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Emplacement and Release of Brines from the Subsurface

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Abstract

Groundwater contamination by dense brines is addressed from a theoretical and experimental perspective. Numerous human activities have released denser-than-water aqueous solutions into the subsurface, including acid mine drainage, landfill leachates, nuclear wastes, and solid rocket fuel wastes. In addition, a number of subsurface remedial approaches propose the injection of dense, viscous aqueous solutions into the subsurface. The literature on brine transport processes in the subsurface is extensive, but has not addressed the unique characteristics that arise from the release and recovery of these solutions. The importance of gravitational and viscous instabilities was recognized, but the criterion developed by Hill in 1952 has not been fully utilized. An experimental program to measure brine dispersion in one-dimensional sand columns has verified the Hill stability criterion for two brines over a range in concentrations and medium permeabilities. In addition, the experimental results have quantified the dispersion coefficients for flows where gravity and viscosity have opposite effects on the displacement mechanisms. These results support the concept that dense brines can become long-term sources of groundwater contamination that will be difficult to detect and remediate.

Introduction and Problem Statement

The impact of brines on groundwater has been recognized for a long time. Freeze and Cherry (1979) define brines as having a total dissolved solids concentration in excess of 100 g L^{-1} to perhaps distinguish this level from seawater that is 33 g L^{-1} . There has been considerable work on the miscible transport of dense aqueous fluids in water-saturated porous media that has direct bearing on the transport and recovery of contaminants present within brines. These mechanisms are also significant during subsurface remediation when dense, reactive fluids are injected and expected to react with contaminants.

Industrial societies generate brines that are impacting groundwater resources and Table 1 lists a few examples of the activities and the resulting contaminants of concern. The oxidation of pyrite minerals produces acid rock drainage that is largely composed of sulfuric acid and is capable of mobilizing toxic metals. Noordstrom et al. (2000) have investigated one of the most extreme cases at an abandoned mine where the solution has an approximate density of 1.4 g cm^{-3} and toxic metal concentrations are in the g L^{-1} range. The low pH and high ionic strength of mine drainage limits metal removal by adsorption and precipitation reactions. The water quality standard listed for zinc in Table 1 is designed to protect aquatic life in surface waters. The final column of Table 1 is the volume of clean water required to dilute one volume of the mine water to reach the water quality goal. For zinc the dilution volume is 10^6 . Landfill leachates are complex mixtures of dissolved organic and inorganic matter that can be denser than water. For a reported dissolved solids concentration of 45 g L^{-1} a fluid density of 1.03 g cm^{-3} was estimated (Christensen et al., 2001). Leachates containing toxic chemicals like vinyl chloride would require a dilution factor of 10^4 to reach drinking water quality objectives. In the United States and the former Soviet Union, nuclear reactor fuel was reprocessed for the production of atomic weapons. This activity produced brines saturated in NaNO_3 that contained very high levels of fission products. The United States placed these wastes in underground storage tanks that leaked while the former Soviet Union released its waste brines into a surface water reservoir that recharged a deep aquifer. To meet drinking water standards for ^{90}Sr and ^{137}Cs requires dilution factors of 10^{10} and 10^8 ,

respectively (Bell and Bell, 1995). The final example in Table 1 is ammonium perchlorate, NH_4ClO_4 , which is a significant component of solid rocket fuel. The perchlorate anion is highly mobile in the subsurface since it is nonvolatile, does not engage in ion exchange reactions, and does not biodegrade under aerobic conditions. A saturated solution of ammonium perchlorate exceeds a proposed drinking water action level by at least 10^7 (Flowers and Hunt, 2000). While there is a long history of freshwater-seawater interactions in coastal aquifers, only a hundred-fold dilution is required to lower the dissolved solids concentration from 33 g L^{-1} to an acceptable level of 0.50 g L^{-1} . Table 1 indicates that there are many contaminants present within brines where a small waste volume has the potential for contaminating large volumes of groundwater.

The subsurface remediation community is also considering releasing water-miscible fluids into the subsurface to accomplish contaminant destruction, isolation, and removal. Table 2 lists various remediation processes, the reactive compounds proposed for injection, reactant concentrations in the injected fluid, and the approximate fluid density and viscosity. Hydrogen peroxide is being injected into soils and aquifers for the destruction of organic matter, and the injected concentrations are high when nonaqueous phase liquids are present as contaminants in the subsurface. In situ bioremediation of halogenated solvents is promoted by methanogenic conditions that are achieved by injecting organic compounds such as sodium lactate at very high concentrations. One means of binding toxic metals to soil and aquifer materials is to add a concentrated liquid solution of calcium polysulfide, CaS_x , that decomposes and releases sulfide for metal precipitation as insoluble sulfides. Another approach to contaminant sequestration is to inject a colloidal silica suspension that gels and forms an impermeable barrier when mixed in situ with NaCl brine. Trapped nonaqueous phase organic liquids can be solubilized by the injection of alcohol mixtures that are usually lighter than freshwater. These reactive, miscible fluids have densities and viscosities significantly different from the ambient groundwater and these properties will determine the transport pathway for the reactant and the mixing processes with the contaminants in the soils and aquifers.

As Tables 1 and 2 have shown, there are many instances where brines and other concentrated solutions miscible with water have been released into the subsurface environment or are planned for injection. These fluids have density and viscosity contrasts with ambient groundwater that will determine their transport in the subsurface either through the release of contaminants associated with brines into flowing groundwater or following the injection of remedial fluids and their eventual recovery.

Figure 1 presents a conceptual model for dense fluid transport in the saturated zone during and after the release of a brine. The aquifer is represented as locally homogeneous and isotropic with a lens and an aquitard having lower permeability. During the release, as represented in Figure 1a, the fluid falls almost vertically through the aquifer, mounds up on the lens, cascades over the edges of the lens and spills onto the confining layer. The continual release exposes the lens and the aquifer's confining layer to the concentrated brine, and depending upon the permeability of the lens and aquitard, some fluid will physically sink and some fluid components will diffuse into these non-flowing regions. Some time after the release was stopped; the aquifer is represented in Figure 1b with pools of dense fluid in the lens and in pockets within the confining layer. Contaminants within the dense fluid are slowly released into the flowing groundwater by molecular diffusion through the stagnant

water followed by advection and dispersion within the aquifer. In spite of the miscibility of these fluids with water, the lack of mixing processes within the trapped regions suggests components of the dense fluids will be slowly released into groundwater, particularly for wastes summarized in Table 1. Similar transport and release scenarios are expected following the injection of concentrated fluids for remediation purposes.

Analysis of Dense Plumes

Research in quantifying fluid stability in variable density systems initially examined convective currents in a fluid subject to vertical temperature gradients when Lapwood (1948) studied temperature-induced instabilities in a water-saturated porous medium heated from below. Wooding (1959) extended the stability analysis to include systems where the solute causes the density contrast. List (1965) extended the analyses of Lapwood and Wooding by studying the mixing zone between two horizontally flowing, stratified fluids in which the heavier fluid overlies the lighter. This system is inherently unstable, but quasi-stable flow regimes can occur when instabilities generated at the source of the heavier fluid are dampened by the physical system. Ostrom et al. (1992) followed List's analysis and attempted to predict the onset of instability, measured during experiments, using dimensionless parameters. Variable density flow and mixing in heterogeneous media was studied experimentally by Schincariol and Schwartz (1990). Schincariol et al. (1997) followed these experiments with numerical investigations that confirmed earlier assertions that all stratified systems are inherently unstable with the onset of instability dependent on the wavelength of the initial perturbation. But in numerical systems, self-propagating numerical errors can perturb the interface and lead to the generation of "phantom" instabilities.

Completely separate from the natural porous media focus summarized above has been an alternative literature based on porous media reactors for product separations. Hill (1952) identified the key characteristics of miscible displacements under the influence of both gravitational and viscous forces. He observed the removal of impurities during commercial sugar production using an adsorptive porous media filter. Once the filter had been spent, it was cleaned by displacing the sugar liquor with clean water until the adsorbed impurities were removed. After cleaning, the water within the filter was displaced by the sugar liquor. Hill observed that downward flow of water and sugar solutions could be either stable or unstable depending on whether density or viscosity dominated. Hill (1952) provided the methodology for determining the stability of miscible displacements by downward flow. Since brines are generally more dense and viscous than the ambient groundwater, Hill's analysis can be used to analyze dispersion regimes during the vertical transport of brines.

Hill's criterion for the stability of miscible displacements is expressed in terms of two dimensionless numbers, a gravity number, N_G , which is the ratio of density driven flow velocity to the imposed pore water velocity:

$$N_G = \frac{k g (\rho_R - \rho_D)}{\mu_D n U_{pore}}$$

where k is permeability, g is gravitational acceleration, ρ_R is the resident fluid density, ρ_D is the displacing fluid density, μ_D is the displacing fluid viscosity, n is porosity, and U_{pore} is the fluid velocity in the pore space, positive downward. Fluid displacements are gravitationally

stable if the gravity number is positive. The second dimensionless number is the mobility number, M , which is the ratio of the viscosity of the resident fluid, μ_R to the displacing fluid, μ_D :

$$M = \frac{\mu_R}{\mu_D}$$

Fluid displacements are viscously stable if M is less than one. The combined criterion for stability of miscible displacements that incorporates both gravitational and viscous factors is

$$N_G > M - 1$$

If the displacing fluid has a higher density and viscosity than the resident fluid, as is the case with brine displacing water, then the mobility ratio is less than one and stable gravity numbers can be negative.

Hill's stability criterion for brine/freshwater miscible displacements is represented by a plot of the mobility ratio as a function of the gravity number in Figure 2. Based upon the stability criterion, the diagram in Figure 2 is subdivided into four distinct regions. Region I ($N_G > 0$, $M > 1$) represents a conditionally stable condition, i.e. displacements are stabilized by gravitational forces, but are destabilized by viscous forces. Region II ($N_G > 0$, $M < 1$) represents an inherently stable condition, i.e. displacements are stabilized by both gravitational and viscous forces. Region III ($N_G < 0$, $M < 1$) also represents a conditionally stable condition, i.e. displacements are destabilized by gravitational forces, but are stabilized by viscous forces. Region IV ($N_G < 0$, $M > 1$) represents an inherently unstable condition, i.e. displacements are destabilized by both gravitational and viscous forces.

Procedures

A laboratory-scale experimentation program was designed to investigate if Hill's stability criterion determines column dispersion. This section summarizes the procedures and apparatus and greater detail is provided in Flowers (2003). The experiments examined the downward displacement of water by brine and brine displacement by water.

Figure 3 shows a schematic of the experimental apparatus employed in this investigation. The brine and freshwater were held in constant head 50-liter Mariotte bottles. The fluid flow rate was maintained by a pulseless flow pump with the flow rate determined manually, and the selection of fluid flowing into the column determined by a three-way valve. Three different porous medium columns were utilized to achieve a range of permeabilities and flow rates. Two different sand sizes were used, the smaller sand passed through a #30 sieve (0.6 mm), but was retained on a #40 sieve (0.43 mm); and the larger sand passed through a #16 sieve (1.18 mm), but was retained on a #20 sieve (0.85 mm). A range of fluid velocities was achieved by using two column diameters as indicated in Table 3. Each column was packed to achieve a homogeneous and isotropic porous medium. The method selected was a wet packing technique similar to that suggested by Oliviera *et al.* (1996). The column was wet packed in 1 cm lifts by sprinkling sand through water, vibrating the whole system, and compacting with a steel rod. Stainless steel disks were placed at the inlet and outlet of the columns in order to achieve plug flow entrance and exit conditions. Tracer tests with the disks flush against each gave dispersion coefficients much less than column dispersion coefficients. The column effluent was passed through a small volume where conductivity

was measured using a Jenway model 1440 meter with a conductivity sensor having a cell constant of approximately 10 cm^{-1} . Conductivity was measured continuously and recorded every 10 seconds. Salt concentration was determined from conductivity readings through a calibration process that recognized the nonlinear relationship between conductivity and the salt at the concentrations used in these experiments.

A typical experiment involved three displacement cycles, where a displacement cycle consisted of approximately three pore volumes of brine displacing the resident freshwater, followed by three pore volumes of freshwater displacing the resident brine. For each flow rate, or after three displacement cycles, the porous media column was degassed by back flushing with carbon dioxide followed by deionized water. The carbon dioxide was at a pressure of approximately 70 kPa and was followed by approximately 10 pore volumes of deionized water to dissolve any residual CO_2 gas.

The data were used to develop an unbiased estimate of U_{pore} and D_{PM} by fitting the measured raw data to the one-dimensional advection-dispersion equation for homogeneous, isotropic saturated porous medium (Freeze and Cherry, 1979):

$$D_{\text{PM}} \frac{\partial^2 C}{\partial x^2} - U_{\text{pore}} \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

Where D_{PM} is the longitudinal dispersion coefficient, U_{pore} is the pore water velocity, C is the concentration, x is the direction of the mean flow path, and t is time. The initial and boundary conditions relevant to this experimental endeavor are:

$$C(x \geq 0, t = 0) = 0$$

$$C(x = 0, t \geq 0) = C_0$$

$$C(x \rightarrow \infty, t \geq 0) = 0$$

The complete solution to this system is (Freeze and Cherry, 1979):

$$C_{\text{CS}}(x, t; U_{\text{pore}}, D_{\text{PM}}) = \frac{C_0}{2} \left[\text{erfc} \left(\frac{x - U_{\text{pore}}t}{2\sqrt{D_{\text{PM}}t}} \right) + \exp \left(\frac{U_{\text{pore}}x}{D_{\text{PM}}} \right) \text{erfc} \left(\frac{x + U_{\text{pore}}t}{2\sqrt{D_{\text{PM}}t}} \right) \right]$$

where $\text{erfc}()$ is the complimentary error function. The parameters U_{pore} and D_{PM} were determined by an iterative technique that produced a minimum of the sum of the squared differences between measured data and model predictions (Toride *et al.*, 1999). Several artificial time and concentration data sets were generated using various known values of U_{pore} and D_{PM} and the iterative technique arrived at known values with an error less than 0.01%.

The mixing behavior in the three columns without density and viscosity contrasts was determined using a series of dilute tracer displacement experiments. Calcium chloride tracer solutions of 0.1 and 0.2 g L^{-1} were substituted for the freshwater and brine using the same analysis procedure for determining the dispersion coefficient. For each column, three experimental cycles were completed for various flow rates that covered the entire range of the pump. The results of the tracer characterization for all three columns are presented in Figure 4. The dispersion coefficients were fitted to a power function of the velocity as indicated in the figure.

Two different salt solutions were chosen as experimental brines. Calcium chloride was chosen because it has a high solubility resulting in dense brines with increased viscosities as shown in Figure 5. Due to limitations of the conductivity meter, 263 g L^{-1} was the maximum calcium chloride concentration utilized. To separate the effects of density from viscosity, potassium chloride was chosen as the second brine since it has a viscosity independent of brine concentration. Table 4 summarizes the specific experimental conditions and the properties of the brines and Table 5 summarizes the mobility number and critical gravity number, $N_{G,c} = M - 1$ for the experiments. Experimental conditions in terms of the stability criterion are shown in Figure 6. The choice of these experimental conditions was to test the tradeoff between viscous and gravitational effects on dispersion, both in cases where gravity is expected to be destabilizing ($N_G < 0$) and when gravity is stabilizing ($N_G > 0$).

Results

Over 380 experiments were conducted to verify the stability criterion given simply by $N_G > M - 1$. The experimental results are given first for gravitational unstable flows, $N_G < 0$ and then for gravitationally stable flows, $N_G > 0$. Tables of fitted parameters and plots of breakthrough curves are given in Flowers (2003). Representative breakthrough curves are shown to demonstrate that mixing processes are only approximately diffusive, but dispersion coefficients normalized by dilute tracer dispersion under identical flow conditions are a convenient means to generalize the results.

Gravitationally Unstable Flows

Figures 7 and 8 show representative breakthrough curves for experimental conditions that span the stability criterion when $N_G < 0$. In Figure 6, the mobility ratio is fixed at 0.65 since 157 g L^{-1} CaCl_2 is the brine in both cases and the critical gravity number is predicted to be $M - 1 = -0.35$. Results for two different velocities are shown that have different gravity numbers. The experimental results for $N_G = -1.06$, are fitted to a dispersion coefficient 10 times the tracer dispersion coefficient at that velocity, while for $N_G = -0.093$ the dispersion was only 1.3 times the tracer dispersion. These results show a qualitative agreement with Hill's stability criterion. In Figure 8, two experiments were conducted with the gravity number fixed at -0.3 by comparing CaCl_2 brines at different concentrations. When the mobility ratio is 0.48 the brine has a dispersion coefficient that is only 0.815 times that of the tracer and viscosity has stabilized and perhaps suppressed the mixing. Hill predicted stability for $N_G > M - 1 = -0.52$. On the other hand, when the mobility ratio is 0.88 gravity overcomes viscous stabilization leading to brine dispersion that is 1.45 times greater than that of a tracer. Hill's criterion would predict that only for gravity numbers greater than -0.12 would stable displacements exist. These two examples show that a combination of gravity and viscosity contrast jointly control tracer dispersion and Hill's criterion is obeyed.

All gravitationally unstable data are represented in Figure 9 as a plot of dispersion normalized by tracer dispersion plotted against gravity number. For gravity numbers that are greater than -0.3 the dispersion coefficients are very close to those determined for dilute tracers. For gravity numbers less than (more negative than) -0.3 there is a consistent increase in dispersion with decreasing gravity number. This trend is demonstrated by the KCl results where the mobility ratio is 1 and the displacement is always gravitationally unstable. The

CaCl₂ brines have different critical gravity numbers that determine when gravitational instabilities dominate over viscous stabilization.

Gravitationally Stable Flows:

As indicated in Figure 6, a series of experiments was conducted at positive gravity numbers where downward flowing freshwater displaced brines. Under these conditions gravity-stabilized displacements can be destabilized by viscosity differences for the calcium chloride brines. This viscous instability does not exist for the potassium chloride displacements since the viscosities are matched. The data set allows for an analysis of enhanced mixing due to viscous fingering as well as suppressed mixing due to gravitational stabilization. As with the brine-displacing-water experimental realizations, the analysis is based on the measured dispersion coefficient normalized by tracer dispersion coefficients at the same velocity for a range of density contrasts, velocities, and when appropriate, viscosity differences.

Figure 10 summarizes the gravitationally stabilized data in a plot of normalized dispersion plotted against gravity number. For gravity number greater than about 1, all experiments exhibit reduced dispersion compared to dilute tracers. As the gravity number decreases, the densest CaCl₂ brine at 263 g L⁻¹ shows a dramatic increase in dispersion at about the gravity number expected for instability predicted from Hill as $N_G < M - 1 = 0.53$. Figure 10 includes an asymptotic normalized dispersion caused purely by viscosity contrast that is described in Flowers (2003). The 157 g L⁻¹ CaCl₂ brine has a normalized dispersion coefficient that increases for gravity numbers less than 0.34, as predicted by Hill's stability criterion. Furthermore, the normalized dispersion coefficients are approaching the predicted asymptotic limit of 3 at the lowest gravity numbers. For the 52 g L⁻¹ CaCl₂ brine, mixing is suppressed at all gravity numbers and the behavior is very similar to the results obtained with the KCl brines. These results demonstrate that viscosity can destabilize gravitationally stable displacements and the experimental onset of the instability is consistent with the stability criterion developed by Hill.

Conclusions

While brines have been recognized as possible groundwater contaminants for some time, conditions are identified where contaminants dissolved within brines will represent long-term sources of groundwater contaminant, in spite of being completely miscible with water. The density-driven flow of brines to the bottom of aquifers and into less permeable regions leads to the emplacement of these brines and their slow release into the flowing groundwater. In addition, a number of subsurface remediation technologies have been based on the injection and recovery of reactive solutions that have densities and viscosities significantly different from ambient groundwater. These situations lead to an experimental program that investigated the displacement of brines by freshwater and freshwater displacement of brines during vertical transport through water-saturated porous media.

The experimental program was driven by a stability criterion developed originally by Hill that accounted for viscous and gravitational effects. Meter-scale sand columns were utilized to measure dispersion of tracers and concentrated brines that spanned Hill's stability regions. The dispersion data were used to arrive at normalized dispersion coefficients as experimental functions of the gravity number that is the ratio of gravitationally driven flow to the imposed

flow. The second dimensionless number is the mobility number that is the ratio of fluid viscosities. These results provide a foundation to address brine transport and emplacement within water-saturated porous media and for the quantitative consideration of contaminants presents within brines.

Additional studies are warranted on the dispersion, emplacement and release of brines from the vadose zone as well as the delivery and recovery of dense brines used for remediation. These results also suggest a means for interpreting the occurrence of groundwater contamination where dense brines might have been released. Under these circumstances, isolated source terms will be difficult to detect and groundwater sampling devices that integrate over the whole aquifer depth will not provide adequate characterization of such sources. As with other examples of groundwater contamination, understanding the sources of contamination is essential in protecting and addressing the long-term recovery of this valuable resource.

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Table 1. Properties of contaminated brines

Occurrence	Source of Brine	Density [g cm ⁻³]	Contaminant	Env. Level	Water Quality Criteria	Dilution Required
Acid Rock Drainage	H ₂ SO ₄	1.4	Zn	23.5 g/L	80 µg/L	10 ⁶
Landfill Leachate	TDS	1.03	Vinyl Chloride	40 mg/L	2 µg/L	10 ⁴
Nuclear Fuel Processing	NaNO ₃	1.5	⁹⁰ Sr	4x10 ¹⁰ Bq/L	10 Bq/L	10 ¹⁰
			¹³⁷ Cs	8x10 ⁹ Bq/L	50 Bq/L	10 ⁸
Solid Rocket Fuel	NH ₄ ClO ₄	1.11	ClO ₄ ⁻	180 g/L	6 µg/L	10 ⁷

Table 2. Brines being considered to promote subsurface remediation.

Purpose	Injected Fluid	Concentration	Density [g cm ⁻³]	Viscosity [cP]
Organics oxidation	H ₂ O ₂	50% (w)	1.2	1.18
Bioremediation by reductive dehalogenation	Sodium lactate	60%	1.31	≈80-160
Metal binding	CaSx	29%	1.27	17
Permeability reduction	Colloidal Silica	40%	1.3	15
	NaCl (catalyst)	6%	1.04	1.1
NAPL mobilization by alcohol	Ethanol + n-pentanol + water	70% 12% 18%	0.811	2.2

Table 3. Column properties.

Column Description	Inside Diameter [cm]	Grain Diameter [mm]	Length of Sand Pack [cm]	Permeability [10 ⁻⁸ cm ²]	Porosity
Small	3.19	0.5	97.1	92.5±0.7	0.382
Low k Large	5.78	0.5	98.2	91.9±0.2	0.366
High K Large	5.78	1.0	96.3	353±2	0.342

Table 4. Physical properties of the experimental brines at 20 degrees Celsius (Lide, 2000) and experimental conditions.

Brine	Concentration [g L ⁻¹]	Density [g cm ⁻³]	Dynamic Viscosity [cP]	Small Column	Low k Large Column	High k Large Column
CaCl ₂	52.1	1.040	1.14	X	X	X
	108	1.084	1.32	X		
	157	1.120	1.51	X	X	X
	208	1.158	1.76	X		
	263	1.198	2.13	X	X	X
KCl	62.3	1.037	0.99			X
	153	1.091	0.99			X

Table 5. Experimental conditions and critical gravity numbers for brine displacing water and water displacing brine.

Brine	Concentration [g L ⁻¹]	Brine Displacing Water		Water Displacing Brine	
		M	N _{G,c}	M	N _{G,c}
CaCl ₂	52.1	0.875	-0.125	1.14	0.14
	108	0.758	-0.242	1.31	0.31
	157	0.663	-0.337	1.51	0.51
	208	0.567	-0.433	1.76	0.76
	263	0.470	-0.530	2.13	1.13
KCl	62.3	1.0	0	1.0	0
	153	1.0	0	1.0	0

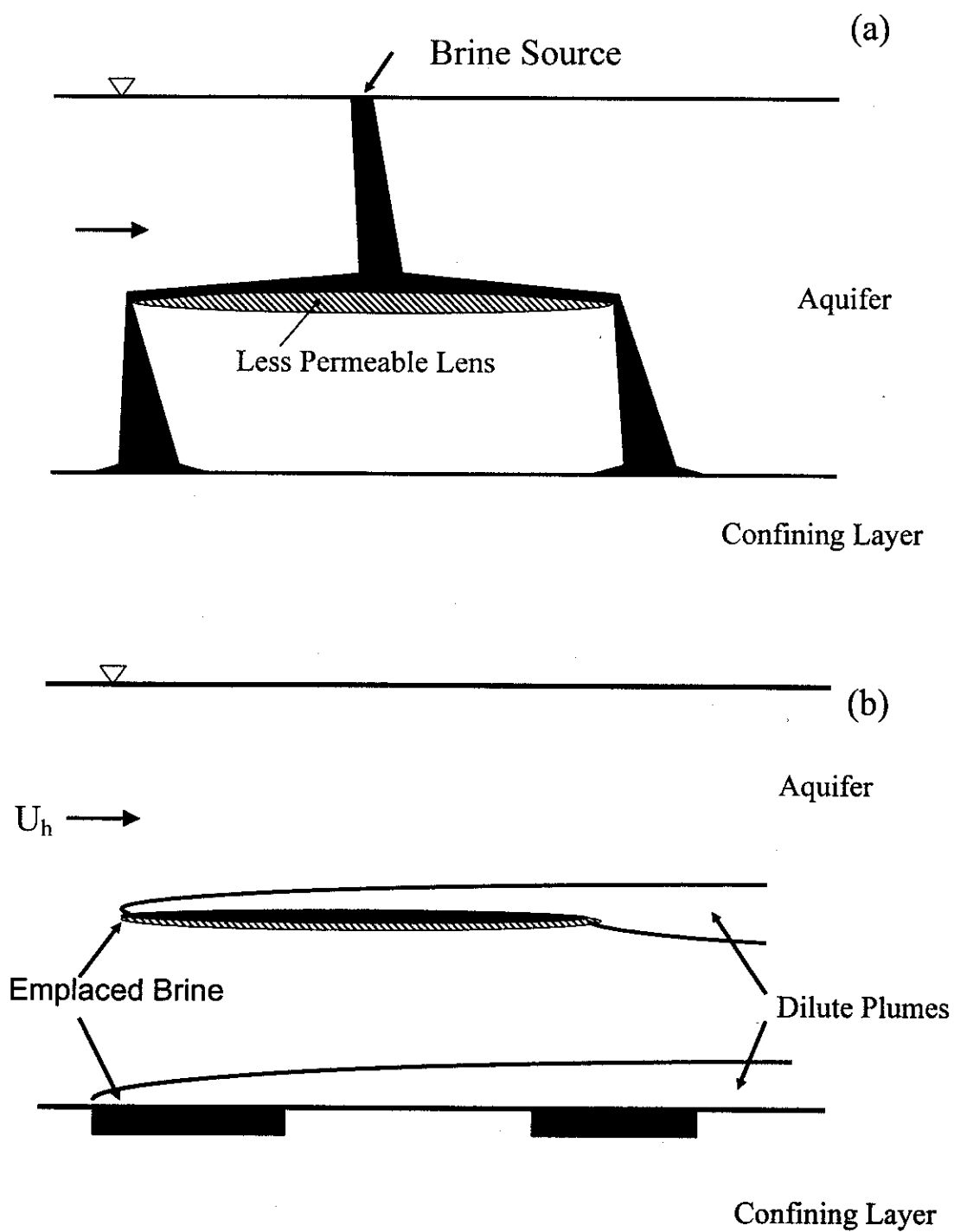


Figure 1. Emplacement and release of dense brines in the subsurface. (a) during emplacement, and (b) after the source has been discontinued.

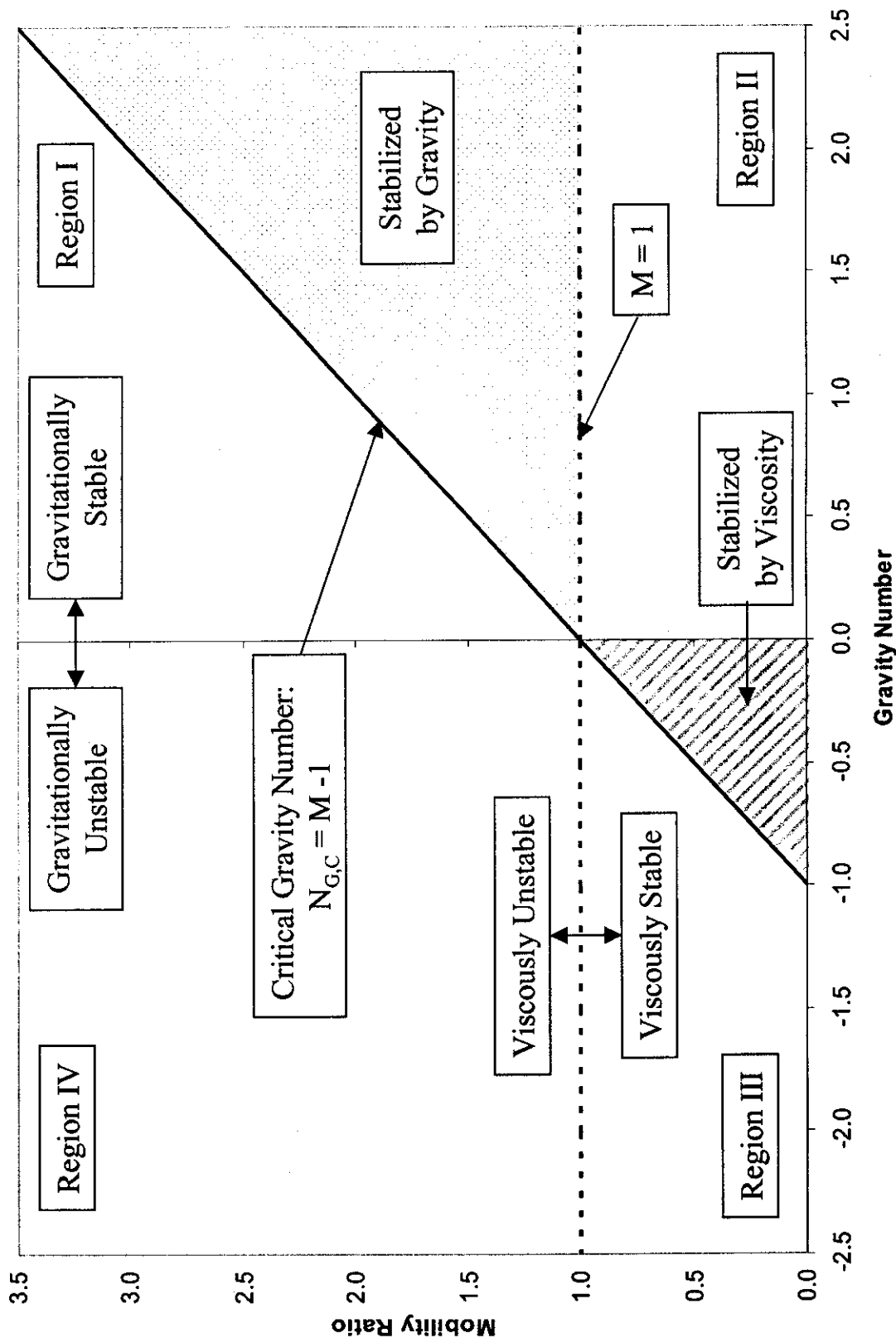


Figure 2. Stability diagram for brine/freshwater miscible displacements.

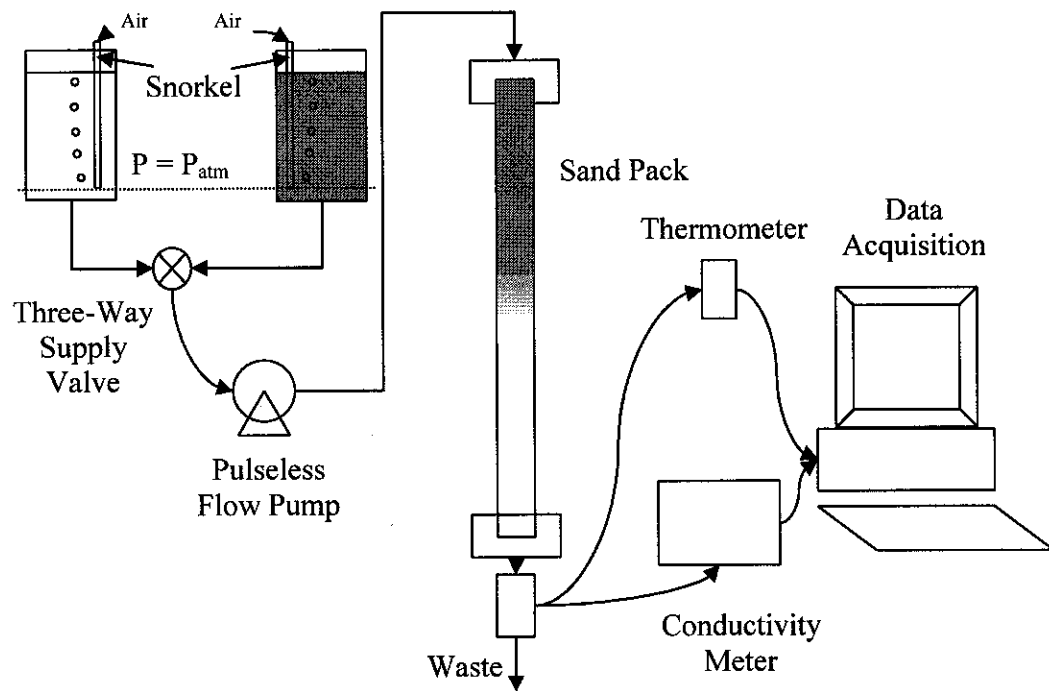


Figure 3 Schematic of laboratory-scale experimental program

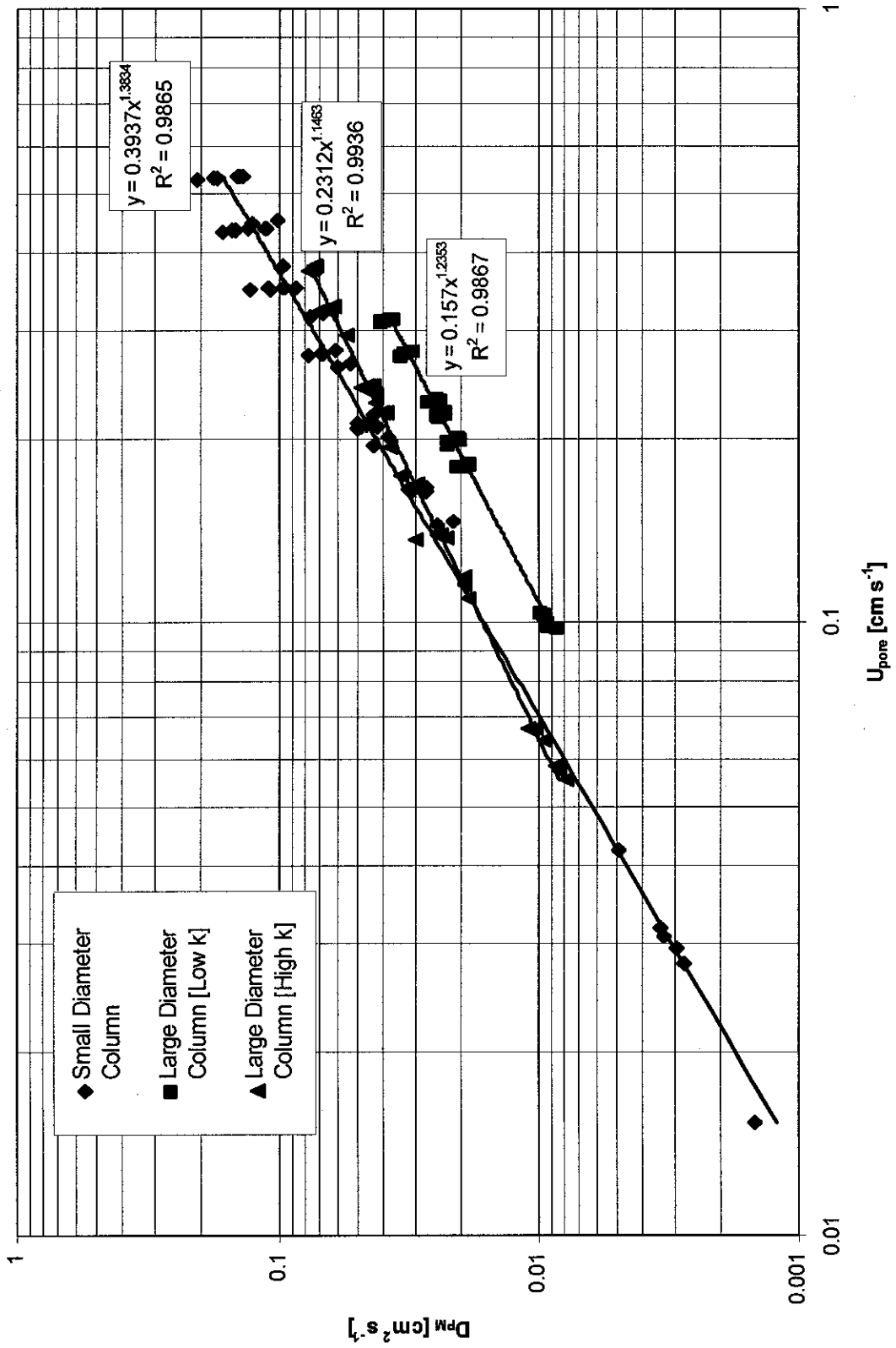


Figure 4 Tracer dispersion coefficients as a function of pore water velocity

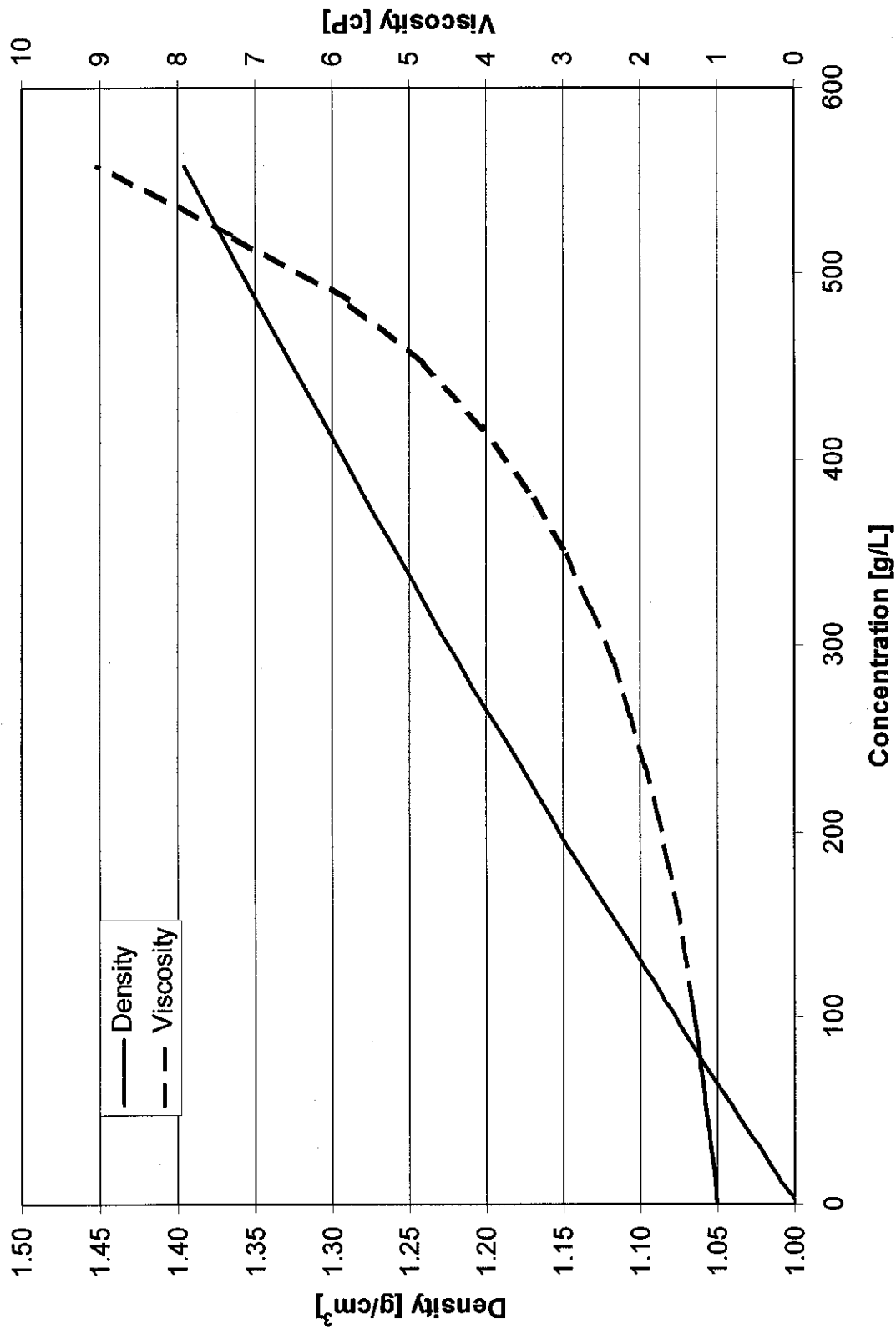


Figure 5 Calcium chloride physical properties as a function of concentration at 20 degrees Celsius [Lide, 2000]

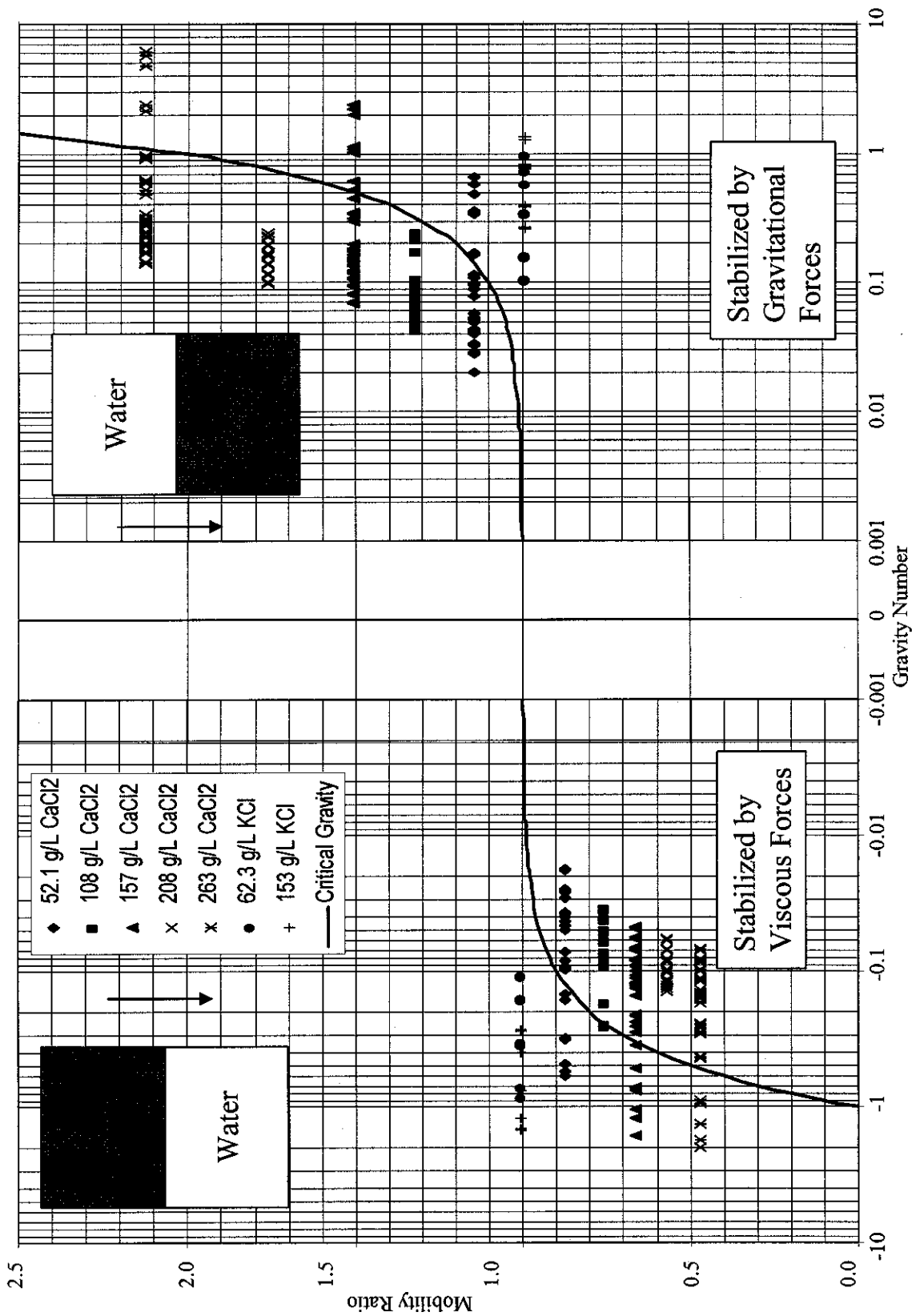


Figure 6. Experiments represented on the stability diagram.

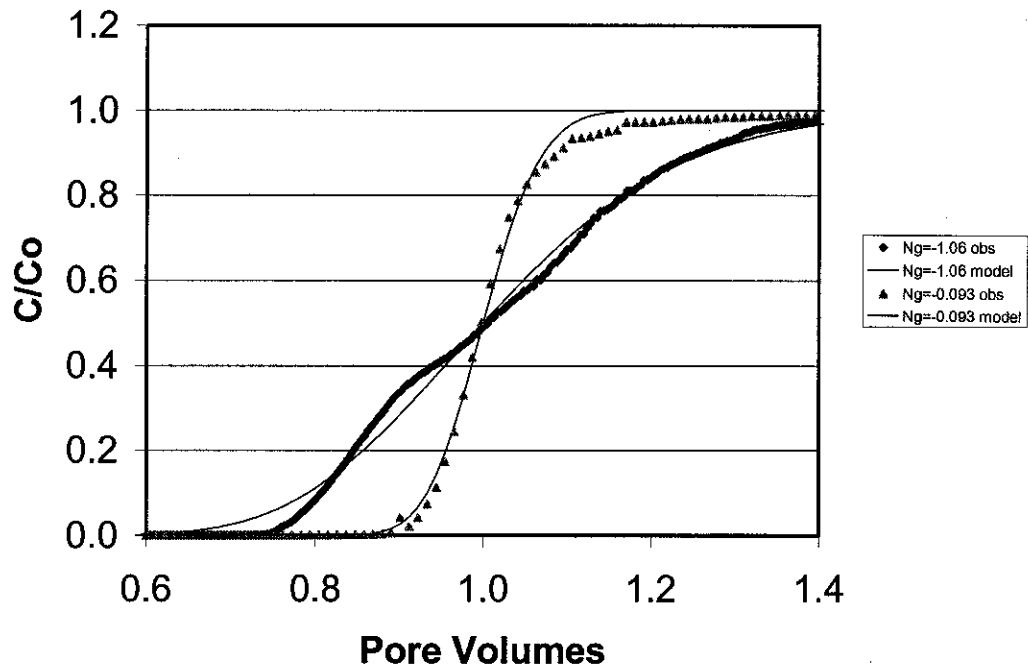


Figure 7. Breakthrough curves of CaCl_2 brines with $M = 0.65$ under stable ($N_G = -0.093$) and for unstable ($N_G = -1.06$) displacement conditions.

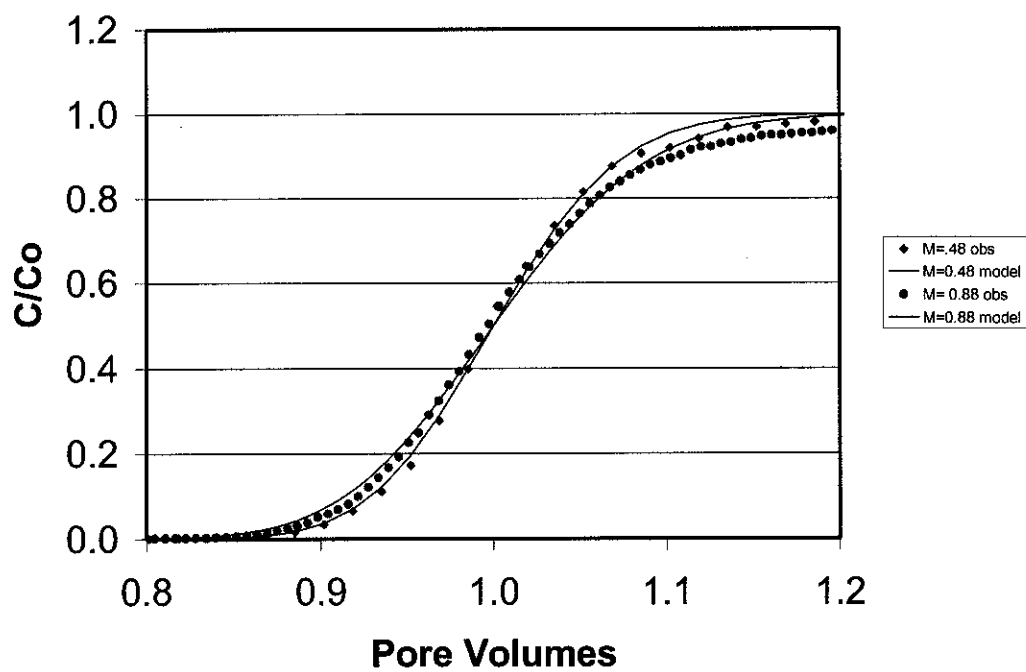


Figure 8. Breakthrough curves of CaCl_2 brines for $N_G = -0.30$ under stable ($M = 0.48$) and for unstable ($M = 0.88$) displacement conditions.

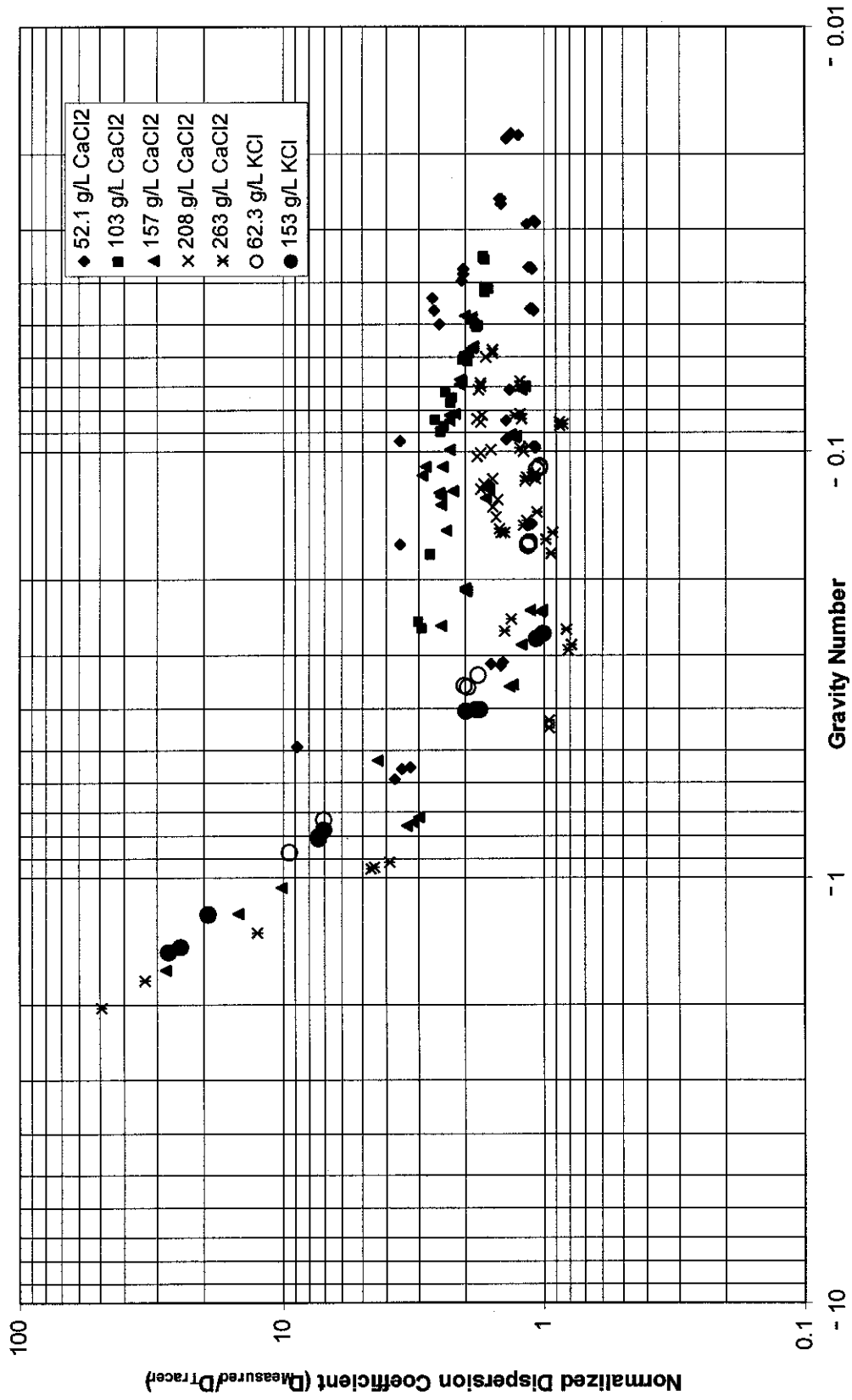


Figure 9. Compiled data for gravitationally unstable displacements

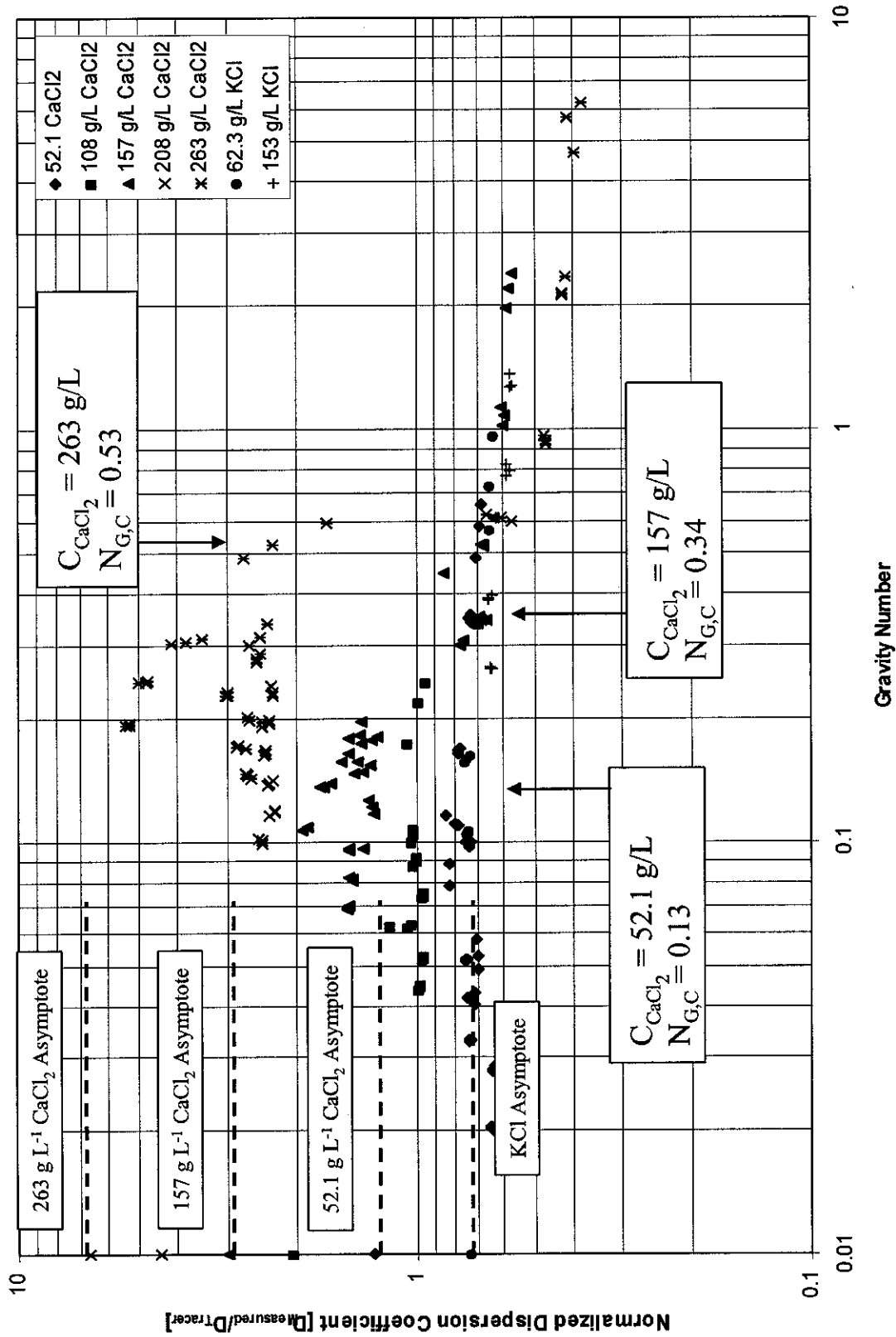


Figure 10. Normalized dispersion coefficients as a function of the gravity number for gravitationally stable displacements. The horizontal dashed line represents asymptotic normalized dispersion coefficients for purely viscous instabilities.