

SOLUBILITY OF GYPSUM IN THE PRESENCE OF SOME METAL IONS IN SODIUM CHLORIDE SOLUTION AND SEAWATER

By

S.K. HAMDONA* AND R.B. NESSIM

* Chemistry laboratory, National Institute of Oceanography and Fisheries,
Alexandria, Egypt.

Key Words : Gypsum, Solubility.

ABSTRACT

The solubility of gypsum in the presence of metal ions of copper, cadmium, zinc and lead in sodium chloride solution 0.7M and seawater has been studied. The solubility decreases in the presence of metal ions in both media in the order Cu > Cd > Zn > Pb. The reduction in solubility of gypsum is greater in seawater than in sodium chloride solution and can be interpreted by the adsorption of metal ions on the surface of gypsum crystals.

INTRODUCTION

The precipitation of calcium sulphate scales poses serious problems in processes such as the evaporative purification of waters and cooling-tower technology (Gill, and Nancollas, 1980). The deposition of scale lowers the heat transfer coefficient and reduces the thermal efficiency. Within heater tubes (Cowan, and Weintritt, 1976) anhydrite scale has been observed next to the metal surface while gypsum was the predominant form of calcium sulphate deposited on top of the anhydrite. Much work has been done in an attempt to characterize the formation products of the scale minerals below which solutions will remain metastable and above which catastrophic formation of solids takes place (Nancollas and Gill, 1979). Glater and Schwartz (1975) made solubility measurements of CaSO₄ hemihydrate and anhydrite and proposed a method of scaling threshold computation as a function of temperature and salinity.

Hamdona, S.K.

In this work, the solubility of gypsum has been measured in the presence of different concentrations of Cu, Cd, Zn and Pb metal ions in sodium chloride and seawater with the aim to reveal the influence of these inhibitors, relevant for industrial practice, on the dissolution process of CaSO_4 .

EXPERIMENTAL PROCEDURE

Calcium sulphate dihydrate crystals were prepared by precipitation from calcium chloride and sodium sulphate solutions as described previously (Liu and Nancollas, 1970). The crystals were aged at least one month before being filtered to obtain the dry powder (specific surface area $0.5 \text{ m}^2/\text{g}$) that was used in the crystal solubility experiments. The specific surface area (SSA) of crystals was measured using a single point nitrogen adsorption apparatus. The crystals were confirmed as gypsum by X-ray powder diffraction (Shimadzu XD-3 diffractometer).

Solutions of metal ions and sodium chloride were prepared using either Reagent Grade (Fisher Sci. Co. and J.T. Baker Co.) or ultrapure (Alfa Chemical Co.) chemicals with triply distilled deionized water. Solutions were carefully filtered through millipore (Maximum pore size 100 nm) filters and diluted as required. Concentrations of the metal ions were determined by Atomic Absorption Spectrophotometer (Perkin Elmer Model 2380) or by exchanging the metal ion (Na, Cu, Cd, Zn and Pb) for hydrogen ion on a Dowex-50 ion exchange resin and titrating the liberated acid with standardized carbon dioxide-free potassium hydroxide (Dilutit, J.T. Baker Co.).

Approximately 1g of gypsum was shaken at $25 \pm 0.2^\circ\text{C}$ with 100 ml of medium (0.7M NaCl solution or seawater $S\%_o = 35\%_o$, 1 atm., pH = 8.2), for at least two months. Before samples were taken, the solid phase was allowed to settle. Since the crystals were quite large, filtering through a fritted glass filter (porosity 3-15 μm) was considered a sufficient measure to exclude solid gypsum from the samples. Shaffer (1967) compared samples from gypsum-saturated seawater and brines after filtering through medium (10-15 μm) and fine (4-6 μm) fritted glass. He found no significant difference in the results. The total concentration of calcium was determined by titration against EGTA and the total concentration of sulphate was determined gravimetrically according to the method of Bather and Riley (1954) and revised by Grasshoff (1976).

RESULTS AND DISCUSSION

Tanji and Doneen (1966) and Tanji (1969) suggested a model to calculate the gypsum solubility in electrolyte solutions up to 0.15M (25°C) taking into account not only ion association but also activity coefficients from extended Debye-Huckel formulae. Many investigators have determined the solubility of gypsum in various media, but rather few determinations have been made in alkaline and alkaline earth metal solutions of ionic strength about 0.7 or in the presence of some metal ions.

1. Solubility of gypsum in sodium chloride solutions :

The first series of solubility experiments was made in sodium chloride solutions 0.7M and 25°C in the presence and absence of some metal ions. The concentrations of metal ions (Cu, Cd, Zn and Pb) ranged from 5 to 100 ppm. Table 1 summarizes the experimental data for each additive, each experiment was made in duplicate or triplicate for certainties. Madgin and swales (1956) and Marshall & Slusher (1966) determined the gypsum solubility in sodium chloride solutions at concentrations close to 0.7M. Dyressen *et al.* (1969) and Elgquist and Wedborg (1975) determined the solubility of gypsum in sodium chloride solutions at different ionic strengths as shown in Table 2. Their results (amounting to about 39.92 m mol/l) are in good harmony with the present ones (39.89 m mol/l).

The influence of added metal ions on the solubility of gypsum is illustrated in Fig. 1 where the solubility profiles show that the solubility of calcium sulphate dihydrate, in sodium chloride solution and in the presence of these metal ions, decreases with successive additions of metal ions. It is possible that the increase in the concentration of the additive ions blocks the active sites on the crystal surface through adsorption, thus decreasing its solubility. It can be seen that the reduction in solubility is in the following order : Cu > Cd > Zn > Pb. It has been observed that at the same ion concentrations the Mg, Cd, Pb and Fe ions markedly reduce the rates of crystallization of calcium sulphate dihydrate (Hamdona *et al.*, 1993).

Hamdona, S.K.

Table (1): Solubility of gypsum in sodium chloride solution 0.7 M and 25°C in the presence and absence of some metal ions.

Medium no.	Additive	(ppm)	Solubility (mM)
1	Pb	-	39.89
2	Pb	5	38.06
3	Pb	10	36.88
4	Pb	20	35.86
5	Pb	50	33.49
6	Pb	75	31.91
7	Pb	100	30.01
8	Zn	5	37.28
9	Zn	10	36.01
10	Zn	20	34.64
11	Zn	50	32.80
12	Zn	75	30.62
13	Zn	100	28.66
14	Cd	5	35.91
15	Cd	10	34.92
16	Cd	20	33.46
17	Cd	50	30.92
18	Cd	75	28.80
19	Cd	100	26.46
20	Cu	5	33.62
21	Cu	10	32.24
22	Cu	20	31.52
23	Cu	50	29.01
24	Cu	75	26.61
25	Cu	100	24.65

SOLUBILITY OF GYPSUM IN THE PRESENCE OF SOME METAL IONS

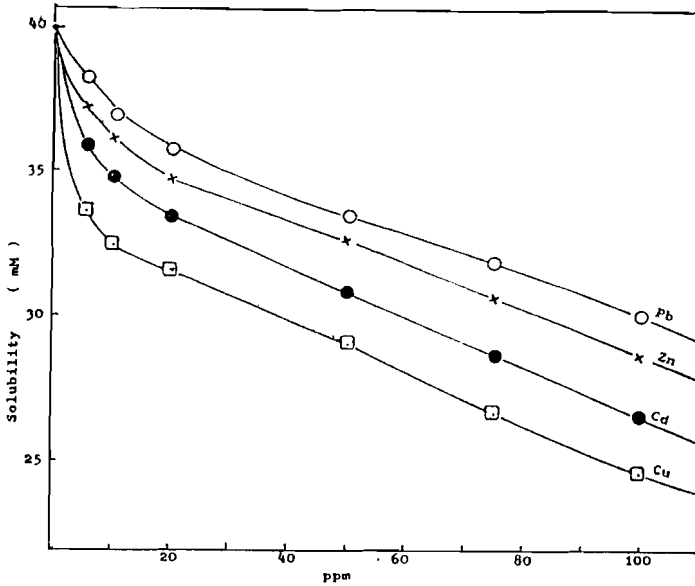
Table (2) : Gypsum solubility at 25°C, 1 atm.

Medium	Gypsum solubility (m mol/l)	References
0.665 M NaCl*	38.83*	Magdin & Swales (1950)
0.678 M NaCl*	38.17*	Marshall & Slusher (1966)
0.700 M NaCl*	39.92	Elgquist & Wedborg (1975)
0.700 M NaCl*	39.89	The present work

* Concentration has been converted from molal to molar scale.

Table (3): Solubility of gypsum in seawater 35 ‰, pH= 8.2, 25°C in the presence and absence of some metal ions.

Medium no.	Additive	(ppm)	Solubility (mM)
26	Pb	-	21.30
27	Pb	5	20.01
28	Pb	10	18.96
29	Pb	20	17.96
30	Pb	50	16.52
31	Pb	75	15.36
32	Pb	100	13.98
33	Zn	5	19.02
34	Zn	10	17.90
35	Zn	20	16.91
36	Zn	50	14.96
37	Zn	75	13.24
38	Zn	100	11.61
39	Cd	5	18.02
40	Cd	10	16.92
41	Cd	20	16.00
42	Cd	50	14.05
43	Cd	75	12.09
44	Cd	100	10.89
45	Cu	5	16.20
46	Cu	10	15.13
47	Cu	20	13.95
48	Cu	50	11.92
49	Cu	75	9.68
50	Cu	100	7.52



Figure(1) : Solubility of gypsum in sodium chloride solution in absence and presence of metal ions, Pb (O), Zn (X), Cd (●) and Cu (□).

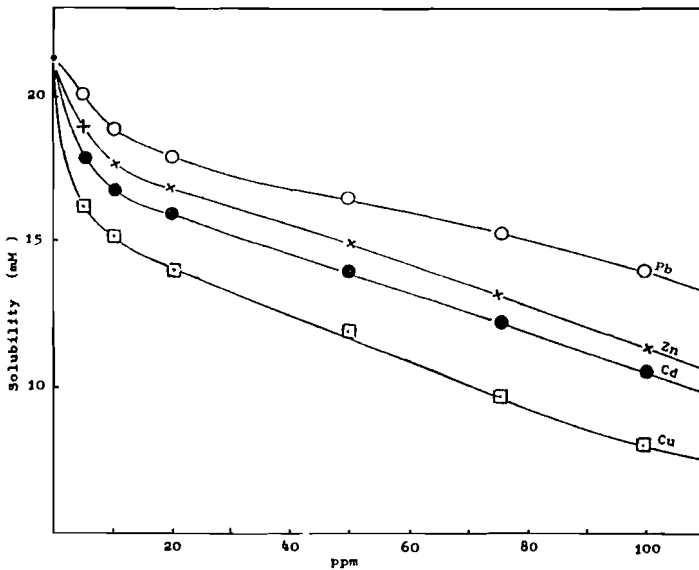


Figure 2 : Solubility of gypsum in seawater in absence and presence of metal ions, Pb, (O), Zn (X), Cd (●) and Cu (□).

2. Solubility of gypsum in seawater

The second series of solubility experiments was made in seawater, $S \text{ ‰} = 35 \text{ ‰}$, 1 atm., $\text{pH} = 8.2$ and at 25°C , in the presence and absence of copper, cadmium, zinc and lead ions. The experimental conditions of solubility are summarized in Table 3. Each experiment was made in duplicate or triplicate. Elgquist and Wedborg (1975) determined the gypsum solubility in standard seawater, their result, 21.10 mM, is in good agreement with the present 21.30 mM as shown in Table 3.

The effect of the presence of these metal ions on the solubility of gypsum in seawater is shown in Fig. 2. The solubility of gypsum decreases with successive additions of metal ions. The order of the reduction in solubility is the same as in sodium chloride solution namely, $\text{Cu} > \text{Cd} > \text{Zn} > \text{Pb}$. It has been observed that the adsorption of these metal ions on the surface of calcium sulphate dihydrate crystals suspensions in artificial seawater follows the same order (Hamdona and Aboul-Naga, 1994). The decrease in the solubility of gypsum in seawater in the presence of these metal ions may, again, be due to the adsorption of these ions on the active sites on the crystal surface. Moreover, the reduction in the value of solubility of gypsum in seawater, 21.30 mM, compared with 39.89 mM in sodium chloride solution may be due to the presence of more interfering ions in seawater.

REFERENCES

- Bather, J.M. and P. Riley, 1954. The chemistry of the Irish Sea. Part I. The sulphate chlorinity ratio. *J. Cons.* Vol. 20 (2): 145-152.
- Cowan, J.C. and D.J. Weintritt, 1976. Water formed scale deposits (Gulf Publ., Co, Houston, 231-356.
- Dyrssen, D, E. Ivanova & K. Aren, 1969. The solubility curves for calcium and strontium sulfates. *J. Chem. Educ.*, 45: 252-254.
- Elgquist, B. and M. Wedborg, 1975. Stability of ion pairs from gypsum solubility: Degree of ion pair formation between the major constituents of seawater. *Mar. Chem.*, 3: 215-225.
- Gill, J.S. and G.H. Nacollas, 1980. Kinetics of growth of Calcium Sulfate crystals at heated metal surfaces. *J. Crystal Growth*, 48:34.

Hamdona, S.K.

- Glater, E.D. and J.L. Schwartz, 1975. "Chemical Equilibriums in the calcium sulfate hemihydrate-Anhydrate system in natural sea-water concentrates" preprint paper, Natl. Div. Environ. Chem., Am. Chem. Soc., 15: 225-231.
- Grasshoff, K., 1976. *Methods of Seawater analysis*, Verlag Chemie Weinheim, New York, 317 p.
- Hamdona, S.K. and W.M. Aboul-Naga, 1994. Adsorption of some metal ions on the surface of calcium sulphate dihydrate crystals in artificial seawater. The 4th Sympo. of the Environ. Prot. is a Must, 10-12 May, 1994, Sheraton, Alexandria, Nat. Inst. of Oceanogr. & Fish. (NIOF), 659-667.
- Hamdona, S.K., R.B. Nessim & S.M. Hamza, 1993. Spontaneous precipitation of calcium sulphate dihydrate in the presence of some metal ions, *Desalination*, B. V. 94: 69-80.
- Liu, S.t. and G.H. Nancollas, 1970. The Kinetics of crystal growth of calcium sulphate dihydrate, *J. Cryst. Growth*, 6: 281-285.
- Madgin, W.M. and D.A. Swales, 1956. Solubilities in the system calcium sulfate-Sodium chloride-Water at 25°C and 35°C. *J. Appl. Chem.*, 6: 482-487.
- Marshall, W.L. and R. Slusher, 1966. Thermodynamics of calcium sulphate dihydrate in aqueous sodium chloride solutions, 0-110. *J. Phys. Chem.*, 70 (12): 4015-4027.
- Nancollas, G.H. & J.S. Gill, 1979. Formation and dissolution of high temperature forms of calcium sulphate scales: The influence of inhibitors. *Soc. Pet. Eng. J.* December, 423-429.
- Shaffer, L.H., 1967. Solubility of gypsum in seawater and seawater concentrates temperatures from ambient to 65°C. *J. Chem. Eng. Data*, 12: 183-189.
- Tanji, K.K., 1969. Solubility of gypsum in aqueous electrolytes as affected by ion association and ionic strength up to 0.15 M and at 25°C. *Environ. Sci. Technol.*, 3: 656-661.
- Tanji, K.K. and L.D. Doneen, 1966. Predictions on the solubility of gypsum in aqueous salts solutions. *Water Resour. Res.*, 2: 543-548.