Prediction of Gypsum Solubility and Scaling Limits in Saline Waters

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Gypsum solubility in natural seawater and agricultural drainage water was measured at temperatures between 25 and 70 °C. Solubilities at higher ionic strengths were also measured in natural water samples augmented with magnesium chloride. Scaling thresholds were evaluated graphically from solubility data. These results were compared with calculated values based on various computation models. A computation scheme based on extended Debye–Hückel theory was used as the basis for this work. The computer program finally developed in this paper provides read out of solubilities as well as scaling thresholds for gypsum. The program is practical for engineering use showing a variation of less than 5% from experimentally derived values.

Application of membrane processes to desalination of natural waters is often limited by deposition of calcium sulfate scale. The ambient temperature modification, gypsum ($CaSO_4{\cdot}2H_2O$) may foul electrodialysis or reverse osmosis membrane surfaces as process water is concentrated. Gypsum scaling is also a serious problem in cooling towers where it is desirable to minimize the volume of makeup water.

Rapid methods for scaling threshold evaluation are essential for establishment of necessary operating parameters. This is especially important when processing waters of continually varying composition such as waste waters of municipal, industrial, or agricultural origin. This paper deals with an improved computer program for assessment of gypsum solubilities and scaling thresholds in various mixed electrolyte backgrounds. Calculated values are compared with experimental results. Baseline solubilities of gypsum in seawater are also compared with literature values.

Two natural waters selected for this research were natural seawater and agricultural tile drainage water. Both waters are vulnerable to gypsum scaling but the problem is especially acute with agricultural runoff because of its low total salinity and high calcium sulfate ion product. Each of these waters was augmented with magnesium chloride at fixed concentration levels in an effort to alter their ionic background and thereby affect the solubility of gypsum. In this manner, the computer model could be tested over a wider range of solution parameters. It is also known that calcium sulfate solubility is enhanced in magnesium augmented solutions (*7*). An assessment of this effect on observed and calculated scaling thresholds is an additional objective of this work.

Models for Gypsum Solubility Evaluation

Any model used for this aqueous system must first take into account changes in activity with ionic strength. Secondly, it must deal with any significant ion pairing, which may lower ionic strength and thus depress the activity of a sparingly soluble salt, e.g., calcium sulfate. Both of these concepts are ignored in an old "rule of thumb" calculation (*6*), which claims that gypsum scale can be prevented by keeping the product of Ca^{2+} and SO_4^{2-} concentrations (both expressed as parts per million) below 500 000. This method is overly simplistic since process waters show wide variations in background ionic composition. Other empirical scale prediction methods published by Stiff and Davis (*18*), Denman (*6*), and Metler and Ostroff (*14*) show some improvement but are limited in general applicability.

Classical electrolyte solution theory has also been used as a basis for calcium sulfate solubility prediction in studies published by Lu and Fabuss (*11*), Tanji (*20*), Marshall, Slusher, and Jones (*13*) and Marshall and Slusher (*12*). Outstanding among these references is the work presented by Marshall and associates. Using the theory of ion association (*5*), extended Debye–Hückel theory (*10*), and experimental data, Marshall's group devised a computer program to determine the scaling threshold of calcium sulfate modifications in aqueous solutions. By this model, scaling thresholds of gypsum ($CaSO_4{\cdot}2H_2O$), hemihydrate ($CaSO_4{\cdot}{}^1/_2H_2O$), and anhydrite ($CaSO_4$) can be predicted over a temperature range of 30–200 °C. A recent paper by Yeatts, Lantz, and Marshall (*22*) reports good agreement between experimental and calculated solubilities of gypsum in three different brackish waters. In the present work, the computation scheme has been modified and applied to other natural waters.

All experimental data used by Marshall et al. to develop and test their computer program were derived from synthetic salt solutions. Information required by the program (input data) was the saline water's molal magnesium and calcium concentration, the molal sulfate to calcium ratio, and the ionic strength, $I = {}^1/_2\sum m_iz_i^2$. In the preceding equation, m_i is molality and z_i charge of the ith species. Input data were derived from initial water composition based on chemical analysis. Magnesium concentration is especially important because of significant magnesium sulfate ion pairing. The program's output was maximum concentration factor (CF) preceding incipient scaling of each calcium sulfate modification at various temperatures. This CF value was given in three forms, molal CF (the ratio of final to initial ionic strength), molar CF (the ratio of initial to final solution volume), and CF in terms of a weight fraction of dissolved solids. This program intelligently uses a combination of theory and empirical data to account for the effects of dissolved ions and temperature on the scaling threshold. Good results were obtained when the program was tested on synthetic or model solutions by the Marshall group. Satisfactory agreement between experimental and program calculated values was also reported for hemihydrate and anhydrite in natural seawater at elevated temperatures by Glater and Schwartz (*8*).

Motivation for the present research developed from the need for a realistic method for prediction of gypsum scaling limits in reverse osmosis equipment. Scale prediction is especially important in desalting plants where excessive blowdown cannot be tolerated. General applicability of the Marshall program to this end raises a number of unanswered questions. First, how accurate are the program's predictions with respect to real systems (e.g., where chemical analyses are often plus or minus 5%)? Second, is it practical for general use? Third, and lastly, does it break down at high ionic strengths or high magnesium levels? Another objective of this work arose from the scarcity of experimental solubility data on gypsum in actual seawater. The only published reports by Tanaka et al. (*19*) and Posnjak (*16*) were derived from abnormal and synthetic seawater, respectively.

Experimental Section

Solubility equilibrations were carried out in concentrates of agricultural runoff, taken on April 4, 1974, from Firebaugh, Calif., and sand-filtered seawater, obtained from Marineland of the Pacific located in Palos Verdes, Calif. To prepare concentrates,

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Table I. Fundamental Data for Seawater and Firebaugh Water

Density and Composition of Seawater Concentrates and Magnesium-Augmented Solutions (Measured Densities in kg/L at 20 °C)

CF	level of Mg^{2+} augmentation (times ambient): ambient [Mg^{2+}]	1.50×	2.00×	2.50×	3.00×
1.00	1.025	1.026	1.029	1.031	1.033
2.00	1.050	1.051	1.056	1.060	1.065
3.00	1.074	1.077	1.082	1.088	1.096
3.50	1.087	1.089	1.095	1.102	1.110
4.00	1.099	1.102	1.108	1.116	1.125
4.50	1.116	1.115	1.127	1.130	1.140

Analysis of CF 1.00 Seawater after Boiling with HCl (All Values in ppm)

dissolved ion	level of Mg^{2+} augmentation (times ambient): ambient [Mg^{2+}]	1.50×	2.00×	2.50×	3.00×
calcium	384	384	383	382	381
magnesium	1298[a]	1944	2585	3224	3862
sodium	10768[a]	10755	10724	10703	10682
potassium	377[a]	387	386	385	384
boron	6[a]	6	6	6	6
sulfate	2702[a]	2699	2691	2686	2681
bicarbonate	0	0	0	0	0
chloride[b]	19118	20990	22813	24650	26480
nitrate	0[a]	0	0	0	0
TDS	34653	37165	39588	42036	44476

Density and Composition of Firebaugh Water Concentrates and Magnesium-Augmented Solutions (Measured Densities in kg/L at 20 °C)

CF	level of Mg augmentation: ambient [Mg^{2+}]	2.00 × [Mg^{2+}]	CF	level of Mg augmentation: ambient [Mg^{2+}]	2.00 × [Mg^{2+}]
1.00	1.006	1.004	3.00	1.013	1.015
1.50	1.009		3.50	1.012	1.017
2.00	1.010	1.009	4.00		1.018
2.50	1.011		4.50		1.021

Analysis of CF 1.00 Firebaugh Water after Boiling with HCl

dissolved ion	level of Mg^{2+} augmentation: ambient [Mg^{2+}]	2.00 × [Mg^{2+}] [c]	dissolved ion	level of Mg^{2+} augmentation: ambient [Mg^{2+}]	2.00 × [Mg^{2+}] [c]
calcium	383	383	sulfate	3620[d]	3620
magnesium	199[d]	399	bicarbonate	0	0
sodium	1320[d]	1320	chloride[e]	659[d]	949
potassium	6[d]	6	nitrate	82[d]	82
boron	13[d]	13	TDS	6282	6772

[a] Abstracted from ref 4. [b] Chloride was modified to include F^- and Br^- in seawater plus added HCl. [c] Minute density difference was neglected in these calculations. [d] Analyses by California Water Resources Laboratory. [e] Chloride modified to include added HCl.

the water was first acidified to pH 4 with hydrochloric acid to prevent alkaline scale and gently boiled (removing CO_2) to beyond the maximum concentration factor desired. At this point the concentrated solution contained a calcium sulfate precipitate from which it was filtered. The precipitate was rinsed several times with distilled water until the final rinse contained no measurable magnesium and less than 1 ppm sodium. The rinses were added to the saline concentrate with enough distilled water to dilute the concentrated solution to a desired concentration factor.

From this stock solution less concentrated samples were obtained by further dilution. The density of each solution was measured with a hydrometer for heavy liquids accurate to ±0 001 g/mL. Solutions were added to 250-mL Erlenmeyer flasks containing a Teflon stirring bar and an excess of reagent grade finely powdered gypsum. The flasks were sealed and equilibrated with stirring in an isothermal water bath, following the technique previously described (*1*). Each sample was then filtered, diluted, and analyzed for calcium with a Perkin-Elmer Model 303 atomic absorption spectrophotometer (AAS) following standard procedures (*15*). To check the accuracy of this method, gypsum was equilibrated at 25 °C in distilled water and the resulting solution analyzed for calcium. The average value was found to be 0.015 20 ± 0.000 05 m, which is in satisfactory agreement with other values reported by Yeatts and Marshall (*23*), 0.015 23 ± 0.000 16 m, and Hullet and Allen (*9*), 0.015 28 ± 0.000 03 m. Confidence in this experimental method was thus established.

Because AAS introduced the bulk of observed standard deviation, a computerized regression technique was devised to improve the accuracy of data reduction. Absorptions by calcium standards of 2.00, 4.00, and 6.00 ppm were measured before and after running each set of samples. The computer performed a least-squares fit on the absorbance of both sets of standards. By assuming the dirft of AAS to be linear with time, we used the program to calibrate each sample with an appropriate interpolation between the two sets of standards.

Fresh Marineland seawater was analyzed for Mg^{2+}, SO_4^{2-}, Ca^{2+}, and Na^+ by AAS. The results were very close to those reported by Badger (*4*) for normal seawater, with the exception that calcium was about 6% lower. Raw Firebaugh water was analyzed by the state of California Department of Water Resources Laboratory. Total dissolved solids were evaluated from conductance measurements by using standard literature values. In order to augument samples with magnesium, a stock solution was prepared such that 20 mL contained 0.0547 mol of magnesium chloride. Ten, twenty, thirty, and forty milliliters were added per liter of CF 1 seawater before concentrating in order to achieve 1.50, 2.00, 2.50, and 3.00 times the ambient seawater magnesium concentration. For Firebaugh water, only one augmented solution was prepared with magnesium at 2.00 times ambient. All necessary data required to calculate the concentration of significant ions in any solution are given in Table I. Results of equilibrium solubility experiments are given in Table II. Not all of the data could be presented here because of the magnitude collected during the course of these experiments. The data are presented in their entirety in ref 2.

Analyses of these raw waters have a dual motivation. First, gypsum solubility data is valid only for very similar waters. Without a knowledge of the background ions in solutions, little can be said about gypsum's solubility. Second, the major intent of this paper deals with the feasibility of Marshall's model for prediction of gypsum solubility. In order to test this model, both solubility data and background chemical analyses are required.

The Computer Program

It was found desirable to add two extentions to the Marshall computer program. First, since most analyses are made on the basis of parts per million (ppm), this concentration unit was more convenient than molality; for this reason a preprocessor was added to read data for a given sample in ppm and calculate the four original parameters ([Ca^{2+}], [Mg^{2+}], [SO_4^{2-}]/[Ca^{2+}], I), thus reducing the hand calculations involved. One merely enters the concentration (in ppm) of calcium, magnesium, sodium, potassium, boron, sulfate, bicarbonate, chloride, and nitrate. The computer now performs all remaining operations. A second addition to the program involved directly obtaining gypsum solubility in a water sample. From Marshall's model, logic was devised by using a modified method of successive approximations to zero in on solubility. The printout value is expressed

Table II. Experimental Solubilities of Gypsum

Natural and Mg^{2+}-Augmented Seawater Concentrates
(All Values in ppm Ca^{2+})

temp, °C	CF	level of Mg^{2+} augumentation (times ambient): ambient $[Mg^{2+}]$	1.50×	2.00×	2.50×	3.00×
25	1.00	1236	1286	1418	1449	1509
	2.00	1342	1371	1520	1534	1576
	3.00	1307	1353	1457	1435	1452
	3.50	1254	1312	1398	1354	1356
	4.00	1198	1184	1284	1252	1231
	4.50	1149	1139	1216	1145	1098
50	1.00	1260	1343	1453	1478	1565
	2.00	1376	1448	1542	1608	1663
	3.00	1341	1446	1505	1527	1548
	3.50	1300	1360	1442	1443	1463
	4.00	1236	1255	1354	1342	1352
	4.50	1177	1211	1292	1254	1223
70	1.00	1231	1365	1393	1563	1548
	2.00	1377	1479	1540	1716	1671
	3.00	1349	1472	1524	1645	1634
	3.50	1333	1425	1472	1584	1558
	4.00	1281	1337	1410	1490	1457
	4.50	1218	1275	1287	1335	1340

Natural and Mg^{2+}-Augmented Firebaugh Concentrates at 25 °C
(All Values in ppm Ca^{2+})

	level of Mg^{2+} augmentation			level of Mg^{2+} augmentation	
CF	ambient $[Mg^{2+}]$	2.00 × $[Mg^{2+}]$	CF	ambient $[Mg^{2+}]$	2.00 × $[Mg^{2+}]$
1.00	476	504	3.00	445	474
1.50	458		3.50	450	473
2.00	452	478	4.00		476
2.50	450		4.50		474

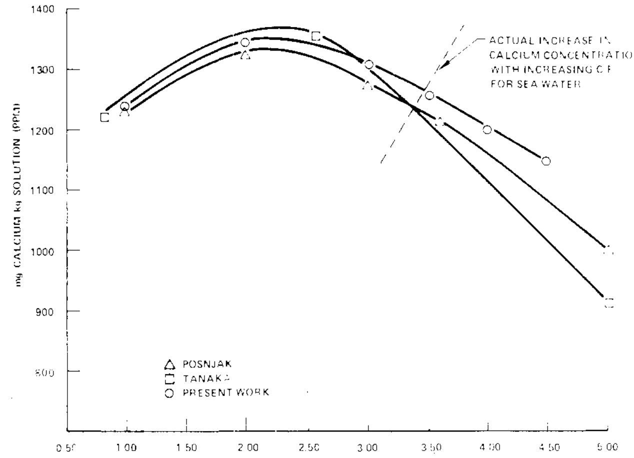

Figure 1. Experimental solubilities of gypsum in seawater concentrates at 30 °C by various investigators.

as ppm of Ca^{2+}, although alternative units can easily be substituted. This modification was installed in an effort to directly mimic the solubility experiments. Solubility output could also be practically applied when the need to dissolve a quantity of gypsum in a particular saline water arises.

While this work deals only with gypsum at temperatures below 70 °C, a similarly modified general program has been devised for all three forms of calcium sulfate, within a temperature range of 0–300 °C. Calculated values using the modified program to predict gypsum solubility in the analyzed saline waters and their concentrates are tabulated in Table III. The accuracy of this model can be determined by comparing these results with

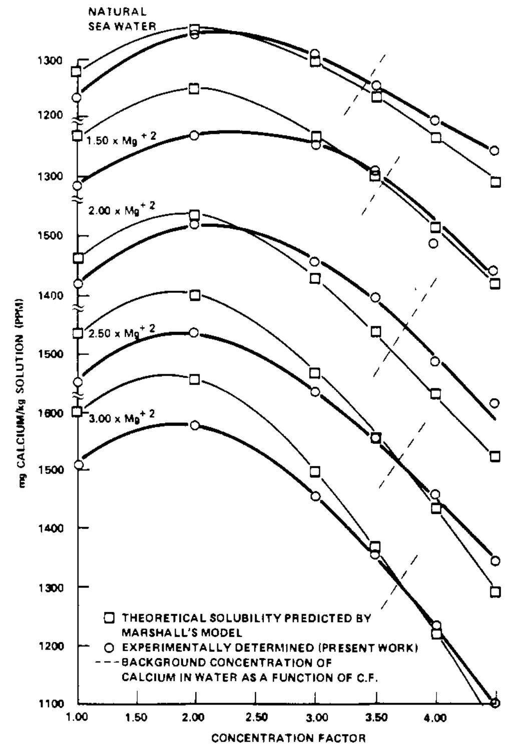

Figure 2. Calculated and experimental solubilities of gypsum in seawater concentrates at 25 °C with various levels of magnesium augmentation.

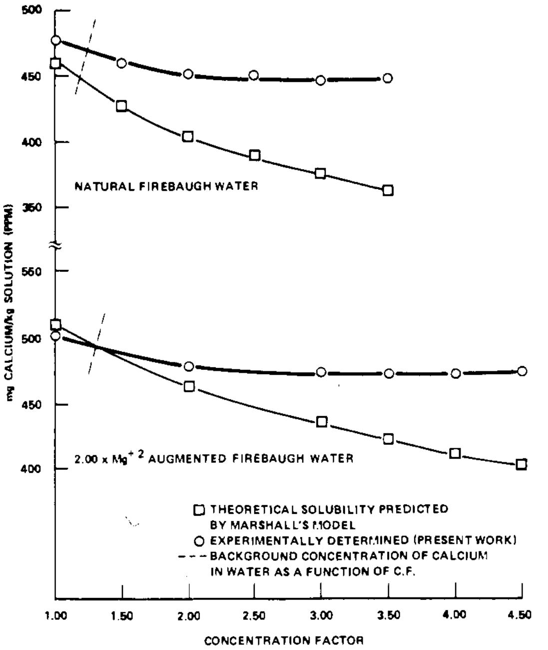

Figure 3. Calculated and experimental solubilities of gypsum in Firebaugh water concentrates at 25 °C with two levels of magnesium augmentation.

experimental data presented in Table II.

Results and Discussion

Figure 1 is a plot of experimental gypsum solubilities as a function of seawater concentration factor at 30 °C. A literature search revealed only two other studies of gypsum solubility in seawater. Agreement with the work of Posnjak (*16*) and Tanaka (*19*) is generally good. This is impressive considering the fact that Posnjak worked with synthetic seawater and Tanaka with diluted natural seawater which was normalized in Figure 1 by a multiplication factor described in ref 2. This figure, rising to

Table III. Theoretical Solubilities of Gypsum Calculated by the Modified Marshall Program

Natural and Mg^{2+}-Augmented Seawater Concentrates (All Values in ppm Ca^{2+})

		level of Mg^{2+} augmentation (times ambient)				
temp, °C	CF	ambient [Mg^{2+}]	1.50×	2.00×	2.50×	3.00×
25	1.00	1277	1373	1458	1534	1603
	2.00	1351	1451	1533	1601	1659
	3.00	1294	1370	1486	1467	1494
	3.50	1236	1297	1336	1358	1366
	4.00	1167	1211	1230	1233	1220
	4.50	1087	1112	1120	1088	1051
50	1.00	1310	1416	1512	1591	1665
	2.00	1373	1481	1568	1640	1700
	3.00	1304	1385	1445	1488	1519
	3.50	1240	1306	1350	1376	1386
	4.00	1166	1217	1242	1249	1241
	4.50	1085	1118	1131	1112	1075
70	1.00	1290	1404	1503	1591	1670
	2.00	1367	1485	1581	1662	1731
	3.00	1316	1410	1485	1542	1585
	3.50	1262	1344	1404	1446	1472
	4.00	1199	1268	1311	1336	1345
	4.50	1129	1182	1214	1216	1201

Natural and Mg^{2+}-Augmented Firebaugh Concentrates at 25 °C (All Values in ppm Ca^{2+})

	level of Mg^{2+} augmentation			level of Mg^{2+} augmentation	
CF	ambient [Mg^{2+}]	2.00 × [Mg^{2+}]	CF	ambient [Mg^{2+}]	2.00 × [Mg^{2+}]
1.00	460	511	3.00	375	435
1.50	428		3.50	363	423
2.00	406	465	4.00		412
2.50	389		4.50		403

Table IV. Experimental and Theoretical Gypsum Scaling Thresholds for Magnesium-Augmented Seawater and Firebaugh Water Solutions in Volumetric CF Units

temp, °C	Mg^{2+} level × ambient	Marshall model program	Marshall model graph	exptl
		Seawater		
25	1.00	3.40	3.42	3.45
	1.50	3.53	3.56	3.58
	2.00	3.61	3.63	3.75
	2.50	3.64	3.68	3.69
	3.00	3.64	3.69	3.70
50	1.00	3.41	3.43	3.55
	1.50	3.55	3.58	3.70
	2.00	3.63	3.67	3.87
	2.50	3.67	3.72	3.87
	3.00	3.67	3.73	3.91
70	1.00	3.46	3.48	3.62
	1.50	3.63	3.67	3.78
	2.00	3.74	3.77	3.96
	2.50	3.81	3.86	4.12
	3.00	3.83	3.91	4.12
		Firebaugh water		
25	1.00	1.17	1.17	1.23
	2.00	1.29	1.30	1.30

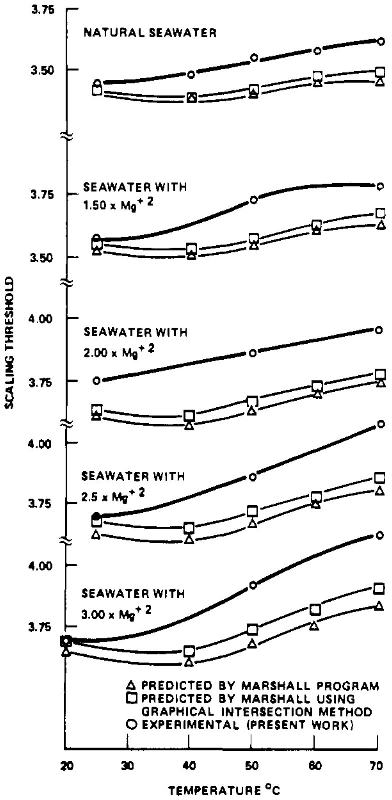

Figure 4. Calculated and experimental scaling thresholds of gypsum in seawater concentrates with various levels of magnesium augmentation between 20 and 70 °C.

a maximum and then declining, is typical of solubility trends of sparingly soluble salts in concentrated electrolyte backgrounds. It is important at this point to distinguish between equilibrium solubility and scaling threshold. The solid lines represent solubility as a function of concentration factor. Superincumbent to these solubility isotherms in Figures 1, 2, and 3 are dashed line segments representing the actual increase in calcium concentration which would occur as the solution is concentrated. The CF at which a dashed calcium concentration line intersects a solid solubility line defines the molar scaling threshold.

Values given in Table II for 25 °C are shown graphically in Figures 2 and 3 as typical of the data in these tables. Deviation of this model from experiment rarely exceeded 7%. Trends are very similar, suggesting the error to be systematic. A Student's *t* distribution (*21*) was found for a large representative portion of the 120 data points which represent 666 separate measurements. These points showed that an interval of ±6 ppm was generally sufficient for 50% confidence. Thus, about half of the reported mean values of experimentally found data points deviate 6 ppm or less from the true value, on the basis of our standards. The standards were evidently well calibrated since gypsum solubility measurements in pure water fell within 0.05% of reported values. Since experiment and model often deviate by 100 ppm for seawater concentrates and 50 ppm for brackish water concentrates, the model's fidelity with experiment is not exact but is tolerable for most practical applications. It is also important to point out that waters used in this study are not simple ionic systems. Firebaugh water has a weight ratio of sulfate to total dissolved solids (TDS) of about 0.58 compared with a ratio of 0.0078 for seawater. On the other hand, seawater has an ionic strength which is very high for any present models of solubility.

Table IV shows a comparison of experimental and calculated molar scaling thresholds. The last column gives experimental values which were derived by intersection of dashed concentration lines with the heavy solid experimental solubility lines. The two preceding columns give scaling thresholds predicted by the Marshall program in two different ways. Data in the first column were obtained directly from program readout. The second column represents calculated scaling thresholds obtained by intersection of the dashed concentration line with the light solid line. The solid line in this case was drawn from gypsum solubilities predicted by the program. Data for seawater are plotted in Figures 2 and 4.

The 50% confidence interval of the experimentally determined scaling thresholds is less than 0.5% based on an error in solubility measurements of ±6 ppm. The difference between experimentally found scaling thresholds and those predicted by the Marshall model is as high as 7%. The expression relating molal CF with molar CF seems to introduce no significant error in Firebaugh water at low ionic strengths, below 0.2. However, it causes the prediction to be 1% low at $I = 2.5$, with the error increasing to 2% low at $I = 4.3$. This is probably due to the fact that correlations between ionic strengths, TDS, and density for the combination of salts in Marshall's sea salt solution are different from those in unusual brackish waters. For example, ionic ratios in Firebaugh water show marked deviation from Marshall's model solution. This error could be overcome by correlating TDS and density with the solution's actual ionic makeup.

It is evident from Figure 3 that magnesium chloride increases the peak solubility of gypsum in brackish waters. This effect is most pronounced at higher temperatures which is consistent with literature reports (*7*). Magnesium chloride addition can also strongly increase the ionic strength. In Figure 2, the slopes of seawater curves increase with additional magnesium chloride due to the fact that ionic strength is increasing faster with concentration factor in the more highly augmented solutions. Thus, the peak solubility occurs at increasingly lower CF's after which the solubility of gypsum falls off more sharply with increasing magnesium chloride addition. This causes the scaling threshold to occur sooner, implying lower gypsum scaling limits, were not the entire graph shifted upward by ion association resulting in neutral $MgSO_4^0$ species.

This can be characterized as a tradeoff situation. The effect of sulfate association with magnesium is more pronounced at high temperatures and lower levels of magnesium augmentation where it results in higher scaling thresholds. At lower temperatures and higher levels of magnesium augmentation, the ionic strength is increasing so rapidly with increasing CF that addition of more magnesium chloride produces no additional benefits. In Firebaugh runoff, the unique water composition results in a different situation as shown in Figure 3. Here the high ratio of sulfate to ionic strength gives the curve a constant downward slope due to the common ion "salting out" effect. Because of the low ionic strength, magnesium chloride addition will increase the scaling threshold continuously up to magnesium levels approximately 60 times ambient.

For most waters it can be assumed that the modified Marshall program is a feasible means for the prediction of gypsum scaling thresholds. The difference between values calculated by the program and those found by experiment showed a variance ranging from 0 to 7%. Although these deviations are significant and reproducible under controlled conditions, they may be trivial in practice for a number of reasons. First is the uncertainty of the feed water's chemical composition which may be limited in analytical accuracy from 1 to 100%. Second is the variation in water composition with season, rainfall, etc. This is especially significant with agricultural drainage waters such as Firebaugh water (*3*). It should be noted, for example, that an error of 5% in both calcium and sulfate analysis can cause an error on the order of 6% in predicted scaling threshold. Temperature is still another variable which, while easily controlled in the laboratory, will fluctuate with time, and even within the system in the field. The solubility of gypsum is not very strongly dependent on temperature (well under 1%/°C), so it is dubious that this will add significantly to uncertainties in scaling threshold when compared to other unknowns. In total these unknowns tend to dwarf the 3% average error introduced by quickly evaluating the scaling threshold by computer program rather than by time consuming experimentation. In spite of these uncontrollable variations, the Marshall program is presently satisfactory for engineering purposes. Further slight improvement could be made by adding empirical first- and second-order terms to the equations which relate ionic strength to activity of $MgSO_4^0$ or other ion pairs. One could also devise a correlation relating TDS, density, and the individual ions in the sample to further improve results.

Before use of the results presented here, it is important to note that both Marshall's program and the present work consider equilibrium solubilities only. Departure from equilibrium may result from supersaturation which is due to slow rates of crystal nucleation and growth. Laboratory studies have shown that gypsum is indeed capable of high levels of supersaturation (*17*). Certain pretreatment chemicals, such as sodium hexametaphosphate, can temporarily enhance solubility and thus increase the transient scaling threshold. This effect may result in scaling thresholds well above those predicted by either the program or any equilibration studies.

Another note concerning the application of this work is that chemical analysis for scaling predictions must be made on the most concentrated portion of the solution. For instance, in membrane desalination processes, the boundary layer on the membrane often contains up to twice the salt concentration of the bulk. Obviously the program cannot be used to predict scaling thresholds based on feed composition of such a system. If brine is blown down before this concentration is reached by the bulk solution, scale may still form on the membrane where the solution is more concentrated than in the bulk. For certain systems, such as the UCLA 1-in. tubular reverse osmosis module, concentration polarization can be predicted to within ±5%. In this case scaling thresholds for the boundary layer can be estimated by dividing CF predicted for the bulk by the concentration polarization factor. This assumes that all salts are rejected equally by the membrane; however, this method provides reasonable results with reasonable effort.

The following are some recommendations to aid in use of the modified Marshall program for rapid and practical scaling threshold evaluation. First, when a brackish water is analyzed, two-place accuracy is required for meaningful results. Second, precise models should be developed for temperature and chemical concentration gradients in any system in which they are significant. Third, research should be done on supersaturation and crystal growth phenomena, and the effects of scaling threshold agents on transient solubility of gypsum in field equipment.

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Literature Cited

(1) Adler, M. S., MS Thesis, UCLA School of Engineering and Applied Science, Los Angeles, CA, 1974.
(2) Adler, M. S., Glater, J., McCutchan, J. W., University of California, UCLA-ENG-7503, Water Resources Center Desalination Report No. 59, 1975.
(3) Antoniuk, D., McCutchan, J. W., Report UCLA School of Engineering and Applied Science, UCLA-ENG-7368, Aug 1973.
(4) Badger, W. L., et al., *U.S. Off. Saline Water, Res. Dev. Prog.* Rep., **No. 25** (1959).
(5) Davies, C. W., "Ion Association", Butterworth, London, 1962, pp 162–175.
(6) Denman, W. L., *Ind. Eng. Chem.*, **53**, 817 (1961).
(7) Glater, J., Murdia, K. S., Dooly, R., *Desalination*, **14**, 197 (1974).
(8) Glater, J., Schwartz, J., *J. Chem. Eng. Data*, **21**, 47 (1976).
(9) Hullet, G. A., Allen, L. E., *J. Am. Chem. Soc.*, **24**, 667 (1902).
(10) Lewis, G. N., Randall, M., "Thermodynamics", 2nd ed., McGraw-Hill, New York, 1961, pp 332–343.
(11) Lu, C. H., Fabuss, B. M., *Ind. Eng. Chem. Process Des. Develop.*, **7**, 206 (1968).
(12) Marshall, W. L., Slusher, R., *J. Chem. Eng. Data*, 13, 83 (1968).
(13) Marshall, W. L., Slusher, R., Jones, E. V., *J. Chem. Eng. Data*, **9**, 187 (1964).
(14) Metler, A. V., Ostroff, A. G., *Environ. Sci. Technol.*, **1**, 815 (1967).
(15) Perkin-Elmer Corp., "Analytical Methods for Atomic Absorption Spectrophotometry", Norwalk, CT, 1973.
(16) Posnjak, E., *Am. J. Sci.*, **238**, 559 (1940).

(17) Reddy, S. R., Glater, J., McCutchan, J. W., *NWSIA J.*, **3**, 11 (1976).
(18) Stiff, H. A., Davis, L. E., *Trans. Am. Inst. Min. Metall. Pet. Eng.*, **195**, 25 (1958).
(19) Tanaka, Y., Nakamura, K., Hara, R., *J. Chem. Soc. Jpn., Ind. Chem. Sect.*, **34**, 779 (1931).
(20) Tanji, K. K., *Environ. Sci. Technol.*, **3**, 656 (1969).
(21) Wilson, E. B., "Introduction to Scientific Research", McGraw-Hill, New York, 1952, pp 239-242.
(22) Yeatts, L. B., Lantz, P. M., Marshall, W. L., *Desalination*, **15**, 177 (1974).
(23) Yeatts, L. B., Marshall, W. L., *J. Chem. Eng. Data*, **17**, 163 (1972).

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Solubility of Aluminum Sulfate in Aqueous Ethanol at 30 and 80 °C

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The solubility of aluminum sulfate in 85–100% by weight aqueous ethanol has been reexamined at 30 and 80 °C. A technique has been developed for producing a stable solution of ~1% $Al_2(SO_4)_3$ by weight in 97% ethanol relatively rapidly. Starting with this stock solution, we prepared lower concentration ethanol systems for equilibration by addition of water. Stock solution is also distilled azeotropically to produce aluminum concentrations in solution as high as ~4% by weight as aluminum. Such solutions are slightly deficient in sulfate due to volatilization of sulfuric acid esters during distillation. Solubilities of $Al_2(SO_4)_3$ are found to be higher than those reported earlier in the 95–100% ethanol region. This is explained by the observation that anhydrous (calcined) aluminum sulfate and aluminum sulfate hydrates equilibrated in ethanol by previous workers are extremely slow in dissolving. Solid phases in equilibrium with ethanolic solutions are found, in general, to be hydrated basic aluminum sulfates containing monoethyl sulfate.

Anhydrous aluminum sulfate is normally prepared by heating the corresponding hexadecahydrate in air in the vicinity of 400 °C. The resulting material has a characteristic X-ray diffraction pattern. Our interest was in determining whether a lower temperature polymorph existed. Whereas there are many potential routes to such a material, equilibration in the ethanol–water system seemed appropriate and convenient. Gee (*6*), for example, reported anhydrous aluminum sulfate in equilibrium with ethanol-water at temperatures as low as 30 °C. Exploratory experiments based upon Gee's work led to the finding that the system is more complex than earlier work had anticipated. Indeed, some of the discrepancies in the reported literature (*2*, *3*, *4*, *12*) on the solubility of aluminum sulfate in ethanol-water systems may have been the consequence of kinetic factors and failure to attain thermodynamic equilibrium.

In view of the apparent complexity of the aluminum sulfate–ethanol–water system, it was decided to approach equilibrium from a new direction and to pay special attention to the composition of solids in equilibrium with higher concentration ethanol solutions.

Experimental Section

The stock solution of aluminum sulfate was prepared by adding 10 mL of saturated aqueous reagent grade $Al_2(SO_4)_3$ solution to 450 mL of boiling USP absolute ethanol (99.8% by weight) in a Waring blender. The $Al_2(SO_4)_3$ solution had been adjusted to 0% basicity by adding sulfuric acid; i.e., the total molar sulfate concentration in solution was adjusted to exactly 1.50 times the molar aluminum concentration. After 5 min in the blender the slurry formed was allowed to equilibrate at room temperature. In approximately 5 h the coarse, gritty solids completely dissolved to give ~1% $Al_2(SO_4)_3$ in ~97% ethanol. One such stock solution, for example, contained 1.03% by weight aluminum as $Al_2(SO_4)_3$ after standing at room temperature for 6 months. Stock solution concentrations of $Al_2(SO_4)_3$ as high as 2.90% were achieved by equilibrating the Waring blender slurry at room temperature after having initially decanted off some of the clear liquor. These procedures for making stock solution are preferred over dissolution of crystalline hexadecahydrate in absolute alcohol, a process which takes several days at elevated temperature.

Table I. Equilibration Time in a Representative Ethanol-Water-Aluminum Sulfate System at 30 °C

time (after water introduction), days	Al concn in solution, wt % $Al_2(SO_4)_3$
0	1.04
3	0.33
4	0.085
5	0.05
6	0.045
7	0.04
10	0.04

Table II. Estimated Precision of Analytical Data

anal. for	coef of variation
Al	2
SO_4	1
H_2O[a]	1.5
C	7

[a] By Karl Fischer titration.

Deionized water was added slowly to $Al_2(SO_4)_3$ stock solution at room temperature with vigorous agitation to produce the solid–liquid systems to be equilibrated. All such systems were equilibrated a minimum of 6 days. Equilibration temperatures were 30 ± 1 and 80 ± 1 °C.

Gee (*6*) equilibrated ethanol–water–aluminum sulfate systems for a minimum of 4 days. In the present investigation a 6-day minimum time was required, as illustrated in the following example. To a sample of 1% $Al_2(SO_4)_3$ stock solution was added sufficient water to produce a 93% by weight ethanol concentration in the final equilibrium clear liquor. Ethanol concentrations are always based upon the ethanol and water contents, to the exclusion of soluble aluminum and sulfate. The system was equilibrated at 30 °C, and uniform slurry samples were withdrawn periodically. Solids were separated by centrifuge, and the clear liquor was analyzed for aluminum. Results are given in Table I.

In order to obtain data for a more concentrated ethanol system, 1% $Al_2(SO_4)_3$ stock solution was distilled in the presence

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