the shape of the resulting grout plume, and found this to be the case. Achieving a high degree of grout saturation in the plume is necessary for low permeability.

We investigated a multiple-injection technique to solve the problem of achieving high grout saturation in an unsaturated formation. According to this technique, several injections of aqueous grout are made, allowing time for each one to gel before the next injection. Each injection drains away, leaving residual saturation which gels in place. The gelled residual saturations of the several injections accumulate to achieve a high saturation of gelled grout in place.

To demonstrate the multiple injection technique, eight sand columns were prepared. In each column, the sand was saturated with grout from below using gravity head and then gas pressure was applied from above to drive the liquid out, simulating drainage to near field capacity. (Bottom boundary conditions made it impossible to achieve the desired degree of desaturation by gravity drainage.) After gelling, the permeability of the sandpack was measured, and then the grout injection was repeated.

Eight columns were made from Lucite tubes with overall length 16.5 cm and 4.46 cm. i.d. A 200 mesh stainless steel screen was mounted 0.5 cm from the bottom of the tube to hold the sand inside the column. A layering and tapping technique was used to pack OK-1 sand into the tube to a final depth of 11.5 cm. The columns were initially dry. Column M7 was flushed with CO_2 to achieve higher liquid saturation. The sandpacks were desaturated to residual water saturation in the sand column by blowing through air or CO_2 until no more water emerged from the bottom of the column.

Two different gas-drive techniques were used to desaturate the columns. In columns M1, M5, and M6, gas pressure was applied only until the grout liquid level reached the top of the sand. In the other columns, gas pressure was applied until no more grout was driven out the bottom of the column. This represents a severe drainage condition, in that gas permeability of the grouted column was forced that might not have drained. The comparable sets of columns (M1 and M2, M3 and M5, and M4 and M6) thus may be considered to bracket the condition that would exist in the field.

Gas permeability of columns M1 through M6 was measured with humidified air, and expressed as equivalent hydraulic conductivity. Liquid permeability of columns M7 and M8 was measured by monitoring the rate of fall of a water column standing atop the grouted sand.

The results in Table II show that the permeability of sand grouted with colloidal silica decreased with each successive injection, eventually reaching quite low values. In columns M3 and M4, the final permeability was forced to be high by gas blown through the column before the grout cured; in the field, grout might not have drained so rapidly. The actual reduction of permeability with each successive injection will depend upon the capillary pressure and relative permeability curves of the particular soil or sand grouted.

CROSSLINKED POLYSILOXANES (PSX)

Gels based on polysiloxanes (or silicones) are inert in a broad range of chemical and biological environments and are commercially available in a broad range of room temperature vulcanizable (RTV) formulations. Linear silicones, such as polydimethyl siloxane, can be cross linked by the addition of a polyfunctional silylhydride to a vinyl group attached to a divinyl-terminated siloxane, or by cross linking linear or slightly branched siloxane chains having reactive end groups such as silanols.

RTV silicone elastomers are available with a wide range of starting viscosities and final cure state. Two-component systems consist of one liquid containing the siloxane polymer (typically containing vinyl groups) and a separate liquid containing the a cross linking agent that contains siloxanes with Si-H groups. When mixed, the crosslinking reactions can occur. A catalyst, such as chloroplatinic acid, is used to accomplish the addition reaction at ambient temperatures.

Two commercial candidate systems were selected for investigation based on their initially low viscosity. These are designated PSX-A and PSX-B. When prepared according to the manufacturer's recipe, the PSX-A produces a fairly rigid, rubbery material. The PSX-B produces a much more jelly-like material because it is under-crosslinked. This material remains tacky after curing and can heal itself if torn and rejoined; this may be beneficial for a subsurface barrier in case of seismic disturbance. In an effort to reduce both the cost of the final gel and the viscosity of the starting mixture, both the PSX materials were prepared using various amounts of a miscible, low-molecular-weight polydimethyl siloxane with viscosity of 5 centistokes as a diluent. The results for these curing studies is summarized in Table III.

The viscosities for a number of the PSX-A mixtures were measured (in the absence of the cross linking agent, which was considerably lower in viscosity than the siloxane polymer, and so would tend to lower the initial viscosity) in a Couette

TABLE II
Multiple Injections of Colloidal Silica

Sample#	M1	M2	M3	M5	M4	M6	M7	M8
Gas pressure drainage-technique	blown to top of sand	blown through	blown through	blow to top of sand	blown through	blown to top of sand	blown through (CO_2)	blown through
K before first injection (cm/s)	not measured, similar to M5			7.7E-3	not measured, similar to M5		9.0E-3	1.1E-3
First Injection Gel Composition	GS-A 65 g/L KCl		GS-B 70 g/L KCl		CS-B 70 g/L NaCl		CS-A 65 g/L KCl	
K after first injection (cm/s)	2.5E-5	5.1E-4	2.1E-4	2.9E-5	1.1E-3	3.8E-5	3.2E-5	2.4E-5
Second Injection Gel Composition	CS-A 55 g/L KCl		CS-B 55 g/L KCl		CS-B 55 g/L NaCl		CS-A 65 g/L KCl	
K after second injection (cm/s)	a	a	9.8E-6	a	3.5E-6	a	b	1.3E-8
Third injection Gel Composition	no further injections						CS-A 65 g/L KCl	
K after third injection (cm/s)							b	<1E-8

a: Gas flow too low to measure, hydraulic conductivity <1E-8 cm/sec

b: Not determinable

TABLE III
Diluted Crosslinked Polysiloxane Systems

Siloxane	Wt % Diluent	Time to Gel
PSX-B	20.8	24 hr
PSX-B	40.0	72 hr
PSX-B	59.9	did not gel
PSX-B	79.6	did not gel
PSX-A	20.0	24 hr
PSX-A	40.0	30 hr
PSX-A	60.0	48 hr
PSX-A	80.0	100 hrs

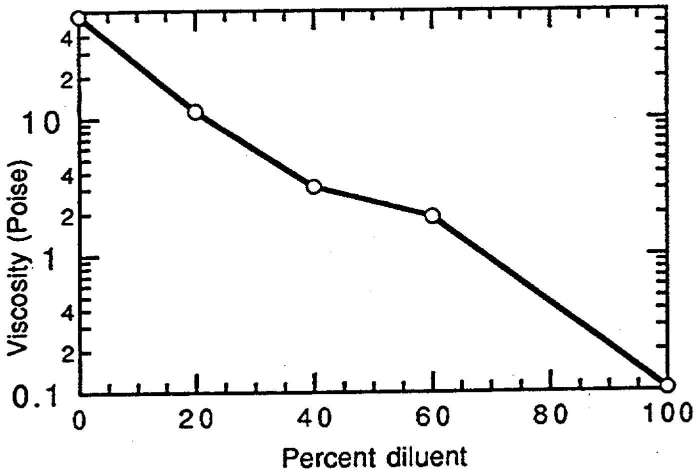

Fig. 6. Viscosity of uncured PSX-A, diluted.

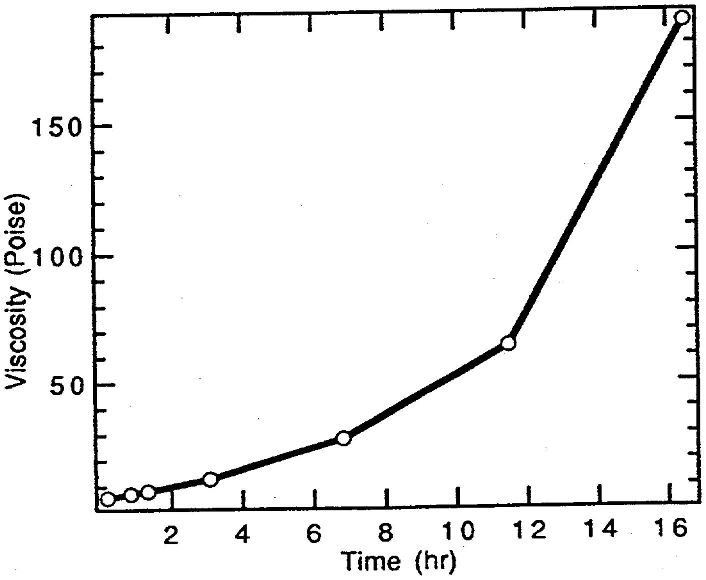

Fig. 7. Viscosity of PSX-B during cure.

viscometer. The mixtures were all Newtonian fluids, and the viscosity is plotted as a function of the fraction of diluent in Fig. 6. Mixtures of the PSX-A containing approximately 60-80% of the 5 centistoke diluent produced reasonably rigid gels and had starting viscosities low enough to allow emplacement. The viscosity of PSX-B, mixed with its crosslinker and not diluted, was also monitored in a Couette viscometer as it cured; data are shown in Fig. 7.

A batch of PSX-B was also poured into a column of Hanford sand. Although the Pt-catalyzed curing system is sensitive to poisoning by environmental contaminants, the PSX-B was unaffected by the sand. The grouted sand was then subjected to a head of distilled water for permeability measurement; measurements during 60 days indicate a hydraulic conductivity of 4×10^{-8} cm/sec. As with the tests of CS grout, this number may be an overestimate due to evaporation.

SUMMARY AND FUTURE WORK

Experimental results reported here show that colloidal silica can be made to gel reproducibly by controlling its pH and ionic strength (or salinity). When colloidal silica is injected into sand in such a manner as to achieve nearly complete saturation of the pore space, and gels in place, the resulting formation is practically impermeable to water flow and can constitute an effective barrier to the transport of contaminants. Control of gel time in situ is complicated by multivalent ions adsorbed in the soil, which accelerates gellation. This acceleration can be mitigated by appropriately preflushing the soil to displace the exchangeable multivalent ions. Achieving a high degree of saturation (of any kind of grout) in the pore space is difficult in an unsaturated formation, as the grout tends to slump, leaving only residual saturation in place. This can be overcome by using several injections of grout in sequence, so that the residual saturations of successive grout injections accumulate to reach the required low permeability.

Polysiloxanes can be diluted with silicone fluid to reduce viscosity without losing the ability to cure, and when emplaced, effectively block water flow. The Pt-catalyzed system studied here, although reported to be sensitive to chemical poisoning, was not adversely affected by the Hanford soil.

Future work will concentrate on demonstrating at increasing spatial scales the emplacement of plumes in unsaturated sand, and developing procedures for multiple injections in sand under various conditions of permeability and saturation. A field demonstration of plume emplacement is anticipated for 1994.

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