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**COMMENTS ON THE POSSIBLE EFFECTS OF ADDITIVES
ON SCALING BY GEOTHERMAL BRINES**

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COMMENTS ON THE POSSIBLE EFFECTS OF ADDITIVES ON SCALING BY GEOTHERMAL BRINES

Abstract

Some of the general phenomena of scale formation by geothermal brines are examined. Particular emphasis is placed on the interactions between additives and brines, and a formal structure for those interactions is developed based on a discussion of thermodynamic, thermochemical, and kinetic behavior.

However, we cannot make definite predictions at this time. An example of a simple additive to silica-containing brine is given to illustrate the concepts. Although the discussion indicates that in general additives are not beneficial, it does not rule out their use, especially if ancillary processes, such as mineral recovery, are considered.

Introduction

There are numerous questions about exactly what will occur with regard to scaling and corrosion when Imperial Valley brines are expanded through a nozzle in the LLL total flow power turbines. The purpose of this paper is to briefly examine the phenomenon of scaling and to discuss possible ways to avoid it.

Implicit in the formulation of the LLL total flow concept are several hypotheses that require careful examination:

- Scale formation and precipitation are separate phenomena.
- Scale formation is a purely kinetic phenomenon. Therefore it may be prevented by using appropriate construction materials, physical means, or additives in the input brine.

We will examine these hypotheses from both general thermodynamic and kinetic points of view.

Scale Formation

The formation of scale is evidence that a solid phase has formed resulting from a physical or chemical change. The scale could have originated from a gas, a liquid, or a liquid-gas phase. Since scale is a solid phase, it has formed because the system has been forced to

cross some thermodynamic phase boundary. When such a process occurs in a gas, liquid, or liquid-gas mixture, precipitation always occurs. However, scale formation need not follow.

Immediately, it is clear that a condition leading to precipitation is a

necessary but not sufficient condition for scale formation. This is so since scale formation is very analogous to crystallization which is partially a kinetic phenomenon. Intuitively, the kinetic phenomenology of scale formation is obvious. One can conceive of precipitation of material which then does not stick to the surface of its container.

The analogy between scaling and crystallization allows us to break the kinetics of scale formation into heterogeneous and homogeneous parts. Loosely, this corresponds to nucleation followed by the growth stages of crystallization. In the case of scale formation, heterogeneous kinetics are applicable to a larger class of phenomena than nucleation. These phenomena also include various intramolecular phenomena that ultimately lead to the adhesion of the scale to some substrate. However, nucleation is probably still an important phenomenon. The homogeneous stage of scale formation corresponds to the growth of the scale layer once nucleation and adhesion have taken place.

Usually, heterogeneous kinetic phenomena have an induction period. This induction period is the delay between the time the reactants come into physical contact and the time the reactions actually start. Usually, induction periods for a given, defined set of reactants are:

- Quantitatively nonreproducible.
- Qualitatively effected by trace impurities, surface physical adsorption processes, and surface chemisorption processes.

Both heterogeneous and homogeneous kinetics are affected by catalysts and poisons. Catalysts are materials which do not partake in the reaction, but which increase the reaction rates. Poisons, correspondingly, decrease reaction rates. Perhaps, scaling can be prevented by the use of catalysts or poisons in the heterogeneous or homogeneous kinetic stage. Generally, the induction period is affected by so many factors that finding the desired catalyst or poison may be practically impossible. Note also that once the nucleation and adhesion stage have actually commenced, "ordinary" kinetic phenomena take over.

Speed for Attainment of Equilibrium

Prevention of scaling by physical means may be done by altering the speed with which equilibrium is attained; particularly by lowering the pressure since this is easy to do at very rapid rates. By slowing down the rate at which equilibrium is attained, it may be possible to avoid precipitation and, therefore, scale formation. (Raising pressures or changing temperatures are relatively slow processes. Intuition and experience in-

dicate that equilibrium is relatively easily attained under these circumstances.) Inert gases and fluids can attain pressure equilibrium at rates which correspond to sonic velocities. Intuition, however, indicates that an accompanying chemical equilibrium may not be attained very rapidly. (This is true for many chemical systems but is not always the case. For example, in chemical explosive reactions, chemical equilibria

are also attained at rates similar to sonic velocities.)

It is exceedingly important to examine the rates at which chemical equilibrium are attained in the LLL total flow turbine. We must clarify the effects of pressure drop. First of all, there are probably very few chemically inert molecular species present at high pressures in the brine. If there were, the rule of thumb would be that the reaction rates would not be dependent on the pressure drop to a first approximation. However, almost the total pressure drop is due to CO_2 , H_2S , and H_2O . All of these are important reactants in the brine. Their release causes two concerns: (1) the shift in chemical equilibrium (this point will be discussed in the next section), and (2) the rate at which equilibrium is attained.

We have no general rules to predict rates for attaining the new equilibrium on pressure release. (Some rules of thumb could be invoked if we had some idea of the form of the kinetic rate laws. We know of no data that applies to this problem.) In this case, it may very well be that intuition is correct and that the rates for attainment of equilibrium are slow enough so as not to cause precipitation and scale formation in the required time frame. However, preliminary data on the expansion of brine solution in nozzles shows that scale does form in the nozzles. Careful tests of scale formation in nozzles are required since the details of nozzle design become important considerations, e.g., stagnation surfaces, etc.

Effects of Additives

Using additives to simply prevent scale formation may be economically feasible. If this isn't possible, it may be reasonable to use additives for a combination of power production and mineral recovery. We will consider this further in our conclusions.

Additives will have two interrelated effects. First, they will affect the thermochemical equilibria; and, second, the resulting reactions will be kinetically affected.

Let us consider the entire LLL full flow power generation system from a generalized thermodynamic point of view.

The brine is in equilibrium when it is in the ground. (A true thermodynamic equilibrium is not present. Heat is constantly flowing toward the earth's surface

and being dissipated. However, in a local time sense, it is reasonable to postulate an equilibrium condition.) This equilibrium is easily written as

$$\sum_{n, (P=P_o, T=T_o)} a_n R_n$$

$$= K_1 \sum_{m, (P=P_o, T=T_o)} b_m p_m \quad (1)$$

where R_n are the reactants, a_n and b_m are the mole numbers, p_m are the products, P is the pressure of inert molecular species, and T is the absolute temperature. Associated with this equilibrium is an equilibrium constant K_1 . Note that equilibrium as expressed in Eq. (1) has $P = P_o$ and $T = T_o$ so that the pressure

and temperature of inert molecular species are constant. Gaseous molecular species such as H_2O , CO_2 , H_2S , etc. are in the equation in terms of reactants and products, R and p . The equilibrium in Eq. (1) is really the result of many reactions, e.g.

each of which has its own equilibrium constant.

When the brine is expanded through a nozzle, the entire set of equilibria changes

$$\sum_{n, (P=P_f, T=T_f)} a_n R_n = K_2 \sum_{m, (P=P_f, T=T_f)} b_m p_m, \quad (3)$$

where the pressure and temperature are those at given spatial regions in the nozzle and in the turbine. The equilibrium constant K_2 will be the one appropriate to the region of interest. It is during this process of expansion and temperature change that precipitation and scale formation occur. That additives can change the kinetics of these reactions is of course clear. The question is whether one can hope to find the appropriate additive.

The addition of some number of additives can now be introduced. Presumably, the additives are to be introduced into the input brine stream. Denote these additives by

$$\sum_k C_k A_k,$$

where C_k are the mole numbers and A_k are the additives. Equation (1) now becomes

$$\sum_{n, k (P=P_o, T=T_o)} (a_n R_n + c_k A_k) = K_3 \sum_{m' (P=P_o, T=T_k o)} b_{m'} p_{m'}, \quad K_3 \neq K_1. \quad (4)$$

Similarly, the set of Eqs. (2) is now changed, and all the individual equilibrium constants are different. Now when the brine is expanded, a new equilibrium is obtained where the new form of Eq. (3) will contain the additives. The kinetics will also be affected. However, since there are now $(n + k)$ reactants and (m') products, statistically it is clear that while the rates for some of the reactions in the set of:

will be decreased, others will be increased. Furthermore, as the brine well gets older, the equilibria in Eqs. (1), (3), and (4) will change.

The composition of the spent brine that is reinjected into the ground is different from the original composition. For example, CO_2 and H_2S will have been almost

completely lost. SiO_2 will precipitate as will other components. Therefore, as the brine well gets older, the additives that initially proved useful in decreasing the kinetics would need to be changed. Also, different additives would be required for brine wells in different locations.

Specific Examples of the Effect of an Additive

Fournier¹ reports that silica forms soluble complex ions derived from $\text{NaHSiO}_2 \cdot n\text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_2 \cdot n\text{H}_2\text{O}$ at a pH greater than 9. Thus, adding a base to raise the pH of a silica solution above 9.0 will tend to keep the silica in solution. The phenomenology of additives can be illustrated by examining some of the equilibria involved when a base is added to the high-salinity brines of the Imperial Valley.

In low-pH solutions, silica exists primarily in the form of monomers and polymers of silicic acid. Polymerization occurs rapidly at near neutral pH.^{1, 2} As the pH is further increased, soluble complex ions begin to form, as shown by the following equilibria:

As base (OH^-) is added, H^+ will be removed as in Eq. (9) and the equilibria shown in Eqs. (7) and (8) will be shifted to the right. Thus, silica will be in a soluble form.

As the pH is increased, insoluble hydroxides will tend to form as follows:

Amphoteric hydroxides, such as $\text{Al}(\text{OH})_3$, $\text{Pb}(\text{OH})_2$, and $\text{Zn}(\text{OH})_2$, will precipitate and then redissolve as high pH values are reached.

Silica tends to coprecipitate with gelatinous metal hydroxides such as $\text{Fe}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$. This coprecipitated silica will not be readily available for the reactions in Eqs. (7) and (8) because of rate considerations.

As the pH is increased, the sulfide equilibria will concurrently shift to the right.

1. R. O. Fournier, "Silica in Thermal Waters; Laboratory and Field Investigations," in Proc. Symposium on Hydrogeochemistry and Biogeochemistry, Tokyo, 1970 (Clarke Co., Washington, D. C., 1973), vol. 1, pp. 123-139.
2. G. B. Alexander, J. A. C. S. **76**, 2094 (1954).

As base is added, the S^{2-} concentration increases. As it increases, insoluble sulfides will start to precipitate as follows:

The carbonate equilibria are:

As base is added, these equilibria will shift to the right causing an increase in CO_3^{2-} concentration. As it increases, insoluble carbonates will begin to precipitate:

The cation in the base can also enter into reactions. The cheapest available base, CaO , will react as:

As CaO is added, the Ca^{2+} concentration will increase causing precipitation of insoluble Ca salts as in Eq. (23).

The above equations merely illustrate the interaction of some of the equilibria involved when a simple additive is introduced into a complex geothermal brine. There are many more reactions which we have not analyzed.

Although the addition of a base might prevent silica from forming scale in the turbine, the concomitant precipitates would cause severe erosion. Therefore, the use of a base to prevent scaling would depend on the development of an economical process to remove the precipitate from the brine before it reached the turbine. Such a process could be of value for mineral recovery.

More complex materials, such as organic additives, could react extensively by oxidation, reduction, polymerization, etc. in the hot brine. The effect of such reaction products would be very difficult to predict.

Conclusions

Scaling and precipitation are inter-related phenomena. We have discussed the general concepts of scale prevention by physical means, and, that physical control does not appear to be an attractive approach.

The phenomenology for additive-brine interactions indicates that, in general,

additives will not have a beneficial effect on scale control. The concepts were illustrated by the use of a specific example. However, we have also shown that it may be possible to consider some additives for scale control which may be economically attractive because they allow mineral recovery. However, in

this case, ancillary process problems may require consideration (e. g., removal of erosive precipitates). A detailed analysis of that situation would be required. Such an analysis would require detailed data on the

very complex equilibria in the geothermal brines. Such data is presently nonexistent. However, even with such data, it would be necessary to exercise considerable care in the choice of specific additives.

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