

Modelling Halite Formation and Brine Densities: Comparison of Non-Marine and Seawater Brines

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ABSTRACT

Historically, seawater has been a convenient source for much of the world's sodium chloride (NaCl, common salt) because of its ready availability. The production process, which depends on crystallization over a range of experimentally-established brine densities, relies on a consistent seawater chemical composition. Attempts to harvest sodium chloride and other salts from non-marine brines, however, cannot use the seawater criteria since the solubilities of salts in solution and their relationship to brine densities are different for different ionic compositions.

Solubilities of salts in highly saline and complex brines can now be precisely modelled using the ion interaction formalism developed by Pitzer. This involves the estimation of activity coefficients (γ) to calculate activity ($\alpha = \gamma m$) from concentration (m). Activity coefficients represent the changes in free energy for water and ionic species which are caused by the association and interaction of ions in concentrated salt solution. The activities are not only dependent on the salinity but also on the particular ions contributing to the salinity.

In the Murray-Darling Basin in south-eastern Australia, waste irrigation waters have been evaporated for the commercial recovery of salts. By comparison with seawater, these waters have higher concentrations of calcium and magnesium and lower sodium concentrations. As a consequence the model predicts that more gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) will form prior to sodium chloride saturation, and that there will be lower yields of sodium chloride compared to seawater brines. The model also predicts that because of the higher Mg content, there will be a more restricted suite of "bittern" salts from the waste irrigation water than from seawater.

Experimental data showed that saturation with gypsum occurred at lower densities for waste water brines than for marine brines and that there were also discrepancies between the two waters for the relationships of density and halite saturation. Regulation of the recovery of salts from other than seawater brines requires that a field criterion, such as density, can be predicted in relation to the brines chemical composition, particularly at halite saturation. Volumetric properties of multi-component electrolyte solutions, such as density and partial molal properties, have been computed using the Pitzer formalism in conjunction with a Gibbs free energy minimization algorithm, linked to a thermodynamic data base. This allows density and saturation indices to be modelled simultaneously for waters having a wide range of chemical composition.

INTRODUCTION

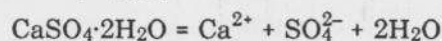
Thermochemistry of saline waters

Analytical concentrations of ions in aqueous solutions only approximate the activity, or effective concentration, in very dilute solution where conditions approach the ideal, and ionic interaction is minimised. The ratio of the activity of a solute species (α) to its concentration (m) is called the activity coefficient (γ) and has values near unity only in very dilute aqueous solutions, that is at low ionic strengths. Ionic strength is a measure of salinity defined as

$$I = \frac{1}{2} \sum m_i z_i^2$$

where m is molal concentration and z is ion charge.

Estimation of solubilities is based on equilibrium chemical thermodynamics where the solution of, for example, gypsum is considered as the reaction



and the equilibrium constant

$$K_{\text{eq}} = \frac{[\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] \times [\text{H}_2\text{O}]^2}{[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]}$$

TABLE 1

Chemical composition of evaporation pond waters at Wakool compared with seawater

Site		1	2	3	4	5	Seawater
Composition molal	Na	0.214	0.390	0.735	1.351	3.147	0.468
	K	0.00033	0.00050	0.00085	0.00008	0.00059	0.0102
	Ca	0.016	0.028	0.053	0.063	0.075	0.010
	Mg	0.045	0.084	0.159	0.299	0.708	0.053
	HCO ₃	0.0030	0.0010	0.0014	0.0014	0.0027	0.0023
	Cl	0.314	0.581	1.093	1.992	4.436	0.546
	SO ₄	0.017	0.030	0.050	0.061	0.060	0.028
	pH	7.6	8.3	8.1	8.6	8.2	8.2
	TSS g L ⁻¹	19	35	65	114	237	36
	Ionic strength	0.418	0.770	1.434	2.506	5.437	0.696
Mole ratio	Na/Cl	0.681	0.671	0.672	0.678	0.709	0.858
	Ca/Cl	0.0519	0.0476	0.0485	0.0314	0.0169	0.0188
	Mg/Cl	0.1437	0.1442	0.1459	0.1501	0.1595	0.0973
	SO ₄ /Cl	0.0526	0.0512	0.0456	0.0307	0.0136	0.0518

where [species] represents activity. Activity of solid gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) = 1, so that

$$K_{\text{eq}} = [\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] \times [\text{H}_2\text{O}]^2$$

which is the solubility product (K_{sp}) of gypsum. In a water which has not reached gypsum saturation, the Ion Activity Product (IAP, $[\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] \times [\text{H}_2\text{O}]^2$) will be less than the K_{sp} .

The use of activities, rather than of analytical concentration, in the calculation of solubilities incorporates the effects of the association and the interaction of ions in concentrated aqueous salt solutions (Pitzer, 1973). The activity coefficient (γ_i) of a solution component (i) is related to the excess Gibbs free energy (G^e).

$$RT \ln \gamma_i = \left(\frac{\partial G^e}{\partial n_i} \right)_{n_j, T, P}$$

The Pitzer representation of the excess Gibbs free energy of an aqueous solution is:

$$\frac{G^e}{RT} = f(I) + \sum_i \sum_j \lambda(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k$$

The first term of the equation is only dependent on ionic strength. The second expansion term incorporates ionic strength dependent binary coefficients for the effects of interactions between pairs of ions, and the third term is to account for triple ion interactions which are important in very saline brines. The parameters for the Pitzer equations for complex

multi-component systems have been derived from experimental data on simple binary and ternary mixtures (Harvie et al., 1984).

In this paper activity coefficients and solubilities have been calculated using the Pitzer formulations in the Chemix module of the CSIRO Thermochemistry System (Turnbull and Wadsley, 1988). The paper presents an assessment, by comparison with seawater, of the chemistry and potential salt yields of a non-marine brine as it evaporates to halite saturation and beyond. Field samples are compared with modelled evaporations. Density measurement, rather than chemical analysis, is the preferred method of monitoring the commercial evaporation of saline waters. In order to develop an industrially acceptable aid to process control, the Chemix program has been extended to density modelling. This procedure has been validated against published values for simple binary solutions and experimental and reported values for more complex brines. Differences between densities for gypsum and halite saturation in seawater and the non-marine brines are discussed.

RESULTS AND DISCUSSION

In Table 1, seawater data is compared with data from evaporation ponds supplied by waste irrigation waters in the district of Wakool, NSW. Site 1 is inlet water and sites 2-5 are sequential ponds. The mole ratios of the inlet water at Site 1 show that Na is a smaller proportion, and Ca and Mg a

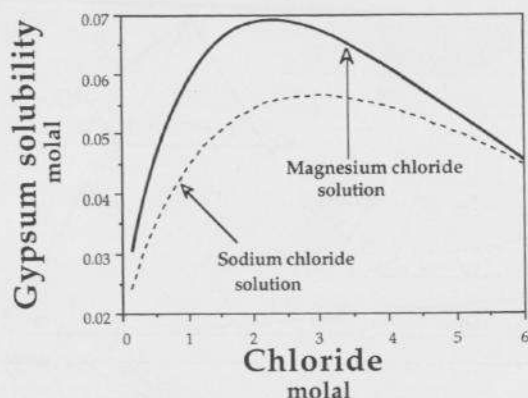


Fig. 1. Compaction of gypsum solubility at 25°C in solutions of different salts according to calculation based on the Pitzer equations.

larger proportion, of the cation equivalents in the Wakool water, compared to seawater. Variations in Ca/Cl and SO₄/Cl for the more evaporated waters are consistent with calcite (CaCO₃) and gypsum (CaSO₄·2H₂O) formation.

The chemical characteristics of the brines formed by evaporation of the Wakool waters will be different from a seawater-derived brine because of the different ionic composition. For example, gypsum solubility depends on its IAP which varies in the presence of different ions because the activity coefficients are affected by ion interaction. This is illustrated in Fig. 1 by comparison of the solubilities of gypsum in NaCl or MgCl₂ solutions of comparable chloride concentration.

Similar calculations allow the prediction of comparative yields of gypsum and halite from seawater and the Wakool water under equilibrium conditions at 25°C. Figure 2 shows the grams of salt expected as the waters evaporate (increasing ionic strength). It is apparent from these data that gypsum saturation occurs at a much lower ionic strength (1.28 molal)

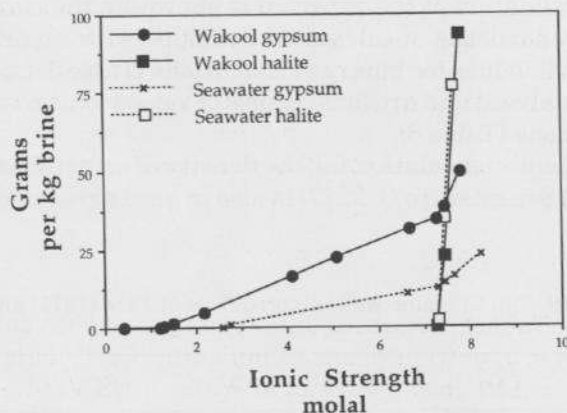


Fig. 2. Predicted yields of gypsum and halite from Wakool water compared with seawater.

TABLE 2

Predicted compositions for seawater and Wakool brines at halite saturation

Composition molal	Wakool	Seawater
Na	4.319	5.167
K	0.0066	0.109
Ca	0.030	0.011
Mg	0.912	0.589
Cl	6.344	6.035
SO ₄	0.064	0.220
Ionic strength	7.346	7.294

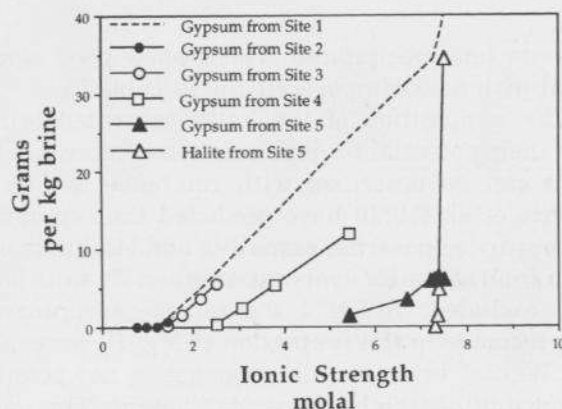


Fig. 3. Predicted yields from sequential ponds.

with evaporating Wakool water than with seawater (2.58 molal).

As would be expected from the higher Ca content, there is a higher gypsum yield predicted from the Wakool water compared to seawater. Halite reaches saturation at similar ionic strengths in both brines (Wakool, 7.346 molal; seawater, 7.294 molal; Table 2). However, the potential halite yield is also controlled by the composition of the brine and a comparison of the sodium and chloride contents of the two brines at halite saturation (Table 2) indicates that 15% less halite would be expected from the Wakool brine compared with a seawater brine because of the lower sodium content.

Gypsum contamination of halite is reduced in solar salt field operations by its successive removal from the concentrating brine in a number of ponds prior to halite precipitation. Figure 3 illustrates this procedure with modelled evaporation of the waters between Sites 2, 3, 4 and 5 and from Site 5 to halite saturation. Site 1 evaporation shows total gypsum yield as in Fig. 2. Table 3 gives the compositions of the modelled, evaporated brines, from which the

TABLE 3
Predicted compositions of evaporated brines

	Composition (molal) predicted for		
	Site 3	Site 4	Site 5
Na	0.734	1.353	3.108
K	0.0009	0.0016	0.0002
Ca	0.048	0.061	0.056
Mg	0.158	0.293	0.688
HCO ₃	0.0040	0.0035	0.0025
Cl	1.093	2.011	4.583
SO ₄	0.052	0.057	0.053
Ionic strength	1.431	2.504	5.441

gypsum has precipitated. These show good agreement with field sample analyses in Table 1.

The composition of the halite-saturated brines and their potential for precipitation of more soluble salts can be described with reference to Fig. 4. Harvie et al. (1980) have predicted that epsomite, hexahydrate, kieserite, carnallite and bischofite will form from seawater evaporation when Ca salts have been excluded. On Fig. 4, this represents a progressive increase in the proportion of Mg. However, for the Wakool brine such a sequence is not possible because of the high initial Mg content. This is in accord with the equilibrium thermodynamic modelling, at 25°C, which predicts that only carnallite and bischofite will form at very high concentration.

Density prediction

The differences in the chemical behaviour of the Wakool brine compared to a seawater brine have been related to ionic strengths. However, the same formalism which has enabled precise solubility predictions can be used to calculate volumetric properties, like density, for complex aqueous solutions (Monnin, 1989). Chemical processes such as gypsum and halite saturation could then be predicted in relation to the densities of evaporating brines of other than marine composition.

The Chemix program has been extended to include equilibrium density calculations at 25°C, by

TABLE 4

Standard molal volumes (V_0 cm³ mol⁻¹) used in Chemix for density model. The Cl⁻ value was accepted from Millero (1971) and other values then calculated from molecular data (Monnin, 1989)

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	OH ⁻	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
V_0	-1.15	9.04	-18.24	-21.93	-4.2	-4.18	24.33	17.83	14.09

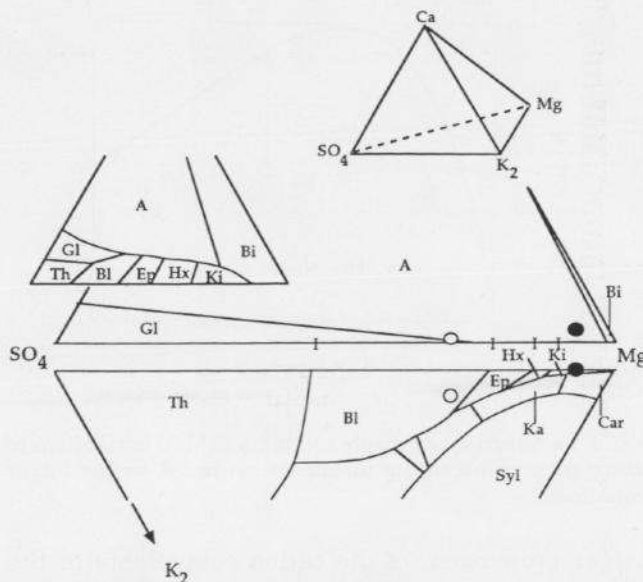


Fig. 4. The compositions (mole percentages of the components of each face) for Wakool (•) and seawater (o) are shown on a portion of the Jänecke projection (Stewart, 1963) of predicted mineral phases in the presence of halite at 25°C for the six-component system Na-K-Mg-Ca-Cl-SO₄-H₂O (Eugster et al., 1980). The diagram represents the region of low K₂, low Ca along the SO₄-Mg edge of the back and base faces of the reference tetrahedron (inset, upper right). The inset diagram (top left) is a schematic representation of the thin wedge of phases at low Ca and SO₄ concentrations which are not discernible at a true scale. Phases are shown as: A, anhydrite (CaSO₄); Gl, glauberite (Na₂Ca(SO₄)₂); Th, thenardite (Na₂SO₄); Bl, bloedite (Na₂Mg(SO₄)₂·4H₂O); Ep, epsomite (MgSO₄·7H₂O); Hx, hexahydrate (MgSO₄·6H₂O); Ki, kieserite (MgSO₄·H₂O); Bi, bischofite (MgCl₂·6H₂O); Car, carnallite (KMgCl₃·6H₂O); Ka, kainite (KMgClSO₄·H₂O); Syl, sylvite (KCl).

the incorporation of a suitable algorithm including pressure variation of Pitzer's ion interaction coefficients derived by Monnin (1989) and standard partial molal volumes calculated for ionic species (Table 4). Validation of the program is shown by the close correspondence of calculated densities with experimental values for binary salt solutions (Table 5) and for analysed and artificial brines of varied ionic compositions (Table 6).

Chemix calculation for the density of an artificial Dead Sea mixture (1.2227) is also in good agreement

TABLE 5

Comparison of experimental values for densities of binary salt solutions at 25°C (Lo Surdo et al., 1982) and values calculated in Chemix

Binary salt solution molality	Density (g cm ⁻³)		Binary salt solution molality	Density (g cm ⁻³)	
	Experimental	Predicted		Experimental	Predicted
NaCl			MgCl ₂		
0.78000	1.02793	1.0282	0.30126	1.02024	1.0205
0.96189	1.03479	1.0350	0.60791	1.04282	1.0430
1.62667	1.05913	1.0594	1.00671	1.07094	1.0710
3.60582	1.12494	1.1253	2.55235	1.16890	1.1693
4.30838	1.14629	1.1466	3.27113	1.20958	1.2102
5.15380	1.17080	1.1712	4.11680	1.25431	1.2548
5.99350	1.19407	1.1944	5.27571	1.31086	1.3107
Na ₂ SO ₄			MgSO ₄		
0.36623	1.0418	1.0421	0.28074	1.03024	1.0322
0.52712	1.06046	1.0608	0.71303	1.07877	1.0834
0.65576	1.07500	1.0754	1.08966	1.11922	1.1265
0.75671	1.08623	1.0867	1.28035	1.13907	1.1477
0.96067	1.10837	1.1089	1.74576	1.18602	1.1980
1.26034	1.13972	1.1403	2.15267	1.22503	1.2402
1.46960	1.16077	1.1614	2.39917	1.24778	1.2650

TABLE 6

Comparison of experimental and calculated densities for analyzed and artificial brines. Densities were determined by pycnometer measurements at 25°C and converted using water density from Lo Surdo et al., 1982

Brines	Composition (molal)							Density (g cm ⁻³)	
	Na	K	Mg	Ca	Cl	SO ₄	HCO ₃	Experimental	Predicted
Analyzed									
A	3.321	0.0031	0.6164	0.0906	4.696	0.0414	0.0032	1.1624	1.1610
B	1.735	0.0017	0.3491	0.0858	2.444	0.0493	0.0022	1.0976	1.0941
Artificial									
1	2.753	0.0161	0.2448	0.0107	3.145	0.0674		1.1179	1.1173
2	0.745	0.0051	0.0676	0.0088	0.865	0.0188		1.0334	1.0335
3	0.702	0.0062	0.0413	0.0022	0.781	0.0071		1.0290	1.0290
4	0.054	0.0096	2.9521	0.2320	6.415	0.0037	0.0096	1.2093	1.2091
5	3.774	0.0355	0.7242	0.0389	5.211	0.0444	0.0355	1.1812	1.1766

with calculated (1.2230) and experimental values (1.2233) quoted by Monnin (1989).

The prediction of density along the evaporation path for waters of different compositions is illustrated in Fig. 5 by comparison of seawater and Wakool water. Dead Sea water has been included because of its high Mg content, which is also a distin-

guishing feature of the Wakool water. The Wakool water reaches gypsum saturation at a significantly lower density (1.040) than seawater (1.085), while the values for halite saturation are only slightly different (Wakool, 1.205; seawater, 1.215). For Dead Sea water, halite is predicted to be saturated at a density of 1.231.

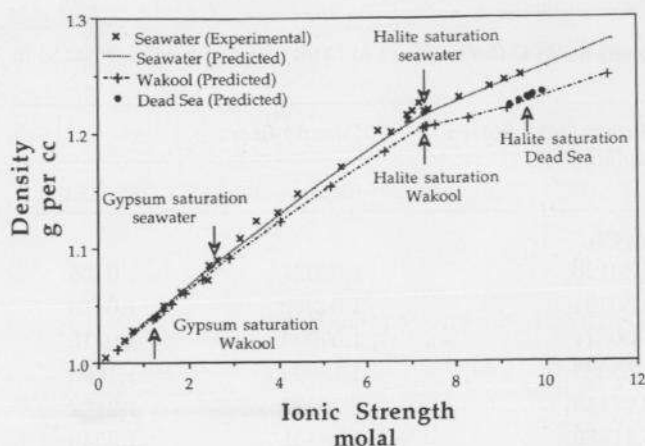


Fig. 5. Comparison of predicted densities for equilibrium evaporation at 25°C for seawater, Wakool water and Dead Sea brines up to concentrations beyond halite saturation. Experimental seawater values from Baseggio (1974) and Brantley et al. (1984).

CONCLUSIONS

Salt solubilities for brines of a wide range of chemical composition can be predicted in relation to brine density using the Chemix thermodynamic program. This capability provides chemical control for management of salt harvesting from non-marine brines. Prior to density modelling, relationships were only known for seawater brines based on empirical data.

In comparison to seawater, the Wakool water has

- a higher potential yield of gypsum precipitating at lower densities,
- a lower potential halite yield at slightly lower density, and
- a reduced suite of bittern salts because of the high Mg content.

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