Modeling of nucleation rate in supersaturated calcium sulfate solutions

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ABSTRACT

Salt accumulation in Southwestern areas relying on Colorado River water is inevitable. Salt removal from water depends on reverse osmosis (RO) treatment. But, Ro recovery is limited by scaling reactions. Antiscalant chemicals are added during RO and pH is controlled to avoid scaling. There is currently no means to rapidly screen antiscalant for use in RO treatment of specific waters. This work is aimed at development of a rapid screening test for antiscalant selection. Steps in the investigation included experiments for the following purposes:

- To understand the relationship between degree of supersaturation and induction time of precipitation of calcium sulfate
- Impact of antiscalant on the homogeneous nucleation rate and the induction time
- Modeling of those variables (degree of supersaturation, dose of antiscalant and induction time)

MOTIVATION

Total Dissolved Solids (TDS) levels in the lower Colorado River are about 750 mg/L and water delivered to the Tucson area via the Central Arizona Project (CAP) canal brings 200,000 MT of salt to Tucson each year. Essentially none leaves, making salt accumulation inevitable. Eventual salt management via RO treatment in the Southwest is likely. The chart below compares the water composition of CAP water and typical Southern Arizona potable groundwater. Aquifer salt concentrations are projected to increase by about 5 mg/L per year in Tucson area aquifers.

Water Quality Constituent (mg/L)	Tucson Water Production Wells	CAP Water
Total Dissolved Solids	259	~750
Hardness (as CaCO ₃)	119	270
Sodium	40	112
Chloride	17	104
Calcium	39	56
Magnesium	5	31
Sulfate	45	280
Alkalinity	126	98
TOC	<1	3.5

The table below shows concentration and solubility data for CAP water species that may contribute to membrane scaling

Precipitate	Ion Concentration	log (ion product)	log K _{SO}	Degree of Saturation
BaSO ₄ (s)	[Ba ⁺²] = 1.17 × 10 ⁻⁶ M [SO ₄ ⁻²] = 2.81 × 10 ⁻³ M	-8.48	-10.0	827.83
CaSO ₄ (s)	[Ca ⁺²] = 2.0 × 10 ⁻³ M	-5.25	-4.85	9.95
CaCO ₃ (s)	[CO ₃ ⁻²] = 1.0 × 10 ⁻⁵ M	-7.7	-8.48	150.64

It is known that reverse osmosis recovery is limited by scaling. The solution to this problem is to find antiscalants capable of minimizing brine produced by reverse osmosis treatment.

BACKGROUND

- Osmosis and Reverse Osmosis principles

$$\text{Recovery} = 100\% * \frac{Q_p}{(Q_p + Q_c)}$$

Permeate recovery which is expected to be 80% is limited to avoid membrane scaling.

- Membrane scaling :
 - 1.- provokes severe flux decline on the membrane
 - 2.- shortens membrane life
 - 3.- increases the maintenance cost
 - 4.- Increases energy consumption of the treatment process

NUCLEATION RATE THEORY

- Nucleation : start of the precipitation process
- When the solubility of a solution is exceeded and it is supersaturated, the molecules aggregated into clusters (nuclei)
- Gibbs free energy change required to form a cluster is :

r : spherical cluster radius
σ : solid-liquid interfacial tension
G_v: free energy per unit volume
v : molar volume (74.69 cm³/mol for gypsum)
k : Boltzmann constant
T : absolute temperature

$$\Delta G = -\frac{4}{3}\pi r^3 G_v + 4\pi r^2 \sigma$$

The first term shows the energy decrease due to bond formation in the solid. The second term shows the free energy increase due to surface tension (σ) of the new interface. When the slope of the overall free energy change (ΔG) becomes negative, nucleation is spontaneous. The nucleation rate, i.e., the number of nuclei formed per unit time per volume can be calculated as follows :

$$B_0 = A \exp \left[\frac{-16\pi\sigma^3 v^2}{3k^3 T^3 (\ln S)^2} \right]$$

A : pre-exponential factor
S : degree of supersaturation
B₀ : nucleation rate
If r < r_c: the particles will dissolve or evaporate. If r > r_c: the particles will continue to grow. When some particles reach the size of r_c and pass the activation barrier further growth of particles will lead to decrease of ΔG_v.

This equation shows that the nucleation rate is controlled by three factors: degree of supersaturation, the temperature and the interfacial tension.

STRATEGY FOR PREVENTION OF SCALING

- Addition of antiscalant

Antiscalant additives affect nucleation rate, crystal growth of calcium sulfate. Adsorption of these additives onto crystal growth sites of nascent crystals alters their surface proprieties to avoid crystal growth.

Progressive addition of antiscalant increases the induction time (t_{ind}) for crystal formation in supersaturated solutions, in effect delaying nucleation in scale formation.

METHODS AND RESULTS

- Methods
 - 1.- Supersaturated equimolar solutions of calcium sulfate prepared by mixing of CaCl₂.2H₂O and Na₂SO₄
 - 2.- Solutions are continuously stirred by use of a jar tester
 - 3.- Each 3-5 minutes samples are taken from the jar tester beakers to get their absorbance using a spectrophotometer.
 - 4.- Tests are run with/without antiscalant to determine the induction time of precipitation of calcium sulfate

- Results

Figure 1. 42.08 degree of supersaturation of calcium sulfate with 0 and 2 ppm of antiscalant

Figure 2. Degree of supersaturation versus induction time of calcium sulfate solutions for different addition of amount of antiscalant

CONCLUSION

- Induction time for calcium sulfate precipitation decreases with an increase of the degree of supersaturation and increases with addition of antiscalant in a range of 1-2 ppm
- Antiscalant increases the surface energy and the activation barrier, slowing the nucleation rate
- Homogeneous nucleation rate can be used to rapidly assess antiscalant efficiency
- Antiscalant is widely use in seawater desalination plants in California, Australia and Middle East Gulf countries