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EFFECT OF CARBON DIOXIDE ON THE
PERMEABILITY OF SYNTHETIC HANFORD SALT CAKE

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ABSTRACT

In well-drained salt cakes where no capillary-held mother liquor was present, the reaction between NaOH and $\text{CO}_2(\text{g})$ produced enough solids to lower the permeability by a factor of 20. This same reaction lowered the permeability by at least three orders of magnitude when the salt cake was saturated with mother liquor. Thus, while the reaction between CO_2 and NaOH can dry the liquids in Hanford salt cake, the permeability is decreased to such an extent that use of this method becomes impracticable.

EFFECT OF CARBON DIOXIDE ON THE PERMEABILITY OF SYNTHETIC HANFORD SALT CAKE

INTRODUCTION

At the Energy Research and Development Administration's (ERDA) Hanford site liquid radioactive wastes from fuel reprocessing are being solidified by evaporation to salt cake. Slurries containing liquid concentrate and solids are pumped from a crystallizer-evaporator to storage tanks where the solids are allowed to settle, forming a salt cake which is essentially sodium nitrate (NaNO_3). This NaNO_3 salt cake contains some radionuclides, principally cesium-137. The liquid phase is about 5M sodium hydroxide (NaOH) saturated with NaNO_3 and containing varying amounts of sodium nitrite (NaNO_2) and sodium aluminate (NaAlO_2). Further reduction of the liquid volume is accomplished at the evaporator by pumping supernatant liquids from the tanks and as much of the drainable liquid as possible from saturated salt cakes via salt wells which reach to the bottom of the tank. Liquids are pumped to a practical limit. Some liquids which are held by capillary action as a residual heel remain. Since there does not seem to be any mechanical method for removing this nonpumpable liquid heel and since these liquids must be prevented from leaving the tank in the event of tank wall failure, a method of immobilizing the drainable liquor or displacing it toward the salt well was needed.

One method of immobilizing the nonpumpable liquors is to convert them to a solid by using carbon dioxide gas. In the process of converting the NaOH to a hydrated sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$) the permeability of the salt cake may be lowered. How much the permeability will be lowered is the subject of this paper.

THEORY

PERMEABILITY

Darcy^[1] investigated the flows of water through packed beds of sand and developed the empirical equation

$$Q = KA \frac{h_1 - h_2}{l} \quad (1)$$

where Q = volume rate of flow downward through the column

A = cross-sectional area of the column

l = length of the column

$h_1 - h_2$ = head of water (driving force)

K = proportionality factor depending upon the fluid and porous medium.

Later work defined K to be equal to k/μ where μ is the viscosity of the working fluid and k depends solely on the porous medium; *i.e.*, the permeability. From this work the generalized form of Darcy's equation was found to be

$$v_s = - \frac{k}{\mu} \left(\frac{dP}{ds} \cdot \frac{dz}{ds} \cdot \frac{\rho g}{1.0133 \times 10^6} \right) \quad (2)$$

where s = distance in the direction of flow, (cm)

v_s = volume flux across a unit area of the porous medium, (cm³/s)

z = coordinate the direction of flow, (cm)

ρ = density of the working fluid, (g/cm³)

g = acceleration of gravity (980.665 cm/s²)

$\frac{dP}{ds}$ = pressure gradient along s , (atm/cm)

μ = working fluid viscosity (centipoise)

k = permeability (darcies, d)

1.0133×10^6 = conversion from atmospheres (atm) to dynes/cm².

For horizontal flow of incompressible fluids such as water or mother liquor, $dz/ds = 1$ and $dP/ds = dP/dx$ and the above equation reduces to

$$v = - \frac{k \cdot dP}{\mu dx} \quad (3)$$

or

$$Q = \frac{kA(P_1 - P_2)}{\mu l} = \frac{kA}{\mu} \left(\frac{\Delta P}{l} \right) \quad (4)$$

upon integration,

where A = cross sectional area (cm²)

l = length of sample (cm)

P_1 = high pressure (atm)

P_2 = low pressure (atm).

In previous work^[2] it was established that equation 4 could be used for gases if low pressures were used and the flow rates were not corrected for gas slippage (Klinkenberg^[1]) or from standard conditions to real conditions (temperature and pressure). Therefore no presentation will be made here for the form of Darcy's equation as applied to gases.

When CO₂ reacts with NaOH in the presence of moisture, three products are possible depending upon the temperature. These products are given by the following reactions:^[3]

In a waste tank the first of these reactions will take place since the temperature is 40° to 50° C due to radio-isotope decay heat. However the Hassler cell was not set up to do work at elevated temperatures so the last reaction takes place in the salt cakes studied here.

EXPERIMENTAL

Salt cakes for this work were prepared by saturating 5M NaOH, 2M NaNO₂, 2M NaAlO₂ solution with NaNO₃ at 90° to 100° C. This solution was then cooled to 50° C with constant agitation. Agitation of the mixture at 50° C continued for 24 hr after which it was cooled to room temperature. Both NaAlO₂ and NaNO₃ were commercial grade chemicals, whereas the NaOH and NaNO₂ were of higher quality.

A schematic of the Hassler cell which was used to obtain permeability data appears in Figure 1. When loading the cell a coarse stainless screen (~25 mesh) was placed on top of the bottom plug followed by a fine (~100 mesh) stainless steel screen. These screens provided better gas flow at the base of the sample. To provide sample uniformity a Plexiglas tube was inserted into the cell and a thick salt slurry was poured into the Plexiglas tube. A thin stainless steel rod was used to work out any trapped air and voids in the salt slurry and insure an evenly packed cake. After draining the excess liquid through the salt core, the Plexiglas cylinder was removed and a coarse stainless steel screen placed on top of the salt. Upon completing the assembly of the cell, the Hassler pressure (see Figure 1) was increased to 1.8 kg/cm² (25 psig) and dry nitrogen gas was forced through the cake to remove any residual liquids.

FIGURE 1
HASSLER CELL SCHEMATIC

After the gas flowed through the sample for several hours no more liquid drained.

A Brooks Instrument Company (Model 5830-1FLA) or Datametrics (Model 800LM) flow meter and associated transducer was used to measure the flow rates. Output from the flow meter was read from a Keithly Instrument, Inc., digital voltmeter (Model 163). Working gas pressures at the top and bottom of the sample and their difference were measured using a mercury manometer and 100 cm cathotometer. Readings could be made to the nearest 0.003 cm. A pressure gauge calibrated from 0 to 60 psi was used to measure the Hassler pressure.

Initial permeability data were taken using dry $N_2(g)$ after which $CO_2(g)$ was passed through the sample at ambient temperature for about 12 hours. The new permeability was determined using $N_2(g)$ again. The sample was then removed from the cell and the dimensions measured using a set of calipers capable of measuring ± 0.002 cm. Data obtained before and after treatment with CO_2 were reduced to a plot of $-\frac{Q}{A}$ versus $\frac{\Delta P}{\ell}$ and the slope $\left(\frac{k}{\mu}\right)$ determined using a least squares computer program.

In one experiment the residual liquid was removed slowly using $CO_2(g)$ instead of nitrogen. This should give the change in permeability of salt cake which lies below the liquid level in a waste tank as opposed to the change in a well-drained salt cake.

RESULTS

As can be seen from Table I, the decrease in salt cake permeability can be as high as a factor of 20 for drained salt cake to more than a factor of 10^3 for salt cake

saturated with mother liquor. The large scatter in the data suggests the difficulty in obtaining a reproducible packing of the salt in the Hassler cell.

TABLE I
EFFECT OF CO₂ ON SALT CAKE PERMEABILITY

	<u>K₁*</u> <u>darcies</u>	<u>K₂*</u> <u>darcies</u>	<u>K₁/K₂</u>
SC-S-10	1.37	0.070	20
SC-S-11	0.771	0.150	5.1
SC-S-12	1.93	1.57	1.2
SC-S-13	0.819	0.321	2.6
SC-S-23	-	<0.002	~10 ³

*K₁ = permeability before CO₂ injection.
K₂ = permeability after CO₂ injection.

CONCLUSIONS

From the data it is evident that for a well-drained salt cake the permeability can be decreased by an order of magnitude and for a salt cake containing capillary-held liquids this decrease can exceed three orders of magnitude. Thus one can expect that above the liquid level within a salt cake in a waste tank the permeability of Hanford salt cake can go from about 2 d^[2] to about 0.2 d as CO₂ reacts with the NaOH. If CO₂ is injected below the liquid level within the salt cake, the permeability will drop below 0.002 d. These changes might be mitigated somewhat if the reaction does not go all of the way to Na₂CO₃·10H₂O because the tank temperature exceeds 35° C. Hence some residual liquids may remain in the pore space. In order for additional reaction between NaOH(g) and CO₂(g) to occur the gas pressure must be increased to force the liquid to become mobile. The effective permeability of the salt to the gas

will be lowered by a factor of 2 to 10 depending upon the degree of saturation of the salt by the mother liquor.^[1] Dissolution of CO_2 in the liquid as HCO_3^- followed by diffusion and reaction is considered to be too slow to be of any use. Complete reaction between $\text{CO}_2(\text{g})$ and $\text{NaOH}(\text{aq})$ to form $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ may occur since there is an excess of water present.

In order to force $\text{CO}_2(\text{g})$ into the salt cake a good hermetic seal will have to be made between the injection tube and the salt. Decreasing the permeability will make this hermetic seal more difficult to form. A decrease in the permeability of the salt will also decrease the radial range of the $\text{CO}_2(\text{g})$ [*i.e.*, $\text{CO}_2(\text{g})$ will tend to go up rather than out through the salt cake].

While this method might be useful for drying salt cakes above the liquid level within the salt cakes (capillary-held plus free-standing liquids), its application to the drainable liquid portion of the salt cake system is dubious at best.

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REFERENCES

1. Amyx, Bass, and Whiting, Petroleum Reservoir Engineering: Physical Properties, McGraw-Hill, New York (1960).
2. D. M. Strachan, *Permeability, Capillarity, and Pore Volume of Hanford Salt Cake*, ARH-ST-129, Atlantic Richfield Hanford Company, Richland, Washington, November 1975.
3. J. F. Smith, Comprehensive Inorganic Chemistry, Vol. 1, M. C. Sneed and R. C. Brasted, eds., D. Van Nostrand Company, Inc., Princeton, New Jersey (1957).

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