CALCIUM SULFATE SCALE IN THE PETROLEUM INDUSTRY

By

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I. INTRODUCTION

Oilfield scale is defined as the precipitation of hard, adherent deposits of inorganic solid originating from aqueous media. This constitutes sulfate and carbonate of the alkaline earth metals calcium, barium and strontium and complex salts of iron. Generally, the process of the scale deposition occurs when the product solubility of a compound considered is exceeded. The formation of scale, such as calcium sulfate, has long recognised as one of the serious problems in oil and gas production leading to reduced production rates as flow becomes restricted.

Calcium sulfate scale found in the oilfield is in the form of gypsum ($CaSO_4.2H_2O$) which is the most stable form at temperatures of 40 °C or less at atmosphere pressure. Above this temperature, anhydrite ($CaSO_4$) may be found, although hemihydrate ($CaSO_4.1/2H_2O$) may form under certain conditions. The reaction for precipitation of calcium sulfate is as follows :

$$\underset{(aq)}{Ca^{+2}} + \underset{(aq)}{SO_4^{-2}} \longrightarrow \underset{(solid)}{CaSO_4}$$

The solubility of calcium sulfate in distilled water is 2080 mg/l at 25 °C. Calcium sulfate scale arises from several causes, such as temperature, dissolved salts, pressure, and time. The main points of this paper are focused on nomenclature, chemical structure, the occurrence of calcium sulfate scale, example of calcium sulfate scale in the petroleum industry, and calculation of calcium sulfate solubility in brine.

II. NOMENCLATURE

The various names commonly used to describe components and phases of the system CaSO4.H2O are listed in Table - 2.1.

Table - 2.1
Nomenclature in the system CaSO4.2H2O.

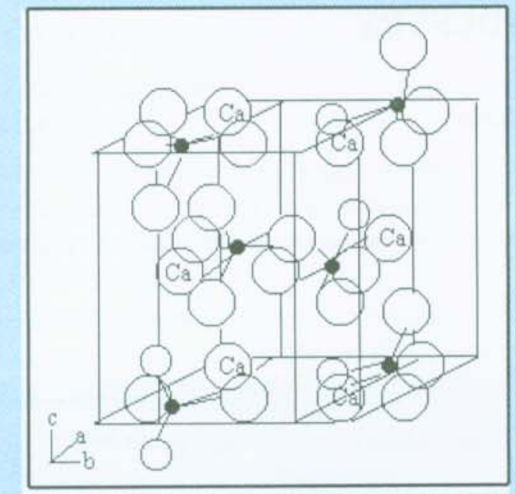
Formula	
$CaSO_4.2H_2O$	Gypsum also called Selenite, Satin-par, calsium sulphate dihydrate, alabaster, rock gypsum (gypsum is an impure form).
$CaSO4.1/2H_2O$	Hemi-hydrate also called plaster of Paris, bassanite, α and β Hemi Hydrate, calcined gypsum.
$CaSO_4$ (metastable)	γ CaSO4 (soluble anhydrite, dehydrated hemihydrate
$CaSO_4$ (Stable to 1200°C)	anhydrite (b-CaSO4, insoluble anhydrite, dead burned gypsum.
$CaSO_4$ (stable above to 1200°C)	$CaSO_4$

III. STRUCTURE

The structure of anhydrite is different from that of barite group. Bragg believes the difference to be due to smaller size of the calcium ion. A three dimensional view of the structure in Figure - 3.1 illustrates the packing together of the Ca ions and tetrahedral SO_4 groups. The large calcium ions are packed between SO_4 groups, and dark areas are sulfur atoms.

IV. THE OCCURENCE OF $CaSO_4$ SCALE

The purpose of this section is to demontrate and record the available information on factors that affect the crystallization or solution of calcium sulfate. These are: effect of temperature, dissolved salts content, pressure and time.



Source : Crystal structure of minerals, 1965, Bell. G and Sons, Cornel University

Figur – 3.1
Structure of anhydrite.

A *Effect of temperature*

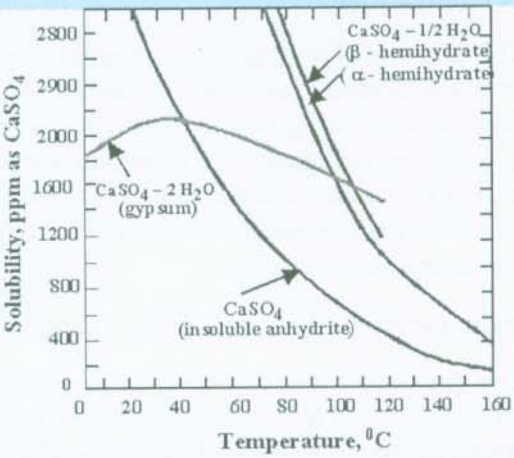
Generally, gypsum is the stable form at low temperature, whereas anhydrite is formed at higher temperature. Gypsum solubility increases with temperature up to about 40 °C, then decrease with temperature as shown in Figure – 4.1.

This is quite different from the temperature-solubility behaviour of $CaCO_3$. Firtsly, gypsum is considerably more soluble than $CaCO_3$ in normal temperature range of interest. The solubility of $CaSO_4$ in distilled water is 2080 mg/l, while solubility of $CaCO_3$ in distilled water is 53 mg/l. Secondly, the maximum in the gypsum curve explains that an increase in temperature could either increase or decrease the solubility of gypsum depending on which part of the temperature curve it is concerned with. This is decidedly different from $CaCO_3$ where an increase in temperature always decreases the solubility.

Note that above about 40 °C, anhydrite becomes less soluble than gypsum, so it could reasonably be expected that anhydrite might be the preferred form of $CaSO_4$ in deeper, hotter wells. Actually, the temperature at which the scale changes form from gypsum to anhydrite or hemi-hydrate is a function of many factors, including dissolved salt content, pressure, flow conditions and the speed at which different forms of $CaSO_4$ can precipitate from solution. The curve for the solubility of anhydrite intersects the solubility curve for gypsum at 42 °C. This is transition point of gypsum-anhydrite. Above 100 °C, anhydrite will precipitate directly in a stirred or flowing system. If the system is quiescent, hemi-hydrate solubility becomes limiting. Conversion to anhydrite could be expected with time.

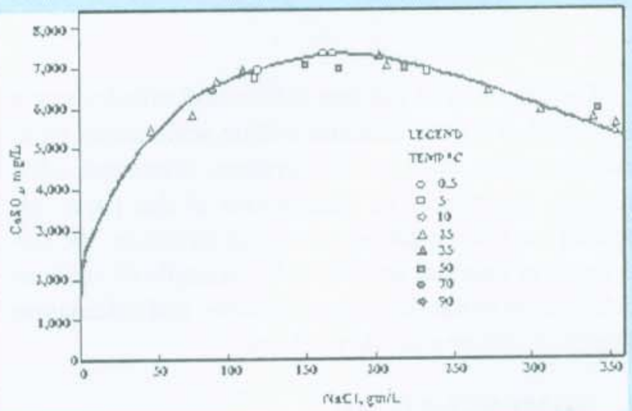
B. *Effect of dissolved salts*

The presence of NaCl or dissolved salts other than calcium or sulfate ions increases the solubility of gypsum or anhydrite, up to a salt concentration of about 150,000 mg/l. Further increases in salt content decrease $CaSO_4$ solubility. This case is described in Figure – 4.2.



Source : Water- formed scale deposit by Cowan, J.C and Weintritt, D.J.

Figure - 4.1
Solubility of calcium sulfate in pure water

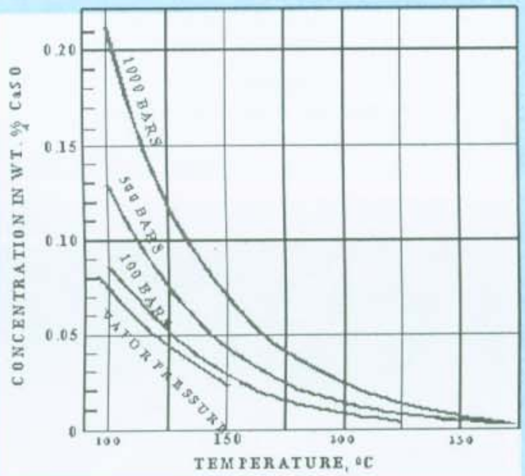


Source : Solubility of Calcium Sulfate in Brine, SPE Paper 4353.

Figure - 4.2
Solubility of Gypsum in Brine at temperature from 0 to 90 °C.

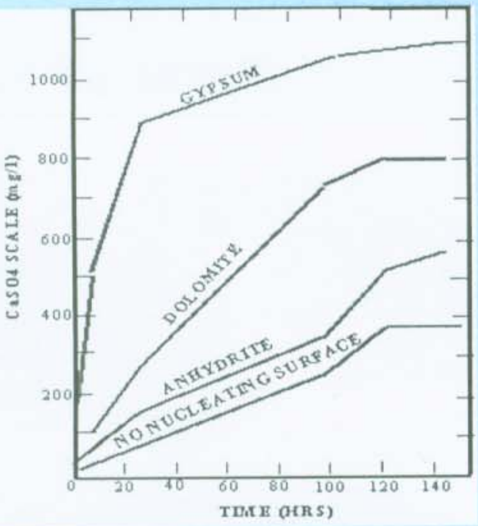
C. *Effect of pressure*

The solubility of calcium sulfate in water increases with pressure. The effect of increased pressure is physical, resulting in a reduction in the size of the calcium sulfate molecule. Although rather large increases in pressure are necessary to effect a significant change in molecular size, the effect of pressure can be important and beneficial in injection wells where appreciable pressure may be developed. The effect of pressure and temperature on anhydrite solubility is shown in Figure - 4.3.



Source : Am. J. of Sci., Vol. 261, 1963, p.61.

Figure - 4.3
Effect of pressure and temperature on CaSO4 (anhydrite) solubility



Source : J. Pet. Tech. Vol. 20, 1968, p.559 – 664

Figure - 4.4.
Calcium sulfate scale rate

D. *Effect of Time*

Upon release of pressure, a supersaturated solution is obtained that deposits gypsum for a period of time (see Figure - 4.4).

V. EXAMPLE OF CALCIUM SULFATE SCALE IN THE PETROLEUM INDUSTRY

Normally, oil or gas wells are drilled and allowed to produce without additional stimulation process. This is called primary production. Primary production technique usually results in a large amount of oil being left in place, and the petroleum industry has recognized this potentially recoverable hydrocarbon source and has developed techniques, secondary recovery methods, to increase the total recovery.

One of the most succesful methods of secondary recovery is water flooding, a process in which water is pumped down an injection well to flush or remove oil from the formation as it moves along to a producing well. The oil, along with the injected water and connate water, is recovered at the well. Although this method has been highly successful and is in wide use today, it is fraught with many problems. A major one is *scale*. Numerous types and combinations of scale occur in water flooding operation. This section show several examples of calcium sulfate scale occurred in the petroleum industry.

Figure – 5.2
Calcium sulfate scale adhering to inside of wooden water tank on a waterflood operation

Figure – 5.1
Calcium sulfate scale formed in 3-inch nipple
in 3 months from waterflood

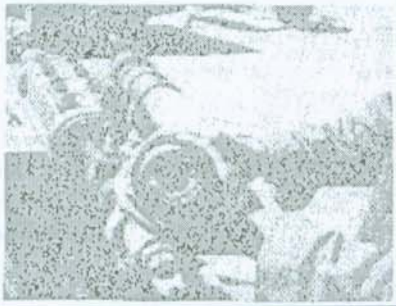
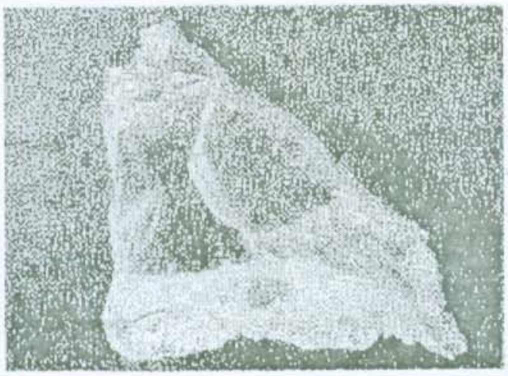


Figure – 5.3
Calcium sulfate scale
in rubber discharge hose pump

Figure – 5.4
Calcium sulfate sacle on meter-run
screens

Source : Courtesy U.S. National Museum.

Figure – 5.5
Anhydrite (the natural form)



Source : Courtesy U.S. National Museum.

Figure – 5.6
Clear gypsum crystal
with yellow sulfur band along bottom

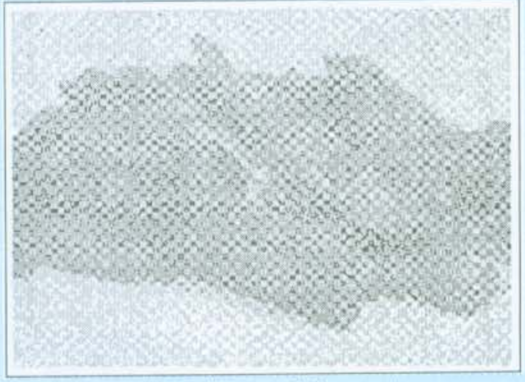


Figure – 5.7
Large crystal of gypsum
produced from brine recovery operation

VI. CALCULATING CALCIUM SULFATE OLUBILITY IN BRINE

Skillman's method is a method used for calculating calcium sulfate solubility in brines and converted available solubility data into a form suitable for use by operating engineers. This method is based on the classical thermodynamic approach. Using the brine analysis in Table - 6.1, the following calculation is an example of the the application of Skilman's method.

1. Calculations ionic strength (Table 6.2 and 6.3, input expressed as mg/l)

U = [2.2 (Na) + 5.0 (Ca) + 8.2 (Mg) +1.4 (Cl) + 2.1 (SO_4) + 0.8(HCO_3)] x 10^{-5}

U = [2.2 (1257) + 5.0 (808) + 8.2 (242) +1.4 (2025) + 2.1 (2428) + 0.8(443)] x 10^{-5}

U = 0.17

Table –6.1
Typical Subsurface Brine Analysis Used In Example of Calculation of Skillman et al Calcium Sulfate Stability Index

	mg/l	mco/l
Na	1,257	54.7
Ca	808	40.4
Mg	242	19.9
Cl	2,025	57.1
SO_4	,428	50.5
HCO_3	443	7.3
pH	7.3	

U.S. Pat. No. 3,454,677, July 8, 1969.

2. Determine solubility product constant

(Figure - 6.1)

K vs U at 95 °F

When U = 0.17, K = 4.65 x 10^{-4}

3. Determine common ion concentration

(Table - 6.4)

x = [(2.5 Ca – 1.04 SO_4)] x 10^{-5}

x = [2.5(808) – 1.04(2428)] x 10^{-5}

x = 0.5 x 10-2 M/L

4. Calculate solubility

$$S = 1000\sqrt{X2 - 4K - X}$$

where :

S = Solubility gypsum in milliequivalents/litre

K = Thermodynamic solubility product constant of gypsum.

X = Excess common ion concentration (either calcium or sulfate ion moles/litre).

S = 38.4 meg/l

$$S = 1000\sqrt{25}X10^{-4} + 18.6X10^{-4} - 0.5X10^{-4} - 0.5X10^{-2})$$

S = 38.4 meg/1

Table – 6.3
Solubility Product Constants (K) for Calcium Sulfate at Uniform Ionic Strength Intervals at 50, 95, 122, 176 °F

Ionic Strength,U	Solubility Product Constant K at			
	50°F	95°F	122°F	176°F
0.00	1.02 x 10^{-4}	1.02 x 10^{-4}	1.25 x 10^{-4}	0.89 x 10^{-4}
0.10	3.04	3.29	3.31	2.82
0.20	4.99	5.23	5.28	4.67
0.30	6.87	7.11	7.17	6.44
0.40	8.68	8.91	8.96	8.13
0.50	10.41	10.64	10.68	9.75
0.60	12.07	12.30	12.30	11.30
0.70	13.65	13.88	13.85	12.78
0.80	15.16	15.39	15.32	14.18
0.90	16.60	16.83	16.71	15.52
1.00	17.96	18.20	18.02	16.79
1.25	21.05	21.29	20.96	19.79
1.50	23.69	23.93	23.46	22.22
1.75	25.90	26.12	25.52	24.39
2.00	27.67	27.88	27.18	26.22
2.25	29.03	29.22	28.47	27.73
2.50	30.00	30.15	29.40	28.92
2.75	30.60	30.71	30.01	29.81
3.00	30.84	30.90	30.32	30.42
3.25	30.77	30.77	30.36	30.73
3.50	30.39	30.34	30.15	30.76
3.75	29.76	29.66	29.73	30.51
4.00	28.90	28.75	29.13	29.97
4.25	27.85	27.66	28.37	29.14
4.50	26.65	26.43	27.49	28.02
4.75	25.34	25.13	26.52	26.58
5.00	23.98	23.80	25.48	24.83
5.25	22.60	22.49	24.42	22.74
5.50	21.26	21.27	23.36	20.30
5.75	20.02	20.20	22.33	17.49
6.00	18.93	19.35	21.38	14.28

U.S. Pat. No.3, 454, 677, July8. 1969

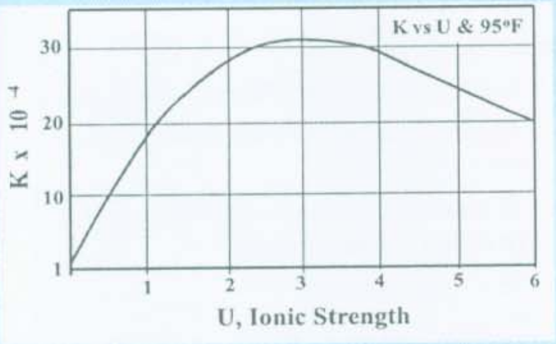


Figure – 6.1
Ionic strength, U vs solubility product, K

Table 6.4
Formula For Calculating
Common Ion Concentration

(The common ion concentration is the absolute difference between the molar concentration of calcium and sulfote ion)

1. When concentration are reported as ml/l
   $X = (2.5.Ca - 1.04\ SO4 \times 10^{-4}$
2. When concentration are reported as meq/l
   $X = [(Ca - 1.04\ SO4)] \times 10^{-4}$

U.S.pat. No. 3, 454, 677, Juli 8, 1969.

The actual concentration of calcium sulfate in the brine is 40.4 meq/l as limited by the calcium concentration. Therefore, the water trends to be scaling since the actual concentration exceeds the calculated solubility.

VII. CONCLUSIONS

Explanation mentioned above is obtained from several literatures, and can be concluded as follows:

1. Calcium sulfate scale arises from several causes, such as temperature, dissolved salts, pressure and time.
2. Gypsum is the stable form at low temperature, whereas anhydrite is formed at higher temperature. Gypsum solubility increases with temperature up to about 40 °C, then decreases with temperature.
3. With increasing salt concentration, the solubility of gypsum or anhydrite increases, up to a salt concentration of about 150, 000 mg/l. Further increase in salt content decreases $CaSO_4$ solubility.
4. The solubility of calcium sulfate in water increases with pressure.
5. A supersaturated solution is obtained that deposits gypsum for period of time.
6. Calcium sulfate solubility in brine can be calculated by using Skilman's method.
7. The occurence of calcium sulfate in oil industry results in the reduction of production rates as flow becomes restricted.

VIII. REFERENCES

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