Geochemical Equilibrium Modeling of the Auburn Thermal Energy Storage Field Test

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October 1979

**Prepared for the U.S. Department of Energy
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**Pacific Northwest Laboratory
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SUMMARY

Since 1976, two field experiments have been completed involving storage of heated water in a shallow, confined aquifer near Mobile, Alabama. These experiments, designed and operated by Auburn University, proved to be successful with respect to energy storage and recoverability. However, significant reductions in well injectivity (permeability) were encountered during the injection phase of the operations. This near-well clogging occurred within the first 24 to 48 hours and may be potentially attributed to a combination of particulate plugging, clay swelling and dispersion, and temperature-induced outgassing. It is speculated that had storage formation water been used as the working fluid, instead of water from an overlying aquifer, loss of well injectivity might have been inhibited or avoided totally. Unfortunately, there is insufficient data to substantiate this hypothesis and subsequent field testing is warranted.

The objective of the study described in this report is to investigate some alternate reservoir damage mechanisms that may have contributed to the loss of well injectivity experienced at the Mobile field site. Specifically, this includes mineral precipitation and/or alteration resulting from:

- 1) increased temperatures and temperature gradients, 2) presence of oxygen, 3) fluid-fluid incompatibility (mixing of two different aquifer waters), and 4) fluid-rock incompatibility (introducing foreign groundwaters into storage aquifer sedimentary matrix).

The primary investigatory tool used in the study is an Electric Power Research Institute computer program (EQUILIB), which is based on equilibrium chemical thermodynamics. The computer code was utilized to simulate changes in mineralogy and groundwater chemistries due to the interaction of the sediment material and two differing aquifer waters at temperatures of 55°C, 100°C, and 150°C. Conclusions are primarily based on the 55°C results since this was the maximum operating temperature for the Auburn experiment. The main conclusions of this study are:

- 1) Hydrothermal reactions, oxidation reactions, fluid-fluid incompatibility, and fluid-rock incompatibility do not provide reasonable explanations for the observed loss in well injectivity. Results predicted by EQUILIB imply mineral precipitates such as hematite (iron oxide) and adularia (potassium aluminum silicate) would be either too small in quantity or too slow in formation to account for the rapid plugging.
- 2) The montmorillonite content in the sediments and the relative salinity difference between the water extracted from the supply well and the ambient water in the storage aquifer are potentially sufficient to cause significant clay swelling and dispersion.
- 3) It is quite possible that outgassing or the formation of bubbles due to decreased gas solubilities with higher temperatures and lower pressure may have contributed to the loss of injectivity. Unfortunately, no dissolved oxygen data are available for the supply well waters.
- 4) Suspended solids may have contributed to the plugging. However, no data are available on the size or density distributions of particles suspended in the groundwater.
- 5) Prior to field development, any candidate Seasonal Thermal Energy Storage (STES) site should be subjected to a well-documented set of laboratory and/or small-scale field tests including:
 - Groundwater
 - cation and anion concentrations
 - dissolved silica
 - pH
 - Eh
 - suspended solids
 - dissolved gases
 - Rock or sediment
 - particulate plugging
 - water sensitivity
 - mineralogy
 - bulk chemistry
 - thermo-mechanical properties
 - thermal diffusivity
- 6) With laboratory and/or small field loop equipment designed to simulate STES operating conditions, simultaneous permeability and stress-strain measurements should be made for site-specific sediment samples being treated with heated groundwater. Emphasis should be on permeability degradation, volumetric strain increases, and water quality alterations.

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INTRODUCTION

Since 1976, two field experiments have been conducted by Auburn University involving storage of heated waters in a shallow, confined aquifer near Mobile, Alabama (Molz et al. 1978, 1979). The first experiment involved injection of $7,570 \text{ m}^3$ of 37°C , filtered water from an electric power plant cooling water canal. Figure 1 shows a plan view of the test facility. The storage aquifer is located between 40 and 62 m below the land surface. The heated canal water was stored for 37 days and then recovered with an overall thermal efficiency of 67%.

The process was inhibited by significant plugging of the injection well. This has been attributed to clay and silt particles suspended in the canal water; filtering above the 5-micron range improved but did not eliminate the problem. Ultimately, the injection was terminated when increased pumping pressure, necessary to maintain reasonable injection volume, resulted in loss of confinement. Subsequent investigations revealed that failure occurred along an abandoned well casing which penetrated the clay confining layer in the vicinity of the main injection well. This failure was subsequently corrected by pressure grouting.

A second experiment, utilizing the same storage aquifer, involved a 79-day injection of $55,345 \text{ m}^3$ of 55°C boiler heated water. The water source was a partially confined aquifer located between 25 m and 34 m below the land surface. The water was stored for 50 days and then retrieved over a 41-day period. The recovery efficiency was 65% over a temperature range of 55°C to 33°C . Ambient groundwater temperature was 20°C . Figure 2 is a schematic of this second experiment. It is important to note that the supply water was extracted from an overlying aquifer and, therefore, the system did not represent a true doublet configuration.

Clogging of the injection well again proved to be a major operational difficulty. Loss of permeability resulted in a decrease in the maximum injection rate from 12.6 l sec^{-1} (200 gpm) to 6.3 l sec^{-1} (100 gpm). Plugging of the well may have been due to the water sensitive nature of the storage

FIGURE 1. Schematic Diagram Showing the Details of the First Project Site near Mobile, Alabama (Molz et al. 1978)

FIGURE 2. Schematic Diagram of the Second Mobile, Alabama, Field Test System (Molz et al. 1979)

aquifer sediments. Montmorillonite clay in the storage aquifer combined with a low cation concentration of the supply water relative to the storage aquifer water may have resulted in swelling and dispersion of clay particles as shown conceptually in Figure 3. Such water sensitivity is a documented phenomenon which lends itself to laboratory identification and field pretreatment (Hewitt 1963, Day et al. 1967, Reed 1972). It is also possible that the supply aquifer water contained suspended solids and/or dissolved gases. Suspended solids could contribute to particulate plugging, and temperature-induced air bubble formation might have also contributed to the plugging.

SWELLING CLAY

PARTICLE PLUGGING

brine

brine

fresh water

fresh water

FIGURE 3. Conceptualization of Clay Swelling and Dispersion

In general, there are other potential reservoir damage mechanisms. Examples include precipitation of minerals due to the mixing of incompatible groundwaters or introducing foreign groundwater into the storage aquifer. Increasing temperatures might conceivably result in hydrothermal alteration of minerals, dissolution, and scaling. Permeability reduction potentially due to

temperature-induced increases in quartz-water adhesion (Danesh 1978) and/or microstructural formation damage (Casse 1974) is also conceivable. The introduction of oxygen and carbon dioxide can change the solution pH and result in production of relatively insoluble oxidation products. Particulate plugging can result from a number of sources including existing formation fines, pipe corrosion products, mineral scale, and solids suspended in the injected water.

The primary objective of this study is to investigate fluid-fluid incompatibility, fluid-rock incompatibility, hydrothermal mineral alterations, and redox reactions with respect to potential contribution to the loss of well injectivity observed at the Auburn field experiments. This investigation was based totally on chemical thermodynamic computer modeling. Unfortunately, since no laboratory experimentation and/or post-experimental field data are available for comparison, the results of this computer study are only of qualitative interest. The remainder of this report includes: 1) descriptions of the initial mineralogy and water chemistry associated with the second Auburn field experiment, 2) description of the computer model employed in this study, 3) description of test cases simulated, and 4) analysis and conclusions.

SEDIMENT AND GROUNDWATER CHARACTERIZATION

Because of the time delay between the field tests and this computer-oriented study, no groundwater samples were available for chemical analysis. Records at Auburn University yielded the partial analyses listed in Table 1. The supply aquifer refers to the near-surface, semi-confined aquifer. The storage aquifer refers to the deeper, confined aquifer utilized for the thermal water storage. Microscopic examination and X-ray diffraction of a single storage aquifer sediment sample resulted in the estimated mineralogy listed in Table 2. The grain size distribution determined by sieve analysis is listed in Table 3.

Because the water chemistry, as reported, did not represent a charge-balanced solution and no additional water samples were available, it was necessary to make assumptions concerning the anion concentrations required to

TABLE 1. Groundwater Chemistries as Supplied by Auburn University

Water Type	Supply Aquifer (Unconfined Aquifer)		Storage Aquifer (Confined Aquifer)	
	mg/l		(mg/l)	
	Sample 1	Sample 2	Sample 1	Sample 2
Na	3.40	0.60	7.60	11.10
Ca	0.33	0.21	0.05	0.38
Fe	0.07	0.07	0.06	0.05
Si	6.30	9.10	10.40	9.70
CaCO ₃	3.80	3.80	176.00	176.00
pH	7.19	7.19	7.38	7.38
Temperature	19.5°C	19.5°C	19.5°C	19.5°C

TABLE 2. Initial Sample Mineralogy Based on Optical Petrography and X-ray Diffraction

Mineral	Composition	Concentration (Vol%)
Calcite	CaCO ₃	3.7
Quartz	SiO ₂	76.5
Hematite	Fe ₂ O ₃	2.5
Muscovite	KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	1.3
Kaolinite	Al ₄ Si ₄ O ₁₀ (OH) ₈	2.8
Alkali Feldspar	(K,Na)AlSi ₃ O ₈	8.3
Plagioclase Feldspar	NaAlSi ₃ O ₈ - CaAl ₂ Si ₂ O ₈	4.5
Montmorillonite	(1/2Ca,Na,K) _{0.7} (Al, Mg,Fe) ₄ (Al,Si) ₈ O ₂₀ (OH) ₄ · nH ₂ O	0.4

maintain a charge balance. Only CO₃²⁻ was used for the charge balance although other negative species, e.g., Cl⁻, OH⁻ are possible. The H⁺ concentration was determined based on the reported pH values. Table 4 reveals the method used for charge balancing the storage aquifer waters. In all cases, the available water analyses were averaged and then arithmetically balanced. One of the major drawbacks in this study was the lack of data on dissolved gases and suspended solids for the two groundwaters. As a result, no conclusions were possible concerning outgassing or particulate plugging.

TABLE 3. Grain Size Distribution from Sieve Analysis

<u>Size Fraction</u>	<u>Weight Percent</u>	<u>Description</u>	<u>Phi Size</u>
18 x 35	0.22	Coarse Sand	0.0-1.0
35 x 120	86.39	Medium Sand Fine Sand	1.0-3.0
120 x 200	4.82	Very Fine Sand	3.0-3.75
200 x 325	4.18	Very Fine Sand Coarse Silt	3.75-4.5
-325	4.39	Coarse Silt and Finer	

TABLE 4. Example Charge Balance for Storage Aquifer

<u>Cation</u>	<u>ppm</u>	<u>moles kg-1</u>	<u>Charge</u>	<u>Total moles</u>
Fe ²⁺	0.055	9.848×10^{-7}	2	1.970×10^{-6}
Na ⁺	9.350	4.067×10^{-4}	1	4.067×10^{-4}
Ca ²⁺	0.220	5.489×10^{-6}	2	1.098×10^{-5}
H ⁺		4.170×10^{-8}	1	4.170×10^{-8}
				4.197×10^{-4}

Anion

$$\frac{4.197 \times 10^{-4} (+)}{2 \text{ mole } (-)/\text{mole CO}_3^{2-}} = 2.098 \times 10^{-4} \text{ moles of CO}_3^{2-} \text{ required}$$

DESCRIPTION OF THE EQUILIB COMPUTER MODEL

Thermal energy storage (TES) in aquifers is somewhat analogous to natural geothermal conditions, although in most cases the temperatures of interest are somewhat lower for TES. As such, it is possible to utilize several tools developed for the geothermal industry. One such tool is an equilibrium chemical thermodynamics computer program developed at Battelle for the Electric Power Research Institute (EPRI). The model (EQUILIB) is based on theoretical

work by H. C. Helgeson (Helgeson et al. 1970). Up to 122 aqueous species, 7 gas species, and 131 mineral components are contained in the associated data base. This includes silicates, oxides, carbonates, sulfides, and sulfates (Shannon et al. 1976).

The computer code includes the factors listed in Table 5. All calculations are based on 1 kg of fluid. New equilibrium mineralogy and water chemistry are calculated at any specified temperature between 25°C and 300°C. Examples of the EQUILIB data base are shown in Figure 4. A generalized flow diagram is shown in Figure 5.

TABLE 5. Categories Included in the EQUILIB Computer Model
(Shannon et al. 1976)

- Temperature
- Cation and anion concentrations
- pH
- Partial pressure of gases
- Activity coefficients for aqueous species
- Ionic strengths affecting chemical activities
- Components controlling oxidation potentials
- Solubilities of solid minerals
- Aqueous phase equilibria
- Total mass balances

FIGURE 4. Example EQUILIB Data Base Entries
Activity Versus Temperature

DESCRIPTION OF TEST CASES

The objective of this study is to analyze some potential alternate causes of formation plugging at the Auburn field test. The following observations are noted:

- The shallow partially confined supply aquifer is low in ionic concentration relative to the storage aquifer, and has unknown suspended solid and dissolved gas concentrations.
- The deeper, confined, storage aquifer water is assumed to be in chemical equilibrium with the formation mineralogy at a temperature of 19.5°C.
- The supply and storage waters were increased in temperature from 19.5°C to approximately 55°C.
- Plugging occurred when the supply aquifer water was used as the working fluid.
- Plugging apparently did not occur when the storage formation water was injected back into the storage aquifer. This water was not heated however (Molz, Auburn University, personal communication).

Based on these observations and a water sensitivity test conducted at Auburn University, (Molz, personal communication), it is probable that the loss in well injectivity resulted primarily from particle plugging and clay swelling and dispersion. The montmorillonite content is less than a percent by weight; however, this is often sufficient to inhibit the flow of low salinity waters (Hewitt 1963). Furthermore, particles in the low micron to submicron range can often reduce permeability (Reed 1972).

Other potential reservoir damage mechanisms amenable to simulation with EQUILIB include:

- mineral precipitation as the working fluid temperature is increased
- mineral precipitation as oxygen is introduced to the system
- mineral precipitation due to the mixing of the potentially incompatible supply and storage formation waters

- mineral precipitation due to a chemical incompatibility between the supply water and the storage aquifer sediment and/or hydrothermal alteration products.

To study these four potential categories, several computer simulations were conducted. The independent variables in the test matrix are listed in Table 6. Not all possible factorial combinations reflect realistic field conditions. The cases actually simulated are listed in Table 7.

TABLE 6. Independent Variables

Working Fluid

- Shallow supply aquifer water
- Deeper storage aquifer water

Temperature

- 20°C
- 55°C
- 100°C
- 150°C

Dissolved Oxygen

- 0 ppm
- 8 ppm

Initial Water Chemistry

- Supply aquifer (Table 1)
- Storage aquifer (Table 1)

Initial Mineralogy

- Storage aquifer (Table 2)

TABLE 7. Computer Test Cases

<u>Input</u>	<u>Oxygen</u>	<u>20°C</u>	<u>55°C</u>	<u>100°C</u>	<u>150°C</u>
1) Supply Water Alone	-	-	X	X	X
2) Supply Water Alone	X	X	X	X	X
3) Storage Water Alone	-	X	X	X	X
4) Supply Water Plus Storage Water	X	X	X	X	X
5) Supply Water Plus Storage Water Plus Minerals	X	-	X	X	X

DATA ANALYSIS AND CONCLUSIONS

For each computer simulation, the following equilibrium data were tabulated: 1) equilibrium mineralogy, 2) type and quantity of new mineral precipitates, 3) fluid temperature and pH, and 4) aqueous species concentrations. It is assumed that if minerals precipitate to any significant degree, decreased formation permeability might result.

MINERAL PRECIPITATION DUE TO INCREASED TEMPERATURES, OXYGEN AND/OR MIXING OF AQUIFER WATERS

Increasing the working fluid temperature and/or oxygen content (Eh) in this case apparently has a negligible effect on mineral precipitation. Hematite, a ferric (iron) oxide, is the only mineral predicted susceptible to precipitation. However, as shown in Table 8, the quantity in moles per kilogram of water is rather insignificant. In addition, mixing the supply aquifer water and the storage aquifer water does not result in deleterious mineral precipitation; therefore, fluid-fluid incompatibility might be discounted as a contributor to the observed formation plugging at the Auburn field tests.

ALTERATION OF THE STORAGE AQUIFER MINERALOGY

This scenario involves combining the aerated heated supply water with ambient temperature groundwater and minerals in the storage aquifer. In actuality a temperature profile will exist in the aquifer such that temperature will decrease with radial distance from the injection well. The concern is that mineral dissolution might occur in the elevated temperature zones and deposition might result in the cooler regions of the reservoir. Conversely, any minerals with retrograde solubility might tend to plug the wellbore region.

Table 9 shows the ionic concentrations in the groundwater and equilibrium mineralogy predicted by EQUILIB for four different injection water temperatures. With respect to the mineralogy at 55°C, it can be observed that EQUILIB predicts that calcite, muscovite, and kaolinite all reacted to some

TABLE 8. Minerals Precipitated Due to Heat, Oxygen and/or Fluid-Fluid Incompatibility

Fluid	Oxygen	Temperature (°C)	pH	Eh	Insoluble Minerals (quantity moles/kg water)
Supply Water Alone	Yes	20	7.19	+0.807	quartz SiO ₂ (0.192E-03) hematite Fe ₂ O ₃ (0.627E-06)
		55	8.36	+0.541	hematite Fe ₂ O ₃ (0.627E-06)
		100	7.77	+0.354	hematite Fe ₂ O ₃ (0.627E-06)
		150	7.34	+0.226	hematite Fe ₂ O ₃ (0.627E-06)
Supply Water Alone	No	55	8.36	-0.215	minnesotaite Fe ₃ Si ₄ O ₁₀ (OH) ₂ (0.418E-06)
		100	7.77	-0.159	hematite Fe ₂ O ₃ (0.627E-06)
		150	7.34	-0.178	hematite Fe ₂ O ₃ (0.627E-06)
Storage Water Alone	No	20	7.38	-0.091	quartz SiO ₂ (0.274E-03) minnesotaite Fe ₃ Si ₄ O ₁₀ (OH) ₂ (0.328E-06)
		55	8.95	-0.268	minnesotaite Fe ₃ Si ₄ O ₁₀ (OH) ₂ (0.328E-06)
		100	8.36	-0.196	hematite Fe ₂ O ₃ (0.492E-06)
		150	7.90	-0.212	hematite Fe ₂ O ₃ (0.492E-06)
Supply Water Plus Storage Water	Yes	20	7.27	+0.367	quartz SiO ₂ (0.234E-03) hematite Fe ₂ O ₃ (0.560E-06)
		55	8.76	-0.079	hematite Fe ₂ O ₃ (0.560E-06)
		100	8.17	-0.120	hematite Fe ₂ O ₃ (0.560E-06)
		150	7.71	-0.151	hematite Fe ₂ O ₃ (0.560E-06)

TABLE 9. Water and Mineral Equilibrium Concentrations at Various Temperatures

Aqueous Species	Moles/kg H ₂ O			
	20°C	55°C	100°C	150°C
N ⁺	0.247-03	0.125-02	0.125-02	0.125-02
Ca ⁺⁺	0.611-05	0.614-04	0.284-03	0.601-03
Fe ⁺⁺	0.492-06	0.318-13	0.193-22	0.288-16
Fe ⁺⁺⁺	0.627-06	0.405-13	0.270-12	0.547-11
Si	0.316-03	0.291-03	0.845-03	0.215-02
CO ₃ ⁻⁻	0.132-03	0.476-02	0.407-02	0.828-02
OH ⁻	0.100-06	-	-	-
H ⁺	0.100-05	-	-	-
O ₂	0.390-03	-	-	-
Al ⁺⁺⁺	-	0.124-05	0.203-05	0.720-05
K ⁺	-	0.690-03	0.234-02	0.233-02
pH	7.27	8.260	7.270	6.760
Eh	-	+0.018	+0.769	+0.361
P _{CO}	-	-	0.047	0.417
Mineralogy				
Calcite (CaCO ₃)	0.100-01	0.537-02	0.606-02	0.186-02
Quartz (SiO ₂)	0.400-02	0.609-02	0.505-02	0.751-02
Hematite (Fe ₂ O ₃)	0.100-02	0.100-02	0.100-02	0.100-02
Muscovite (KAl ₃ Si ₃ O ₁₀ (OH) ₂)	0.100-02	0.280-05	-	-
Kaolinite (Al ₄ Si ₄ O ₁₀ (OH) ₈)	0.100-02	0.707-03	-	-
Microcline (KAlSi ₃ O ₈)	0.100-02	-	-	-
Low Albite (NaAlSi ₃ O ₈)	0.100-02	-	-	-
k-Montmorillonite K _{0.7} (Al,Mg,Fe) ₄ (Al,Si) ₈ O ₂₀ (OH) ₄ · nH ₂ O	0.100-02	-	-	-
Adularia (KAlSi ₃ O ₈)	-	0.164-02	-	-
Zoisite (Ca ₂ Al ₃ Si ₃ O ₁₂ (OH))	-	0.228-02	0.160-02	0.377-02
Ca-Montmorillonite (1/2Ca) _{0.7} (Al,Mg,Fe) ₄ (Al,Si) ₈ O ₂₀ (OH) ₄ · nH ₂ O	-	-	0.280-02	-
Total	2.00-02	1.710-02	1.65-02	1.41-02

extent and that the minerals adularia and calcium montmorillonite would be formed as products. Similarly, the feldspars microcline and low-albite apparently react and zoisite is a predicted reaction product. As the injection water temperature is increased, there is a net decrease in the amount of solid material within any volume of rock equilibrated at these temperatures. To maintain a mass balance, there is an increase in the aqueous species concentration of the fluid. This might indicate that as the temperature decreases with increasing distance from the well, precipitation may become the rule. If the fluid is saturated with respect to certain mineral species at elevated temperature near the well, transport of the fluid to a lower temperature or pressure environment could result in precipitate formation. The consequences of such precipitation would depend, in part, on the quantity and density of the precipitate and the interstitial makeup of the sedimentary matrix. However, kinetics is one additional factor that should also be considered.

Based on the equilibrium predictions of EQUILIB, it might be argued that hydrothermal mineral alteration contributed to the plugging observed at the Auburn test site. However, the results predicted by EQUILIB should be viewed with caution and considered to be qualitative only. Because of problems such as thermodynamic inconsistencies in the data base, results predicted by complex geochemical computer codes (EQUILIB) may not always be accurate. For example, a questionable prediction of EQUILIB is the formation of zoisite, a high-pressure phase usually associated with low to medium grade metamorphic rocks. Using results of EQUILIB also assumes that the heated supply water, storage aquifer water and storage aquifer mineralogy have achieved a stable equilibrium. This assumption becomes quite restrictive if the temperature under consideration is as low as 55°C, since reaction rates of rock-forming minerals with aqueous solutions may be extremely slow. As illustrated in Figure 6 for a simple reaction, the dissociation of quartz in water exhibits a large increase in reaction rate constant as temperature increases. At 55°C, dissolution and/or precipitation of quartz will eventually result in the equilibrium value, shown in Figure 4. However, hydrothermal reactions probably

sensitivity (clay swelling and dispersion), particulate plugging, and outgassing of dissolved air represent the most reasonable explanations for the loss of injectivity in this specific case. More detailed study might reveal that temperature-induced increases in quartz-water adhesion and/or microstructural deformation may have been contributing factors. Table 10 is a summary of the potential contributors to the Auburn formation damage. A qualitative estimate of the relative likelihood of each mechanism is also given. Those considered "high" are discussed further in the appendices.

TABLE 10. Potential Damage Mechanisms for the Auburn Field Tests

<u>Mechanism</u>	<u>Qualitative Potential</u>	<u>Comments</u>
<u>Temperature-Induced Phenomena</u>		
• Mineral precipitation	Low	Mathematical modeling potential for dissolved oxygen in the supply aquifer
• Outgassing	Moderate	
• Increased quartz-water adhesion	Unknown	No available data
• Microstructural deformation	Unknown	No available data
<u>Fluid-Fluid and Fluid-Rock</u>		
<u>Chemical Incompatibility</u>		
• Clay swelling and low dispersion undocu-	High	Significant montmorillonite, salinity water injection
• Mineral precipitation (fluid mixing)	Low	mented lab and field data Mathematical modeling
• Mineral precipitation (oxidation)	Low	Mathematical modeling
<u>Fluid-Rock Physical Incompatibility</u>		
• Suspended solids	Moderate	Potential for micron and sub-micron particles in the supply aquifer water
• Existing formation from particles	Moderate	Sediment suspended in water the storage aquifer

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APPENDIX A

GENERAL DISCUSSION ON CLAY SWELLING AND DISPERSION

Consolidated and unconsolidated sands and silts often contain montmorillonite which may undergo volume changes when the electrolyte content of the groundwater is changed (Hewitt 1963, Mungan 1965).^(a) If the rock is subjected to injection waters of lower salinity than the ambient formation waters, certain clays may swell and significantly increase in volume. Furthermore, during the expansion process the edges of the flat clay plates can become frayed and small particles dispersed within the sandstone matrix. This can lead to particulate plugging.

Formation damage refers to a reduction in permeability due to swelling of indigenous clays or by the dispersion and movement of indigenous particles. Basically, the spacing between repeating layers of montmorillonite clay is altered when the degree of hydration is changed by varying the salt content of the formation waters. Because these clays are commonly distributed in the pores or connection channels in the rock, the clay minerals can quickly obtain "swelling" equilibrium with any new formation waters. In other words, any change in brine composition may upset equilibrium and cause the clays to expand (Hewitt 1963). The common swelling clay minerals are montmorillonites, some mixed-layer clays, and certain types of illite. In general, the amount of swelling is increased with a decrease in fluid salinity and, therefore, a concentrated brine would cause the least permeability damage and fresh water the most.

For example, when mica (a common sandstone constituent) containing the potassium ion (interplanar basal spacing $10 \text{ \AA}$) is contacted with a fluid low in potassium content, a cationic exchange or chemical reaction can occur with layer hydrated ions of sodium or calcium. The interplanar spacing can thus increase to $15 \text{ \AA}$ (Reed 1972). During the swelling process, the normally flat

(a) References cited in Appendices are listed in References of main text.

plates can have their edges frayed and broken, thus generating fines which are free to migrate and plug interstices. Clay-sized particles are flocculated or held together by electrostatic forces. The reduction of cation concentration by groundwater dilution can also promote particle dispersion or deflocculation. These dispersed particles are then free to migrate within the formation.

The Berea sandstone is used as an example of an extremely water sensitive rock. Both particle dispersion and swelling are apparent damage mechanisms. Figure A-1 reveals the degree of permeability reduction as a function of sodium content of waters being pumped through the sandstone core. Permeability alterations are manifested by the sharp declines observed during the 0.1 N NaCl and distilled water floods. The reason the permeability decline is only 28% during the 0.1 N NaCl flood is that the salinity is high enough to partially inhibit clay dispersion even though the clay surfaces are Na saturated. When the core is washed free of salt during the distilled water flood leaving the clays in a freshwater environment, the permeability declines nearly to zero (Hewitt 1963).

The total clay content of the Berea sandstone is only 7% by weight on the average. To determine the approximate content of montmorillonite in the Berea sandstone, a test using methylene blue can be employed. The methylene blue test is based upon empirical data suggesting that non-montmorillonite clays absorb negligible amounts of methylene blue, as compared to montmorillonite clays. The results reveal a montmorillonite content in Berea of between 0.5 and 1.0% by weight. Therefore, rather small quantities of interstitial clay material can, in certain circumstances, cause significant reductions in formation permeabilities. It is important to note, however, that many sandstones and unconsolidated sands are not particularly water sensitive.

For a potential TES reservoir, it will be necessary to identify the water sensitivity nature of the original formation rock and alteration products, if any. This is necessary, because hydrothermal alteration might in certain circumstances lead to the synthesis of swellable montmorillonite (Day et al. 1967).

The presence, cause, and magnitude of water sensitivity in most reservoir rocks can be recognized by a combination of the following techniques:

CLAY PLUGGING

FIGURE A-1. Reduction in Liquid Permeability Associated with Decreased Salinity Water (Hewitt 1963)

1. single phase permeability measurements with gas and a series of brines of decreasing salinity on extracted core plugs to determine if permeability varies with salinity
2. x-ray diffraction analysis to detect swelling clays (montmorillonite, mixed-layer clays and certain types of illite)
3. physical swelling tests to determine the actual swelling capacity of indigenous clay minerals
4. microscopic examination of rock thin sections to determine the distribution of clay minerals relative to the pore system.

To inhibit water sensitivity problems, chemical pretreatment is possible. It is necessary to introduce a material that will adhere to both external and interlayer surfaces of clay minerals. Hydroxy-aluminum (OH-Al) solutions followed by a few days of freshwater treatment appear to successfully inhibit clay swelling problems in the field. The polymeric cations adsorb tenaciously on the clay mineral surfaces and tend to undergo further polymerization during aging in fresh water. The chemical can be applied in the field by injecting 0.1 M OH-Al having an OH/Al ratio of 2.0, overflushing with fresh water, and allowing it to age for perhaps 2 days before putting the well on production (Hewitt 1963).

The addition of ammonia in a concentration as low as 0.013 kg/kg of water also appears to inhibit potential hydrothermal production of montmorillonite (swelling) clay. Ammonium-mica and analcite are generally formed instead of montmorillonite (Day et al. 1967). Finally, it should be noted that the potential problem of clay swelling and dispersion in a thermal energy storage system can probably be minimized by using the storage formation water as the working fluid. In other words, the doublet concept may, in itself, minimize any potential water sensitivity problems. Furthermore, the relatively high permeability reservoirs desirable for thermal energy storage may in general be less water sensitive than many lower permeability oil reservoir sands.

APPENDIX B

GENERAL DISCUSSION ON PARTICULATE PLUGGING

Particulate plugging refers to the bridging or lodging of small particles (fines) in the interstices of flow channels in a sandstone (Figure B-1). Such plugging can significantly decrease the permeability of the reservoir. In general, potential sources of particles include: 1) existing fines or particles (sand and silt), 2) disaggregation products, 3) suspended solids in the injection fluid stream, 4) mineral scale and pipe corrosion deposits, and 5) frayed and dispersed clay particles.

The potential for and magnitude of formation permeability damage depends upon the particle size distribution, the sandstone or unconsolidated sediment pore size distribution, and the fluid density, viscosity, and flow velocity. Damage could be manifested as a "filter cake" at the sand face (well surface) or as plugs (bridges) within the flow channels of the sandstone itself.

Particle plugging has been analyzed in the laboratory by flowing liquid water with various suspended solid loads through sandstone cores. Pressure buildup and effluent particle load are continuously monitored. Figures B-2 and B-3 show examples of particle distribution and pressure buildup curves for tests done on Berea sandstone.

With liquid water as the working fluid, particle plugging can be simulated with a statistical random-walk computer model (Donaldson et al. 1977). The mathematical model, based on Poiseuille capillary flow equations, results in reasonable reproduction of laboratory data.

SOURCES

- SUSPENDED SOLIDS IN THE INLET AIR
- DISLODGED ROCK FRAGMENTS
- FRAYED CLAYS
- PIPE CORROSION PRODUCTS
- MINERAL SCALE
- MICROBES

RESULTS

- BRIDGING
- FILTER CAKE

SOLUTIONS

- PROPER RESERVOIR SELECTION
- PROPER OPERATING CONDITIONS
- CHEMICAL PRETREATMENT
- SAND SCREENS

FIGURE B-1. Conceptualization of Particulate Plugging

FIGURE B-2. Particle Size Distribution for Solids Pumped into Berea Sandstone Cores (Donaldson et al. 1977)

FIGURE B-3. Pressure Buildup and Particle Flux in the Effluent for Berea Tests (Donaldson et al. 1977)

APPENDIX C

TEMPERATURE-INDUCED PERMEABILITY ALTERATIONS

Several experimental studies have demonstrated temperature effects on the absolute permeability of unconsolidated sands and consolidated sandstones (Greenberg et al. 1968, Afinogenov 1969, Weinbrandt 1972, Casse 1974, Aruna 1976, and Danesh et al. 1978). In general, the main observations derived from these studies are:

1. a 50 to 100% decrease in liquid water permeability due to an increase in fluid temperatures from 25 to 100°C
2. no definitive changes in oil or nitrogen permeability
3. a 15 to 80% recoverability in liquid permeability as the working fluid temperature is reduced to 25°C
4. a hysteresis effect, i.e., cumulative increase in amount of irrecoverable permeability with successive temperature cycles.

Figures C-1, C-2, and C-3 illustrate example permeability values as a function of temperature. Figure C-1 reveals data from a flow test on Ottawa sand with filtered deionized water as the flowing fluid (Danesh 1978). The degree of irrecoverable permeability and the hysteresis phenomenon are evident from the data. Figures C-2 and C-3 are based on similar tests on consolidated sandstones (Weinbrandt 1972). No temperature cycling was performed in these tests, however.

Several explanations for this temperature sensitivity have been proposed by various authors. Greenberg suggested mechanical and thermal stresses in conjunction with chemical reactions may be responsible for the permeability reductions. Afinogenov hypothesized porosity reductions or changes in the physiochemical properties of the fluid-rock system. Casse concluded that decreases in liquid water permeability could not be attributed to bulk fluid property changes, i.e., viscosity and density, or to thermally induced mechanical stresses because similar permeability decreases were not observed for mineral oil or nitrogen. He suggests that a temperature-dependent rock-fluid interaction is the dominant factor. Aruna carried this argument one step

FIGURE C-1. Water Permeability Versus Temperature, Ottawa Sand (Danesh et al. 1978)

FIGURE C-2. Effect of Temperature on Absolute Permeability of Boise Sandstone (Weinbrandt 1972)

FIGURE C-3. Effect of Temperature on Absolute Permeability of Berea Sandstone (Weinbrandt 1972)

further by hypothesizing that the permeability reduction may be due to temperature-dependent increases in the attractive forces between water and quartz, the principal constituent of sand. He based this hypothesis on the observation that similar permeability decreases were not observed for limestone.

This proposed increase in quartz-water adhesion with increased temperature has been explored by Danesh and his coworkers. They noted that a molecular-force transition zone apparently exists at a solid-liquid interface and that this zone can be hundreds or thousands of molecules thick. The viscosity within this zone may be significantly higher than that of the bulk fluid (Kirk et al. 1970). Danesh explains that "the water molecules at the interface are less inclined to separate and hence result in a higher viscosity." He admits, however, that this explanation is quite vague and that additional investigation is required.

Soseman (1965) also suggests that the surfaces of some solids such as quartz can react with water and thus form a boundary layer of variable thickness. This relative immobilization and associated liquid-solid momentum transfer might result in a reduction in the effective size of porous flow

channels (Churayev et al. 1970). Thus, in media supporting significant micro-capillary flow, surface effects may become important. The effect of temperature on the mobility of water through porous media cannot be adequately explained by induced changes in bulk water viscosity alone (Danesh et al. 1978).

Unfortunately, there is insufficient evidence to totally support this "increased adhesion" hypothesis. The primary problem is the lack of experimental data and adequate control. For example, in the Danesh experiments, the samples were exposed to an effective stress on the order of 1000 psig and then heated with elevated temperature fluids. No sample deformation (strain) measurements were reported, however. Therefore, it is not possible to determine whether time and/or temperature-dependent sample deformation is an alternate explanation for the observed permeability reductions. The limited recoverability of permeability upon cooling might be correlated with elastic deformation. The irrecoverable permeability reduction might be attributed to inelastic (nonlinear) sample deformation. Such sample strains might be indicative of microstructural damage corresponding to: 1) thermally-induced anisotropic microstructural stresses, 2) thermal fatigue, and/or 3) hydrolytic weakening (silicate hydrolysis).

Figure C-4 is a representation of an ideal thermal expansion/contraction cycle for an unconfined soil or rock specimen. The total thermal dilation E_{total} at any point C is the sum of the observed recoverable elastic expansion (E_{α}) and any irrecoverable inelastic dilation (E_R). A partial time-dependent reduction in the magnitude of E_R has been observed in hard rocks (Therumalai 1970). The explanation is that E_R reflects microstructural damage of the sample and that the magnitude of new damage decreases with successive cycles. Figure C-5 is a plot of temperature versus E_R at its maximum value (usually within 3 to 5 cycles). These particular data are for hard rocks. The microstructural damage, quantified by E_R , may be due to micro-cracking and fragmentation. Figure C-6 reveals the elastic unconfined expansion of the granodiorite sample. It should be emphasized that if the sample were confined to simulate lithostatic loading, the rock would be stress cycled

FIGURE C-4. Ideal Thermal Expansion Cycling for Rock Material

to a greater degree as the temperature is cycled. Microstructural damage could conceivably contribute to permeability reductions in sandstones due to pore-throat constriction and/or particulate plugging. Unfortunately there are no similar data for sands or sandstones subjected to thermal cycling. Furthermore, the limited mechanical fatigue data currently available for sandstones was measured under dry conditions at room temperature. Figure C-7 is an example of these data (Haimson 1977).

Flow experiments such as those discussed earlier suffer from the lack of adequate sample strain and acoustic activity monitoring. The inhomogeneity and anisotropy of microstructural thermoelastic and strength properties of consolidated or unconsolidated aggregates is such that sample damage cannot be ignored as a possible contributing factor to observed permeability reductions. This, in combination with the potential for fatigue and hydrolytic weakening, dictates that aggregates should not be considered purely elastic bodies even at relatively low effective stress levels. Temperature and time-dependent

FIGURE C-5. Rock Response to Induced Thermal Stresses
(Therumalui et al. 1970)

deformation monitoring in the form of volumetric strain measurements is necessary in any future flow experiments. Only by simultaneous measurement of permeability, volumetric strain, and acoustic emissions can one begin to address the physics and chemistry associated with the available empirical results.

FIGURE C-6. Thermal Expansion of Test Rocks in Atmosphere and Reduced Environmental Pressure (Therumalai et al. 1970)

FIGURE C-7. S-N Curves in Uniaxial and Triaxial Compression in Terms of Percentage of Respective Monotonic Compressive Strengths (C) (Haimson 1977)

APPENDIX D

SUMMARY OF POTENTIAL PERMEABILITY DAMAGE MECHANISMS

Table D-1 summarizes example formation damage mechanisms that should be considered at a TES candidate site. Prior to development of a field site, carefully preserved rock or sediment samples and associated groundwater samples should be tested in the laboratory under simulated field conditions. Example conditions include: temperature, effective stress, deviatoric stress, suspended load, sandface flow rates, and chemical additive concentrations. Such screening experiments could in many cases elucidate potential reservoir damage mechanisms and/or unacceptable water quality alterations. Once a potential site has been determined as a leading candidate, an on-site field test loop should be considered in conjunction with reservoir pretreatment should it be warranted. Loss of production/injection well permeability can often be irreversible and as such, when possible, precautions should be taken to detect this potential and employ preventative measures.

TABLE D-1. Example Potential TES Reservoir Alteration Mechanisms

- Particulate plugging
- Mineral dissolution and scaling
- Clay swelling and dispersion
- Increased quartz-water adhesion
- Microstructural alteration
- Bulk compressibility changes
- Hydrolytic and oxidation reactions
- Water quality alterations

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