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**Oil Recovery Improvement Through Profile
Modification by Thermal Precipitation**

**Final Report for the Period
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ABSTRACT

The objective of this research project has been to investigate the potential for using temperature-dependent (thermal) precipitation of chemicals to reduce the porosity and permeability of porous rocks. The method consists of injecting hot water that is saturated in a chemical that will precipitate upon cooling. Through this process, the permeability of thief zones in oil reservoirs could be reduced, allowing improved recovery by secondary and tertiary recovery processes.

The chemical literature was reviewed for environmentally safe chemicals that have a suitable temperature-dependent solubility for the thermal precipitation process. Four suitable chemicals were identified: boron oxide, potassium carbonate, sodium borate, and potassium chloride.

An experimental apparatus was constructed to test the thermal precipitation process at high temperatures and pressures. Data was collected with clastic Berea sandstone cores using two chemicals: potassium carbonate and sodium borate. Data was also collected with limestone cores using potassium carbonate. The porosities and permeabilities were measured before and after being treated by the thermal precipitation process.

A theoretical study of the process was also conducted. A model for predicting the fractional reduction in porosity was developed that is based on the temperature-dependent solubility of the chemical used. An empirical model that predicts the fractional reduction in permeability in terms of the fractional reduction in porosity was then developed for Berea sandstone. Existing theoretical models for estimating the permeability of porous media were tested against the measured data. The existing models, including the widely-used Carman-Kozeny equation, underpredicted the reduction in permeability for the thermal precipitation process.

This study has shown that the thermal precipitation process has considerable potential for the controlled reduction in porosity and permeability in geologic formations. A design study to determine how the process would work in the field is recommended.

EXECUTIVE SUMMARY

Many oil fields are abandoned while they still contain significant reserves of oil because it is uneconomical to continue producing oil from them. Reservoir heterogeneities are the major cause of the low volumetric sweep efficiencies found in many oil recovery projects. Improved oil recovery processes, e.g., water, steam, carbon dioxide, or miscible gas injection, can effectively sweep oil from high permeability zones (thief zones) but will often by-pass oil in lower permeability zones. In many cases, the oil content of the by-passed zone is greater than that of the swept zone.

The objective of this research project has been to investigate the potential for using temperature-dependent (thermal) precipitation of chemicals to reduce the porosity and permeability of high permeability zones. The method consists of injecting hot water that is saturated in a chemical that will precipitate upon cooling. Through this process, the permeability of thief zones in oil reservoirs could be reduced, allowing improved recovery by secondary and tertiary recovery processes.

The chemical literature was reviewed and 16 chemicals were identified as having a suitable temperature-dependent solubility. Material Safety Data Sheets were obtained and reviewed for these chemicals to determine any safety, health, and environmental hazards. From this review, four chemicals were identified as being suitable for the thermal precipitation process: boron oxide, potassium carbonate, sodium borate, and potassium chloride.

An experimental apparatus was constructed to test the thermal precipitation process at high temperatures and pressures. Data was collected with clastic Berea sandstone cores using two chemicals: potassium carbonate and sodium borate. Data was also collected with limestone cores using potassium carbonate. The porosities and permeabilities were measured before and after being treated by the thermal precipitation process. The thermal precipitation process successfully lowered the permeability of the samples tested in the laboratory. Permeability reductions of 50% were observed in Berea sandstone for reductions in porosity of 15%. Reductions in permeability in Indiana limestone were virtually 100% for the same reduction in porosity. The data for Berea sandstone are shown in the following figure.

A theoretical study of the process was also conducted. A model for predicting the fractional reduction in porosity was developed that is based on the temperature-dependent solubility of the chemical used. This model is given by

$$\frac{\Delta\phi}{\phi} = \left(\frac{M_h - M_l}{M_h + M_w} \right) \left(\frac{\rho_h}{\rho_p} \right) S_s .$$

where M_h and M_l are the mass of chemical dissolved at high and low temperature in a mass of water, M_w . The density of the solution at high temperature is ρ_h and the density of the precipitated solid is ρ_p . The fraction of the pore space containing the injected solution is S_s .

An empirical model that predicts the fractional reduction in permeability in terms of the fractional reduction in porosity was then developed for Berea sandstone. The simplest model for predicting the permeability reduction is given by

$$\frac{\Delta K}{K} = 1 - \exp\left\{-5 \frac{\Delta \phi}{\phi}\right\}.$$

Existing theoretical models for estimating the permeability of porous media were tested against the measured data. The existing models, including the widely-used Carman-Kozeny equation, underpredicted the reduction in permeability for the thermal precipitation process.

This study has shown that the thermal precipitation process has considerable potential for the controlled reduction in porosity and permeability in geologic formations. A design study to determine how the process would work in the field is recommended.

1. INTRODUCTION

Many oil fields are abandoned while they still contain significant reserves of oil because it is uneconomical to continue producing oil from them. Reservoir heterogeneities are the major cause of the low volumetric sweep efficiencies found in many oil recovery projects. Improved oil recovery processes, e.g., water, steam, carbon dioxide, or miscible gas injection, can effectively sweep oil from high permeability zones (thief zones) but will often by-pass oil in lower permeability zones. In many cases, the oil content of the by-passed zone is greater than that of the swept zone.

A number of methods to divert injected fluids from depleted, high permeability zones to oil-bearing, low permeability zones have been proposed. While many of these methods show promise, reliable, cost effective methods for improving oil recovery by profile modification through plugging high permeability zones are still needed.

The purpose of this project is to evaluate a new method to reduce the permeability of porous media. This method is based on the temperature-dependent solubility of chemicals in water and the precipitation of those chemicals when the temperature is reduced.

In this process, a hot solution that is saturated (or nearly saturated) with the chosen chemical is injected into the porous medium. The chemical used must have a high solubility in water at high temperature and a much lower solubility at ambient temperature. Once the solution reaches the desired location, it is allowed to cool, precipitating the excess chemical that cannot remain in solution. To control where precipitation occurs, the porous medium can be preheated by injecting hot water or steam.

This report summarizes a theoretical and experimental study of the thermal precipitation process.

2. BACKGROUND

A variety of reservoir permeability reduction processes are in use and are being developed. Some of the processes that result in permeability reduction are naturally occurring or are the result of normal oil production operations, e.g., diagenesis over geologic time, barium and strontium sulfate scale deposition during oil production, and asphaltene deposition in oil reservoirs during miscible gas flooding. At the high temperatures and pressures found in geothermal reservoirs and during steam injection activities, dissolution and precipitation of silica can also result in a significant permeability alteration. Permeability reduction caused by such normally occurring processes are described in Section 2.1.

In Section 2.2, processes used to deliberately modify injection profiles by reducing the permeability are discussed. These include plugging of high permeability thief zones by the placement of gels, by in-situ chemical reactions, by the injection of dispersed solids or other plugging agents, and by lowering the residual oil saturation through precipitating salts within a reservoir.

In Section 2.3, models are described for chemical precipitation and dissolution processes in geological formations.

2.1 Permeability Reduction by Naturally Occurring Processes

Naturally occurring processes play a major role in the alteration of porosity and permeability of a formation. Over geologic time, unconsolidated sediments are slowly cemented by the precipitation of various chemicals, most commonly silica or calcite. This process, known as diagenesis, is a strong function of the temperature and pressure of the rock-fluid system.

The porosity and permeability of petroleum reservoirs can also be altered by normal hydrocarbon recovery processes. Barium, strontium, and calcium sulfate can precipitate due to the incompatibility between injected saline water and reservoir connate water in a waterflooding process or from changes in the temperature and pressure of the fluid during recovery operations. Permeability impairment can also occur from asphaltene deposition during miscible gas flooding of oil reservoirs. Silica can also be dissolved near the wellbore and precipitate in the formation during steam injection activities.

2.1.1 Diagenesis

Diagenesis is the changes that occur in the character and composition of sediments, beginning from the moment of deposition and lasting until the rocks are destroyed. The major forms of diagenesis are compaction, cementation, and lithification. Compaction is a change in grain packing by rotation, translation, fracturing, and plastic deformation of grains. Cementation and lithification are mainly the result of chemical precipitation of a binding agent or the chemical welding of adjacent detrital grains, but can include metamorphosis of the grains themselves. One of the major changes that occurs in the bulk physical properties of rocks from diagenesis is an alteration of the porosity and permeability.

2.1.2 Temperature and Pressure Effects

Much research has been conducted on the effect of temperature and confining pressure on the absolute permeability of silica based porous media. Weinbrandt et al. (1975) measured decreases in permeability of approximately 50% for Boise and Berea sandstones as the temperature increased from 77 to 176°C. Aruna (1976) studied changes in permeability with temperature for a variety of materials, working fluids, and confining pressures and reported that an increased confining pressure resulted in a decrease in permeability. This decrease in permeability has been attributed to stress-induced silica dissolution at grain contacts and the re-precipitation of the silica at lower-stress surfaces (Aruna, 1976; Dibble, et al., 1983). This theory follows from the linear relationship between surface stress and chemical potential. Because the surface chemical potential is highest at the contact point, the solubility of silica in water is highest at that location. Quartz and amorphous silica (opal-A) have a low solubility at room temperature, but at elevated temperatures their solubility increases sharply, as shown in Fig. 1 (Krauskopf, 1967).

Solution pH is another important factor influencing the extent and rate of silica dissolution. Krauskopf (1976) and Iler (1955) have shown that silica solubility remains relatively constant below a pH of 9 but increases sharply at higher pHs.

When bicarbonate ions in steam generator feedwater decompose to carbon dioxide and hydroxyl ions, the carbon dioxide partitions to the vapor phase and the hydroxyl ions partition to the liquid phase. This causes the pH of the liquid phase to increase sharply. Some of the hydroxyl ions react with remaining bicarbonate ions to form carbonate ions, which also are quite alkaline. Measurements on samples of liquid effluent collected from field generators show that about one-third to one-half of the alkalinity is from carbonate ions and the rest is from hydroxyl ions (Reed, 1980).

Reed (1980) determined the rate of silica dissolution of quartz sand during core floods at various temperature and pH conditions. At room temperature the silica concentrations in the effluent at all pH levels were below the detection limit of 1 mg/L, which represents an insignificant dissolution rate. The silica concentration increased significantly with both temperature and solution pH, especially above 350°F, as shown in Figs. 2 and 3. Dissolution was only observed on the inlet face of the sample; the effluent end of the core did not show any evidence of mineral dissolution. Reed noted that the permeability of natural sandstone cores usually decreased during flow of the hot water. The permeability decline may have been caused by the reprecipitation of dissolution products in the downstream end of the core.

Morrow et al. (1981) reported the effects of temperature-induced geochemical changes on fluid flow through granite under simulated in-situ conditions around a borehole in a nuclear waste repository. Tests were run for intact samples with initial permeabilities of several hundred nanodarcies and for samples containing fractures. In all cases, the permeabilities decreased between 1 and 2 orders of magnitude during flow tests, with the rate of reduction being higher at higher temperatures. At 200°C, permeability dropped by an order of magnitude over a 1-month period, whereas at 310°C, the permeability dropped within a few days to 5% of the initial value. The dissolution of quartz and feldspar and the subsequent redeposition of these minerals within cracks at a lower temperature was found to be the major cause of reduction of permeability. Mineral deposition was due mainly to decreasing solubility along the temperature gradient.

Variations of physical factors other than temperature can also affect the permeability of fractures within granite. Increased effective stress will tend to close cracks and inhibit

flow, but will enhance the solubility of minerals in the rock by pressure solution. A decrease in flow rate can increase the amount of time available for chemical reactions within the rock. Temperature gradients, as well as ground water chemistry, in-situ stresses, fracture density, and rock mineralogy can all affect permeability (Morrow, et al., 1981).

Moore et al. (1982) studied the chemical reactions accompanying fluid flow through granite in a temperature gradient. In these tests, distilled water was flowed radially through the granite cylinders. The rate of permeability change varied with temperature and flow rate, which in turn controlled the amount of mass transfer from high to low temperature zones in the granite. Silica, possibly in the quartz phase, was the major precipitated mineral. The silica concentration in the solutions increased with temperature and pressure. The silica content of the discharged fluids was also sensitive to reductions in flow rate, which increased the fluid-granite reaction times at all temperatures.

2.1.3 Scale Formation

Formation water normally contains a variety of dissolved solids in equilibrium with the surrounding rock. During the production of oil, this water is also produced. During production, however, the temperature and pressure of the water are altered, changing the thermodynamic equilibrium conditions for the dissolved solids. This change in equilibrium can result in the water becoming supersaturated in some dissolved solids. To regain equilibrium, these solids commonly precipitate as scale. Common chemicals that precipitate are barium, strontium, and calcium sulfate.

2.1.4 Asphaltene Deposition in Miscible Gas Flooding

Gas and waterflooding of oil reservoirs are the most common ways to improve oil recovery. The interaction between the injection fluid and reservoir oil can precipitate asphaltic particles from the oil and lower the permeability of the formation. Although the miscible displacement of oil with propane does not result in significant precipitation of asphaltenes within the pores, the bulk mixing of propane and oil can promote asphaltene flocculation, pore plugging and permeability impairment, which can result in a severe loss of fluid production. One experimental study reported a reduction in permeability of about 60 percent from the precipitation of asphaltenes (Danesh et al, 1988). The mechanism of asphaltene precipitation is very complex and not well understood.

2.2 Permeability Reduction by Injecting Plugging Agents

During waterflooding, the more permeable strata (thief zones) are depleted of oil first. One way to prevent wasteful circulation of water through high permeability thief zones is to selectively plug these zones with particles, gels, or chemical solutions. In this section various permeability reduction techniques are described.

2.2.1 Injection of Solids

One way to reduce the permeability of thief zones is to inject solids into the formation (Meadors, 1957; Showalter, 1972). The particle size is selected so that they will enter the larger pores of the most permeable zone (or fractures) but will not enter the smaller pores of the less permeable zone. The particles enter the pores and travel some distance and then form a bridge. The subsequent build-up of particles behind the bridge

then plugs the zone. By incorporating a swelling agent with the particles, the plugging agent can be wedged in place.

One unusual method of plugging a thief zone is by injecting a material at a temperature higher than its melting point and allowing the material to cool and solidify in the reservoir (Sharp, 1989).

2.2.2 Injection of Gels

Gels are a complex mixture of polymeric solids. Several researchers have described the use of different types of gels for reducing the permeability of highly permeable zones in underground formations (Allison and Purkaple, 1988; Navratil and Mitchell, 1989; Jennings and Hoefner, 1989; Ryles, 1989). Although gels are presented here as a method of profile modification, they can be considered a method to increase the viscosity of the fluids, rather than reduce the permeability within the porous media. Two problems in using gels are getting the mixture into the formation before gelation occurs and preventing the mixture from entering permeable strata that are not to be plugged. The time required for gelation is influenced by temperature, pH, and metal content of the gel.

Seright (1988) developed mathematical models that describe the plugging of low permeability zones when zonal isolation techniques are not used. Richardson (1971), Richardson and Scheuerman (1973), and Suman et al. (1974) described a process where an aqueous solution is injected containing a dissolved salt of a metal that precipitates as a gelatinous, hydrous or hydrated metal oxide or hydroxide. Torrest (1987) showed that by adjusting the pH within the porous media, the precipitation time of a hydrated aluminium oxide gel can be controlled. Permeability reductions of up to 98% of the initial permeability were observed in this process.

2.2.3 Injection of Incompatible Chemical Solutions

Precipitation of solids caused by chemical reactions due to mixing of incompatible solutions can also reduce the permeability of underground formations. When incompatible solutions are injected in the reservoir, a reduction of permeability away from the wellbore can take place. This process may enhance the efficiency of the flood by reducing the permeability deep in the formation.

A two-stage treatment using a chemical solution was presented by Hower and Ramos (1956) to partially plug high permeability zones. In this process, a chemical solution is injected into the formation that is strongly adsorbed on the rock surfaces. After a small water spacer is injected, a second solution is then injected that reacts chemically with the first solution to form a water-insoluble, gelatinous precipitate. Extensive laboratory tests have shown that this type of precipitate is a more effective agent in reducing permeabilities than crystalline materials.

Needham et al. (1974) described a combination process that involves injecting a dilute polymer solution that adsorbs on the rock surface. The polymer solution is then followed by an aluminium citrate solution. Aluminum ions are retained in the polymer that was adsorbed on the rock surface. The aluminum citrate solution is displaced by a second polymer solution and then by brine. Permeability reduction occurs when the polymer in the second polymer cycle by crosslinking with aluminum ions, form a layered structure. Reduction in brine permeability after treatment ranged from factors of 3 to 4,170 for several sandstones. This permeability reduction was more resistant to elution than that obtained with a single polymer treatment.

Experiments conducted by Parmeswar and Willhite (1988) show that permeability reduction by the combination process was limited to the inlet end of the core. It was found that the amount and distribution of permeability reduction is related to both polymer and aluminum retention. Changing the treatment sequence to aluminum citrate/brine/polymer/brine yielded a deeper penetration into the core of the affected zone. Both the magnitude and persistence of the permeability reduction were comparable to or better than those obtained with the original process. In most cases, the permeability increased with distance from the core-inlet, due to the nonuniform distribution of retained aluminum.

Scale deposition often results from the incompatibility between injected saline water and reservoir connate water in a waterflooding process. Todd and Yuan (1992) describe barium and strontium sulfate scale formation in porous media during both flowing and static conditions. In all core tests, the scale concentration reduced significantly from the core front to the rear. Visual examination of cores after experiments using a scanning electron microscope (SEM) indicated that the crystal precipitation was not different between the static and flowing conditions. Temperature had a large effect on scaling crystal morphology and a higher scaling rate was observed at the elevated temperature. From the SEM views of the crystals grown at different temperatures, both in static and flowing solutions, it was observed that the crystals precipitated at elevated temperatures were more perfect and have fewer crystal faces.

A significant limitation to the data of Todd and Yuan is that precipitation was not uniform in the core. The reported porosity and permeability data reflect core averages, not local values. Thus, any correlation between the porosity and permeability suggested by their data does not necessarily have universal applicability to estimating permeability reduction as a function of porosity reduction. The data of Todd and Yuan are discussed below.

2.3 Models of Chemical Precipitation and Dissolution Processes

Many processes, such as sandstone acidizing and enhanced oil recovery, rely on the injection of reactive fluids into a permeable medium. The interaction between the injected fluids and rock minerals may lead to mineral dissolution, migration of the dissolved mineral, and the subsequent precipitation of the mineral elsewhere in the reservoir. Several studies have been conducted that model the precipitation/dissolution processes in the absence of precipitate migration and pore plugging.

Walsh, et al. (1982) developed a general model for mineral dissolution and precipitation within a porous medium during convective transport. The model was based on the assumptions of local equilibrium, negligible dispersion, and no migration of precipitated solids. The last assumption severely limits the model because experimental studies have demonstrated that precipitated solids can migrate with the fluid.

Sharma and Gang Wu (1989) extended Walsh et al.'s model by incorporating the migration of precipitated solids in a permeable medium. This extended model attempts to characterize the local permeability reduction by incorporating precipitated grain-size and pore-size distributions into one of the two dominant plugging mechanisms. These plugging mechanisms are solid deposition on pore walls (surface adsorption) and trapping of mobile particles in small pore throats. If the precipitated solid size is comparable to the mean pore throat size, the dominant mechanism for particle trapping is size exclusion. The case where the solid size is much smaller than the pore throat size, i.e., where surface adsorption becomes important, is not considered in their paper.

During the migration of precipitated solids in a permeable medium, the region of constant composition of solids that precede and succeed composition changes represents a wave. A numerical study of these waves reveal that they develop and move through the system in a manner similar to that of gas or liquid chromatography (Walsh, et al., 1984). The structure of these waves have three essential features. First is the mineral sequence of the wave that defines the order of the existing mineral phases in the core (Sharma and Gang Wu, 1989). Determining the mineral sequence is usually possible only with a numerical model. Second is the coherence of the wave, which requires that the concentration velocities of all elements in a wave to be equal. Third is that the solution downstream of a solid which has disappeared across a wave must remain in equilibrium with that solid.

The model for precipitation and dissolution processes with precipitate migration developed by Sharma and Gang Wu (1989) shows that the lowest solid migration wave velocity, which is the precipitation/dissolution wave velocity, is obtained when no solids flow. These authors also showed that solid migration is always retarded when solid trapping occurs across the migration wave. The number of precipitation/dissolution waves determines the number of damaged regions. Damaged regions are zones in the permeable media where solid precipitates are captured and cause permeability loss. The higher the number of precipitation/dissolution waves, the larger the number of damaged regions.

Sharma and Gang Wu also investigated the effect of relative pore and particle size on wave behavior. When the particle size is larger than the maximum pore size, all precipitated minerals are trapped and no migration of solid occurs. When the particle size is less than the minimum pore size, all precipitate mineral migrates and there is no trapped solid. In this case, the solid migration wave coincides with the salinity wave. This solution is referred to as the complete solid migration solution, where no permeability reduction occurs. When the particle size is comparable to the mean pore size, the partial solid migration numerical solution to the equations is obtained.

3. DESCRIPTION OF THERMAL PRECIPITATION PROCESS

The thermal precipitation process will reduce the permeability of geological formations by precipitating chemicals in the pores from temperature-dependent changes in chemical solubility. In the first step of the process, hot water or steam is injected into the formation to preheat it. Because of the heterogeneities in the permeability and fluid mobility, the zones already swept will be preferentially heated. After preheating the high permeability zone to the desired distance from the wellbore, a slug of hot water which is saturated (or nearly saturated) with the chosen chemical is injected. The chemical used must have a high solubility in water at high temperature and a much lower solubility at reservoir temperature.

Once the chemical saturated slug of hot water reaches the desired location, it is allowed to cool. The cooling precipitates the chemical, plugging the pores and reducing the permeability of the high permeability zone. Subsequent injection of low temperature fluids would sweep other regions of the reservoir as the flow is diverted away from the plug.

The location of where the plug is created can be controlled by how much the formation was pre-heated. Formation temperatures and the depth of penetration of the pre-heated regions can be calculated from procedures developed for thermal oil recovery operations. For example, the methods of Lauwerier (1955) or Myhill and Stegemeier (1978) can be used for hot water and steam injection, respectively.

The amount by which the permeability is reduced in the plug can be controlled by the selection of the chemical used, the temperatures used in the process, the amount of chemical injected, and how the slug is allowed to cool. It can be cooled by shutting the well and letting conduction to the surrounding formation lower the temperature or by continued injection and letting convection push the slug into cooler regions of the formation. Less precipitation is expected if the slug is cooled by conduction, because only one pore volume of water saturated with chemical would be available to precipitate in one pore volume of rock. If the slug is pushed into cooler regions, an energy balance between the hot water and the reservoir rock would control how much chemical is precipitated in one pore volume of rock. In this case, substantially more than one pore volume of water saturated with chemical could precipitate.

Experiments conducted by Todd and Yuan (1992) show that crystals precipitated in porous media from the same brines under static conditions and flowing conditions do not show significant differences in external crystal morphology. This suggests that the mechanism of crystal precipitation is not altered from static to flow conditions. Thus, the crystalline structure for precipitation by conductive or convective cooling may be identical.

Oil recovery during the thermal precipitation process would be enhanced during the preheating period from the proven recovery mechanisms that occur when injecting the hot fluids (Willman, et al., 1961). This would improve the project economics, even in reservoirs where traditional thermal recovery methods are not appropriate for the entire project.

Holbrook et al. (1957) reported that precipitating a salt within a reservoir reduces the residual oil saturation. They did not discuss the effect of precipitation on permeability reduction, however. It may be possible that porosity reduction due to precipitation may cause a displacement of oil from the reservoir, which may result in a lower residual oil saturation.

3.1 Thermal Precipitation by Conduction

In this variation of the thermal precipitation process, the reservoir is preheated to the desired temperature by steam or hot water injection and then the chemical-saturated hot water is injected into the preheated zone. Once the chemical-saturated water has reached the desired location, injection is stopped and the hot solution is allowed to cool by conduction to the surrounding formation. Precipitation of the chemical takes place as the solubility declines with the declining temperature. Cooling by conduction will allow the chemical from one pore volume of solution to be precipitated.

For the case of cooling by conduction, the reduction in porosity can be calculated from a material balance on the dissolved chemical. The fractional reduction in porosity can be expressed in terms of the ratio of the volume of chemical precipitated, V_p , and the total pore volume before precipitation, V_t .

$$\frac{\Delta\phi}{\phi} = \frac{V_p}{V_t} \quad (3.1)$$

The volume of chemical precipitated is calculated from the difference in the mass of chemical dissolved at the high and low temperatures, M_h and M_l , respectively,

$$V_p = \frac{M_h - M_l}{\rho_p} \quad (3.2)$$

where ρ_p is the density of precipitated chemical. The mass of chemical is either measured or found from its solubility in a saturated solution at the different temperatures.

The total pore volume can be expressed in terms of the volume of solution, V_s , and the fraction of the pore space occupied by the solution, S_s . The fraction of the pore space occupied by the solution is called its saturation. The total pore volume can then be expressed as

$$V_t = \frac{V_s}{S_s} \quad (3.3)$$

The volume of the solution is determined from its mass and density at high temperature:

$$V_s = \frac{M_h + M_w}{\rho_h} \quad (3.4)$$

where M_w is the mass of water in the solution and ρ_h is the solution density at high temperature.

Data presented by Sohnle and Novotny (1985) show the solution density for potassium carbonate and sodium borate, as a function of temperature to be nearly linear for

a given concentration. An expression for the density of a solution of potassium carbonate was obtained from a linear regression of these data:

$$\rho_h(T,W) = 0.01055X + \rho_w(T) . \quad (3.5)$$

A similar expression was found for sodium borate

$$\rho_h(T,W) = 0.087069X + \rho_w(T) , \quad (3.6)$$

where X is the chemical concentration in weight percent and ρ_w is the density of pure water as a function of temperature, T , in $^{\circ}\text{C}$.

The chemical concentration is given by

$$X = \frac{M_h}{M_h + M_w} . \quad (3.7)$$

The fractional reduction in porosity can be determined by combining the above equations to yield

$$\frac{\Delta\phi}{\phi} = \left(\frac{M_h - M_l}{M_h + M_w} \right) \left(\frac{\rho_h}{\rho_p} \right) S_s . \quad (3.8)$$

3.2 Thermal Precipitation by Convection

In this method the reservoir is preheated as before. Rather than shutting in the injection well, however, injection continues and the chemical saturated slug is pushed into the cooler regions of the reservoir. As the slug is pushed beyond the preheated zone, it is cooled by convection and precipitation takes place. An energy balance between the reservoir rock and the slug of hot solution will give the amount of precipitation that would take place in this process.

The enthalpy, Q , required to raise the temperature of a bulk volume of reservoir, V_R , initially at temperature, T_l , to a final high temperature, T_h by injecting hot saturated solution at temperature T_h is given by:

$$Q = V_R M_R (T_h - T_l) , \quad (3.9)$$

where M_R is the volumetric heat capacity of the reservoir. The enthalpy of the solution available to heat the reservoir is given by:

$$Q = V_s M_s (T_h - T_l) , \quad (3.10)$$

where M_s is the volumetric heat capacity of saturated solution. The heat of solution is small compared to the enthalpy required to heat the formation and can be neglected.

If Eqs. 3.9 and 3.10 are equated, the volume of solution required to heat a given volume of formation can be determined:

$$V_s = \frac{V_R M_R}{M_s} . \quad (3.11)$$

The volume of solution can also be determined in terms of the volume of precipitate formed by combining Eqs. 3.2 and 3.4,

$$V_s = V_p \left(\frac{M_h + M_w}{\rho_h} \right) \left(\frac{\rho_p}{M_h - M_l} \right) . \quad (3.12)$$

If Eqs. 3.11 and 3.12 are equated, the volume of precipitate generated in the affected reservoir volume can be determined:

$$\frac{V_p}{V_R} = \left(\frac{M_h - M_l}{M_h + M_w} \right) \left(\frac{\rho_h}{\rho_p} \right) \left(\frac{M_R}{M_s} \right) . \quad (3.13)$$

The pore volume where precipitation occurs can be expressed in terms of the volume of reservoir affected:

$$V_i = \phi V_R . \quad (3.14)$$

Combining Eqs. 3.13 and 3.14, the ratio of the volume of the precipitate formed to the pore volume over which precipitation occurs for the thermal precipitation by convection process can be obtained. This ratio is the fractional reduction in porosity:

$$\frac{\Delta\phi}{\phi} = \left(\frac{M_h - M_l}{M_h + M_w} \right) \left(\frac{\rho_h}{\rho_p} \right) \left(\frac{M_R}{\phi M_s} \right) . \quad (3.15)$$

For typical thermal properties, the fractional reduction in porosity is about three times greater for thermal precipitation by convection than for thermal precipitation by conduction.

4. IDENTIFICATION OF CHEMICALS

The most important property in selecting a chemical for use in the thermal precipitation process is its solubility as a function of temperature. In particular, a high solubility at high temperature and a low solubility at low temperature is desired. The chemical literature were reviewed to identify chemicals that have the appropriate solubility variation with temperature. A total of 16 chemicals were identified. These chemicals are listed in Table 1. The physical and chemical properties of these chemicals were then reviewed to identify any safety, health, or environmental problems that may occur with the use of those chemicals. From this review, a short list of chemicals was developed that would be considered suitable for use in the thermal precipitation process. These chemicals are boron oxide, potassium carbonate, potassium chloride and sodium borate. The solubilities of these chemicals are presented in Fig. 4 (Perry, et al., 1963).

5. EXPERIMENTAL SYSTEM

The purpose of the apparatus is to measure the pressure drop across a core sample before and after temperature dependent precipitation (thermal precipitation) for different chemical solutions. From this data the change in permeability can be determined for the different conditions.

The objective is achieved by first measuring the pressure drop across the core at room temperature, then pumping a saturated solution into the core at high temperature. The core is then allowed to cool to room temperature and the new pressure drop is measured. A saturated solution at ambient temperature is used for the final permeability measurement to prevent redissolution during the measurement. From these data, the initial and final permeabilities are calculated. The porosity of the sample before and after thermal precipitation is also measured.

This chapter contains an overview of the apparatus that was constructed to study reduction in permeability from the thermal precipitation process. The apparatus was designed for the high temperature and pressures involved in the process. A description of the operating procedures for the apparatus is also provided.

5.1. Description of Apparatus

The apparatus consists mainly of an Injection system, a Precipitation system, and a Measurement system. A schematic of the experimental apparatus is shown in Fig. 5.

5.1.1. Injection System

This system consists of a water reservoir with a 5 μm filter, a positive displacement pump, and a back pressure regulator to control the system pressure. Most of the tubing in the system was 316 stainless steel. To minimize corrosion, monel was selected for the tubing that will contain the hot chemical solution.

5.1.2. Precipitation System

This system consists of an oven to provide isothermal conditions for the elevated temperature runs, a mixing vessel to provide a means to saturate the hot water with the desired chemical at high temperature and pressure, a Hassler type of core holder, and a desaturation vessel to allow final cooling and precipitation of the solution to occur prior to being passed through the back pressure regulator. A filter was installed after the desaturation vessel to prevent solids migration through the back pressure regulator.

5.1.3. Measurement System

This system consists of various pressure gauges and pressure transducers to monitor system pressures and a solubility measurement system to measure the chemical saturation of the solution at high temperature and pressure. A detachable piece of tubing was installed downstream of the mixing vessel to measure the saturation of the chemical in the solution at high temperature and pressure after it leaves the mixing vessel.

Following thermal precipitation and the final permeability measurement, the core is in a saturated state at room temperature with a solution of the chemical used in the

precipitation experiment. The difficulty with measuring the final porosity is that when the core is dried, the chemical still dissolved at room temperature will precipitate, biasing the measurement. The following procedure describes how the final porosity measurement can be corrected to eliminate this bias.

A saturated solution at room temperature containing W_p grams of chemical per gram water will have a solubility expressed as:

$$S = W_p / \text{gm water.} \quad (5.1)$$

Drying the core will remove the water, leaving the previously dissolved chemical as a solid precipitate. The weight of water removed by drying, W_w , can be determined by subtracting the final dry core weight, W_{df} , from the weight of the saturated core, W_s :

$$W_w = W_s - W_{df}. \quad (5.2)$$

The weight of solids precipitated during drying, W_{pd} , is calculated by multiplying the solubility at room temperature by the weight of water removed by drying, W_w ,

$$W_{pd} = (S)(W_w). \quad (5.3)$$

The total weight of precipitate in the core from thermal precipitation and from drying, W_t , can be measured by subtracting the core's initial dry weight, W_{di} , from it's final dry weight, W_{df} :

$$W_t = W_{df} - W_{di}. \quad (5.4)$$

The total weight of precipitate can also be expressed as the sum of the weights of the chemical precipitated during drying, W_{pd} , and during thermal precipitation, W_{pt} :

$$W_t = W_{pt} + W_{pd}. \quad (5.5)$$

Equating equations 5.4 and 5.5 provides an expression for the weight of precipitate from thermal precipitation alone:

$$W_{pt} = W_{df} - W_{di} - W_{pd}. \quad (5.6)$$

The volume occupied by the chemical precipitated during thermal precipitation, V_p , is found by dividing the weight of precipitate by the chemical's specific gravity, SG :

$$V_p = W_{pt} / SG. \quad (5.7)$$

This volume represents the pore volume occupied by the chemical precipitated as a result of thermal precipitation.

To calculate the final porosity after treatment (but before drying) the precipitated chemical volume, V_p , is subtracted from the initial pore volume. The initial pore volume is the initial porosity, ϕ_i , multiplied by the bulk volume, BV . This value is then divided by the core bulk volume to give the final porosity:

$$\phi_f = (\phi_i * BV - V_p) / BV. \quad (5.8)$$

6. EXPERIMENTAL RESULTS

One inch diameter cores of Berea sandstone and Indiana Limestone with lengths varying from three to five inches were used for the tests. The cores selected did not show any significant visual heterogeneities and were considered to have fairly uniform petrophysical properties. The cores were fired to desensitize indigenous clays, following the procedure outlined by Shaw, et al. (1991). Prior to each test, the porosity and permeability of all cores were measured.

For each test, a core was saturated with the chemical solution at room temperature, the mixing vessel was filled with solid chemical, and the oven heated to the desired temperature. After the apparatus reached temperature equilibrium, water was injected into the system until a minimum of about five pore volumes of the solution passed through the mixing vessel and the core. Dissolution of the chemical occurred as the water passed through the mixing vessel. After the desired volume of solution was passed through the core to saturate it, the oven was turned off and the system cooled to ambient temperature. This cooling allowed the precipitation of the chemical within the core. After cooling, the permeability of the core was measured using a saturated chemical solution at ambient temperature as the injection fluid. Using a saturated solution at ambient temperature prevented the dissolution of the precipitate during the final permeability measurement. The porosity of the core after precipitation was also measured, as previously discussed.

The thermal precipitation process was applied to ten Berea sandstone cores with potassium carbonate and two with sodium borate. The high temperatures used ranged from 80 to 160 °C and all eight cores were cooled by conduction to 24 °C (room temperature). The resulting fractional reductions in porosity ranged between 5 and 20 percent, while the corresponding fractional reduction in permeability ranged between 26 to 63 percent. The data for the individual cases are presented in Table 2.

The measured fractional reductions in porosity are compared to those predicted by Eq. 3.8. As shown in Fig. 6, the measured porosity reduction for potassium carbonate were lower than those predicted if the solutions were fully saturated. The test results using sodium borate show better correlation with the predicted results, suggesting that the solutions of sodium borate were closer to being fully saturated. This lack of complete saturation was confirmed with the solubility device. No attempt was made, however, to achieve a fully saturated solution at high temperature for these tests.

The measured fractional reductions in permeability are plotted in Fig. 7 as a function of the measured fractional reduction in porosity. For comparison, the data of Todd and Yuan (1992) are also shown. The trend in permeability reduction was similar, even though the chemical processes were dissimilar.

The morphology of the precipitate following the thermal precipitation process was examined with a Scanning Electron Microscope. Potassium carbonate precipitated fairly uniformly over the entire pore wall, forming a layer of precipitate. The crystals themselves were relatively small. No evidence of fines was observed. Sodium borate, however, tended to form larger, individual crystals that attached at random locations in the pores. The effect of these chemicals on permeability was, however, similar.

The thermal precipitation process was also applied to two Indiana limestone cores with potassium carbonate at 80 °C. The resulting porosity and permeability data are shown in Table 3. At porosity reductions on the order of 15%, the cores were virtually plugged. At comparable porosity reductions, the permeability reductions for the clastic Berea

sandstones were on the order of 50%. Thus, the reduction in permeability for the limestone cores was considerably greater than that of the sandstone for the same reduction in porosity. This difference was attributed to the different pore geometries. Because of this, the application of the thermal precipitation process in the field may require additional tests with cores having the appropriate pore geometry.

7. THEROETICAL MODELING

This section discusses models for the reduction in permeability as a function of the reduction in porosity following the precipitation of inorganic solids in a permeable formation. The models are compared to the clastic Berea sandstone data. It is assumed that there is no particle migration and subsequent bridging of pore throats. Fines migration, however, can also be an important factor in permeability reduction following precipitation (Aliaga, et al., 1989). A model for the effects of precipitate migration on permeability has been presented by Gang Wu and Sharma (1989).

7.1 Exponential Model

A simple exponential model for the effect of porosity changes on permeability changes has been proposed by a number of authors, (Rege and Fogler, 1989; McClure, et al., 1979; Lund, 1974),

$$K \sim \exp\{a\Delta\phi\} , \quad (7.1)$$

where "a" is an empirical constant. For this model, the corresponding change in permeability can be expressed as:

$$\frac{\Delta K}{K} = 1 - \exp\left\{-\frac{a\Delta\phi}{\phi}\right\} . \quad (7.2)$$

Figure 8 compares this model to the experimental data presented in Fig. 7. The best fit was obtained for a value of "a" equal to 5.

Although this model provides a reasonably accurate, easy-to-use description of the permeability reduction from precipitation, it does not provide any insight into the petrophysical changes that occur upon precipitation.

7.2 Power Law Model

Empirical studies have shown that the dependence of permeability on porosity can be described with a power law function.

$$K = c\phi^b . \quad (7.3)$$

This model is often used when correlating core data to determine porosity-permeability transforms. Rumpf and Gupte (1971) reported that the best match to unconsolidated beds is obtained when the exponent, "b", is equal to 5.5. Schwartz and Banavar (1989) reported that the exponent "b" is equal to 3.5 for binary mixtures of different sizes of grains. Bourbie and Zinszner (1985) reported that the porosity exponent for the well-sorted, constant-grain size Fontainebleau sandstone is 7.33 or 3.05 for porosities less than and greater than 8%, respectively. Doyen (1988) reported that the porosity exponent for the Fontainebleau sandstone is 3.8 for porosities above about 5%. These exponents were considered to be somewhat low because the permeabilities were not corrected for the Klinkenberg effect.

For this model, the corresponding change in permeability can be expressed as:

$$\frac{\Delta K}{K} = 1 - \left(1 - \frac{\Delta \phi}{\phi}\right)^b \quad (7.4)$$

This model is compared to the experimental data in Fig. 9 for different values of "b". The best fit was obtained for a value of "b" equal to 5, which is close to the value recommended by Rumpf and Gupte.

7.3 Capillary Tube Model

Perhaps the first theoretical approach to modeling the permeability of a porous medium was to assume that the medium behaved like a bundle of straight-walled capillary tubes. Such models are based on the Hagen-Poiseuille equation for laminar flow in a capillary tube. By comparing the Hagen-Poiseuille equation to Darcy's law, it can be shown that the permeability of a single capillary tube is given by

$$K_{\text{tube}} = \frac{r^2}{8} \quad (7.5)$$

This permeability is based on the use of the cross sectional area of the tube in Darcy's law. This permeability differs from that of a porous medium in that the area used in Darcy's law includes the area of the solids. The permeability of a porous medium is found from the effective permeability of an individual pore by multiplying the tube permeability by the porosity. Thus,

$$K = \phi \frac{r^2}{8} \quad (7.6)$$

The porosity of the porous medium is equal to the area of the tube divided by the effective bulk area associated with the tube:

$$\phi = \frac{\pi r^2}{\pi r_e^2} \quad (7.7)$$

where r_e is the effective radius of the bulk medium associated with each tube. Combining Eqs. 7.6 and 7.7 yields

$$K = \frac{r^2}{8} \phi^2 \quad (7.8)$$

This equation is particularly useful for determining the effect of precipitation on the permeability because the effective radius associated with each tube does not change as precipitation occurs. Thus, the permeability calculated with this form of the capillary tube equation depends only on the change in porosity.

By comparing Eq. 7.8 with Eq. 7.3, it can be seen that the bundle of capillary tubes model is simply the power law model with an exponential factor $b=2$. From Fig. 9, however, it can be seen that the model provides a poor fit to the measured data.

A more general approach to the change in permeability following a change in porosity for capillary tubes was presented by Schechter and Gidley (1969). This model extended the capillary tube model to include "collisions" between growing tubes during acidizing of petroleum-bearing formations to increase the production rate. When an expanding pore collides with a nearby pore, they combine into a single pore with a much larger effective flow area. The resulting change in permeability is given by

$$\frac{\Delta K}{K} = 1 - \left(1 - \frac{\Delta \phi}{\phi}\right)^2 \exp\{2\Delta \phi\} . \quad (7.9)$$

For the case of precipitation, the pores will shrink and collisions can be considered as the breaking of a large pore into two smaller pores. In this case, $\Delta \phi$ will always be negative and the effect of pore collisions will decrease the effect in porosity changes on permeability changes. Because the capillary tube model without the collisions significantly underpredicts the change in permeability, allowing collisions makes the model even worse.

7.4 Carman-Kozeny Model

A significant limitation to the use of the capillary tube models to predict permeabilities is that pores are not circular, nor are they all aligned with the direction of flow. If the Hagen-Poiseuille equation is modified to account for the different size, shape, and orientations of the pores in a porous media, an improved model for the permeability can be obtained. The most common of these models is the Carman-Kozeny equation (Wyllie and Gregory, 1955; Wyllie and Gardner, 1958; and Dullien, 1975).

The Carman-Kozeny equation can be expressed in several equivalent forms:

$$K = \frac{\phi}{k_o \left(\frac{L_e}{L}\right)^2 S_p^2} , \quad (7.10)$$

$$K = \frac{\phi^3}{k_o \left(\frac{L_e}{L}\right)^2 S_b^2} , \quad (7.11)$$

$$K = \frac{\phi^3}{k_o \left(\frac{L_e}{L}\right)^2 (1 - \phi)^2 S_g^2} , \quad (7.12)$$

where k_o is a shape factor to account for the pores not having a circular cross section, $(L_e/L)^2$ is the tortuosity to account for the fact that many of the pores that the fluid passes through are not aligned with the overall flow direction. Typical values for the shape factor

and tortuosity are 2.5 and 2, respectively. S_p , S_b , and S_g are the specific surface areas of the medium (surface area per pore, bulk, and grain volume, respectively). The specific surface area is a measure of the average pore size in the medium.

The change in permeability following precipitation is not easy to determine from these equations because it is not clear how precipitation affects all of the factors. If the precipitate uniformly coats the pore walls, as indicated in this study, the shape factor, tortuosity and bulk volume will likely not change significantly during precipitation. The surface area will likely change, however, so the specific surface area will not be constant.

The Carman-Kozeny equation has been used to model the reduction of permeability in geologic formations caused by the precipitation of quartz (Leder and Park, 1986; Angevine and Turcotte, 1983). These authors did not present any data to validate their respective models, however. In both studies, Eq. 7.12 was used, except that Angevine and Turcotte used a value of 8 for the porosity exponent in the numerator. Both sets of authors assumed that the shape factor, tortuosity, and specific surface area per grain volume did not vary during precipitation. The assumption of the constancy of the specific surface area (per grain volume) is particularly questionable when the grain volume is changing from precipitation.

Under the assumptions of Leder and Park, the change in permeability as a function of the change in porosity is given by

$$\frac{\Delta K}{K} = 1 - \frac{\left(1 - \frac{\Delta \phi}{\phi}\right)^3}{\left(1 - \frac{\Delta \phi}{1 - \phi}\right)^2} \quad (7.13)$$

For the model of Angevine and Turcotte, the exponent in the numerator would be 8 instead of 3. The resulting change in permeability is plotted in Fig. 10. From this figure, it can be seen that neither the model of Angevine and Turcotte or of Leder and Park accurately represented the change in permeability following chemical precipitation. The absolute porosity for this plot was assumed to be 16%. The change in permeability is relatively insensitive to the absolute porosity, as long as the porosity is much less than one.

If it is assumed that the shape factor, tortuosity, and specific surface area per bulk volume do not change with precipitation, Eq. 7.11 becomes identical to the power law model described by Eq. 7.3 with $b=3$. This model is similar to that proposed by Camp (1964). For a capillary tube, however, the specific surface area per bulk volume is proportional to the square root of the porosity. Thus, Eq. 7.11 becomes identical to the capillary tube model of Eq. 7.8 and the power law model of Eq. 7.3, with $b=2$. As seen in Fig. 9, these power law models underpredict the change in permeability. Thus, the assumption that the specific surface area per bulk volume is constant is not supported.

For spherical grains having a known packing lattice, the specific surface area can be calculated. Taylor et al. (1990) calculated the changing porosity and specific surface area when a biofilm was assumed to grow with a uniform thickness within a network of packed spheres. They then used Eq. 7.11 to estimate the resulting permeability as the biofilm grew and plugged the medium. The resulting reduction in permeability for this model is also shown in Fig. 10. The fit of this model to the experimental permeability reduction data was

poor. Thus, including a changing specific surface area did not improve the ability of the Carman-Kozeny model to predict permeability reduction in a porous medium.

It is concluded that the Carman-Kozeny equation does not provide a good model for the reduction in permeability following chemical precipitation in a porous medium.

7.5 Sinusoidal Model

A major limitation to the application of the capillary tube models, including the Carman-Kozeny equation, is that they assume that the cross sectional area of a pore remains constant along its length. Actual pores have a varying cross sectional area. Because the permeability of a tube is a function of the square of the tube radius, chemical precipitation in a pore throat would have a significantly greater effect on the permeability than precipitate in a pore body. Thus, incorporating a varying area can result in an improved model for the permeability.

One way to model a pore having a changing cross sectional area is to assume that the pore bodies and pore throats are connected capillary tubes having a constant radius, with a step change in radius between the pore bodies and pore throats (Dullien, 1975; Verma and Pruess, 1988). In these models, the local permeability is assumed to depend only on the local pore radius. A major limitation to this type of model is that it neglects the viscous dissipation the flow separation eddies that occur at the abrupt expansion into a pore body (Azzam and Dullien, 1977). Sinusoidal pore shapes can also be used (Chu and Ng, 1989). Because the pore radius changes slowly, flow separation eddies will probably not be created.

In sinusoidal models, the radius is expressed as

$$r(x) = r_m + (r_p - r_m) \sin\left(\frac{2\pi}{L} x\right), \quad (7.14)$$

where r_p is the radius of the pore body, r_m is the mean radius of the pore, and L is the length of the pore. The mean radius of the pore is defined as

$$r_m = \frac{r_p + r_t}{2}, \quad (7.15)$$

where r_t is the radius of the pore throat. This pore geometry is shown in Fig. 11.

A constriction factor is defined as the ratio of the pore body radius to the pore throat radius,

$$\gamma = \frac{r_p}{r_t}. \quad (7.16)$$

Combining Eqs. 7.15 and 7.16 to eliminate the pore throat radius yields

$$r_p = \frac{2\gamma r_m}{1 + \gamma}. \quad (7.17)$$

Substituting Eq. 7.17 into Eq. 7.14 yields

$$r(x) = r_m \left[1 + \sqrt{2\beta} \sin\left(\frac{2\pi}{L}x\right) \right] . \quad (7.18)$$

where

$$\beta = \frac{1}{2} \left(\frac{2\gamma}{1+\gamma} - 1 \right)^2 . \quad (7.19)$$

7.5.1 Porosity of Sinusoidal Model

The porosity is the pore volume of the capillary tube divided by the appropriate bulk volume associated with an individual tube. The pore volume is given by

$$PV = \pi \int_0^L r^2 dx . \quad (7.20)$$

If Eq. 7.18 is substituted into Eq. 7.20 the following expression for pore volume is obtained:

$$PV = \pi r_m^2 L (1 + \beta) . \quad (7.21)$$

The bulk volume is given by

$$BV = \pi r_e^2 L , \quad (7.22)$$

where r_e is the equivalent radius for each pore in the porous media.

The porosity is then

$$\phi = \frac{r_m^2}{r_e^2} (1 + \beta) . \quad (7.23)$$

If the porosity is assumed to be reduced from uniform precipitation of a material in the pores, it can be shown that the new radius of the pores is given by

$$r' = (r_m - \alpha) \left[1 + \left\{ \frac{(\gamma - 1)}{(\gamma + 1) \left(1 - \frac{\alpha}{r_m} \right)} \right\} \sin\left(\frac{2\pi}{L}x\right) \right] , \quad (7.24)$$

where α is the average reduction in pore radius from precipitation. The parameters r_m and γ refer to the initial pore size, not the pore size after precipitation has occurred.

Substituting Eq. 7.24 into Eq. 7.20 and integrating yields the pore volume after precipitation:

$$PV = \pi r_m^2 L \left(1 - \frac{\alpha}{r_m}\right)^2 \left(1 + \frac{\beta}{\left(1 - \frac{\alpha}{r_m}\right)^2}\right). \quad (7.25)$$

Since the bulk volume associated with each pore has not changed, the porosity is given by

$$\phi' = \frac{r_m^2}{r_0^2} \left(1 - \frac{\alpha}{r_m}\right)^2 \left(1 + \frac{\beta}{\left(1 - \frac{\alpha}{r_m}\right)^2}\right) \quad (7.26)$$

The change in porosity from precipitation is given by

$$\frac{\Delta\phi}{\phi} = 1 - \left(1 - \frac{\alpha}{r_m}\right)^2 \frac{1 + \frac{\beta}{\left(1 - \frac{\alpha}{r_m}\right)^2}}{1 + \beta}. \quad (7.27)$$

7.5.2. Permeability of Sinusoidal Model

The permeability at any position in the capillary tube is assumed to be equal to that of a straight-sided capillary tube having the same local radius. For a straight walled capillary tube, the local permeability is

$$K(x) = \frac{r^2(x)}{8}. \quad (7.28)$$

The permeability of a pore is found by integrating the permeability along the pore:

$$\frac{1}{K_{\text{tube}}} = \frac{1}{L} \int_0^L \frac{dx}{K(x)} . \quad (7.29)$$

Substituting the radius of the tube from Eq. 7.18 into Eqs. 7.28 and 7.29 and integrating yields

$$K_{\text{tube}} = \frac{r_m^2}{8} [1 - 2\beta]^{\frac{3}{2}} . \quad (7.30)$$

To obtain the conventional permeability, which is based on the bulk flow area that includes the area of the solids associated with the tube, the permeability for the tube must be corrected for the area. Because the local area associated with the tube varies with position along the tube, an average area will be taken. The ratio of the average area of the tube to the average bulk area, however, is simply the porosity. The permeability of a solid containing sinusoidal pores is then

$$K = \phi K_{\text{tube}} . \quad (7.31)$$

Substituting Eqs. 7.23 and 7.30 into Eq. 7.31 yields

$$K = \frac{r_m^4}{8r_o^2} [1 - 2\beta]^{\frac{3}{2}} (1 + \beta) . \quad (7.32)$$

The permeability after the uniform precipitation of material along the pore walls can be calculated using Eq. 7.29, only using Eq. 7.24 for the tube radius instead of Eq. 7.18. The resulting effective permeability of a tube is

$$K' = \frac{r_m^2}{8} \left(1 - \frac{\alpha}{r_m}\right)^2 \left[1 - \frac{2\beta}{\left(1 - \frac{\alpha}{r_m}\right)^2}\right]^{\frac{3}{2}} . \quad (7.33)$$

The conventional permeability following precipitation is found from

$$K' = \phi' K'_{\text{tube}} , \quad (7.34)$$

or

$$K' = \frac{r_m^4}{8r_o^2} \left(1 - \frac{\alpha}{r_m}\right)^4 \left[1 - \frac{2\beta}{\left(1 - \frac{\alpha}{r_m}\right)^2}\right]^{\frac{3}{2}} \left[1 + \frac{\beta}{\left(1 - \frac{\alpha}{r_m}\right)^2}\right]. \quad (7.35)$$

The change in permeability from precipitation is given by

$$\frac{\Delta K}{K} = 1 - \frac{\left(1 - \frac{\alpha}{r_m}\right)^4 \left[1 - \frac{2\beta}{\left(1 - \frac{\alpha}{r_m}\right)^2}\right]^{\frac{3}{2}} \left[1 + \frac{\beta}{\left(1 - \frac{\alpha}{r_m}\right)^2}\right]}{(1 - 2\beta)^{\frac{3}{2}}(1 + \beta)}. \quad (7.36)$$

The change in permeability as a function of the change in porosity can be found by combining Eqs. 7.27 and 7.36 and eliminating α/r_m . The resulting expression is

$$\frac{\Delta K}{K} = 1 - \left[1 - \frac{\Delta\phi}{\phi}(2 + \beta) + \left(\frac{\Delta\phi}{\phi}\right)^2(1 + \beta)\right] \frac{\left[1 - \frac{2\beta}{1 - \frac{\Delta\phi}{\phi}(1 + \beta)}\right]^{\frac{3}{2}}}{1 - 2\beta}. \quad (7.37)$$

For the case of a conventional capillary tube, $\beta=0$ and Eq. 7.37 reduces to

$$\frac{\Delta K}{K} = \frac{2\Delta\phi}{\phi} - \left(\frac{\Delta\phi}{\phi}\right)^2, \quad (7.38)$$

which is equivalent to power law model of Eq. 7.4 with $b=2$.

This model for permeability reduction is compared to the experimental data in Fig. 12 for various constriction factors, γ . The best match to the data is obtained when the constriction factor of the pores before precipitation is six, or $\beta=0.255$. This constriction factor is a reasonable value for the ratio of pore body to pore throat diameters of many geologic formations. Most pores are much longer than they are wide and are randomly oriented. Since each pore body in a clastic formation is normally connected to an adjacent pore body, the effective pore body width will be much wider than the pore throat width.

The sinusoidal model for permeability reduction, like the corresponding model with step changes in radius, allows the permeability to be reduced to zero while pore space

remains in the medium. The porosity remaining after the permeability has been reduced to zero is called the critical porosity. Although models for the permeability reduction have been developed in terms of the critical porosity (Verma and Pruess, 1988; Graham, 1973), no simple way to determine the critical porosity has been presented.

7.6 Statistical Network Model

Another approach to modeling the permeability of a porous medium is by assuming that the medium consists of a network of randomly-distributed interconnected pores. Unlike the previous models discussed, the network models allow a distribution of pore sizes to be considered.

Taylor et al. (1990) calculated the reduction in permeability as a function of the reduction in porosity following the growth of a uniform thickness biofilm in the network for several of the "cut-and-random-rejoin" models. In these models, the network is constructed by randomly distributing a set of cylindrical pores in a plane. A second plane containing a different random distribution of pores is then placed beside the first and the pores that overlap are joined. The process of adding planes of randomly distributed pores is continued until the network has been created. An arbitrary pore size distribution can be used. They did not present any data to support their models, however.

Taylor et al. considered several cut-and-random-rejoin models and recommend one presented by Mualem (1976) for predicting permeability reduction. The resulting reduction in permeability was found to depend strongly on the pore size distribution parameter, z , with a greater permeability reduction for more uniform pore sizes, e.g., higher values of z . For the soils they studied, the value of z is about 2.0. From Fig. 13, however, it can be seen that this model significantly underpredicts the experimentally measured permeability reductions.

A separate network model was presented by Bryant et al. (1993a). In their model, the pore network was obtained by direct measurement of the location of about 8,000 randomly packed spheres. The permeability was then calculated by assuming a conic frusta between all of the individual pores (Bryant et al., 1993b). A layer of cementation was assumed to grow uniformly over all surfaces and the permeability and porosity of the network recalculated. The resulting reduction in permeability is also shown in Fig. 13. This network also underpredicted the measured permeability reduction.

Bryant et al. (1993a) claimed that the pore structure of actual networks is correlated, not random. Because of this, the resulting permeability reduction in actual pore networks will be greater than those predicted with random networks. As seen in Fig. 13, the permeability reduction of the Bryant et al. model, which included real pore structure correlation, was greater than that of the random Taylor et al. model, which did not.

8. CONCLUSIONS

This study of the thermal precipitation process has been successfully completed. The process has shown to successfully plug porous media under conditions that normally encountered in geologic formations.

- 1. Analytical models were developed for predicting the fractional reduction in porosity for the cases when the solution is cooled by either conduction or convection.**
- 2. The chemical literature was reviewed for chemicals that have the proper solubility properties to be used for the thermal precipitation process. The MSDS, safety, health, and environmental problems associated with these chemicals have been reviewed. Based on this review, boron oxide, potassium carbonate, potassium chloride, and sodium borate are the only chemicals are recommended as being suitable for the thermal precipitation process.**
- 3. An experimental apparatus was designed and constructed to study permeability reduction by thermal precipitation.**
- 4. An extensive set of experimental data was obtained for the thermal precipitation of potassium carbonate and sodium borate in Berea sandstone. Data was also obtained for potassium carbonate in a limestone cores. These data included porosity and permeability measurements of the cores, both before and after treatment with the thermal precipitation process.**
- 5. The reduction in permeability at a given reduction in porosity for limestone was considerably greater than that of sandstone. The reduction in permeability appears to depend on pore geometry.**
- 6. Theoretical models predicting the permeability reduction from thermal precipitation were reviewed and compared to the experimental data from Berea sandstone. Most existing models, including the Karman-Cozeny equation, were found to significantly underpredict the actual reduction in permeability. Improved models for the permeability reduction were then developed.**
- 7. A design study to determine how the thermal precipitation process would be implemented in the field is recommended. A study of the applicability of this process to provide a barrier around hazardous and radioactive waste sites is also recommended.**

NOMENCLATURE

English

a	= Empirical constant
b	= Empirical constant
BV	= Bulk volume of core
c	= Empirical constant
K	= Permeability
K'	= Permeability after precipitation
K_{tube}	= Permeability of capillary tube, based on tube area
K'_{tube}	= Permeability of capillary tube after precipitation, based on tube area
K_f	= Final permeability
K_i	= Initial permeability
K_o	= Shape factor in Carmen-Kozeny equation
L	= Length of core
L_e	= Length of fluid flow path
M_h	= Mass of chemical dissolved in water at temperature T_h
M_l	= Mass of chemical dissolved in water at temperature T_l
MR	= Volumetric heat capacity of the reservoir
M_s	= Volumetric heat capacity of saturated solution
M_w	= Mass of water that dissolves chemical
PV	= Pore volume
PV'	= Pore volume after precipitation
Q	= Enthalpy
r	= Radius of capillary tube
r'	= Radius of pore after precipitation
r_e	= Effective radius of matrix around capillary tube
r_m	= Mean radius of sinusoidal pore
r_p	= Radius of pore body
r_t	= Radius of pore throat
S	= Solubility
S_b	= Specific surface of core (per bulk volume)
S_g	= Specific surface of core (per grain volume)
SG	= Specific gravity of chemical used in thermal precipitation
S_p	= Specific surface of core (per pore volume), cm^{-1} .
S_s	= Fraction of pore volume occupied by solution

T_h	= Initial high temperature
T_l	= Final low temperature
V_p	= Volume of precipitated solids
V_R	= Bulk volume of formation
V_s	= Volume of solution
V_t	= Total pore volume
W_{df}	= Final dry weight of core, after treatment and drying
W_{di}	= Initial dry weight of core before thermal precipitation
W_p	= Weight of chemical in solution
W_{pd}	= Weight of chemical precipitated during drying of the core
W_{pt}	= Weight of solids precipitated during thermal precipitation
W_s	= Weight of core saturated with chemical solution following thermal precipitation
W_t	= Total weight of solids precipitated from treatment and drying
W_w	= Weight of water removed from the core during drying
x	= distance along sinusoidal pore
X	= Mass fraction of chemical in solution

Greek

α	= Thickness of precipitate layer
β	= Parameter in sinusoidal pores
γ	= Construction factor of pore
$\Delta\phi$	= Reduction in porosity
Δk	= Change in permeability
ϕ	= Porosity
ϕ_f	= Final porosity
ϕ_i	= Initial porosity
ρ_h	= Density of solution at high temperature
ρ_p	= Density of precipitated solids
ρ_w	= Density of pure water, gm/cc.

REFERENCES

- Aliaga, D. A., Gang Wu, Lake, L. W., and Sharma, M. M., "Barium and Calcium Sulfate Precipitation, Dissolution, and Migration Inside Sandpacks," paper SPE 19765 presented at the 64th Annual Technical Conference and Exhibition, San Antonio, TX, Oct. 8-11, 1989.
- Allison, D. J. and Purkale, D. J., "Reducing Permeability of Highly Permeable Zones in Underground Formations," U.S. Patent 4,773,481, Sept. 27, 1988.
- Aruna, M., "The Effect of Temperature and Pressure on Absolute Permeability of Sandstones," PhD dissertation, Stanford U., Stanford, CA, 1976.
- Angevine, C. L. and Turcotte, D. L., "Porosity Reduction by Pressure Solution: A Theoretical Model for Quartz Arenites," Geol. Soc. Am. Bul., Vol. 94, pp. 1129-1134, Oct. 1983.
- Azzam, M.I.S. and Dullien, F.A.L., "Flow in Tubes with Periodic Step Changes in Diameter: A Numerical Solution," Chemical Engineering Science, Vol. 32, pp. 1445-1455, 1977.
- Bourbie, T. and Zinszner, B., "Hydraulic and Acoustic Properties as a Function of Porosity in Fontainebleau Sandstone," J. Geophy. Res., Vol. 90, No. B13, pp. 11,524-11,532, Nov. 10, 1985.
- Bryant, S. L., Mellor, D. W., and Cade, C. A., "Physically Representative Network Models of Transport in Porous Media," AIChE J., Vol. 39, No. 3, pp. 387-396, March 1993a.
- Bryant, S. L., King, P. R., and Mellor, D. W., "Network Model Evaluation of Permeability and Spatial Correlation in a Real Random Sphere Packing," Transport in Porous Media, Vol. 11, pp. 53-70, 1993b.
- Camp, T. R., "Theory of Water Filtration," J. Am. Soc. Civ. Eng., Vol. 90, pp. 1-3, 1964.
- Chu, C. F. and Ng, K. M., "Flow in Packed Tubes with a Small Tube to Particle Diameter Ratio," AIChE, J., Vol. 35, No. 1, pp. 148-158, Jan. 1989.
- Danesh, A., Krinis, D., Henderson, D. G., and Peden, M. J., "Asphaltene Deposition in Miscible Gas Flooding of Oil Reservoirs," Chemical Engineering Reservoir & Design, Vol. 66, No. 4, pp. 339-344, July. 1988.
- Dibble, W. E. Jr., Nur, A., and Potter, J. M., "Porosity Reduction in Sandstone," paper SPE 11970 presented at the 1983 SPE Annual Technical Conference and Exhibition, San Francisco, Sept. 5-8, 1983.
- Doyen, P. M., "Permeability, Conductivity, and Pore Geometry of Sandstone, J. Geophy. Res., Vol. 93, No. B7, pp. 7729-7740, July 10, 1988.
- Dullien, F. A. L., "Single Phase Flow Through Porous Media and Pore Structure," Chem. Eng. J., Vol. 10, pp. 1-34, 1975.

- Gang Wu and Sharma, M. M., "Model for Precipitation and Dissolution Processes with Precipitate Migration," *AIChE. J.*, Vol. 35, No. 8, pp. 1385-1390, Aug. 1989.
- Graham, R. A., "A Quantitative Determination of Microstructure on Gas Permeability of UO_2 and Ni Sintered Bodies," M.S. Thesis, Univ. of Fla., Gainesville, 1973.
- Holbrook, O. C., and George G. B.: "Secondary Recovery of Oil From Reservoirs by Successive Precipitation," U.S. Patent 2,903,065, August 7, 1957.
- Hower, F. W., and Ramos, J., "Selective Plugging of Injection Wells by In Situ Reaction," Secondary Recovery Symposium, Halliburton Oil Well Cementing Co, Wichita Falls, Tex., Nov. 19-20, 1956.
- Iler, R. K., "The Colloid Chemistry of Silica and Silicates," Cornell U. Press, New York City, pp. 4-13, 1955.
- Jennings, R. A., Jr. and Hoefner, L. M., "Method to Improve Use of Polymers for Injectivity Profile Control in Enhanced Oil Recovery," U.S. Patent 4,848,464, July 18, 1989.
- Krauskopf, K., "Introduction to Geochemistry," McGraw-Hill Book Co. Inc., New York City, 1967.
- Lauwerier, H. A., "The Transport of Heat in an Oil Layer Caused by Injection of Hot Fluid," *Applied Scientific Research*, Vol. A5, pp. 145-150, 1955.
- Leder, F. and Park, W. C., "Porosity Reduction in Sandstone by Quartz Overgrowth," *Am. Assoc. of Pet. Geol. Bul.*, Vol. 70, No. 11, pp. 1713-1728, Nov. 1986.
- Lund, K., "On Acidizing of Sandstone," Ph.D. Dissertation, Univ. of Mich., Ann Arbor, 1974.
- McClure, L. C., Fogler, H. S., and Kline, W. E., "An Experimental Technique for Obtaining Permeability-Porosity Relationships in Acidizing Porous Media," *Ind. Eng. Chem. Fundam.*, Vol. 18, pp. 188-191, 1979.
- Meadors, G. V., "Selective Plugging Procedure for Improving Secondary Recovery Operations," U.S. Patent 2,800,184, July 23, 1957.
- Moore, D. E., Morrow, C., and Byerlee, J., "Chemical Reactions Accompanying Fluid Flow Through Granite in a Temperature Gradient," *Geochimica et Cosmochimica Acta*, Vol. 47, pp. 445-453, Nov. 29, 1982.
- Morrow, C., Lockner, D. M., and Byerlee, J., "Permeability of Granite in a Temperature Gradient," *Journal of Geophysical Research*, Vol. 86, No. B4, pp. 3002-3008, April 10, 1981.
- Muallem, Y., "A New Model for Predicting the Hydraulic Conductivity of Unsaturated Porous Media," *Water Resour. Res.*, Vol. 12, No. 3, pp. 513-522, 1976.
- Myhill, N. A. and Stegemeier, G. L., "Steam Drive Correlation and Prediction," *J. Pet. Tech.*, pp. 173-182, Feb. 1978.

- Navratil, M. and Mitchell, S. M., "Composition and Methods for Reducing the Permeability of Underground Strata," U.S. Patent 4,836,285, June 6, 1989.
- Needham, R. B., Threlkeld, C. B., and Gall, J.W., "Control of Water Mobility Using Polymers and Multivalent Cations," paper SPE 4747 presented at the 1974 SPE Improved Oil Recovery Symposium, Tulsa, April 22-24, 1974.
- Parneswar, R., and Willhite, P. G., "A Study of the Reduction of Brine Permeability in Berea Sandstone with the Aluminium Citrate Process," SPE Reservoir Engineering, Vol. 3, pp 959-966, August 1988.
- Perry, J. H., Chilton, C. H., and Kirkpatric, S. D., "Perry's Chemical Engineers Handbook," Fourth Edition, McGraw Hill Book Company, New York, 1963.
- Reed, M. G., "Gravel Pack and Formation Sandstone Dissolution During Steam Injection," Journal of Petroleum Technology, pp 941-949, June 1980.
- Rege, S. D. and Fogler, H. S., "Competition Among Flow, Dissolution, and Precipitation in Porous Media," AIChE J., Vol. 35, No. 7, pp. 1177-1185, July 1989.
- Richardson, E. A., "Plugging a Subterranean Formation by Homogeneous Solution Precipitation," U.S. Patent 3,614,985, October 26, 1971.
- Richardson, E. A., Scheuerman, R. F., "Plugging Solution Precipitation Time Control," U.S. Patent 3,730,272, May 1, 1973.
- Rumpf, H. and Gupte, A.R., "Einflüsse der Porosität und Korngrößenverteilung im Widerstandsgesetz der Porenströmung," Chem. Ing. Tech., Vol. 43, p. 367, 1971 (in German).
- Ryles, G. R., "High Temperature Profile Modification Agents and Methods for Using Same," U.S. Patent 4,865,129, Sep. 12, 1989.
- Schechter, R. S. and Gidley, J. L., "The Change in Pore Size Distribution from Surface Reactions in Porous Media," AIChE J., Vol. 15, No. 3, pp. 339-350, May 1969.
- Schwartz, L. M. and Banavar, J. R., "Transport Properties of Disordered Continuum Systems," Phys. Rev. B., Vol. 39, No. 16, pp. 965-970, June 1989.
- Seright, R. S., "Placement of Gels to Modify Injection Profiles," New Mexico Petroleum Recovery Research Center, SPE/DOE 17332, April 1988.
- Sharma, M. M. and Gang Wu., "Model for Precipitation and Dissolution Processes with Precipitate Migration," AIChE Journal, Vol. 35, No. 8, pp 1385-1390, Aug. 1989.
- Sharp, A. K., "Procedure for Improving Reservoir Sweep Efficiency Using Paraffinic or Asphaltic Hydrocarbons," U.S. Patent 4,842,070, June 27, 1989.
- Shaw, J. C., Churcher, P. L., and Hawkins, B. F., "The Effect of Firing on Berea Sandstone," SPE Formation Evaluation, pp. 72-78, Mar. 1991.
- Showalter, E. W., "Method for Improving the Injection Profile of a Water Injection Well," U.S. Patent 3,677,343, July 18, 1972.

- Sohnel, O. and Novotny, P., "Densities of Aqueous Solutions of Inorganic Substances," Elsevier Science Publishers B.V., Amsterdam, 1985.
- Suman, G. O., Richardson, E. A., Scheuerman, R. F., "Hydrated Metal Oxide Deposition," U.S. Patent 3,854,538, December 17, 1974.
- Taylor, S. W., Milly, P. C. D., Jaffe, P. R., "Biofilm Growth and the Related Changes in the Physical Properties of a Porous Medium: 2. Permeability," Water Resour. Res. Vol. 26, No. 9, pp. 2161-2169, Sept. 1990.
- Todd, A. C. and Yuan, M D., "Barium and Strontium Sulfate Solid Solution Scale Formation at Elevated Temperatures," SPE Production Engineering, pp. 85-92, Feb. 1992.
- Torrest, R. S. and Huang, S. H., "Alumina Precipitation in Porous Media for Profile Control," SPE 16251, presented at the SPE International Symposium on Oilfield Chemistry, San Antonio, Texas, Feb. 4-6, 1987.
- Verma, A. and Pruess, K., "Thermohydrological Conditions and Silica Redistribution Near High-Level Nuclear Wastes Emplaced in Saturated Geological Formations," J. Geophysical Res., Vol. 93, No. B2, pp. 1159-1173, Feb. 10, 1988.
- Walsh, M. P., Bryant, S. L., Schechter, R. S., and Lake. L. W., "Precipitation and Dissolution of Solids Attending Flow through Porous Media," AIChE J., Vol. 30, No. 2, pp. 317-328, March 1984.
- Walsh, M. P., Lake, L. W., and Schechter, S. R., "A Description of Chemical Precipitation Mechanisms and Their Role in Formation Damage During Stimulation by Hydrofluoric Acid," Journal of Petroleum Technology, Sept. 1982.
- Weinbrandt, R. M., Ramey, H. J. Jr., and Casse, F. J., "The Effect of Temperature on Relative and Absolute Permeability of Sandstones," SPEJ, pp. 376-84, Oct. 1975.
- Willman, B. T., Valleroy, V. V., Runberg, G. W., Cornelius, A. J., and Powers, L. W., "Laboratory Studies of Oil Recovery by Steam Injection," J. Pet. Tech., pp. 681-690, July 1961.
- Wyllie, M. R. J. and Gardner, G. H. F., "The Generalized Kozeny-Carman Equation," World Oil, pp. 121-128, March 1958.
- Wyllie, M. R. J. and Gregory, A. R., "Fluid Flow Through Unconsolidated Porous Aggregates: Effect of Porosity and Particle Shape on Kozeny-Carman Constants," Industrial and Engineering Chemistry, Vol. 47, No. 7, pp. 1379-1388, July 1955.

Table 1 Chemicals Studied

Ammonium Nitrate
Barium Chlorate
Barium Hydroxide
Boron Oxide
Calcium Nitrate
Potassium Carbonate
Potassium Chlorate
Potassium Chloride
Potassium Nitrate
Potassium Nitrite
Sodium Borate
Sodium Chlorate
Sodium Chloride
Sodium Hydroxide
Sodium Nitrate
Sodium Nitrite

Table 2. Summary of Experimental Data for Berea Sandstone

Test No.	Temp °C	Chemical Injected	Permeability Reduction			Porosity Reduction		
			K _i (md)	K _f (md)	$\Delta K/K_i$	ϕ_i	ϕ_f	$\Delta\phi/\phi_i$
1	80	K ₂ CO ₃	120.0	88.6	26.0	21.0	19.9	5.1
2	80	K ₂ CO ₃	61.0	43.1	29.1	19.6	18.3	6.5
3	127	K ₂ CO ₃	110.0	61.0	45.0	22.0	19.3	12.8
4	127	K ₂ CO ₃	99.0	51.0	48.5	21.3	19.1	10.0
5	127	K ₂ CO ₃	37.0	15.8	57.0	19.7	16.2	17.7
6	160	K ₂ CO ₃	211.0	89.0	59.7	24.4	19.5	20.0
7	160	K ₂ CO ₃	496.0	75.0	0.848	25.52	17.5	0.314
8	180	K ₂ CO ₃	302.0	2.0	0.993	25.0	12.0	0.519
9	80	Na ₂ B ₄ O ₇	907.0	303.0	63.0	26.4	23.9	9.5
10	80	Na ₂ B ₄ O ₇	413.0	192.0	53.5	25.8	22.1	16.7

Table 3. Summary of Experimental Data for Limestone

Test No.	Temp °C	Chemical Injected	Permeability Reduction			Porosity Reduction		
			K _i (md)	K _f (md)	$\Delta K/K_i$	ϕ_i	ϕ_f	$\Delta\phi/\phi$
1	80	K ₂ CO ₃	13.1	0	100	18.2	15.0	17.4
2	80	K ₂ CO ₃	12.05	0.52	96	18.7	16.4	12.4

Figure 1. Effect of Temperature on Quartz and Amorphous Silica Solubility in Pure Water

Figure 2. Quartz Sand Dissolution During Flow of Water as a Function of Temperature and pH

Figure 3. Quartz Sand Dissolution During Flow of Water as a Function of Temperature and pH

Figure 4. Chemical Solubility as a Function of Temperature

Figure 5. Schematic of Experimental Apparatus

Figure 6. Comparison of Measured and Calculated Fractional Reduction in Porosity for Potassium Carbonate

Figure 7. Measured Fractional Reduction in Permeability

Figure 8. Exponential Permeability Reduction Model

Figure 9. Power Law Permeability Reduction Model

Figure 10. Carman-Kozeny Equation Permeability Reduction Model

Figure 11. Schematic of Sinusoidal Pore

Figure 12. Sinusoidal Permeability Reduction Model

Figure 13. Network Permeability Reduction Models

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