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A STUDY OF SCALE AND NONCONDENSABLES
IN AN EVAPORATOR

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A STUDY OF SCALE
NONCONDENSABLES IN AN EVAPORATOR

ABSTRACT

The EPRI Geopressured Wellhead Project as described in C. K. GeoEnergy Corporation Agreement No. RP1671-4 has considered using a flash evaporator designed by Stone and Webster Engineering Corporation, or equivalent, to produce steam which will be heated and used in a steam turbine. Various possible arrangements for power production are discussed in the C. K. GeoEnergy Corporation proposal. In most of these arrangements there are potential problems with the brine chemistry related to scale formation. Emphasis of our research has been on the brine chemistry associated with the flash evaporation process. Specifically, we used the saturation index as defined by Mason Tomson of Rice University to predict scaling tendencies. Associated with the vaporization of the brine droplets are critical mass transfer and heat transfer processes which could have an effect on the scaling. From detailed investigation of these processes, scaling should not be a major problem in the evaporator.

The EPRI Geopressured Wellhead Project as described in C. K. GeoEnergy Corporation Agreement No. RP1671-4 has considered using a flash evaporator designed by Stone and Webster Engineering Corporation, or equivalent, to produce steam which will be heated and used in a steam turbine (Fig. 1). A number of possible arrangements for power production are discussed in the C. K. GeoEnergy Corporation proposal. In all of these arrangements, there are potential problems of scale formation. Emphasis of this research has been placed on the brine chemistry and associated scaling tendency during the flash evaporation process. The objectives of the research project are:

1. To study the scale formation potential as the pressure is dropped and CO₂ is lost from the brine and;
2. To predict and measure the fraction of noncondensables which remain in the steam phase.

The scaling tendency of the brine represented by a saturation index, SI, can be calculated with the following equation developed by Mason Tomson of Rice University:

$$SI = \log \frac{T_{Ca} Alk^2}{P_{X_{CO_2}}} + 5.89 + 1.549 \times 10^{-2} T - 4.26 \times 10^{-6} T^2 - 7.44 \times 10^{-5} P - 2.526 I^{1/2} + 0.920 I$$

T_{Ca} - Molar = ppm Ca/40,000

Alk - Molar = ppm HCO₃⁻/61,000

P - psi

X_{CO_2} - mole fraction or volume fraction CO_2 in the gas

T = °F

I - Molar ionic strength $\sim 1.5 \times 10^{-5}$ conductance ($\mu\text{mhos/cm}$)
 $\sim \text{ppm TDS}/56,000$

A semiquantitative interpretation of the various SI levels is presented in Figure 2. If it is assumed that the key variables which can be altered are T and P, the constant SI isopleths can be constructed (Fig. 3). Figure 3 will be quite useful in quick estimations of how various T and P changes might affect the tendency of the brine to scale. The qualitative interpretations attached to the various SI levels are probably correct to within only 0.3 SI units, at best. Illustrated on the diagram are two extreme scenarios for the brine flashing. In the top scheme, ABD, it is assumed that the pressured drops to 15 psia rapidly and then the temperature drops to about 220°F more slowly. In the bottom flash path, ACD, the opposite order is assumed. The difference with respect to scale formation can be seen in the diagram. Unfortunately, once a nucleus of scale forms it will grow larger and is not redissolved because the brine is thermodynamically supersaturated with respect to calcite formation.

It was assumed in constructing the isopleths in Fig. 3 that the mole fraction of CO_2 in the gas phase remained constant, however, this may not be true in a flash evaporator which tends to lessen the severity of the scaling problem. Mass transfer

calculations for typical flow rates, etc., have been performed to estimate the actual order of the T/P effect on a droplet and the magnitude of CO₂ exchange rate relative to the residence time in the evaporator. In general, preliminary calculations of mass transport and heat transport were performed to define the flash evaporator operating conditions. If the heat transfer (temperature drop) is faster than the mass transfer (pressure drop), the scaling potential will be lowered.

The flash evaporator is shown in Fig. 4 along with the inlet and outlet conditions as described in the Stone and Webster model. The following assumptions were made for the evaporator:

1. The pressurized brine will be sprayed into a flash evaporator 2 ft. in diameter and 10 ft. tall.
2. The hydraulic residence time will be 3 seconds.
3. After leaving the nozzle in the evaporator, the brine will form droplets 0.1 cm. in diameter.
4. The droplets will fall through the steam for about 1 second, based on Stoke's Law Terminal Velocity of 5 ft./sec. for 5 ft. before encountering the evaporator wall or the accumulated brine in the bottom of the evaporator.

CALCULATION OF CO₂ AND CH₄ EQUILIBRIUM CONCENTRATIONS

Steam production = 6,460 lb/hr.

For brine containing 100 ppm CO₂

$$\text{CO}_2 \text{ production} = 146,000 \text{ lb/hr.} \times \frac{100}{10^6}$$

$$= 14.6 \text{ lb/hr.}$$

The partial pressure of CO_2 is proportional to the moles of CO_2 , assuming ideal gas behavior.

$$\text{moles H}_2\text{O} = \frac{6,460 \text{ lb/hr.}}{18 \text{ lb/lb-mole}} = 359 \frac{\text{lb-mole}}{\text{hr}}$$

$$\text{moles CO}_2 = \frac{14.6 \text{ lb/hr.}}{44 \text{ lb/lb-mole}} = 0.033 \frac{\text{lb-mole}}{\text{hr.}}$$

$$\text{mole fraction CO}_2 (x_{\text{CO}_2}) = \frac{0.033}{359 + 0.033} = 9.2 \times 10^{-4}$$

$$\begin{aligned} \text{partial pressure CO}_2 (P_{\text{CO}_2}) &= 9.2 \times 10^{-4} \times 760 \text{ mm} \\ &= 0.70 \text{ mm Hg} \end{aligned}$$

The partial pressure of CH_4 can also be calculated giving the following value:

$$P_{\text{CH}_4} = 18.9 \text{ mm Hg}$$

After obtaining values for the partial pressures of CO_2 and CH_4 , their concentrations can be readily calculated from Henry's Law,

$$x_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{K_H}$$

where Henry's Law constant (K_H) is 5.38×10^6 at 280°F

$$\begin{aligned} x_{\text{CO}_2} &= \frac{0.70 \text{ moles CO}_2}{5.38 \times 10^6 \text{ moles H}_2\text{O}} \\ &= 1.3 \times 10^{-7} \text{ moles CO}_2 / \text{moles H}_2\text{O} \end{aligned}$$

$$\begin{aligned} \text{concentration of CO}_2 &= 1.3 \times 10^{-7} \frac{\text{moles CO}_2}{\text{moles H}_2\text{O}} \times \frac{44 \text{ g/g-moles}}{18 \text{ g/g-moles}} \\ &= 0.32 \text{ ppm} \end{aligned}$$

The equilibrium concentration of CO_2 is 0.32 ppm. This means that the CO_2 concentration is reduced from 100 ppm to 0.32 ppm

in the evaporator. Similarly the equilibrium concentration of CH_4 was calculated and found to be 0.30 ppm. This corresponds to a reduction of 1000 ppm CH_4 in the brine entering the evaporator to 0.30 ppm leaving and entering the disposal well.

MASS TRANSFER FROM DROPLETS IN FLASH EVAPORATOR

In order to obtain information about mass transfer in the evaporator, we assumed diffusion from a stagnet sphere. The equation for this stagnet sphere model is as follows:

$$1 - \Delta' = - \frac{6}{\pi^2} \sum_{N=1}^{\infty} \frac{1}{N^2} \exp\left[-\frac{4N^2 \pi^2 Dt}{Y^2}\right]$$

where

Δ' = fraction of gas (CO_2 or CH_4) remaining at time, t

Y - diameter of droplet

D = diffusion coefficient

t - time in seconds

for the flash evaporator conditions

$D = 5 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 100°C

$t = 1 \text{ sec.}$

$Y = 0.1 \text{ cm}$

Tables are available in mass transport books of $4Dt/Y^2$ vs Δ' . Therefore, it is not necessary to solve the complete equation to obtain mass transport data. Evaluating for the flash evaporator for CO_2 ,

TABLE 1

MASS TRANSFER FOR CO₂

Fraction CO ₂ Remaining Δ'	$\frac{4Dt^*}{y^2}$	Diffusion only time-sec	Diffusion and Convection	
			Low Range t/30 sec.	High Range t/90 sec.
0.78	0.005	0.25	0.008	0.0027
0.58	0.02	1	0.033	0.011
0.22	0.10	4.9	0.082	0.027
0.004	0.80	39	0.65	0.22

*Diffusion Coefficient (D) 5×10^{-5} cm/sec at 100°C

$$\frac{4Dt}{Y^2} = \frac{4 \times 5 \times 10^{-5} \times 1}{(0.1)^2} = 0.020$$

From a table of Δ' vs $\frac{4Dt}{Y}$ values,

$$\Delta' = 0.58$$

The Δ' values obtained using the static sphere model measures only diffusion. Internal circulation (convection) also occurs in the drop causing increased mass transport. Based on other investigations using CO_2 , convection effects cause the mass transport to increase from 50 to 70 fold. We made a number of calculations for a low of 30 fold increase and a high of 90 fold for internal circulation. These data are shown in Table 1. Similar calculations were made for CH_4 and are shown in Table 2.

TABLE 2
MASS TRANSFER FOR CH₄

Fraction CH ₄ Remaining Δ	$\frac{4Dt}{y^2}$	Diffusion only time-sec	Diffusion and Convection	
			Low Range t/30 sec.	High Range t/90 sec
0.78	0.005	0.14	0.0047	0.0016
0.58	0.02	0.56	0.019	0.062
0.22	0.10	2.8	0.093	0.031
0.004	0.80	22.4	0.74	0.25

$$*D_{CH_4} = 8.6 \times 10^{-5} \text{ cm}^2/\text{sec at } 100^\circ\text{C}$$

HEAT TRANSFER CALCULATIONS

According to the proposed Stone and Webster model, the brine enters the flash evaporator at a temperature of 280°F and leaves to enter the disposal well at a temperature of 220°F. This heat transfer associated with the temperature drop was studied using the following steps:

1. Determine the boiling point of the brine.
2. Calculate the number of calories of heat required to vaporize 4.4% of the brine.
3. Calculate average temperature reduction in droplet required to produce calories from #2.
4. Relate average temperature reduction to temperature reduction along radius.
5. Develop heat transfer equations based on temperature change center of sphere to the surface.
6. Calculate the time required to move the calories in #2 to the surface.
7. Correct for internal circulation.

DETERMINE THE BOILING POINT OF THE BRINE

In order to calculate the boiling point of the brine, the 130,000 ppm total dissolved solids are assumed to be chloride for use in calculating the boiling point elevation. Using the basic equation,

$$\Delta T_b = K_b M \quad \text{where}$$

ΔT_b = the boiling point elevation

K_b = Boiling point elevation constant

M - molal concentration

The boiling of the brine entering the flash evaporator is calculated to be 375°K and 216°F

HEAT REQUIRED TO VAPORIZE THE BRINE

According to the Stone and Webster model, 4.4% of the brine will be evaporated. Using the volume of the spherical droplet of brine ($\frac{4}{3} \pi r^3$) and the radius being 0.05cm, the volume of the brine drop is calculated to be $5.2 \times 10^{-4} \text{ cm}^3$. Assuming the density of the brine is 1.0 g/cm^3 , the mass of the droplet is $5.2 \times 10^{-4} \text{ g}$. Since only 4.4% of the brine is vaporized, the mass vaporized is $2.3 \times 10^{-5} \text{ g}$. (The heat required for vaporization is readily calculated as the product of mass of the brine and the heat of vaporization. This calculation yields a value of 0.012 cal.). The temperature drop due to brine vaporization can be determined from the following equation:

$$\Delta H = C_p X M (T_F - T_0) \text{ where}$$

$$\Delta H = \text{heat capacity of droplet} = 0.956 \text{ cal/gC}^\circ$$

M - mass of brine vaporized

The final temperature determined from this calculation is 113°C or 237°F. This is the average temperature when 4.4% of the brine is vaporized. It is a linear function which makes it possible to interpolate to find the average temperature at other degrees of vaporization.

It is necessary to determine the position within the sphere which has the average temperature. It is reasonable to assume that the average temperature occurs at the radius within the spherical drop in which internal volume is equal to the external volume. For the spherical drop with a diameter of 0.1cm and a radius of 0.05cm, this radius is 0.04cm. The average temperature can be assumed to be at a radius of 0.04cm.

The heat flow through the wall of the spherical droplet of brine can be evaluated using the equation for heat conduction within a sphere.

$$Q \frac{dr}{r^2} = -4\pi K dt$$

$$Q \int_{r_1}^{r_2} \frac{dr}{r^2} = -4\pi K \int_{T_1}^{T_2} dt$$

K = thermal conductivity of water
= 0.0016 cal/cm sec. °C

by substitution

$$Q = \frac{4 \times 3.14 \times 0.0016 \text{ cal/sec } ^\circ\text{C} (\bar{T}_2 - 102.2)}{(1/0.04 - 1/0.05)}$$

$$= 0.0041 \text{ cal/sec } ^\circ\text{C} (\bar{T} - 102.2)$$

with the heat as a function of the average temperature, a temperature differential within the drop can be set up and evaluated.

$$- \frac{\partial \bar{T}}{\partial t} = \frac{Q \text{ (cal/sec)}}{C_p \text{ (cal/g } ^\circ\text{C}) \times M \text{ (g)}}$$

$$- \frac{\partial \bar{T}}{\partial t} = \frac{0.0041 (\bar{T} - 102.2)}{0.956 \times 5.2 \times 10^{-4}}$$

on evaluating and setting up definite integrals

$$\int_{\bar{T}_I}^{\bar{T}_F} \frac{d\bar{T}}{\bar{T} - 102.2} = .8.24 \int_{t_0}^{t_F} dt$$

and

$$t = 0.12 \ln \frac{\bar{T}_I - 102.2}{\bar{T}_F - 102.2}$$

This equation can be used to calculate the time necessary for various temperature drops and corresponding heat flows. This equation accounts only for conduction, the heat transfer will be much faster if convection effects are considered. The same convection effect factors of 30 and 90 are used for heat transfer as was used in mass transfer. The results are shown in Table 3.

With comparable mass transport and heat transfer information in Tables 1 and 3, and comparison of the times necessary for the transfers to take place will enable us to predict with some certainty if the heat transfer will occur faster than mass transfer. Data from Tables 1 and 3 are shown in table 4. The table shows that it takes 8 msec for 22% of the CO_2 to leave the brine droplet and enter the vapor phase whereas 25% of the heat is removed from the droplet in only 0.7 m-sec. At points with higher percentage vaporization, the rate of heat with respect to mass transfer is more pronounced.

SUMMARY

This research was designed to predict the scaling

tendency in a flash evaporator as designed by Stone and Webster. Based on mass transport and heat transport calculations, we feel that the path from A to D in Figure 3 is closer to the ACD route than the ABD route. This means that there is very little likelihood of scale forming in the evaporator.

TABLE 3
HEAT TRANSFER FOR CO₂

			Conduction Only t-sec	Conduction & Convection	
% Vap	Temp. °C	Temp. °F		Low Range t/30 t-msec	High Range t/90 t-msec
0	138	280	0	0	0
25	132	270	0.022	0.7	0.2
50	126	259	0.05	1.6	0.5
75	119	242	0.09	3.0	1.0
100	113	234	0.14	4.7	1.6

TABLE IV

COMPARISON OF MASS TRANSFER AND
HEAT TRANSFER DATA

Heat Transfer		Mass Transfer	
% Vap	time m-sec Low Range	%CO ₂ in Vapor	time m-sec Low Range
25	0.7	22	8
50	1.6	42	33
75	3.0	78	82
100	4.7	100	650

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Figure 1. Liquid and vapor phase train showing relative position of the flash evaporator. Brine will be admitted to the flash evaporator via a control valve. The brine will be directed tangentially onto the tank walls.

Scale of Approximate (± 0.3)
Saturation Index Values

SI Values		Comment
<u>Supersaturated</u>	2.5	Instantaneous Uncontrollable Scale, probably
	2.0	Controllable with Inhibitors
	1.5	CaCO ₃ Precipitation will Probably Begin in a Few Minutes
		Metastable
	0.0	Equilibrium Gas-Brine-Solid
<u>Subsaturated</u>		Subsaturated
	2.0	Probably Not a CaCO ₃ Brine

Figure 2

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Temperature vs. Pressure Constant Saturation Index Isopleths for Brine as
in Sweetlake or Pleasant Bayou #2 Wells

FIGURE 3

FIGURE 4

FLASH EVAPORATOR