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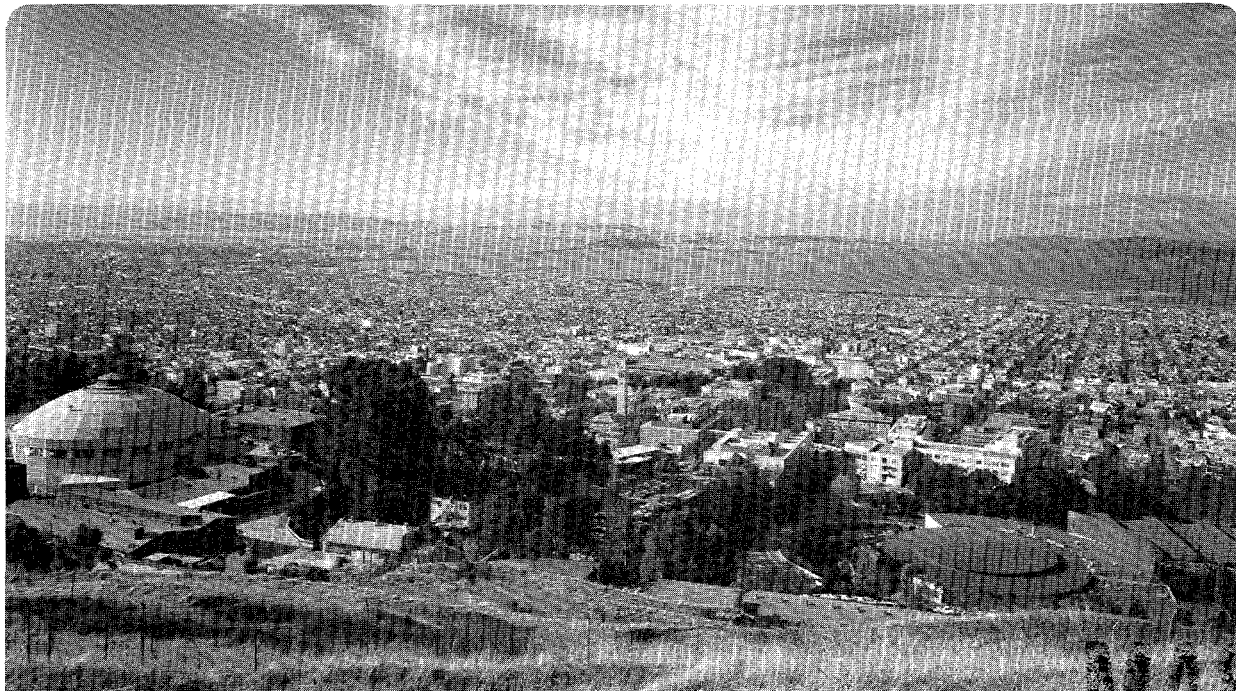## UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

Injectable Barriers for Waste Isolation

P. Persoff, S. Finsterle, G.J. Moridis, J. Apps,
K. Pruess, and S.J. Muller

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INJECTABLE BARRIERS FOR WASTE ISOLATION

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ABSTRACT

In this paper we report laboratory work and numerical simulation done in support of development and demonstration of injectable barriers formed from either of two fluids: colloidal silica or polysiloxane. Two principal problems addressed here are control of gel time and control of plume emplacement in the vadose zone. Gel time must be controlled so that the viscosity of the barrier fluid remains low long enough to inject the barrier, but increases soon enough to gel the barrier in place. During injection, the viscosity must be low enough to avoid high injection pressures which could uplift or fracture the formation.

Control of gel time of colloidal silica grout is achieved by adjusting the pH and ionic strength; for crosslinkable polysiloxane the gel time is controlled by adjusting the catalyst concentration. Grouts with desired gel times are designed to compensate for the effects of soil chemistry. For colloidal silica, gel acceleration results from Ca ions released by ion exchange between the grout and the soil. Strategies to control this effect include preflushing to displace Ca, precipitating Ca in place, or use of special colloids that contain no exchangeable Na. For polysiloxane, gel acceleration results from the catalytic effect of certain metals in the soil. To test the grout gel time in the soil, the injection pressure was monitored as grouts were injected into sandpacks.

When grout is injected into the vadose zone, it slumps under the influence of gravity, and redistributes due to capillary forces as it gels. We have developed a new module for the reservoir simulator TOUGH2 to model grout injection into the vadose zone, taking into account the increase of liquid viscosity as a function of gel concentration and time. We have also developed a model to calculate soil properties after complete solidification of the grout.

The numerical model has been used to design and analyze laboratory experiments and field pilot tests. We present the results of computer simulations of grout injection, redistribution, and solidification.

INTRODUCTION

Permanent barrier systems for contaminant isolation are emerging as an alternative to treatment or disposal of contaminated soil (Dwyer 1994; Noll et al., 1992; Voss et al., 1993; Moridis et al., 1993). Vertical barriers, or cut-off walls, can be formed by slurry trenching or jet grouting, in which the soil is replaced with a clay or cement material. Formation of horizontal bottom barriers is more difficult because barrier material must be emplaced remotely. One promising approach for the formation of horizontal bottom barriers is the use of injectable barriers formed from liquids that are injected into the soil through inclined or horizontal wells, and gel in place (Figures 1 and 2). Such materials could also be used for vertical barriers.

Grout placement is critical to the formation of injectable barriers. When grout is injected into the subsurface, consideration must be given to the likelihood that the grout plume will move before it solidifies or gels. This problem was previously studied by Karol (1982) who demonstrated the effect of flowing groundwater on the ultimate shape and location of a plume of cement grout injected into
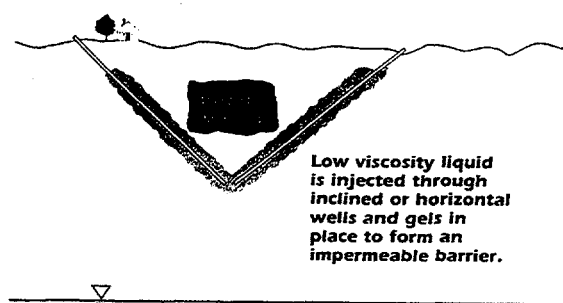

Low viscosity liquid is injected through inclined or horizontal wells and gels in place to form an impermeable barrier.

Figure 1. Schematic of bottom barrier emplaced under buried waste through inclined wells.

Intersecting grout plumes form continuous barrier
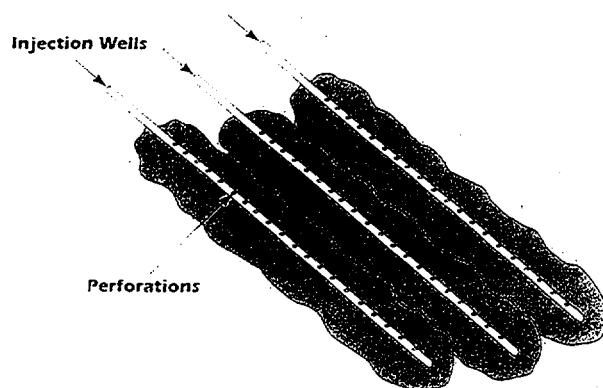

Injection Wells

Perforations

Figure 2. Schematic of formation of horizontal injectable barriers. Barrier fluid(s) are injected, at pressures below lithostatic, so as not to fracture the formation or cause surface uplift. Fluid is injected into the porous formation through horizontal wells, and permeates 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 then congeals, gels, or sets in place. Several intersecting plumes would be emplaced to form horizontal barrier in situ.

saturated sand. In the applications shown in Figs. 1 and 2, a barrier is to be emplaced by injection in the vadose zone. In this application the effects of gravity and capillarity are important. Essentially, the injected grout plume is drawn downward by gravity and is dispersed by capillarity; both effects continue atdecreasing rates as the viscosity of the grout increases and as the grout changes from a Newtonian liquid to a non-Newtonian liquid and finally solidifies. The time scale of these changes, referred to as gel time, must be slow enough to allow complete injection without excessive injection pressure which would uplift the formation (generally limited to 20 kPa per meter of depth [1 psi per foot]), and fast enough to solidify the plume in its intended location.

In this paper we report laboratory work done to control and measure gel time for two types of grout, both in the presence and the absence of soil; and numerical simulation to predict the location and other properties of an injected plume. Two types of grout were studied: an aqueous grout comprised of colloidal silica (CS), which is made to gel by addition of brine, and a non-aqueous grout comprised of polysiloxane (PSX) which is crosslinked by the addition of a catalyst. These grouts were selected for study on the basis of low toxicity, low initial viscosity, and controllable gel time. Gel times were measured by visual assessment of gel state (Sydansk, 1990) and checked by rheometry in which both the viscous and elastic components of flow resistance were measured. A numerical simulator was developed to model grout flow during and after emplacement, and results of simulations were used to guide laboratory and field tests. Results of a sandbox injection are compared to a simulation.

MATERIALS

Colloidal Silica Grout (CS)

The use of CS for blocking flow in porous media originated in the petroleum industry (Bennett et al, 1988; Jurinek et al, 1991; Seright and Martin 1991) and has recently been transferred to the field of environmental protection (Noll et al., 1992; Yonekura and Kaga 1992). Essentially, the colloid is stabilized by a negative charge on the particles and a surrounding double layer of counter-ions. The colloid is destabilized and gels when the repulsive forces caused by the negative charge are overcome, and particles approach each other and form inter-particle siloxane (Si-O-Si) bonds. Gelling is accomplished either by increasing the ionic strength to compress the double layer, or by introducing a divalent ion which can attract two particles together.

Generally the negative charge needed to

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stabilize the colloid is produced by adding NaOH, which raises the pH and ionizes silanol (Si-OH) groups on the particle surface to Si O$^-$. However, we found (Persoff et al. 1994) that when the colloid is injected into soil, the Na ions are exchanged for Ca ions on clay particles in the soil, and the Ca ions in the aqueous phase cause uncontrolled rapid gelling of the grout. Two strategies to overcome this problem are reported elsewhere (Persoff et al 1994). For this work we used a standard alkaline colloid (Nyacol 1440, PQ Corporation, Valley Forge, PA) gelled by addition of 20% by volume of NaCl brine, and a newly developed alumina-modified colloid (Nyacol DP5110) gelled by addition of 20% by volume of CaCl$_2$ brine.

Polysiloxane Grout (PSX)

The second grout studied is a divinyl-terminated polydimethylsiloxane. Cross-linking occurs at the vinyl terminations in the presence of a platinum catalyst. The initial viscosity of the grout is determined by the polysiloxane chain length, and the rate of gelling is determined by the concentration of catalyst. To meet the requirement for low initial viscosity, a new product was formulated for this project, designated 2-7154-PSX-10; with catalyst 2-0707 (Dow Corning, Midland, MI).

The soils used in this work were taken from two potential test sites: the Hanford formation at the 200 East site of the Hanford Reservation in Washington state, and from a quarry near East Sacramento, California (ESQ sand). Both soils showed similar effects in these tests.

METHODS

We conducted experiments to control the gelling rate of grouts both in the absence of soil (jar tests and viscometry) and in the presence of soil (jar tests and column tests). In the jar tests, the gel time of all materials was measured by a qualitative visual assessment of gel state (Sydansk 1990). Gel states were assigned numbers: 1 represents no change from initial viscosity; 2, increased viscosity, still Newtonian; 3 through 8, increasing yield stress and elasticity of non-Newtonian viscoelastic fluids; 9, rigid gel; and 10, ringing rigid gel. Although crude, the jar test has the advantage that the gel state can be measured in the presence of soil, which cannot be done in viscometric methods. However, jar tests do not reproduce the ratio of soil solid to injected liquid that would obtain in the field. To examine gel time under those conditions, grout was injected into packed columns of soil, while the injection pressure was monitored. The column dimensions and flow rate in these tests were designed to reproduce

approximately the flow rates that would occur in a planned field test injection. In the planned field injection, 1 m^3 of grout would be injected for 2 hr at a constant volumetric rate from a point source into a soil with 36% porosity. This would yield a spherically symmetric injection with a radius of 87 cm. In the field test, the grout front would advance at a power-law decreasing rate; in the column tests, the injection rate was held constant at 1.4 mL/min through a 2.54 cm i.d. column. This resulted in grout reaching the outlet of the 87-cm long column in 2 hr, thus reproducing the grout flow on an average basis. To obtain data needed for simulations, selected grout formulas were also measured in a Contraves rheometer or in a Rheometrics dynamic mechanical spectrometer; for these tests soil could not be included.

To develop grout formulas, various concentrations of curing agent were added to the CS or PSX, and gelling was monitored. The principal problems to be overcome for CS grout were premature gelling caused by chemical interaction between the grout and the soil, and acceleration of gel time caused by dyes that would be used to detect grout plumes in the soil. For PSX grout, the soil also accelerates gelling, but to a lesser degree, and the effect of soil can be compensated for by reducing the amount of catalyst.

RESULTS

Design of grouts with controllable gel times in soil

The fundamental problem for controlling gel time of CS grout is that Na ions in the grout are exchanged for Ca ions adsorbed on clay in the soil. This effect is illustrated in Fig. 3. Even if no NaCl is added to the colloid, the Na present in the colloid is sufficient to cause premature gellation, as shown in Figure 4. Figure 4 also shows that preflushing the sand with 4% NaCl brine is sufficient to eliminate the problem. The salinity of the preflush (4% NaCl), is greater than that of the grout (1% NaCl). To avoid formation of a high-salinity fast-gelling mixing zone at the front where the grout displaces the preflush, the preflush is followed by a 1% NaCl rinse before the grout is injected. With this technique, preflushing the soil to displace Ca makes injection of CS grout feasible.

However, preflushing is not acceptable in situations where it would mobilize contaminants in the soil. For this reason, we continued searching for a CS system that would gel controllably in soil and not require preflushing. A newly developed CS (Nyacol DP5110) solved this problem (Figure 5).

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This CS is surface-modified by isomorphic substitution of alumina, which causes a permanent (i.e., not pH-dependent) surface charge. This grout gels at the same time in soil as with no soil.

For PSX grout3/, Figure 6 shows gel time curves with and without ESQ sand. The ESQ sand accelerated the gelling of the grout, but the acceleration can be compensated for by reducing the concentration of catalyst.

For simulations of grout emplacement, data are needed on the viscosity of grout both initially and as it changes from a Newtonian liquid to a viscoelastic liquid, and finally to a solid as it gels. Typical data are shown in Figure 7. Three kinds of data are shown in this Figure: viscosity (measured with a Contraves Couette rheometer), gel state (visually assessed), and Storage and Loss moduli (measured in a Rheometrics dynamic mechanical spectrometer). Motion of grout practically ceases when gel state 2 is reached.

NUMERICAL SIMULATION OF INJECTION

When grout is injected into unsaturated soils, the grout plume slumps under gravity and spreads due to capillary forces, while its viscosity increases and it finally solidifies. In the case of CS, the grout is initially miscible with pore water but eventually it forms a separate phase, while in the case of PSX, the grout is a separate phase at all times. The purpose of grouting is achieved when the grout solidifies, thus changing the original porous medium to a new one with lower porosity and permeability. However, because of the slumping and spreading of the grout plume, the pore space is only partially saturated with grout, and therefore permeability reduction upon gelling is not as great as it would be if the pore space were fully saturated with gelled grout.

We have developed a numerical model to simulate these flow and gelling processes, with the aim of predicting both the eventual location of the
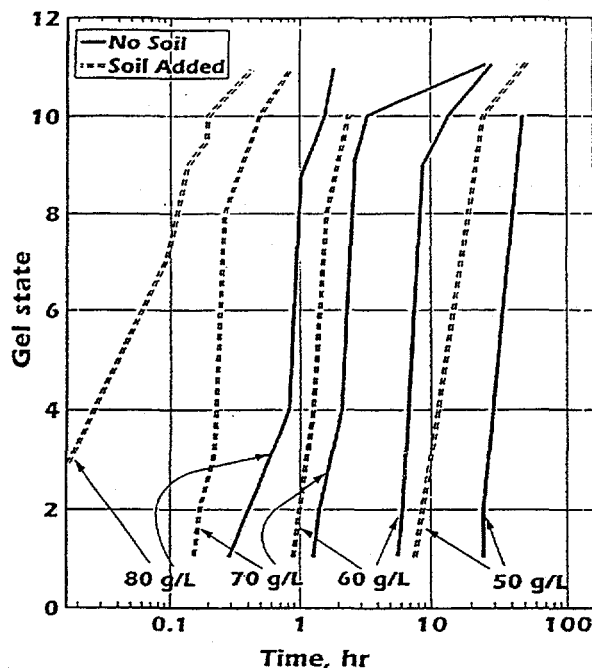
Figure 3. Gel-time jar tests of alkaline colloidal silica, with and without soil. The grout is made by adding 4 mL by volume of brine to 20 mL colloid. The colloid in these tests was Nyacol 1440, and the brines ranged from 40 to 80 g/L NaCl. When 10 g of uncontaminated sand from the Hanford formation was added to 24 mL of grout, the gelling was dramatically accelerated. The Na ions displace Ca ions in the clay by ion exchange, and the Ca ions accelerate the gelling.
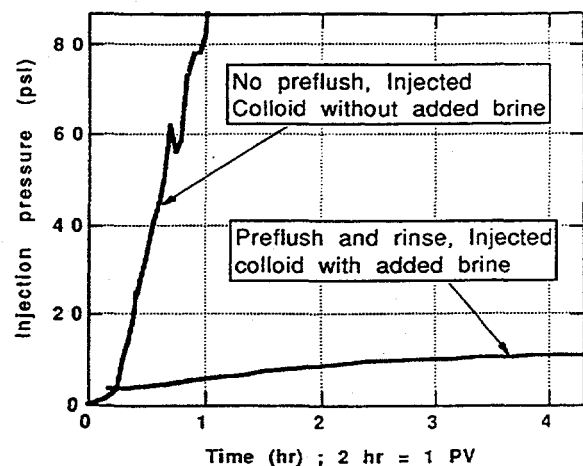
Figure 4. Column injection tests of basic colloidal silica, with and without preflushing. The soil in these tests was ESQ sand, 87 cm long. The colloid was Nyacol 1440. Even if no NaCl brine is added to cause gelling, the Na ions present in the colloid are sufficient to release Ca ions and cause premature gellation. In this test, premature gellation caused excessive injection pressures before the grout reached the outlet of column. When the soil column was preflushed with 2 PV of 4% NaCl and then rinsed with 1 PV 1% NaCl the Ca ions were displaced. Grout (5 parts colloid and 1 part 6% NaCl) was then injected and premature gelling did not occur. Pressure drop was due only to viscous flow through the sandpack.
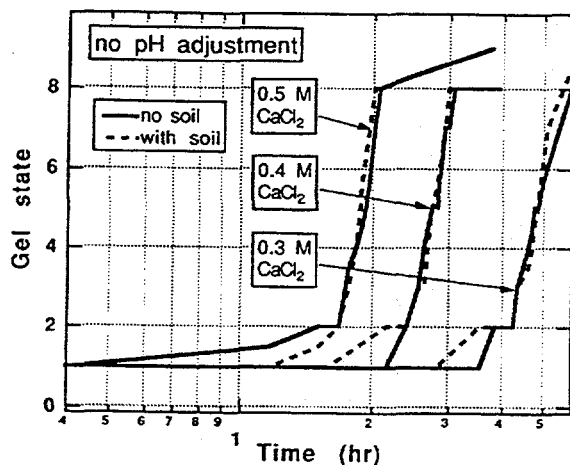
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Figure 5. Gel-time jar tests of neutral, surface-modified colloidal silica, with and without soil. The grout is made by adding one part by volume of brine top five parts colloid. The colloid in these tests was Nyacol DP5110, and the brines ranged from 0.3 to 0.5 M CaCl$_2$. The soil was uncontaminated sand from the Hanford formation. There are no Na ions in the grout, so no additional Ca ions are contributed to the grout by ion exchange. As a result, the grout gels at the same rate whether soil is present or not.
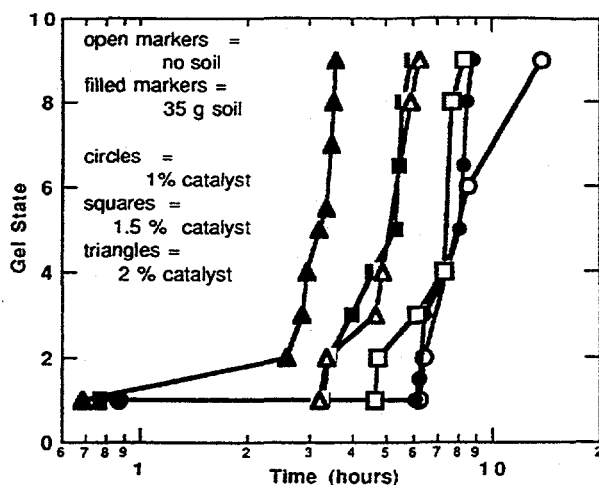

Figure 6. Gel-time jar tests of PSX grout, with and without soil. The grout is made by adding one part by volume of brine top five parts colloid. The soil in these tests was ESQ sand.

plume and the properties of the new porous medium formed by grouting. The new porous medium can then be described for simulation of subsequent grout injections. The numerical model is an extension of TOUGH2 which simulates non-isothermal flows of multicomponent, multiphase fluids in porous and fractured media. The processes of gelling, mixing, and solidification are represented by a Gel Time Curve, Mixing Rule, and Solidification Model. In this paper, we only present a brief description of these rules and an example result; full documentation of TOUGH2 and of these modifications are presented elsewhere [Pruess, 1987, 1991a, Finsterle et al 1994, 1995].

The **gel time curve** specifies the change of viscosity with time. Any explicit viscosity vs. time
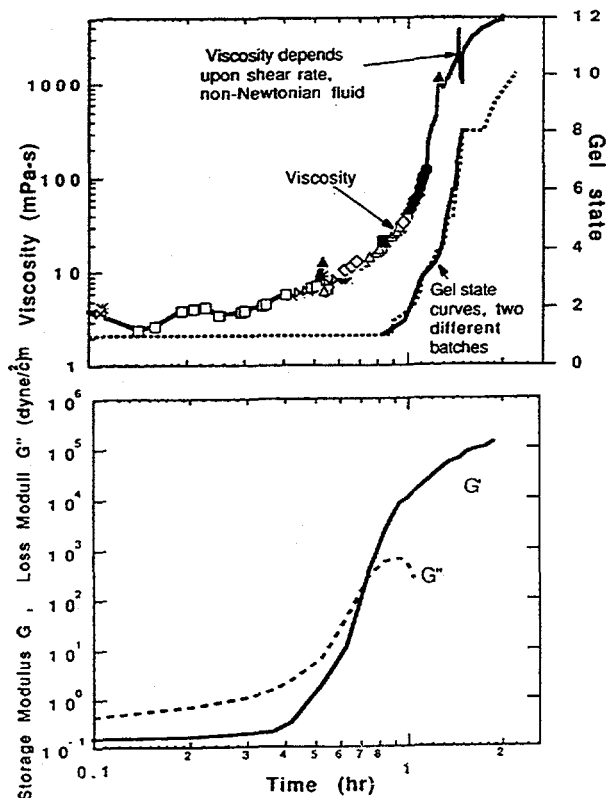

Figure 7. Viscosity during gelling, colloidal silica grout. This grout consisted of 5 parts by volume Nyacol 1440 colloidal silica, pH adjusted, and 1 part 70 g/L NaCl solution. The pH after brine addition was 9.03.
(a) Contraves Couette viscometer data and visual assessment of gel state.
(b) Rheometrics dynamic mechanical spectrometer data, separating viscous and elastic components of viscoelasticity.

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function can be used. We have used curves fit to the data of Fig. 7 (a) ; alternatively, effective viscosity can be calculated from the data of Fig. 7 (b). This latter option is equivalent to specifying a shear rate.

CS grout is miscible with pore water. The **mixing rule** is used to calculate the viscosity as a function of time and mass fraction of grout in the diluted grout. With the linear mixing rule, the viscosity is a weighted average of the viscosities of water and undiluted grout at the same time. At the user's option, other rules can also be used; Todd (1990) suggests a power-law mixing rule. For PSX grout, which is not miscible with water, no mixing rule is needed.

The **solidification model** describes how the grout changes from a liquid with increasing viscosity to a solid, resulting in a new porous medium. Tables 1 and 2 summarizes how the phases are dealt with before, during, and after solidification. After solidification, a new parameter set is calculated for the grouted soil. The parameters to be recalculated are porosity, permeability, relative permeability and capillary pressure functions, and initial liquid saturation. They are basically a function of the final grout content. Note that an initially homogeneous soil becomes heterogeneous with lower porosities and permeabilities in regions with a high final grout content. On the other hand, an initially heterogeneous soil may become more homogeneous on a scale smaller than the plume size, because highly permeable zones are preferentially clogged with grout compared to regions which are already relatively impermeable.

The mixing rule specifies the viscosity of grout that has been diluted with pore water; a high degree of dilution also prevents such a grout from soldifiying. For CS grout, the Solidification Model assumes that all the liquid in the pore space eventually solidifies only if the colloid content in the liquid phase exceeds a certain minimum concentration We found from jar tests that the threshold concentration for solidification is 70 % for DP5110 gelled with CaCl$_2$. PSX grout is not miscible with water, so no diution occurs and it all solidifies. For any kind of grout, after so;lidification, the porosity of the porous medium is reduced by the amount of grout that solidified, the absolute permeability is reduced, and new capillary pressure and relative permeability curves are calculated. Details of these calculations are presented in the user's manual (Finsterle et al. 1994, 1995). The reduction in absolute permeability is calculated by assuming that the CS grout wets the solid phase like water; i.e., partial clogging of the pore space by CS grout is conceptually similar to the permeability reduction due to phase interferences in a multiphase flow system. Since the grout-water mixture is the wetting fluid, one might take the relative permeability function of the non-wetting phase to calculate the absolute permeability of the new porous medium after solidification. For PSX grout, the PSX is assumed to wet the soil better than air but less well than water.

Due to the reduced pore sizes in the new porous medium, the capillary pressure (at any specified water saturation) of the grouted sand is expected to be greater than for the original ungrouted sand. We assume that the pore size distribution is shifted but that its shape is not

Table 1.   Concept and application of Solidification Model for CS grout

Time	Major Component in Phase				Comment
	Air	Water	Grout	Soil	
before solidification	gas	liquid		solid	grout and water are miscible
during solidification	gas	grout-water mixture solidifies if grout con-centration is sufficient		solid	apply solidification model
after solidification	gas	liquid	solid		new porous medium

Table 2.   Concept and application of Solidification Model for PSX grout

Time	Major Component in Phase				Comment
	Air	Water	Grout	Soil	
before solidification	gas	liquid 1	liquid 2	solid	grout and water are immiscible
during solidification	gas		grout solidifies	solid	all grout solidifies
after solidification	gas	liquid	solid		new porous medium

changed. Consequently, the exponents in the commonly used characteristic curves by Brooks-Corey or van Genuchten are not modified, either.

A sandbox demonstration and simulation

One of the goals of this project is to demonstrate formation of a continuous barrier injected from parallel horizontal wells some distance apart; another is to test the numerical simulator. Accordingly, we set up a small sandbox and injected PSX grout simultaneously through two wells; we also simulated the injection numerically. The soil sample, from a semi-arid environment, was sufficiently dry (about 5% saturation) that the aqueous phase could be ignored. Two-phase modeling (PSX and air) was used, with PSX as the wetting phase. To obtain data for simulations, we measured the hydraulic conductivity in sandpacks of Hanford soil using water, and measured the capillary pressure vs saturation curve in a pressure cell, also using water. The hydraulic conductivity of the sand was 8×10^{-2} cm/sec, isotropic. Constants $n = 1.53$ and $a = 7.2 \times 10^{-1}$ Pa for the van Genuchten equation were obtained by fitting the capillary pressure data (Figure 8). To estimate the capillary pressure and relative permeability curves for PSX-air in Hanford sand, we compared the observed capillary rise of water and PSX in glass tubes. The PSX rose one-half as far as water. Therefore we reduced a by a factor of 2; this factor includes the combined effects of surface tension and contact angle. The value of n was unchanged.

The sandbox was 120 cm (4 ft) high, 60 cm (2 ft) wide, and 10 cm (4 inches) deep from front to
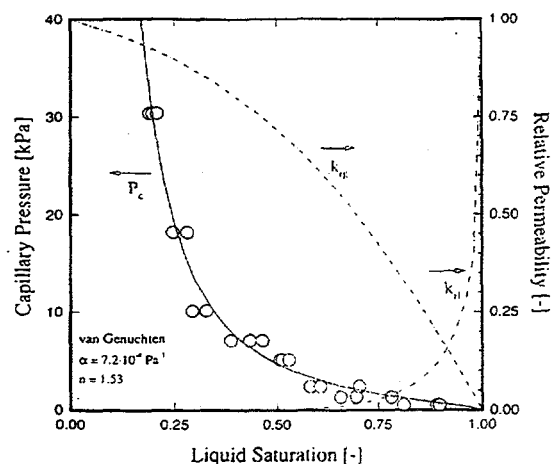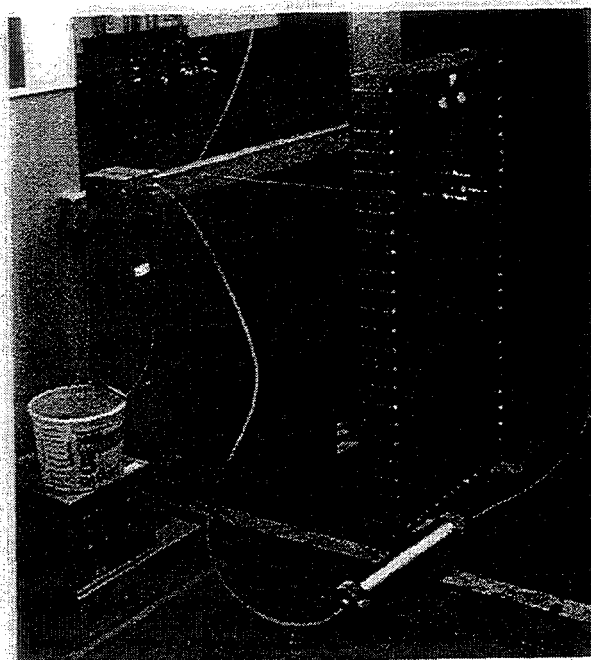
Figure 8. Capillary pressure curve for Hanford sand.

Figure 9. Sandbox experiment, in which two plumes of PSX were injected simultaneously. This photograph shows the syringe pump at left, which pumped water into a transfer cell (bottom), displacing PSX into a four-plex manifold (removed before this photo) that delivered grout to both ends of each of two wells. See also Figure 10.

back (Fig 9). The front and back surfaces were plexiglass to allow us to see the grout plume. Three wells (perforated 1/4 inch o.d. copper tubes) extended horizontally through the front and back surfaces. The wells are visible in the photographs of Figures 9 and 10; injection was through the lower two only (the third well was to permit an additional injection if plumes from the lower two failed to merge). Hanford sand was placed in the box by rolling a hopper with a perforated bottom back and forth over the open top of the box. To avoid disturbing the sand when installing the wells, sand was placed up to the level of the wells, and then the wells were installed, and more sand placed over the wells to the top of the box. This method of packing was not perfect, and a layer of coarser sand was visible at the front side of the box just below the level of the wells. This layer is visible in Figure 10. No such coarse layer was seen at the back of the box. The properties of this layer were not measured. For simulations, the hydraulic conductivity was taken as four times as great as the rest of the sandbox (factor based on backfit trials); the capillary and relative permeability curves were

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adjusted holding van Genuchten's n and α constant as in the solidification model.

PSX grout with 1.25 % catalyst was premixed as a batch and pumped from a transfer cell through a four-plex manifold into both ends of both wells. The penetration of the grout was clearly visible. Figure 10 shows the advance and final shape of the resulting grout plumes at the front and at the back of the box, and compares it to simulations. At the front of the box, where the layer of coarser sand was visible, we saw that grout first moved into the more permeable layer, but eventually was wicked into the finer sand above and below the permeable layer. Comparison of the photographs of the plumes with the simulations shows that the simulator reproduced the general shape of the injection.

SUMMARY AND CONCLUSIONS

Two grouts, colloidal silica and polysiloxane, have been developed that satisfy the requirements of low initial viscosity and controllable gel time in soil. For alkaline colloidal silica, gelling is accelerated uncontrollably by calcium in the soil unless the calcium is displaced by a NaCl preflush. For neutral colloidal silica stabilized by surface modification (Nyacol DP5110), no preflush is necessary.

For crosslinkable polysiloxane grout, the gel time is controlled by catalyst concentration. Soil accelerates the crosslinking of the polysiloxane, but this effect can be compensated for by reducing the catalyst concentration.

A numerical simulator has been developed that incorporates the mixing (if the grout is aqueous), gelling, and solidification of grout. It was used to plan laboratory experiments and field injections. In a sandbox experiment, the simulator accurately calculated the final shape and location of a pair of plumes of PSX grout.

ACKNOWLEDGMENT

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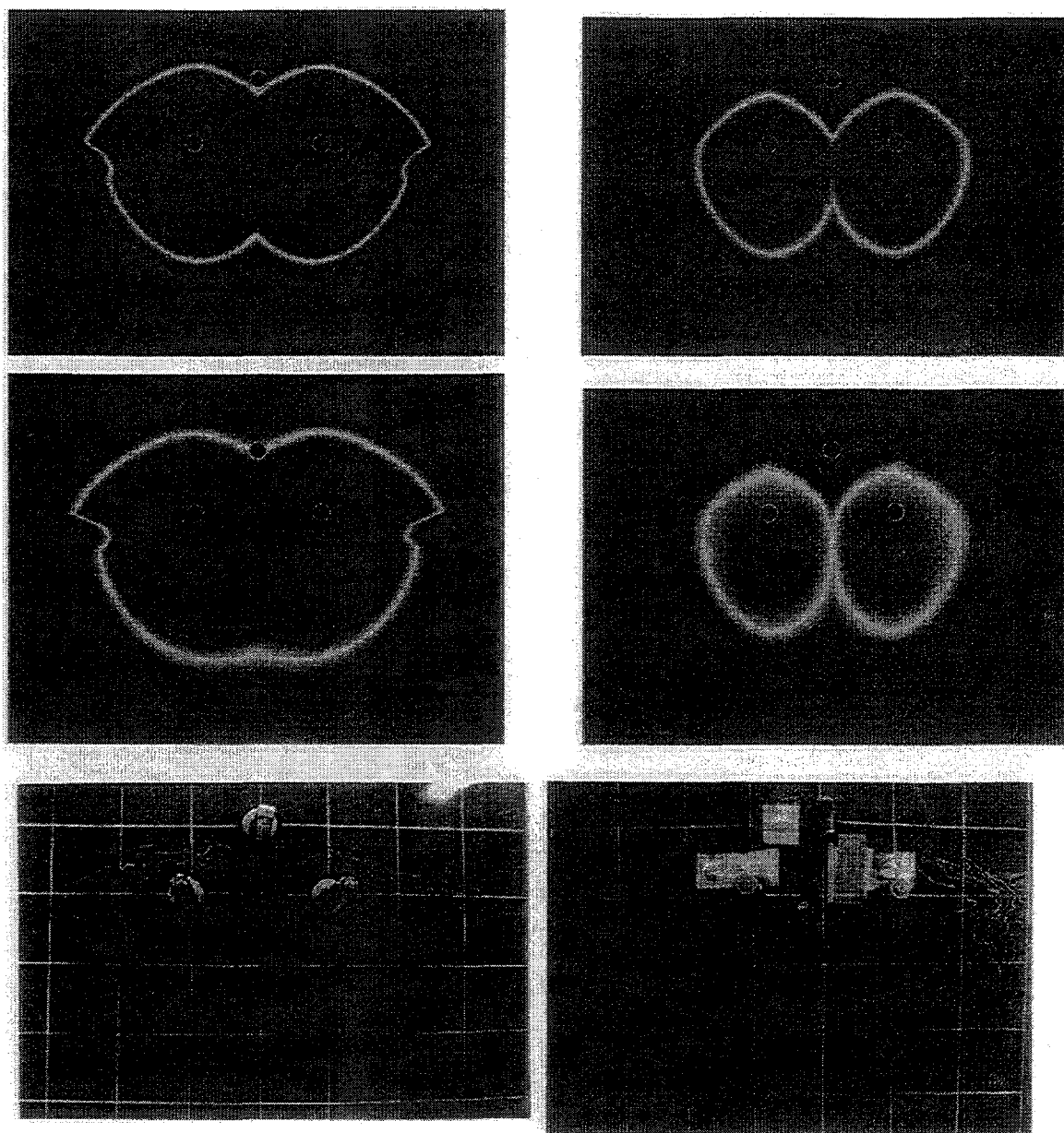Pruess, K, TOUGH2 - A general-purpose numerical simulator for multiphase fluid and heat flow,

Figure 10. Results of sandbox experiment. The left side shows the front of the sandbox (visible in Figure 9); the right side shows the back. Top: calculated grout saturation when injection is complete (2 hr). Middle: calculated grout saturation when gelling is complete. Bottom: photographs of plumes, with contours showing advance.

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