Potential Petrophysical and Chemical Property Alterations in a Compressed Air Energy Storage Porous Rock Reservoir

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POTENTIAL PETROPHYSICAL AND CHEMICAL
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FOREWORD

The Compressed Air Energy Storage (CAES) Technology Program at Pacific Northwest Laboratory (PNL) is sponsored by the Department of Energy, Division of Energy Storage Systems and the Division of Electrical Energy Systems. The program scope includes a group of studies directed at developing a new energy storage technology to improve the cost and efficiency of electrical power utilization and to reduce the dependence on premium fuels such as oil and natural gas. The program has two major thrusts -- Reservoir Stability Criteria Studies and Advanced Concepts Studies, with the following objectives:

Reservoir Stability Criteria

Develop design and stability criteria for long-term operation of underground reservoirs used for CAES in order to accelerate the commercialization of the concept.

Advanced Concepts Studies

Develop and assess advanced CAES concepts that require little or no supplementary firing by premium fuels in order to eliminate the dependence of CAES on premium fuels.

The ultimate objective of this program is to reduce the consumption of natural gas and oil, used for peak-power generation plants, by about 100,000,000 barrels per year. This objective could be accomplished by replacing conventional gas turbine peaking plants currently being used by utilities with CAES plants.

The following documents have been issued by PNL or by subcontractors to PNL reporting the results of the work toward the objectives.

- Technical and Economic Feasibility Analysis of the No-Fuel Compressed Air Energy Storage Concept, D. K. Kreid, BNWL-2065, May 1976.
- FY-1977 Progress Report - Stability and Design Criteria Studies for Compressed Air Energy Storage Reservoirs, G. C. Smith, J. A. Stottlemire, L. E. Wiles, W. V. Loscutoff and H. J. Pincus, PNL-2443, March 1978.
- FY-1977 Progress Report Compressed Air Energy Storage Advanced Systems Analysis, D. K. Kreid and M. A. McKinnon, PNL-2464, March 1978.

- Preliminary Stability Criteria for Compressed Air Energy Storage in Porous Media Reservoirs, J. A. Stottlemire, PNL-2685, June 1978.
- Preliminary Long-Term Stability Criteria for Compressed Air Energy Storage Caverns in Salt Domes, R. L. Thoms and J. D. Martinez, PNL-2871, August 1978.
- Numerical Analysis of Temperature and Flow Effects in a Dry, One-Dimensional Aquifer Used for Compressed Air Energy Storage, G. C. Smith, L. E. Wiles, and W. V. Loscutoff, PNL-2546, February 1979.
- The Effects of Water on Compressed Air Energy Storage in Porous Rock Reservoirs, L. E. Wiles, PNL-2869, March 1979.
- Pacific Northwest Laboratory Annual Report for 1978 to the DOE Division of Energy Storage Systems - Compressed Air Energy Storage Technology Program, W. V. Loscutoff and Staff, PNL-2935, June 1979.
- Incremental Cost Analysis of Advanced Concept CAES Systems, C. A. Knutsen, PNL-3118, September 1979.
- Numerical Analysis of Temperature and Flow Effects in a Dry, Two-Dimensional, Porous-Media Reservoir Used for Compressed Air Energy Storage, L. E. Wiles, PNL-3047, October 1979.

SUMMARY

Successful commercialization of Compressed Air Energy Storage (CAES) systems depends on long-term stability of the underground reservoirs subjected to somewhat unique operating conditions. Specifically, these conditions include elevated and time varying temperatures, effective stresses, and air humidities. To minimize the requirements for premium fuels, it may be desirable to retain the thermal energy of compression. Porous media, e.g., sandstone, may hold promise as elevated temperature reservoirs. For the purpose of this study, a reservoir composed of clean quartz sandstone and injection air temperatures of 300 to 575°K are assumed. Numerical modeling is used to estimate temperature, stress, and humidity conditions within this reference porous media reservoir.

The objective of this report is to present discussion on relative importance to CAES of several potential porous media damage mechanisms. In this context, damage is defined as a reduction in intrinsic permeability (measure of air transport capability), a decrease in effective porosity (measure of storage capability), or an increase in elastic and/or inelastic deformation of the porous material. The potential damage mechanisms presented include: 1) disaggregation, 2) particulate plugging, 3) boundary layer viscosity anomalies, 4) inelastic microstructural consolidation, 5) clay swelling and dispersion, 6) hydrothermal mineral alteration, 7) oxidation reactions, and 8) well casing corrosion. The main objective of this discussion is to place these mechanisms in perspective with respect to anticipated CAES conditions and to suggest which mechanisms are: 1) of academic interest only, 2) readily identified and controlled via engineering, or 3) potential problem areas requiring additional investigation. The following table is a qualitative categorization of the potential porous media damage mechanisms covered in this review.

Estimated Importance of Potential Property Alteration Mechanisms

I. REQUIRES FURTHER INVESTIGATION

- A. Disaggregation and particle plugging
- B. Anomalous viscosity
- C. Water vapor induced consolidation (hydrolytic weakening and pressure solution)
- D. Temperature-induced consolidation (static and dynamic fatigue)

II. POTENTIALLY CONTROLLED BY SITE SELECTION AND/OR ENGINEERING

- A. Clay swelling and dispersion
- B. Casing corrosion
- C. Oxidation of compressor oil

III. NONPROBLEMS

- A. Hydrothermal mineral alterations
- B. Oxidation reactions

DISAGGREGATION

Disaggregation refers to the dislodging of individual grains within porous media. It can potentially occur when cement is preferentially dissolutioned or the matrix is mechanically loaded beyond a certain threshold. Potential causes include: 1) differential thermal expansion and contraction, 2) static or dynamic fatigue, 3) chemical dissolution, 4) hydrolytic weakening, and 5) mechanical erosion. There could be adverse consequences associated with disaggregation, e.g., particulate plugging or matrix consolidation. The consequences could also be beneficial if permeability increases near the wells.

PARTICLE PLUGGING

Particle plugging refers to the bridging or lodging of small particles (fines) in the interstices or flow channels in a porous media. Such plugging can significantly reduce the permeability of the rock. Potential sources of particles include: 1) existing particles or fines, 2) disaggregation products, 3) suspended solids in the injected air, 4) mineral scale and corrosion deposits, and 5) frayed and dispersed clay particles.

BOUNDARY LAYER VISCOSITY INCREASES

In sandstones, the absolute permeability to liquid water appears to decrease significantly with increasing fluid temperature. Conversely, dry gas permeability is apparently not temperature sensitive. No data are available on the sensitivity of humidified gas permeabilities to temperature. One possible explanation for the decrease in liquid water permeability may be that near the liquid-solid interface, chemical attack and dissolution of silica by water may result in the formation of a gel containing elements other than oxygen and hydrogen. This gel, often called anomalous water, may exhibit much higher viscosity than for ordinary liquid water. This may perturb the fluid flow resistance. It is being hypothesized that this will not be a significant problem in CAES, but needs to be experimentally verified.

HYDROLYTIC WEAKENING AND PRESSURE SOLUTIONING

Another possible explanation for the observed temperature sensitivity of liquid water permeability is hydrolytic weakening and pressure solutioning at highly stressed grain to grain contacts. Subsequent solid body rotation and/or inelastic deformation may result in increased consolidation of the porous medium under a sustained effective stress. As with the anomalous viscosity topic, only limited data are available on the effects of liquid and vapor on microstructural deformation.

TEMPERATURE-INDUCED CONSOLIDATION

Even if the porous medium was completely free of interstitial water, the probability of consolidation and permeability degradation due to elevated and cyclical temperatures cannot be currently dismissed. Fluctuating stresses may enhance microcrack extension and coalescence. Creep and fatigue should be explored under reconstituted or simulated field conditions.

CLAY SWELLING AND PARTICLE DISPERSION

Rock formations often contain bentonitic clays which may undergo volume changes if the electrolyte content (salinity) of the ground water is changed. If water of lower than ambient salinity is injected or condensed into the reservoir, certain clay minerals can increase in volume by as much as 50%, thus reducing permeability.

Particles generated from clay plate edges frayed during the expansion and particles released by a deflocculation process may result in particulate plugging. In a CAES operation, condensate is the only potential source of low salinity water. However, most condensation should be in the cooler zones far away from the wells where consequences associated with clay swelling may not be significant.

Water sensitivity or clay swelling potential is relatively easy to discover in the laboratory and pretreat in the field. If it is considered a potential problem, pretreatment with hydroxy-aluminum solutions followed by freshwater flushing might be considered.

MINERAL PRECIPITATION ASSOCIATED WITH RESIDUAL WATER EVAPORATION

The irreducible water in the near vicinity of the well will be gradually vaporized and removed by the warm undersaturated air. During the process, residual brine may approach saturation with respect to certain ionic species. The result may be mineral deposition.

The areas affected by such "infilling" will typically be small diameter interstices, dead end pore space, or lenses of low permeability material within the reservoir. Mineral precipitation should therefore occur only in the volume of pore space originally containing irreducible water and should not have a significant effect on CAES operations.

HYDROTHERMAL MINERAL ALTERATIONS

Hydrothermal alteration refers to changes in mineralogy and/or mineral dissolution and precipitation. The minerals of primary interest include quartz and various silicates, carbonates, and sulfates.

The major parameters controlling hydrothermal alterations include:

1) initial rock composition and microstructure, 2) water availability and composition, 3) temperature, 4) fluid velocity, 5) fluid residence time, 6) rock surface area to fluid volume ratio, 7) pH (hydrogen ion activity), and 8) Eh (redox potential). Both equilibrium solubility and kinetics must be considered in assessing the practical significance of any given hydrothermal reaction.

In a CAES reservoir, it may be necessary to ensure that zones containing irreducible liquid phase water are not heated to any significant degree. The solubilities of minerals in saturated steam or humidified air are probably too low to be of major concern to CAES operation. In general, mineral solubilities are significantly lower in steam than in liquid water as long as the temperature is somewhat below 640° to 650°K, the critical point of water.

REDOX REACTIONS

Confined aquifers are generally anoxic or reducing in nature. Free oxygen will be readily available in a CAES reservoir, however. Oxidation reactions may thus occur and potentially result in the corrosive gases and insoluble compounds that reduce permeability. Oxidation reactions may be of particular interest at the storage zone/caprock interface. Arguments can be presented, however, that indicate potential problems associated with the introduction of oxygen can be eliminated or inhibited by site selection and engineering.

Another type of oxidation reaction may be of some concern. Oil has been found on the sand face in natural gas storage field wells. This oil is presumably from the compressor. Oxidation of this oil with hot air may be a potential problem warranting additional study.

ALTERATIONS IN THERMAL CHARACTERISTICS

Temperature, stress, and liquid phase saturation can affect the thermal conductivity of reservoir rocks. Temperature and pressure have only limited effects on the thermal conductivity, but liquid saturation is a dominant parameter. Conductivity has been observed in the laboratory to decrease by a factor of 4 to 10 when some sandstones go from a liquid saturation of 40% or more to a totally dry state. In general, for brine and air systems, thermal conductivity is proportional to the cube root of the brine saturation for consolidated sandstones and to the square root for unconsolidated sands.

CORROSION

Corrosion of well casings could be a significant problem for a CAES reservoir if liquid water is present. Basically, corrosion will increase as: 1) acidity, 2) oxygen content, 3) liquid content, 4) temperature, and 5) flow rates increase.

Vapor condensation, if any, in the well casing should control the potential for corrosion in a CAES system. Although corrosion may occur in a water vapor environment, it will be significantly reduced from that which would be expected for liquid water.

It appears that corrosion rates of up to 20 mils per year might be expected under high humidity conditions. However, as the humidity decreases, the corrosion rates should also decrease. Average corrosion rates between 1 and 6 mils per year might be reasonable for a CAES facility, although additional data are required to substantiate this estimate.

The effects on well casing material should be characterized as general corrosion that produces an uneven surface. Stress corrosion in casings should not be a problem except possibly in the case of a sulfide bearing reservoir, which may accommodate hydrogen sulfide gases.

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POTENTIAL PHYSICAL AND CHEMICAL PROPERTY ALTERATIONS IN A COMPRESSED AIR ENERGY STORAGE POROUS ROCK RESERVOIR

1.0 INTRODUCTION

The economic and technical feasibility of Compressed Air Energy Storage (CAES) technology depends to a major extent on locating, developing, and maintaining a suitable subsurface reservoir. One possible uncertainty is the physical and chemical response of the reservoir, e.g., sandstone aquifer, hardrock cavern, or salt cavity, to new environmental conditions imposed by CAES operations. For example, in sandstone aquifers the primary focus is on potential changes in permeability, friability, thermo-mechanical strength, and compressibility caused by elevated and cyclical temperatures, effective stresses, deviatoric stresses, humidities, and oxygen facilities.

The range of possible operating conditions, assumed for this study, are as follows: injection air temperature (300°K to 575°K), effective stress (10 to 75 MPa), deviatoric stress (0 to 20 Mpa), reservoir residual water content (5% to 25%), and injection air humidity (0.0 to 0.05 kg H₂O per kg air). Numerical modeling (see section on Reference Reservoir Conditions) is utilized to estimate the underground temperature, pressure, and humidity conditions as a function of time and distance from any given injection well. Based on these conditions and information gathered from the open literature, various consultants, and preliminary laboratory-scale experiments, conclusions are drafted concerning the relative importance of several potential CAES reservoir damage mechanisms.

The potential mechanisms discussed in this study include: 1) disaggregation, 2) particle plugging, 3) anomalous solid-liquid boundary layer viscosity, 4) elastic and inelastic microstructural deformation, 5) clay swelling and/or dispersion, 6) hydrothermal mineral alterations, 7) oxidation reactions, and 8) well casing corrosion.

Arguments are presented to show that some common reservoir alteration mechanisms are not particularly relevant to CAES reservoir conditions. Other

types of reservoir damage may be minimized with appropriate site selection, reservoir conditioning, and/or engineering. Some mechanisms, however, appear to warrant additional investigation due to the lack of laboratory and field data commensurate with the unique CAES reservoir conditions.

A brief description of a reference CAES subsurface environment is also given. Detailed descriptions are deferred to several CAES reports listed in the references. The following reservoir conditions are discussed: 1) spatial and temporal temperature distributions, 2) effective stresses, 3) residual water saturations, 4) humidities, and 5) oxidation potentials.

Berea and Galesville sandstones are used as example reservoir rocks in this report, with Galesville being most typical of a CAES reservoir rock. The characteristics of these sandstones are given in the Appendix. Basically, Galesville is representative of the class of clean quartzose sandstones and Berea represents graywackes which tend to be high in feldspar and clay minerals.

It must be emphasized that areas identified herein as requiring further study are being currently investigated at Pacific Northwest Laboratory (PNL), Los Alamos Scientific Laboratories (LASL), the University of Wisconsin (UWM), and Terra Tek, Inc. These studies include:

- PNL - This study involves the design and construction of a dedicated CAES laboratory facility capable of testing generic and site-specific reservoir samples under reconstituted (simulated) field conditions. These conditions include temperatures, effective stresses, deviatoric loads, and humidities. Investigations will focus on the effects of CAES operation on porous media porosity, permeability, and microstructural deformation. Additional studies involve thermal diffusivity factors.
- LASL - This study is focused on the effects of temperature on sandstone and shale triaxial compressive and tensional strengths.
- UWM - This study involves the effects of elevated temperature dry air flow cycling on the petrophysical properties of porous rocks.
- Terra Tek, Inc. - Emphasis in this study is on creep and thermal fatigue of consolidated and unconsolidated porous materials.

2.0 CONCLUSIONS

Conclusions drawn from this study include:

- To date, no evidence has been found that would preclude the injection, storage, and recovery of moderate temperature air in a porous media reservoir. However, the lack of laboratory and field data commensurate with unique CAES operating conditions results in uncertainties concerning the long-term stability of the reservoir. Thus, additional investigation is required before stability of the reservoir can be guaranteed with an acceptable degree of certainty.
- Potential damage mechanisms requiring additional investigation include: static (time dependent failure) and dynamic fatigue, hydrolytic weakening, pressure solutioning, and anomalous boundary layer viscosities due to silica and water vapor interactions.
- Ongoing experimental studies at Pacific Northwest Laboratory, Los Alamos Scientific Laboratories, University of Wisconsin, and Terra Tek, Inc., should reduce the uncertainties associated with these phenomena. Ultimately, field testing will be required.
- Some porous media studies have been made for liquid water and hydrocarbons, but there is a paucity of experiments conducted with humidified or dry air. This is especially true for elevated and cyclical temperatures.
- Sandstone disaggregation may result from thermal fatigue (temperature cycling), differential thermal expansion, and/or preferential mineral dissolution, but there are insufficient data to quantify the probability for this phenomenon.
- Existing particles and disaggregation products appear to be the only particle sources of significant concern to CAES.
- Particle plugging may be manifested as bridging within the formation or as a filter cake at the well. The cyclic operation of a CAES facility should minimize the effect of particulate plugging.

- Liquid water permeability may decrease with temperature as a result of increased boundary layer viscosities and/or microstructural deformation enhanced by hydrolytic weakening and pressure solutioning.
- Dry gas permeability should be insensitive to temperature. However, due to data inadequacies, no such conclusion is warranted for humidified gas permeability.
- Sandstone compressibility may increase with temperature. This could reduce stresses within the formation, but may also induce measurable porosity and permeability reductions.
- Elevated temperature steam may induce rock softening by the partial destruction of dolomite and kaolinite. Pretreatment with weak ammonia solutions may be necessary to inhibit such rock softening at some sites.
- Some clays can undergo significant swelling and/or deflocculation when exposed to low salinity ground water. In CAES, condensation may supply fresh water, but the condensate zones should be far from the critical near-well zones and thus not pose significant problems.
- Water sensitivity (clay plugging potential) is relatively easy to identify and pretreat in the field. Hydroxy-aluminum solutions have met with considerable success at many oil field wastewater injection facilities.
- Hydrothermal mineral alterations and/or mineral dissolution should not be significant problems for a CAES reservoir since liquid phase water and elevated temperatures should not exist simultaneously near production/injection wells. The solubilities of minerals in humidified air is not well quantified, but qualitative arguments support a significantly lower solubility in vapor as compared to liquid as long as the temperature is below the critical point for water (647°K).
- Most aquifers are essentially devoid of free oxygen and, therefore, CAES operations will result in a perturbation to the ambient Eh conditions in the reservoir. Corrosive gases and various insoluble metal oxides and hydroxides may result if sufficient quantities of water are available.

- Well casing corrosion could be a problem if liquid water, elevated temperatures, and air simultaneously contact the metal. In a steam or humidified air environment, however, casing corrosion should be within acceptable limits with average rates of 1 to 6 mils per year being possible.

3.0 COMPUTER MODELING OF A REFERENCE RESERVOIR

Computer modeling assists the investigator in understanding the complex interactions of temperatures, pressures, and humidities within the reservoir. Such determination of the temporal and spatial variability in these parameters establishes the basis for investigating potential physical and chemical property alterations in the reservoir and changes in operability of the facility. Since a CAES aquifer site does not exist as yet, reference reservoir conditions were assumed for the computer modeling effort.

Conceptual representations of a one-dimensional heat and mass transfer CAES computer model are shown in Figures 1 and 2 (Wiles 1979). Table 1 is a list of parameter magnitudes used for the reference reservoir.

In this idealized case, air is injected at 515°K. The resulting air plume extends radially some 61 m into the reservoir as shown in Figure 3. However, due to sensible heat transfer from the air to the rock, the thermal plume extends to a distance of only 23 m even after 1 year of continual operation. A thermal pillar is formed around each injection well with temperatures rapidly decreasing with radial distance from the wellbore.

The temporal and spatial variations in reservoir temperatures are shown in Figure 4. Naturally, physical and chemical reservoir properties are sensitive to temperature. Also, temperature cycling is important because of possible thermal fatigue effects. Anticipated cycling frequency and magnitude are presented in Figure 5. Output from computer simulations reveals that: 1) the average temperature decreases rapidly with increasing distance from the well, and 2) temperature cycling is depressed as the reservoir is developed thermally in time and as the distance from the well is increased.

The porous rock will also be subjected to pore pressure cycling because of the cyclical operation of a CAES plant. A representative CAES operational schedule and associated variations in pore pressure at the well and at the reservoir boundary are shown in Figures 6 and 7.

FIGURE 1. Single Well Symmetry in a CAES Well Field (Wiles 1979)

FIGURE 2. Single Well Reservoir Geometry (Wiles 1979)

FIGURE 3. Thermal Growth in the Reservoir
(Wiles 1979)

TABLE 1. Reference Reservoir Parameters
(Wiles 1979)

Parameter	Reference Value
Geometry	
Reservoir Diameter (m)	122
Well Diameter (cm)	18
Properties	
Porosity (%)	20
Permeability (m^2)	5.0×10^{-12} (500 md)
Rock Thermal Conductivity ($w/m \cdot ^\circ C$)	2.16
Rock Thermal Capacity ($MJ/m^3 \cdot ^\circ C$)	2.62
Operating Conditions	
Nominal Pressure (MPa)	5.07
Mass Flow Rate	
Injection ($kg/s \cdot m$)	0.18
Extraction ($kg/s \cdot m$)	0.16
Initial Reservoir Temperature ($^\circ K$)	312
Air Injection Temperature ($^\circ K$)	515 (242 $^\circ C$)

FIGURE 4. Thermal Cycling During the First Week of Reservoir Operation (Wiles 1979)

FIGURE 5. Thermal Cycling During the 52nd Week of Reservoir Operation (Wiles 1979)

FIGURE 6. Reference Weekly Reservoir Pressure Cycle (Wiles 1979)

FIGURE 7. Weekly Pressure Cycle (Wiles 1979)

In a CAES reservoir, moisture may be derived from two primary sources: 1) residual or irreducible water left in the porous rock after initial air bubble development, and 2) water vapor entrained in the injected air stream. Example capillary pressure-saturation curves are shown in Figure 8. The curves reveal that a certain percentage of water will remain in the reservoir even after the air bubble has been partially established. For this study, it was arbitrarily assumed that 20% of the pore space is still occupied by liquid ground water. This water resides in isolated low permeability pockets or in small diameter pores which support high capillary forces. The second source of moisture is that injected with the air stream. Figure 9 shows the absolute humidity of initially saturated 311°K air after it has been compressed to 5.0 megapascals (MPa). The upper limit is approximately 0.043 kg of H₂O per kg of injected air. The degree of undersaturation is strongly temperature dependent. Therefore, the ability of the undersaturated air to dewater the near-well zones may also be temperature dependent. However, the solubility of water vapor in air depends on the temperature and pressure at the given point in the reservoir and not just on the injection air temperature. Thus, sensible heat storage capacity of the sandstone may be such that the elevated temperature front will lag the dehydration front, and, therefore, the high injection air temperature may not result in significantly faster dewatering. It may not be possible to inject elevated temperature air far enough into the reservoir because of efficient sensible heat transfer.

The air/water/rock system rapidly attains thermal equilibrium with the injected air. Based on this assumption, it is possible to compute the amount of water vapor associated with the air at any given temperature and pressure. Figures 10 and 11 show the vapor pressure curve for pure water and the air/water vapor solubility relationship.

In CAES operations, undersaturated warm air is injected into the reservoir where it is saturated with water vapor at the given temperature and pressure. This air/vapor mixture is advectively transported further into the reservoir where the temperatures are lower and some of the vapor is condensed.

FIGURE 8. Miscellaneous Capillary Pressure-Saturation Curves (Katz et al. 1959)

FIGURE 9. Saturated Absolute Humidity at 5.0 MPa (Wiles 1979)

FIGURE 10. Saturation Pressure Versus Temperature for Water

During the production phase of the CAES cycle air flows back towards the well, is reheated by rock, picks up additional water vapor, and is transported up the well. Figure 12 presents this two-stage reservoir dewatering process.

Figures 13 through 15 show results of mathematical modeling of this dehydration scheme (Wiles 1979). Figure 13 presents idealized drying for various times at three radial distances from a given well. The residual water content is again assumed to be 20%, the injection air humidity zero, and the air temperature at the sandface 503°K. Figure 14 reveals the effect of temperature on the average dehydration rate. Figure 15 shows how the humidity in the injected air can inhibit the dewatering of the near-well zones.

In a CAES reservoir, significant quantities of free oxygen and carbon dioxide may be available. Typically, a natural confined aquifer will support anoxic conditions. Thus, the CAES scheme might transform the natural environment from a zero or negative Eh to a positive Eh. The concern is that certain

FIGURE 11. Solubility of Water in Air at Various Temperatures and Pressure

oxidation reactions may result in the precipitation of relatively insoluble minerals and that the pH of the system may be altered. The possibility of corrosive gases being generated at the storage zone/caprock interface should also be considered.

The parameters, temperature, effective stress, humidity, and gas composition, are interrelated. Furthermore, the potential for physical or chemical alteration of the reservoir depends, in a rather complex way, on the nature of the rock and the fluids and on the complete set of physicochemical conditions existing in a reservoir. For example, hot dry rock might exhibit adequate stability even under cyclic conditions. However, if liquid water is present,

FIGURE 12. Conceptual Presentation of the Evaporation Process

hydrolysis may result in a totally different response. Similarly, the presence of humidified air may be a controlling factor. A liquid saturated rock may exhibit good property stability as long as the temperature is moderate and free oxygen is not present.

FIGURE 13. Dehydration for Three Locations, 5-Year History (Wiles 1979)

In reviewing the remainder of this report on potential reservoir alteration mechanisms, the reader must remain cognizant of the physicochemical conditions imposed on the system. This includes the possibility of these conditions varying temporally and spatially within the reservoir. Finally, it should be noted that conditions are highly site specific and that stability at one reservoir under one set of operating conditions may not be directly extrapolated to all reservoirs.

FIGURE 14. Effect of Injection Temperature on the Net Reservoir Dehydration Rate (Wiles 1979)

FIGURE 15. Effect of Injection Humidity on Growth of the Dry Front: 505°K Injection Temperature (Wiles 1979)

4.0 DISAGGREGATION

Disaggregation refers to the dislodging of individual grains within a cemented sandstone. Disaggregation can occur when the cement is preferentially dissolutioned or the porous rock is thermally or mechanically loaded or unloaded beyond a certain threshold. Potential causes include: 1) differential thermal expansion, 2) thermal fatigue, 3) chemical dissolution, 4) hydrolytic weakening of quartz and silica, and 5) mechanical impact erosion. As an example, Figure 16 shows how an unconfined sample exposed to elevated temperature water can begin to disaggregate.

GALESVILLE SANDSTONE
50°C, 336 HRS, LIQUID H₂O

GALESVILLE SANDSTONE
300°C, 336 HRS, LIQUID H₂O

FIGURE 16. Example of a Disaggregating Sandstone

While disaggregation could be an adverse phenomenon, causing, for example, particulate plugging or consolidation, it may also result in an increase in permeability if microcracking, grain dislocation, or cement dissolution should occur without subsequent plugging or consolidation. With respect to CAES, the consequences of this potential reservoir phenomenon must be compared for a dry air environment, a humidified air environment, and a liquid water environment. A CAES reservoir will contain either humidified or dry air. The liquid water investigation should yield evidence as to the cause of disaggregation, if any.

4.1 DIFFERENTIAL THERMAL EXPANSION AND THERMAL FATIGUE

Localized differential thermal stresses can result from the inhomogeneity and anisotropy of expansion coefficients for individual minerals and the matrix as a whole. If the resulting differential stresses at grain boundaries are of sufficient magnitude, microcracking might result in the dislocation of intact grains or fragmentation of grains.

If, in addition, thermal stresses are cyclical, fatigue might be exhibited. Fatigue refers to the phenomenon of damage in materials subjected to fluctuating stresses. Fatigue may prove to be a problem in a CAES reservoir, especially if the sand grains are cemented with a material exhibiting a different coefficient of thermal expansion. For example, a rock predominantly composed of quartz grains and cemented with crystalline quartz or silica may respond to cyclical temperatures in a different manner from a sandstone cemented with carbonate minerals. No data are available on static or dynamic fatigue properties of sandstones and shales under anticipated elevated temperature CAES conditions. This area is considered to be of primary interest with respect to reservoir stability and is being investigated on both a macro and micro scale.

4.2 CEMENT DISSOLUTION

Two of the most common sandstone cements are silica (SiO_2) and calcium carbonate (CaCO_3). Quartz solubility in liquid water increases with increasing temperature (Figure 17), and calcite solubility decreases with

FIGURE 17. Solubility in Water of Amorphous Silica Relative to Quartz at the Vapor Pressure of the Solution

increasing temperature (Figure 18). Little data are available concerning the solubility of minerals in a humidified air or saturated steam environment. However, mineral solubilities should be significantly reduced relative to those in liquid water provided that temperatures are maintained below the critical point of water, about 647°K.

4.3 HYDROLYTIC WEAKENING

The presence of water vapor at elevated temperatures might result in the hydrolysis and weakening of chemical bonds. If this occurs at the tips of pre-existing microcracks, these cracks might propagate at stress levels much lower than normally required. This is especially true if microcracks are indeed extensional stress features. Figure 19 shows an example of the effect of humidity on crack propagation velocity or growth rate for silica glass. Such enhanced crack growth can lead to time-dependent failure of the specimen.

FIGURE 18. The Solubility of Calcite in Water up to 573°K at Various Partial Pressures of Carbon Dioxide

FIGURE 19. Effect of Humidity on Stressed Crack Propagation

It is speculated that water vapor hydrolyzes the strong Si-O bonds in quartz and such hydrolysis allows microcracks to lengthen and coalesce at reduced levels of bulk effective stress.

Studies have found that small amounts of dissolved water dramatically reduce the strength of single quartz crystals at 800 MPa and 1173°K (Blacic 1971). No data are available concerning hydrolytic weakening of a sandstone at the temperatures and stress levels pertinent to CAES, however. This phenomenon might conceivably contribute to disaggregation and/or fatigue damage. Similarly, hydrolysis, if it occurs, might contribute to inelastic deformation at grain contacts and subsequent enhanced consolidation and permeability reduction. Therefore, it is recommended that testing with dry and humidified air be performed with static and dynamic thermal loading conditions. Thermal fatigue in conjunction with hydrolytic weakening is considered to have the highest investigation priority for CAES.

5.0 PARTICULATE PLUGGING

Particulate plugging in sandstones is the bridging or lodging of small particles (fines) in the interstices or flow channels with concomitant decreases in permeability (Figure 20). In general, potential sources of particles include: 1) existing fines (sand, silt, and clay); 2) disaggregation products; 3) suspended solids in the injection air stream; 4) mineral scale and pipe corrosion deposits; and 5) frayed and dispersed clay particles.

5.1 PARTICLE SOURCES

A number of mechanisms are possible sources of loose particles within a reservoir. Matrix disaggregation has already been discussed as a potential source of particles. Another source might be suspended solids introduced with the air stream. Assuming 100 micrograms of dust per cubic meter of air (Sehmel 1978) and less than 360 cubic meters of 5.0 MPa air injected per hour, the total dust load is only about 1 gram per day.

If any mineral scale or metal corrosion occurs, these deposits may result in sources of particles. Corrosion products are of concern due to their high susceptibility to sloughing. Dispersed clay particles can, under certain circumstances, cause a significant plugging problem. Corrosion and clay particle dispersion are discussed in subsequent sections of this report.

5.2 POTENTIAL CONSEQUENCES

The potential for and magnitude of formation permeability damage depends on: 1) particle size distribution; 2) sandstone pore size distribution; and 3) air density, viscosity, and flow velocity. Damage could be manifested as a "filter cake" at the sand face (well annulus surface) or as plugs and bridges within the flow channels of the sandstone formation.

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 20. Conceptualization of Particulate Plugging

Particle plugging in sandstones has been analyzed in the laboratory by flowing liquid water with various suspended solid loads through sample cores. Pressure buildup and effluent particle load were continuously monitored. Examples of particle size distributions and pressure buildup curves for Berea sandstones are given in Figures 21 and 22. Particle plugging has also been simulated with a statistical random-walk computer model (Donaldson 1977). The mathematical model, based on Poiseuille capillary flow equations results in reasonable reproduction of laboratory data.

No information is available concerning particle plugging when air is the transport fluid. However, particle suspension and transport should be significantly reduced for air relative to water. For example, at 313°K and 5.0 MPa, the density of air is 56.0 kg/m³ and the viscosity is 0.02 g/sec·cm. For water at the same temperature and pressure, the density is about 1000 kg/m³ and the viscosity is 0.68 g/sec·cm. Also, a CAES flow scheme is cyclical rather than

FIGURE 21. Particle Size Distribution (Donaldson 1977)

unidirectional, and a given well is used for both injection and production. This backflushing may inhibit significant loss in permeability through plugging. Site-specific samples should be tested for susceptibility to particulate plugging, but it is anticipated that a CAES reservoir should not encounter the same magnitude of permeability loss as might be expected for a liquid water injection well.

FIGURE 22. Pressure Buildup and Particle Flux in the Effluent (Donaldson 1977)

6.0 MICROSTRUCTURAL DEFORMATION

In a study of the effects of temperature on sandstones, Weinbrant (1972) observed that liquid water intrinsic permeability tends to decrease and irreducible water content increase when temperature is increased from 298°K to 353°K. As shown in Figure 23, the irreducible water content changes from 19% to 34% on the average. The average liquid permeability, for the five Boise sandstone cores tested, decreases from $2.0 \times 10^{-12} \text{ m}^2$ at 298°K to $0.9 \times 10^{-12} \text{ m}^2$ at 353°K. Figures 24 through 26 are graphical displays of these test data. This observed reduction may be caused by the formation of silica-laden viscosity boundary layers and/or microstructural deformation resulting in a reduced capillary flow potential. Dry gas permeabilities do not seem to be adversely affected. No data are available on the temperature sensitivity of sandstone permeability with humidified air as the working fluid, however.

FIGURE 23. Effects of Temperature on the Irreducible Liquid Saturation for Boise Sandstone (Weinbrandt 1972)

FIGURE 24. Effect of Temperature on the Absolute Liquid Permeability for Boise Sandstone (Weinbrandt 1972)

FIGURE 25. Effect of Heating and Cooling on the Absolute Liquid Water Permeability for Berea Sandstone (Weinbrandt 1972)

FIGURE 26. Effect of Temperature on the Absolute Liquid Water Permeability for Boise and Berea Sandstone Cores (Weinbrandt 1972)

6.1 IRREDUCIBLE WATER CONTENT

The irreducible water content is that amount of water that will remain in the rock after initial development of the air bubble. This water is trapped in small diameter pores which support high capillary retention forces. It is possible that up to 20% or more of the porosity could remain liquid saturated after air is injected into the reservoir and this water will have to be removed via vaporization with the undersaturated air. There is some laboratory evidence that indicates an increase in residual liquid saturation as temperature is increases (Weinbrandt 1972). It may be necessary, therefore, to inject low temperature air until the main body of water has been displaced from what will ultimately be the elevated temperature working air zones.

6.2 PERMEABILITY REDUCTIONS

In laboratory studies, liquid water intrinsic permeability is observed to decrease with increasing temperature. The observed permeability reduction

might be due to thermal expansion and restriction of some flow channels which, if elastically deformed, would recover upon cooling. Figure 27 reveals the temperature dependence of the formation factor (tortuosity) ratio as measured on Berea sandstone cores. Tortuosity is defined as the inverse ratio of the length of a rock specimen to the length of the equivalent path of an electrolyte within it. As such it refers to the path length that fluid must negotiate in traversing the axial dimension of a rock core. Therefore, if tortuosity increases with increasing temperature, permeability might be expected to decrease in some associated manner.

If microstructural damage is induced by increased or cyclical temperatures, permeability may decrease due to particulate plugging and/or irreversible media consolidation. Hydrolytic weakening and pressure solutioning may enhance sandstone consolidation at elevated temperatures.

FIGURE 27. Effect of Temperature on the Inverse Formation Factor Ratio (Brannan and Vongenten 1973)

Plugging might also be caused by gases, such as nitrogen, oxygen, and carbon dioxide, being dissolved in the flowing water. As the temperature increases, the gas solubilities decrease and as a result bubbles may form within the sandstone core. Such bubbles might effectively retard the fluid flow and thus result in the observed permeability decreases. As the water temperature decreases the gases might be reabsorbed and the permeability recovered.

Another possibility is that elevated temperatures may increase the total dissolved silica concentration and the prominence of silica suspensions. These increases may lead to anomalously high viscosities for liquids within small channels. Whether similar problems could be encountered with humidified air is a question, as yet, unresolved.

The above discussion centers around a liquid water or oil saturated system. There is no laboratory or field evidence available to justify the assumption that humidified air would result in a similar permeability decrease. The absolute permeability for dry nitrogen does not decrease significantly as temperature is increased. It is assumed that humidified air permeability would respond somewhere between that observed for dry gas and for liquid water. Experiments with humidified air as the working fluid should be conducted.

7.0 COMPRESSIBILITY

Sandstone compressibility may increase as a function of temperature. Compressibility refers to an incremental change in volume commensurate with an incremental change in pressure at a given constant temperature. An 11% increase in the bulk compressibility of Berea sandstone has been observed for temperature increases from 293°K to 373°K. At 473°K there was a 23% increase (Somerton 1974). Figures 28 through 30 reveal how Berea sandstone bulk compressibility and porosity might vary as a function of effective stress and temperature. Thermally induced increments in mean effective stress for CAES reservoirs might be on the order of 10.0 to 60.0 MPa.

7.1 EFFECTIVE STRESSES

A CAES reservoir will be subject to a variety of superimposed stresses, such as confining stress due to the weight of the overlying rock and sediments, pore pressure due to the compressed air and ambient interstitial water pressure, and incremental stresses due to the nonuniform thermal loading. Effective stress refers to the difference between the confining load on the solid matrix and the interstitial fluid pressure. The weight of the overlying column of rock results in a lithostatic stress on the order of 0.021 MPa/m. Associated with this vertical stress is the radial or horizontal stress component. In geologic areas currently in a state of relaxation, the horizontal stress will be of the same magnitude as the vertical stress. In a region undergoing tectonic activity, the horizontal stress component can be two or three times greater than the vertical component. Conversely, in some areas one of the horizontal stress components can be less than half the vertical.

The fluid inside of the rock is pressurized due to the weight of an overlying column of fluid. Generally this is in the range of 0.009 to 0.011 MPa/m. In confined aquifers, the pore pressure or head can be somewhat greater but will still be less than the lithostatic confining stress. In ground-water wells, oil wells, and geothermal wells, the pore pressure is often reduced due to continual extraction of the fluids. Thus, the difference between the

FIGURE 28. Bulk Compressibility of Berea Sandstone as a Function of Temperature and Effective Stress (Somerton 1974)

FIGURE 29. Effect of Temperature and Hydrostatic Stress on Volume, (Somerton 1974)

FIGURE 30. Effect of Temperature and Hydrostatic Pressure on Porosity (Somerton 1974)

STRESS CONDITIONS

FIGURE 31. Conceptualization of Differences Between Confining Stress, Pore Pressure, and Effective Stress

confining stress and the pore pressure increases. It is this stress difference that is termed the effective stress and if sufficient fluid is withdrawn without natural or artificial recharge, then the effective stress will continue to escalate and consolidation and ground subsidence may occur.

In a CAES scheme, extracted fluid is continually replaced. Consequently, the pore fluid pressure should not vary from ambient by more than 100 to 150 psi and then generally in a positive sense. Cumulative subsidence similar to that seen in heavily pumped ground-water basins is not expected under CAES conditions. Increasing the temperature of the storage formation rock will, however, cause thermal expansion. Most of the overlying sediments are not subjected to thermal loading and tend to inhibit the expansion process in the storage zone. Increased temperatures result in an added component of confining stress on the heated portion of the reservoir. Thus, the effective stress increases. Computer calculations reveal that, for the reference CAES reservoir, increments in vertical and radial effective stress of 10 to 60 MPa may be expected for the heated near-well zones (Friley 1979).

The stress level depends, in part, on the compressibility of the rock. The more compressible the rock, the lower the stress and the greater the deformation. Such deformation might reduce the porosity and permeability of the rock somewhat, however, it may be beneficial in reducing the magnitude of macroscopic stresses. Accordingly, sandstone and shale compressibilities should be investigated at elevated temperatures and pressures. Increased humidity may also tend to increase the compressibility of the medium as a result of physico-chemical alterations on a microscopic level.

7.2 ROCK SOFTENING

Laboratory tests have been conducted with pure minerals, as well as actual reservoir rocks, to study the effects of hydrothermal (hot water or steam) treatments on reservoir rock properties like compressibility. These tests show that hydrothermal treatment with steam may result in increased compressibility which is attributed to thermally enhanced pressure solutioning and/or hydrolytic weakening at grain contacts. Alternate explanations include the partial destruction of dolomite and kaolinite and the synthesis of montmorillonite

clay in the presence of excess silica (Day et al. 1967). Basically, the reaction is dolomite + kaolinite + quartz + water = calcite + montmorillonite. Note that water in the liquid or vapor form is required to support pressure solutioning and hydrolytic weakening of silica and any other hydrothermal activities. Thus, the degree of interstitial dewatering and vapor transport in the elevated temperature zones will control any changes in bulk compressibility.

Changes in compressibility may be inhibited by pretreatment with weak ammonia solutions. The effects of hydrothermal steam treatment on Berea sandstone at 575°K are shown in Table 2. The point-load "hardness" of the rock changes from 228 MPa to 152 MPa on the average. Mineralogical analysis reveals montmorillonite is synthesized from kaolinite, dolomite, and quartz. When dolomite and quartz are reacted in the absence of kaolinite or clay minerals, both montmorillonite and talc can be produced along with calcite (Day et al. 1967). Figure 32 shows the X-ray results for Berea sandstone. It is instructive to compare the pre- and post-steam treatment samples and observe the attenuating influence of the ammonia pretreatment. Again, no data are available for a humidified air environment, nor has hydrolytic weakening and pressure solutioning been adequately investigated.

TABLE 2. Rock Softening in Steam and the Effect of Ammonia Pretreatment (Berea Sandstone, 575°K, 4 days) (Day et al. 1967)

Berea Sandstone	Before Treatment	After Steam	After Steam and Ammonia
Point-load Hardness (MPa)	228	152	317
Mineralogy	quartz, kaolinite, illite, feldspar, chlorite, dolomite	quartz, kaolinite, illite, feldspar, abundant montmorillonite	ammonium-mica kaolinite, quartz feldspar

FIGURE 32. Berea Sandstone X-ray Patterns Before and After Steam Treatment (Day et al. 1967)

8.0 CLAY SWELLING AND PARTICLE DISPERSION

Rock formations often contain bentonitic clays which may undergo volume changes when the electrolyte content of the ground water is changed (Hewitt 1963). 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. During the expansion process the edges of the flat clay plates can become frayed and small particles released within the sandstone matrix. This can lead to particulate plugging which causes a loss in permeability. Similarly, a change in the electrolyte content can result in deflocculation and dispersion of clay particles.

8.1 POTENTIAL OF WATER SENSITIVITY IN CAES RESERVOIRS

In CAES operation, air, not water, is being injected into the reservoir. Therefore, fluid incompatibility problems would appear to be of minimal concern, although one possibility must be considered. Large quantities of water will be evaporated in the near vicinity of the wellbore, transported away from the well, and condensed in the cooler regions of the reservoir. The amount of condensate will depend, in part, on the irreducible water content, the radial temperature profile and the injection air humidity. For example, for totally dry air injected at 500°K into a reservoir of 0.20 porosity, 0.20 irreducible water content $5.0 \times 10^{-12} \text{ m}^2$ intrinsic permeability and 30 m thickness, approximately 5000 kg of water might be condensed each week in the cooler regions of the formation (Wiles 1979). This water may be deposited in a zone containing higher salinity waters. If the mineralogy is water sensitive, particles associated with subsequent clay swelling and dispersion may eventually migrate back toward the well. Although not considered likely, this problem should be investigated for any CAES candidate reservoirs found to be water sensitive.

8.2 POTENTIAL FORMATION DAMAGE

Formation damage refers to a reduction in permeability by the swelling of indigenous clays or by the dispersion and movement of indigenous particles.

Basically, the spacing between the stacked plate structure of bentonite clay is changed when the salt content of the formation waters is varied. 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. The common swelling clay minerals are the montmorillonites, 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 would cause the most.

As an example, when mica (a common sandstone constituent) containing the potassium ion (interplate spacing 10 Å) is contacted with a fluid low in potassium content, a cationic exchange or chemical reaction can occur with layer hydrated ions such as sodium or calcium. The interplate spacing increases to 15 Å (Reed 1972). Figure 33 shows how this volume increase might partially plug a sandstone. During the swelling process, the normally flat plates can have their edges frayed and broken, thus generating fines which are free to migrate and plug interstices. Also, clay-sized particles are often flocculated since the individual particles are held together by electrostatic forces. The reduction in cation concentration by fresh-water dilution can promote deflocculation. These dispersed particles are free to migrate with the formation fluids (air or water) and potentially reduce the permeability.

8.3 EXAMPLE LABORATORY DATA

The Berea sandstone is used as an example since it is extremely water sensitive. Both particle dispersion and swelling are potential damage mechanisms. Figure 34 reveals the degree of permeability reduction as a function of sodium content of waters being flushed through the sandstone core. Permeability alterations are manifested by the sharp declines observed during the one-tenth normal (0.1 N) NaCl and distilled water tests. The permeability decline is only 28% during the 0.1 N NaCl flood because the salinity is high enough to partially inhibit clay dispersion even though the clay surfaces are

SWELLING CLAY

PARTICLE PLUGGING

FIGURE 33. Conceptualization of Clay Swelling and Dispersion

FIGURE 34. Reduction in Liquid Permeability Associated with Decreased Salinity Water (Hewitt 1963)

sodium saturated. When the core is washed free of salt during the distilled water flood, leaving the clays saturated with sodium in a fresh-water 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. The bentonite content in Berea is generally between 0.5 and 1.0% by weight. Therefore, rather small quantities of interstitial clay material can, in certain circumstances and for certain sandstones, cause significant reductions in formation permeabilities. For potential CAES reservoirs, it may be necessary to identify the water sensitivity of the reservoir rock and any alteration products.

8.4 WATER SENSITIVITY RECOGNITION

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

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.

8.5 PRETREATMENT

To inhibit water sensitivity problems in reservoir rocks, chemical pretreatment is possible. It may be necessary to introduce a material that will adhere very tenaciously to both external and interlayer surfaces of clay minerals. Hydroxy-aluminum (OH-Al) solutions followed by a few days of fresh-water treatment appear to successfully inhibit clay swelling problems.

Polymeric cations adsorb 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 appears to inhibit the production of montmorillonite (swelling) clay by elevated temperature steam. Ammonium-mica and analcite ($\text{AlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) are generally formed instead of montmorillonite (Day et al. 1967).

The most obvious solution to clay swelling problems however is to select a reservoir medium with as small a clay content as possible.

9.0 HYDROTHERMAL REACTIONS

With respect to hydrothermal alterations, silicates, carbonates, and sulfates are the primary factors. If elevated temperature liquid water is present, hydrolysis and mineral dissolution and precipitation should be considered. The end products of hydrolytic reactions can be clay minerals. The potential problems associated with clays have been previously discussed. The potential problems associated with mineral scaling are evident in geothermal reservoirs. Fortunately, the working fluid in CAES is either dry air or humidified air. Mineral solubilities should be significantly lower in such an environment.

9.1 HYDROLYSIS

During the hydrolysis process, hydrogen ions in solution are exchanged for alkali (Na,K) and alkaline (Ca,Mg) cations in the silicate rock minerals. For example, forsterite, a magnesium silicate, can be hydrolyzed to yield free magnesium cations, hydroxide ions, and silicic acid as follows:

Kaolinite (clay mineral) can result from the hydrolysis of potassium silicates by the following simplified reaction:

Other clay minerals, e.g., talc, chlorite, illite, and montmorillonite, might be similarly produced from silicates like plagioclase and potassium feldspars. However, these reactions require liquid phase water or possibly steam and are highly pH and temperature dependent. In a CAES reservoir, it may be desirable to ensure that zones containing significant quantities of liquid phase water are not heated to temperatures exceeding about 350°K to

400°K. If water is present, an increase in the available free hydrogen ion concentration will increase silicate hydrolysis and clay mineral production. An increase in the partial pressure of CO_2 because of injected air might favor hydrolysis according to the following reactions:

Silicate hydrolysis rates approximately double for a 10°C temperature increment. In essence, elevated temperatures merely accelerate natural chemical weathering reactions. All of the previously presented arguments concerning available water, water immobility, in situ reactions, and "particle slaking" and plugging apply equally well to hydrolysis products. Silicate hydrolysis can result in: an alkaline or at least less acidic solution, clay forming minerals, residual solids and cations, and weak silicic acid in solution. However, because of temperature and liquid water separation in a CAES reservoir, silicate hydrolysis is not being considered a serious alteration mechanism for a CAES system.

9.2 DISSOLUTION AND PRECIPITATION

The major parameters affecting the dissolution and precipitation of reservoir rock include: 1) initial rock composition and microstructure, 2) water availability and composition, 3) temperature, 4) fluid velocity, 5) fluid residence time, 6) rock surface area to fluid volume ratio, 7) pH or hydrogen ion activity, and 8) Eh or redox potential. Another way of expressing these factors is by categorizing them as: thermodynamics, kinetics, crystallization, adherence, and hydrodynamics.

Solubility or equilibrium between a solid and a solution can be described by an equilibrium constant called the solubility product. The solubility product is equal to the mathematical product of the individual constituent activities. Since most rock-forming materials, e.g., silicates, carbonates, and sulfides, are compounds of weak acids, their solutions are alkaline, and thus pH is an important controlling parameter.

Scaling is manifested as a deposit on rock surfaces, well casings, and surface equipment. Subsequent sloughing of this deposit can result in particles being suspended in the flowing fluid column as well as possible plugging problems. Precipitation can also directly result in the presence of a suspended solid in the solution or a deposit between the sand grains in the formation. Many examples of scaling can be found in the geothermal literature. The primary problems include silica deposition as the temperature is decreased and/or calcite deposition as the temperature is increased or the partial pressure of carbon dioxide is decreased.

Precipitation or scaling may occur when the constituent concentration is such that the solubility product is exceeded. In other words, when the fluid becomes supersaturated with a particular mineral, altering the temperature and/or solution pH may cause the water to become supersaturated with minerals like calcite (CaCO_3) or silica (SiO_2) and may result in scaling. Potential mineral deposition may be calculated if the chemistry of the aquifer fluids and host rocks and the thermodynamic equilibrium characteristics are known (Figures 17 and 18). However, equilibrium predictions can often be misleading. The nucleation and growth of a solid from solution is often a difficult and slow process, and crystals may have difficulty forming even from supersaturated solutions. Thus, reaction kinetics play an important role in potential scaling problems.

Figure 17 presented data on the equilibrium solubility of quartz and amorphous silica as a function of temperature. The quantity of amorphous silica or quartz that can go into solution is maximum at 593°K to 613°K and is substantially reduced at both higher and lower temperatures. With respect to kinetics, the most striking feature of quartz dissolution and precipitation is the large rate constant increase between 298°K and 613°K shown in Figure 35.

FIGURE 35. The Logarithm of the Equilibrium Rate Constant for the Dissociation of Quartz in Water as a Function of Reciprocal Temperature (Apps 1978)

Other minerals that are of interest with respect to scaling problems include magnesium carbonate, calcium sulfate, and barium sulfate. The most interesting observation is that calcium sulfate, like calcium carbonate, has a solubility value that decreases with increasing temperature and that barium sulfate cannot be readily dispersed once it has deposited as scale. The decreasing solubility with increased temperature primarily reflects the decreasing solubility of CO₂ in water as the temperature is increased.

Apparently, the solubility of the above minerals depends on the pressure of CO_2 above the solution since this pressure helps to determine the concentration of dissolved carbonic acid:

Thus, any process that increases the amount of CO_2 available to the solution makes more CaCO_3 dissolve; anything that decreases the amount of CO_2 causes CaCO_3 to precipitate. In the CAES concept, the temperature of the storage formation is being increased and carbon dioxide is being introduced to the reservoir; however, it is being speculated that the unavailability of mobile liquid phase water should eliminate scaling as a significant problem.

As important as hydrothermal alterations and scaling may be to technologies like geothermal or seasonal thermal energy (hot water) storage, for a CAES reservoir the environmental conditions are such that these reactions will probably not be present to any significant degree. In the working air zone, the only available liquid phase water will be the irreducible amount remaining after initial air bubble development. This water will be essentially immobile in its liquid state and will reside in small diameter pores, dead end pores, and low permeability lenses. Hydrothermal alterations associated with this localized quantity of water may have an insignificant impact on CAES operations because of its lack of mobility in the liquid state. Thus, the solubility of minerals in saturated steam or, more realistically, humidified air may be the only important consideration.

9.3 PRECIPITATION DUE TO RESIDUAL WATER EVAPORATION

The irreducible water in the near vicinity of the well will gradually be evaporated and recondensed farther out into the reservoir or transported up to the well. As water is evaporated, the remaining brine may approach saturation with respect to certain dissolved constituents. The result may be deposition and infilling of minerals in channels and pore spaces, subsequently causing a reduction of permeability.

Fortunately the affected regions should typically be small diameter interstices, dead end pore space, or lenses of low permeability within the storage reservoir. The mineral precipitation should occur only in that volume of rock originally containing irreducible water. This is because this water is essentially immobile in its liquid state (Stottlemire 1978). Therefore, any mineral precipitation associated with evaporation of irreducible water should not have a significant effect on CAES operations.

9.4 SOLUBILITY IN STEAM

Some limited results are available on the solubility of quartz in a saturated steam environment (Kennedy 1950; Morey 1951). According to Kennedy (1950):

The solubility of quartz in saturated vapor in equilibrium with liquid and with crystalline quartz, that is along the three phase boundary, is almost immeasurably small until a temperature of 643°K and a pressure of approximately 21.0 MPa are reached. From 643°K to 647°K the solubility in the vapor phase increases rapidly along the three phase boundary, until at 647°K the solubility reaches the value of the liquid at this temperature, 0.023%.

Unfortunately, the duration of the tests was typically from 10 to 100 hr. Thus, there is some uncertainty as to whether or not equilibrium saturation was attained at the lower temperatures and pressures. It is certain, however, that the solubility of quartz in saturated vapor is substantially less than that in liquid and probably does not exceed 0.05% by weight. Figures 36 and 37 present much of the data generated by Kennedy and his coworkers.

FIGURE 36. Isothermal Solubility Curves (Kennedy 1950)

FIGURE 37. Isobaric Solubility Curves (Kennedy 1950)

10.0 REDOX REACTIONS

Natural subsurface environments tend to be anoxic or void of free oxygen. However, free oxygen will be readily available in CAES reservoirs. Certain oxidation reactions may result in relatively insoluble minerals that may reduce permeability. If water is present, increased quantities of silicic and carbonic acid may result. The more common reactions include the oxidation of iron oxides to hematite (Fe_2O_3) or goethite (HFeO_2) and the oxidation of manganese oxides to manganite [$\text{MnO}(\text{OH})$] or pyrolusite (MnO_2).

Of possible concern is the oxidation of sulfide minerals such as lead sulfide (galena) and iron sulfide (pyrite). Pyrite often occurs in shale material. The oxidation reaction produces sulfate ions which can result in the production of sulfuric acid. It is not impossible to go from a pH of 6.0 to a pH of 1.0 to 2.0. Once again, H_2O is a key constituent and hence a CAES environment is somewhat unique relative to normal underground conditions. Figure 38 reveals the stability fields of hematite and magnetite in water. Positive Eh values would correspond to a CAES environment.

Another types of oxidation reaction may be of some concern. Oil has been found on the sandface of some natural gas storage wells. This oil is presumably from the compressor. Oxidation of this oil with hot air may be a potential problem warranting additional study. However, the axial and centrifugal compressors being considered for CAES may minimize this potential problem since these units support a somewhat negligible oil wetted surface relative to natural gas field compressors.

FIGURE 38. Composite Diagram Showing Stability Fields of Hematite and Magnetite in Water

11.0 CORROSION

Previous discussions have focused on potential alterations of reservoir rocks. This final section deals with possible well casing corrosion problems. Potential consequences include equipment failures, blowouts, and corrosion product deposition which might result in free particles.

Corrosion is an electrochemical process requiring an electrical coupling between the carbon steel casing and the formation fluids. A typical corrosion reaction is: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$. Two of the most important cathodic reactions required to complete and sustain the electrochemical corrosion process are: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (gas) and $\text{O}_2 + 2\text{H}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$ (Shannon 1977). This shows that the acidity (pH) and the oxygen content of the brine are extremely important in controlling the corrosion of carbon steels. Basically, corrosion will increase with increases in acidity, oxygen content, liquid saturation, flow rate, and temperature.

Most geothermal systems are liquid or liquid-vapor dominated, support a pH close to neutral, and are essentially anoxic. A CAES reservoir, however, should be a humidified air system at worst, and, therefore, corrosion should be significantly reduced. This assumes that no condensation is occurring in the well and that small local cells are not active at alloy discontinuities and shape bends in the pipe.

11.1 LIQUID WATER ENVIRONMENT

If condensation occurs in the well or excessive drawdown results in production of a brine/air mixture, average corrosion rates will increase with increasing solution acidity. A common way of increasing the acidity is by increasing the dissolved carbon dioxide content. Naturally, CO_2 will be readily available in a CAES operation. The average corrosion rates of 10 carbon steels in 1% NaCl brines are plotted against pH in Figure 39 (Shannon 1977). It has been observed that the effects of dissolved CO_2 become less serious at elevated temperatures, e.g., 423°K to 523°K. This is attributed to the buffering effects of corrosion films, e.g., none at 323°K, FeCO_3 at 423°K, and Fe_3O_4 at 523°K (Shannon 1977).

FIGURE 39. Average Corrosion of 10 Carbon Steels in NaCl-CO₂ Brines Versus pH (Shannon 1977)

The effect of temperature on corrosion is interrelated with pH and salinity. Corrosion rates initially decrease as temperature is increased. This is attributed to the development of a protective Fe₃O₄ film on the metal. However, because the elevated temperatures induce increased salinity, corrosion rates tend to increase after a short period of time. An example of the effects of temperature on corrosion rates is shown in Figure 40. An example of the effects of increased salinity is shown in Figure 41.

Note that the corrosion tests were conducted in an oxygen-free environment. However, it is apparent that the presence of oxygen will increase corrosion rates, especially in high iron or chromium alloys.

FIGURE 40. Average Corrosion of 10 Carbon Steels in CO₂-Biocarbonate Brines (Shannon 1977)

11.2 AERATED STEAM ENVIRONMENT

The literature was examined for data on the corrosion of well casings under environments similar to that expected for a CAES reservoir. Example corrosion data are presented in Table 3. It appears that corrosion rates of up to 20 mils per year (mpy) might be expected under high humidity conditions (Marshall et al. 1957). As the humidity decreases the corrosion rates should also decrease because the electrochemical attack is dependent upon the partial presence of water. Corrosion rates between 1 and 6 mpy might be reasonable over the lifetime of a CAES facility.

FIGURE 41. Average Corrosion Rate of Carbon Steels Versus Salinity (Shannon 1977)

For well casing materials, damage should be characterized as general corrosion producing an uneven surface. Stressed samples have been tested in aerated steam and no crevice cracking was observed. Thus it appears that stress corrosion is not particularly significant for carbon steels if liquid water is not present.

TABLE 3. Corrosion Under Environments Similar to CAES

Metal(a)	Condition	Corrosion Rate	Reference
Carbon Steel ASTM-A285	aerated steam 150 days, 100°C, 1 ATM, velocity <10 m/sec	11 mpy	Tolivia et al. 1975
Carbon Steel	aerated steam 144 days, 30 lb steam to 2 lb air	20 mpy	Marshall et al. 1957
	separated steam 144 days, 140°C	6 mpy	Marshall et al. 1957
Bore Casings API-J55	aerated steam 144 days, 98-108°C 0-5 psig	>10 mpy	Foster et al. 1961
API-H40	aerated steam 144 days, 98-108°C 0-5 psig	>10 mpy	Foster et al. 1961
API-J55	separated steam 144 days, 193°C < 1% moisture	<1.0 mpy	Foster et al. 1961
API-H40	separated steam 144 days, 193°C < 1% moisture	<1.0 mpy	Foster et al. 1961

(a) No data available for N-80 casing which is a possible material for a CAES well.

Assuming a corrosion rate of 20 mpy for the first 3 weeks and 5 mpy after that, a period of 23 years would be required to reduce a CAES well casing thickness by 0.1 in. This appears to represent reasonable stability for a CAES well. Possible corrosion factors not considered in this estimate are erosion due to entrained sand particles and the effects of noncondensable gases.

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APPENDIX

SANDSTONE CHARACTERISTICS

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SANDSTONE CHARACTERISTICS

Table A.1 lists the sandstone classes that may be applicable to CAES reservoirs. The chemical and physical stability to potential CAES operating conditions will depend on specific rock and ground-water properties. Therefore it has been necessary to focus discussion on one or two sample rock types. For this report, the Berea and Galesville sandstones have been used as example reservoir rocks. Only the Galesville is typical of a CAES reservoir rock, however.

Berea sandstone, Mississippian in age, is a light olive gray, uniform, fine-grained graywacke quarried near Amherst, Ohio. The texture is clastic with subangular grains and exceptional homogeneity and isotropy. Figure A.1 presents various magnified views of a section of Berea sandstone. Various mineral phases are identified.

Galesville sandstone, from the Media natural gas field in Illinois, is an example of an actual reservoir rock. Core samples, recovered from a depth of 685 m, reveal a white to grayish-white sandstone with an estimated mean grain size of 0.5 mm. Petrographic examination reveals that the subangular grains are equant to subequant in form. The rock as a whole is moderately sorted and exhibits cyclic parallel bedding of thin, coarse-grained layers and thicker, fine-grained layers. The Galesville sandstone is a quartzose consisting of approximately 98% quartz, 1% feldspar, and 1% kaolinite clay + calcite + mica + opaque minerals. The grains are almost entirely quartz with minor amounts of plagioclase and kaolinite. The cement material is predominantly crystalline quartz with minute quantities of carbonate.

Figure A.2 is a micrograph of the Illinois Galesville sandstone. As compared to the Berea, the permeability variations are quite pronounced. Table A.2 lists some additional property data for the Berea and Galesville sandstones.

TABLE A.1. Sandstone Classifications

TEXTURE	UNCONSOLIDATED - SILT, SAND		CLASSIC		
			CONSOLIDATED - SILTSTONE, SANDSTONE		
COMPOSITION MAJOR FRACTION	SIZE GRADES (mm) 1/256 - 1/16 SILT 1/16 - 1/8 VERY FINE SAND 1/8 - 1/4, FINE SAND; 1/4 - 1/2, MEDIUM SAND; 1/2 - 1 COURSE SAND; 1/2, VERY COURSE SAND				
		CHIEFLY QUARTZ			
	90% QUARTZ	FELDSPAR 10-25%	ROCK CHIPS 10%	QUARTZ AND 25% FELDSPAR	QUARTZ, FELDSPAR ROCK CHIPS, PELITIC MATRIX, ANGULAR GRAINS, TOUGH
10% MINOR FRACTION	QUARTZ SANDSTONE (QUARTZOSE SANDSTONE)	FELDSPATHIC SANDSTONE	LITHIC SANDSTONE	ARKOSE (ARKOSE SANDSTONE) NORMALLY PINK, RED OR LIGHT GRAY	GRAYWACKE-NORMALLY GREENISH GRAY SUBGRAYWACKE-LOW IN FELD- SPAR, ROCK CHIPS, OR LESS ANGULAR GRAINS. TENDENCY TO CHEMICAL CEMENT
CLAY MINERALS OR CLAY-SIZE MATERIALS	ARGILLACEOUS QUARTZ SANDSTONE	ARGILLACEOUS FELDSPATHIC SANDSTONE LOESS - FINE SAND OR SILT MASSIVE, POROUS, COHERENT	ARGILLACEOUS LITHIC SANDSTONE	ARGILLACEOUS ARKOSE	ARGILLACEOUS GRAYWACKE ARGILLACEOUS SUBGRAYWACKE
SILICA OPAL CHALCEDONY QUARTZ	ORTHOQUARTZITE (SEDIMENTARY QUARTZITE) (SILICEOUS QUARTZ SANDSTONE)	FELDSPATHIC ORTHOQUARTZITE (SILICEOUS FELDSPATHIC SANDSTONE)	LITHIC ORTHOQUARTZITE (SILICEOUS SANDSTONE)	SILICEOUS ARKOSE (QUARTZITIC ARKOSE)	SILICEOUS SUBGRAYWACKE
CALCITE OR DOLOMITE	CALCAREOUS QUARTZ SANDSTONE	CALCAREOUS FELDSPATHIC SANDSTONE	CALCAREOUS LITHIC SANDSTONE	CALCAREOUS ARKOSE	CALCAREOUS SUBGRAYWACKE
IRON MINERALS CHIEFLY: LIMONITE GOETHITE HEMATITIE SIDERITE CHAMOSITE	LIMONITIC OR (FERRUGINOSE) QUARTZ, SANDSTONE	LIMONITIC OR HEMATITIC (FERRUGINOSE) FELDSPATHIC SANDSTONE	LIMONITIC OR HEMATITIC (FERRUGINOSE) LITHIC SANDSTONE	LIMONITIC OR HEMATITIC (FERRUGINOSE) ARKOSE	LIMONITIC OR HEMATITIC (FERRUGINOUS) GRAYWACKE LIMONITIC OR HEMATITIC (FERRUGINOUS) SUBGRAYWACKE
CARBON HUMUS-YIELDS CARBONACEOUS DERIVATIVES SAPROPEL-YIELDS BITUMINOUS DERIVATIVES	CARBONACEOUS QUARTZ SANDSTONE BITUMINOUS QUARTZ SANDSTONE	CARBONACEOUS FELDSPATHIC SANDSTONE BITUMINOUS FELDSPATHIC SANDSTONE	CARBONACEOUS LITHIC SANDSTONE BITUMINOUS LITHIC SANDSTONE	CARBONACEOUS ARKOSE BITUMINOUS ARKOSE	CARBONACEOUS GRAYWACKE, ETC. CARBONACEOUS SUBGRAYWACKE, ETC.
MISCELLANEOUS PHOSPHATE (COLLOPHANE) EVAPORITES HALITE AND SYLVITE ANHYDRITE GYPSUM	PHOSPHATIC QUARTZ SANDSTONE, ETC.	PHOSPHATIC FELDSPATHIC SANDSTONE, ETC.	PHOSPHATIC LITHIC SANDSTONE, ETC.	PHOSPHATIC ARKOSE ETC.	PHOSPHATIC SUBGRAYWACKE, ETC.

TABLE A.2. Representative Berea and Galesville Sandstone Properties

	Berea	Galesville
Porosity (percent)	20	18
Permeability (10^{-12} m ²)	2.0-4.0	2.0-25.0
Average Grain Size (mm)	0.25	0.5
Angularity	Subangular	Subangular
Cement	Carbonate Silica	Quartz
Composition (wt percent)		
Quartz	85	98
Feldspars	5	1
Carbonates	1	1
Clays	7	1
Fe-Ti Minerals	2	1
Pore Size Range (microns)	0.5-45.0	0.5-100.0
Thermal Conductivity (J/S·m·k)(dry)	2.2	---
Thermal Diffusivity (m ² /s) (dry)	1.4×10^{-5} m ² /s	---
Montmorillonite Content (wt percent)	0.6	0.0
Poisson's Ratio	0.33	0.30

FIGURE A.1. Berea Sandstone Micrograph

10X

GALESVILLE

100X

FIGURE A.2. Micrograph of Typical Galesville Sample

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