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PHASE EQUILIBRIA IN THE SYSTEM H_2O-NaCl-KCl-MgCl$_2$ RELEVANT TO SALT CAKE PROCESSING*

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Abstract

One of the waste products produced by the recycling of aluminum is salt cake, a mixture of aluminum, salts, and residue oxides. Several methods have been proposed to recycle salt cake; one of these involves high-temperature leaching of salts from the salt cake. The salt composition in salt cake can be approximated as a mixture predominantly of sodium and potassium chloride salts, with lesser amounts of magnesium chloride. In order to better assess the feasibility of recycling salt cake, an experimental study was conducted of phase equilibria in the system H_2O-NaCl-KCl-$MgCl_2$ at pressure, temperature, and composition (PTX) conditions appropriate for high-temperature salt cake recycling. These experiments were designed to evaluate the effect of small amounts (2-10 wt.%) of $MgCl_2$ on solubilities of halite (NaCl) and sylvite (KCl) in saturated solutions (30-50 wt.% NaCl + KCl; NaCl:KCl = 1:1 and 3:1) at elevated P and T.

Introduction

One of the waste products produced by the recycling of aluminum is salt cake, a mixture of aluminum, salts, and residue oxides. In the United States, salt cake is usually landfilled. The increasing cost of landfilling and the environmental concerns over the leachable chloride content in salt cake pose a potential threat to the economics of aluminum recycling. To address the problem of landfilling salt cake, several technologies have been tested or proposed for salt cake recycling (1). One of these involves water leaching of salts from salt cake at elevated temperatures and pressures. For a given quantity of water, leaching at elevated temperatures removes a higher proportion of the salts than is possible at ambient temperatures. In order to test the feasibility of this process, the solubilities of salt-cake salts in water at elevated temperatures must be known. The highly soluble salt portion of salt cake is approximated reasonably well by the quaternary system H_2O-NaCl-KCl-$MgCl_2$. Phase equilibrium (solubility) data for this quaternary system are available for ambient to moderate temperatures for a limited range of compositions (2,3), but data do not exist for temperatures and compositions relevant to high-temperature leaching of salt cake. The goal of the present study was to experimentally determine the phase relations and solubilities in the system H_2O-NaCl-KCl-$MgCl_2$ at elevated temperatures and pressures. This work builds on an earlier detailed study of phase equilibria in the H_2O-NaCl-KCl ternary system (4).

Experimental Procedure

Phase equilibria in the H_2O-NaCl-KCl-$MgCl_2$ system were determined by using the synthetic fluid inclusion technique (5,6). With this technique, small samples of aqueous solution are isolated in a quartz host at elevated temperature and pressure by healing fractures in the quartz. The resulting fluid inclusions contain a sample of the fluid that was in equilibrium at the P-T conditions of the experiments, and they maintain the fluid without loss of material so that it can be examined at ambient conditions.

Synthetic fluid inclusions were trapped by healing fractures in Brazilian quartz. Cylinders of clear, natural inclusion-free quartz, 4.5 mm in diameter and about 6-9 mm in length, were heated to 350°C in an oven and then dropped into cold distilled water. The thermal shock results in the formation of numerous closely spaced fractures that propagate from the edge towards the interior of the quartz cylinder. Any water that may have entered the fractures during the fracturing process was removed by placing the fractured cores in a vacuum oven at 100°C for several hours. A dried, fractured quartz core was placed in a platinum capsule along with a solution of the appropriate composition. All of our experiments were conducted along three pseudo binaries in the H_2O-NaCl-KCl-$MgCl_2$ system. One end member of the pseudo binary was represented by H_2O-$MgCl_2$ solutions with compositions of 2, 5, and 10 wt.% $MgCl_2$. The other end member was represented by a mixture of NaCl and KCl salts, with NaCl:KCl ratios of 1:1 and 3:1. Total salinities of the H_2O-NaCl-KCl-$MgCl_2$ solutions ranged from 30 to 50 wt.%. To obtain the desired bulk compositions,

weighed amounts of the H_2O-$MgCl_2$ solutions were added to the platinum capsules along with weighed amounts of NaCl and KCl. After all components (H_2O-$MgCl_2$ solution, solid NaCl and KCl, quartz core) were loaded, the capsule was sealed with an arc-welder.

Capsules containing quartz and the desired fluid compositions were placed in cold-seal pressure vessels and heated to run conditions. Experiments were conducted at elevated temperature (600°C) and pressure (3 kbar) for a seven-day period. During heating from ambient to experimental conditions, solid NaCl and KCl that had been loaded into the capsule dissolved into the H_2O-$MgCl_2$ solution to provide a one-phase, homogeneous H_2O-NaCl-KCl-$MgCl_2$ solution at final run conditions. Petrographic techniques for proving that the P-T conditions were in fact in the one-phase region during the experiment have been described previously (7). After all experiments were completed, the capsule was quenched to room temperature and weighed to confirm that the capsule did not leak during the experiment. The capsule was then opened, and the quartz core was cut into 1-mm-thick disks and polished for microscopic observations.

When the polished quartz disks are examined under the microscope, they are found to contain numerous small (<1 to 50 μm) cavities filled with a liquid phase, a vapor phase, and one or more solids. The vapor phase is a result of shrinkage of the volume of the liquid phase as it contracts (its density increases) during cooling in the constant-volume cavity. The solids (halite and sylvite) are precipitated when the original solution becomes saturated in NaCl and KCl during cooling. To determine the phase relations in the H_2O-NaCl-KCl-$MgCl_2$ system, the inclusion is heated by using a standard petrographic microscope equipped with a gas-flow USGS-type heating-cooling stage, reversing the P-T path the inclusion followed during cooling from formation conditions to ambient temperature. Dissolution temperatures of salts (halite and sylvite) are measured by means of a thermocouple placed on top of the sample. The accuracy of the microthermometric measurements is estimated to be ±1°C in the temperature range of this study. Note, however, that the ranges in measured dissolution temperatures of salts often exceeded the estimated accuracy of the microthermometric measurements (Table 1). This can be explained by incomplete homogenization of solution to produce minor compositional gradients before and/or during inclusion trapping. Studies of aqueous systems conducted in this laboratory over the past 10 years have shown that the minimum temperature recorded most closely approximates the correct (equilibrium) dissolution temperature.

Results and Discussion

Experiments were conducted using 35 different compositions in the H_2O-NaCl-KCl-$MgCl_2$ system and three industrial salt cake compositions. For each composition, the temperatures of dissolution of halite and sylvite solid phases in the synthetic fluid inclusions were measured during heating of the sample in the heating stage. Experimental results for halite (NaCl) and sylvite (KCl) solubilities in 2, 5, and 10 wt.% $MgCl_2$ solutions along the NaCl/KCl = 1:1 and 3:1 pseudo binaries are presented in Table 1. Also listed are solubilities of NaCl and KCl in pure water, calculated from the data in (6). All of the experimental solubility data, including those for the H_2O-NaCl-KCl ternary, were processed by using statistical methods to generate a set of best fit equations describing total salinity as a function of salt dissolution temperature and $MgCl_2$ content for each composition. Solubilities of the salt-cake salts were found to be adequately represented by the H_2O-NaCl-KCl-$MgCl_2$ system with no corrections required for other, minor salt cake constituents.

Halite and sylvite dissolution temperatures as a function of $MgCl_2$ concentration are shown in Figure 1. The data clearly show the effect of $MgCl_2$ on decreasing the solubility of both halite and sylvite in water. The decrease in halite solubility (increase in dissolution temperature shown on Figure 1) with increasing $MgCl_2$ is greatest for the low-salinity (30 wt.%) solutions and less for the higher-salinity compositions. The results for sylvite are less systematic, although there is a clear increase in dissolution temperature, or decrease in solubility, with increasing $MgCl_2$ concentration. Figure 2 illustrates the effect of total salinity on halite and sylvite dissolution temperatures along three constant $MgCl_2$ concentration isopleths (0, 5, and 10 wt.% $MgCl_2$). Note the much greater effect of $MgCl_2$ on the halite dissolution temperatures compared with that on the sylvite dissolution temperatures.

Halite and sylvite solubility surfaces were obtained by regression of the experimental data to generate equations that predict total salinity as a function of either the halite or sylvite dissolution temperature and the concentration of $MgCl_2$. The halite solubility surface in the NaCl-KCl-$MgCl_2$-H_2O quaternary system with NaCl:KCl = 1:1 is given by:

$$S = \frac{(a + bM + cM^2 + dM^3 + eT)}{(1 + fM + gM^2 + hM^3 + iT)} \quad (1)$$

where S = wt.% NaCl + KCl; M = wt.% $MgCl_2$; and T = dissolution temperature of halite in degrees Celsius. Values of the coefficients (a - i) are listed in Table 2. Equation (1) is valid for total salinities (NaCl + KCl) between 30 and 50 wt.%, temperatures from -19° to 316°C, and $MgCl_2$ concentrations from 0 to 10 wt.%. Equation (1) predicts total salinities with an average residual of ±0.25 wt.% and a maximum residual of 0.43 wt.%.

Table 1. Microthermometric data obtained from synthetic fluid inclusions in the NaCl-KCl-MgCl$_2$-H$_2$O system.

Sample #	NaCl wt (g)	KCl wt (g)	NaCl KCl	MgCl$_2$ (wt.%)	1	2	Tm NaCl (°C) (number)	Tm KCl (°C) (number)	Tm °C NaCl (mean)	Tm °C KCl (mean)
10694-IV	.0083	.0083	1:1	10	30.0	27.7	112-114 (8)	63-80 (8)	113	70
10694-V	.0104	.0104	1:1	10	35.0	32.6	190 (4)	89-90 (4)	190	90
10694-VI	.0104	.0104	1:1	10	35.0	32.6	174-175 (6)	86-89 (6)	174	86
10694-VII	.0129	.0129	1:1	10	40.0	37.3	236-238 (5)	117-118 (5)	238	118
10694-VIII	.0129	.0129	1:1	10	40.0	37.5	234-236 (6)	117-118 (6)	235	117
10694-IX	.0159	.0159	1:1	10	45.1	42.4	280-283 (6)	150-152 (6)	282	150
10694-X	.0159	.0159	1:1	10	45.1	42.5	280-281 (5)	149-150 (5)	280	149
10694-XI	.0194	.0190	1:1	10	49.8	47.2	315-317 (5)	181-183 (5)	316	182
032795-I	.0083	.0083	1:1	5	30.0	30.4	36 (1)	46-48 (5)	36	47
110894-III	.0102	.0103	1:1	5	35.0	33.8			120	73
032795-IIR	.0126	.0126	1:1	5	39.9	38.3	186-195 (8)	92-98 (8)	190	98
032795-IIIR	.0156	.0156	1:1	5	44.9	43.2	245-259 (8)	117-123 (8)	251	119
110894-V	.0191	.0190	1:1	5	50.1	48.8	310-313 (5)	172-173 (3)	311	173
101394-II	.0084	.0084	1:1	2	30.0	29.4	-10 - -11 (3)		-10	
011995-III	.0106	.0106	1:1	2	34.9	34.5	79 (3)	71 (3)	79	71
101394-IV	.0132	.0132	1:1	2	40.1	39.6	180-182 (5)	97 (5)	180	97
101394-V	.0162	.0162	1:1	2	45.1	44.6	243-244 (4)	127-128 (4)	243	127
101394-VI	.0198	.0198	1:1	2	50.1	49.6	289-290 (7)	159-160 (7)	289	159
101394-VII	.0198	.0198	1:1	2	50.1	49.6	295-296 (5)	160-161 (5)	295	161
032795-IV	.0241	.0241	1:1	2	55.0	54.5	329-330 (4)	175-176 (4)	330	176
calculated (3)			1:1	0	25.0				-17 ice	0
calculated (3)			1:1	0	30.0				-19.2	29
calculated (3)			1:1	0	35.0				65	65
calculated (3)			1:1	0	40.0				151	96
calculated (3)			1:1	0	45.0				230	120
calculated (3)			1:1	0	50.0				280	155
032795-VIII	.0124	.0041	3:1	10	29.9	27.7	193-203 (8)	23-54 (6)	196	23 *
102294-V	.0156	.0052	3:1	10	35.0	32.6	260-261 (5)	27-32 (5)	260	30
032795-IX	.0195	.0064	3:1	10	39.8	37.5	310-318 (5)	42 (1)	314	42
032795-X	.0237	.0079	3:1	10	45.2	42.3	260-265 (10)	50-75 (10)	363	70
102294-VI	.0290	.0097	3:1	10	50.0	47.4	388-389 (6)	83-84 (6)	389	84
032795-XI	.0121	.0041	3:1	5	30.0	28.8	132-137 (4)	16-17 (4)	134	17
011995-I	.0154	.0051	3:1	5	35.0	33.7	218-219 (6)	28 (2)	218	28
032795-XII	.0189	.0063	3:1	5	39.9	38.7	274-275 (5)	35-69 (5)	274	35 *
032795-XIII	.0232	.0077	3:1	5	45.0	42.9	326-327 (6)	48-146 (6)	327	48 *
110894-XI	.0285	.0095	3:1	5	50.0	48.0	370-385 (15)	75 (1)	375	75
032795-V	.0129	.0042	3:1	2	30.2	29.7	89-91 (4)	10 (1)	90	10
102294-II	.016	.0053	3:1	2	35.0	34.5	199 (4)	21-162 (4)	199	21 *
032795-VI	.0190	.0065	3:1	2	39.2	38.5	254-260 (6)	26-185 (6)	258	26 *
032795-VII	.0242	.0082	3:1	2	45.1	43.9	318-320 (6)	44-150 (6)	319	44 *
102294-III	.0296	.0099	3:1	2	50.0	49.6	365-368 (8)	69-185 (8)	366	69 *
calculated (3)			3:1	0	25.0				-21 ice	-21
calculated (3)			3:1	0	30.0				30	2
calculated (3)			3:1	0	35.0				180	15
calculated (3)			3:1	0	40.0				260	28
calculated (3)			3:1	0	45.0				316	45
calculated (3)			3:1	0	50.0				365	60

1 - (NaCl+KCl / NaCl+KCl+H$_2$O) x 100
2 - (NaCl+KCl / NaCl+KCl+MgCl$_2$+H$_2$O) x 100
3 - calculated data were obtained, using equations in (6)
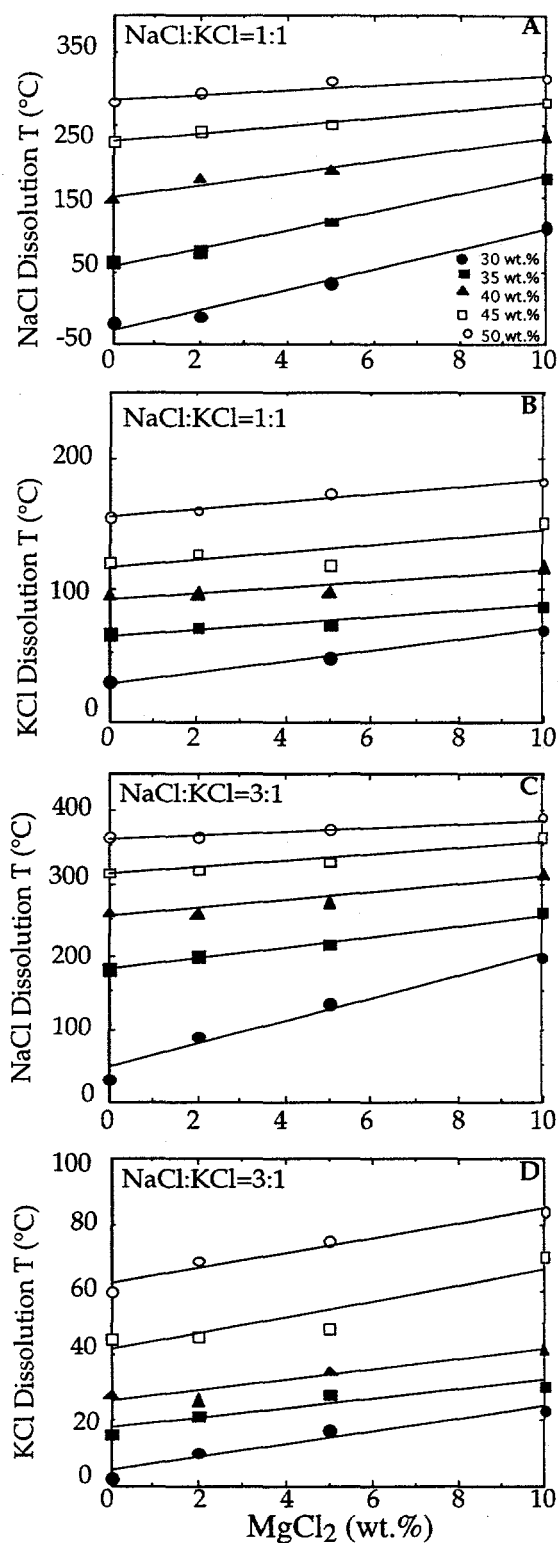* minimum values

Figure 1. Solubilities of halite (A, C) and sylvite (B, D) in the NaCl-KCl-MgCl$_2$-H$_2$O quaternary system for NaCl:KCl ratios of 1:1 (A, B) and 3:1 (C, D) as a function of total salinity and MgCl$_2$ concentration.
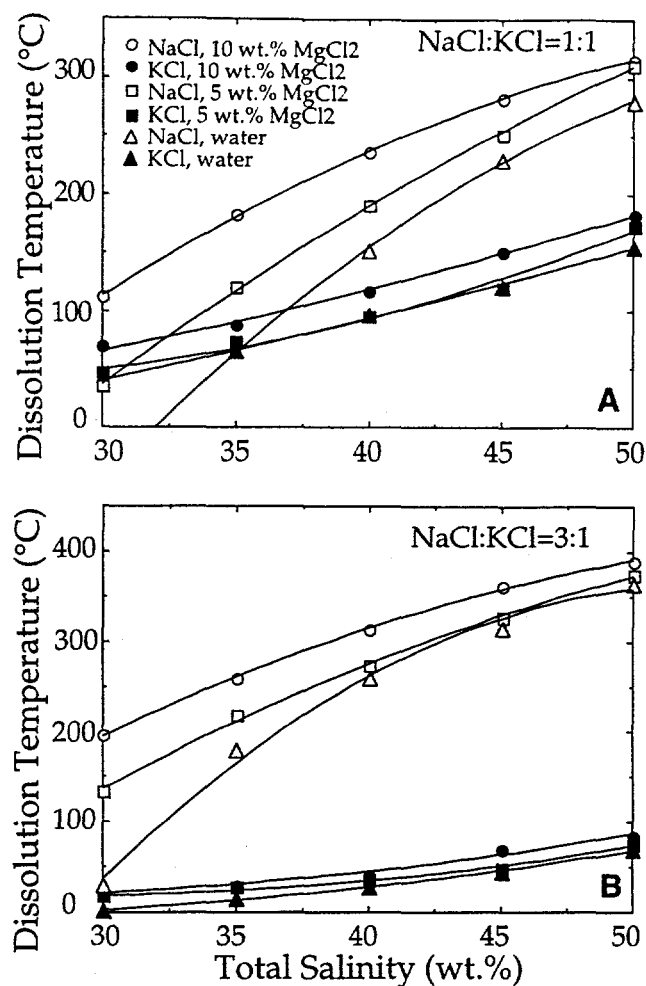

Figure 2. Solubilities of halite and sylvite in the NaCl-KCl-MgCl$_2$-H$_2$O quaternary system for NaCl:KCl ratios of 1:1 (A) and 3:1 (B) as a function of total salinity and MgCl$_2$ concentration.

The sylvite solubility surface in the NaCl-KCl-MgCl$_2$-H$_2$O quaternary system with NaCl:KCl = 1:1 is given by:

$$S = a + bM^{1.5} + cT \qquad (2)$$

where S = wt.% NaCl + KCl; M = wt.% MgCl$_2$; and T = dissolution temperature of sylvite. Values of the coefficients (a - c) are listed in Table 2. Equation (2) is valid for total salinities (NaCl + KCl) between 30 and 50 wt.%, temperatures between 29° and 182°C, and MgCl$_2$ concentrations from 0 to 10 wt.%. Equation (2) predicts total salinities with an average residual of ±0.59 wt.% and a maximum residual of 2.3 wt.% at 119°C.

Table 2. Fitting coefficients for Equations 1 - 4

Coefficient	Equation 1	Equation 2	Equation 3	Equation 4
a	31.23121762	24.56279446	29.29891476	27.8128784
b	0.361953881	-0.14535233	-2.44332121	-2.06728823
c	-0.3304612	0.165011651	0.375081441	0.70441812
d	0.01640298		-0.02266454	
e	0.0178677322		-0.00595165	
f	0.019555796		0.000068065	
g	-0.00808785		-0.0525118	
h	0.000401365		0.008780158	
i	-0.00097248		-0.00050141	
j			-0.00074914	

Figure 3. Halite (top shaded surface) and sylvite (bottom surface) vapor-saturated solubility surfaces in the NaCl-KCl-MgCl$_2$-H$_2$O quaternary system for NaCl:KCl = 1:1, calculated using equations (1) and (2). The halite surface describes NaCl solubility between -19° and 316°C. The sylvite surface describes sylvite solubility from 29° to 182°C. Point "a" (65°C and 35 wt.%) is the cotectic in the NaCl-KCl-H$_2$O ternary system; points "b" (60°C and 33.5 wt.%) and "c" (54°C and 30.8 wt.%) are the cotectics in the NaCl-KCl-MgCl$_2$-H$_2$O quaternary system at 2 wt.% and 5 wt.% MgCl$_2$ concentrations, respectively. Temperatures and compositions along the cotectic were determined by simultaneous solution of the two solubility equations. Temperatures corresponding to the points on the 0 and 10 wt.% MgCl$_2$ projections represent the actual dissolution temperatures of halite and sylvite obtained from synthetic fluid inclusions.
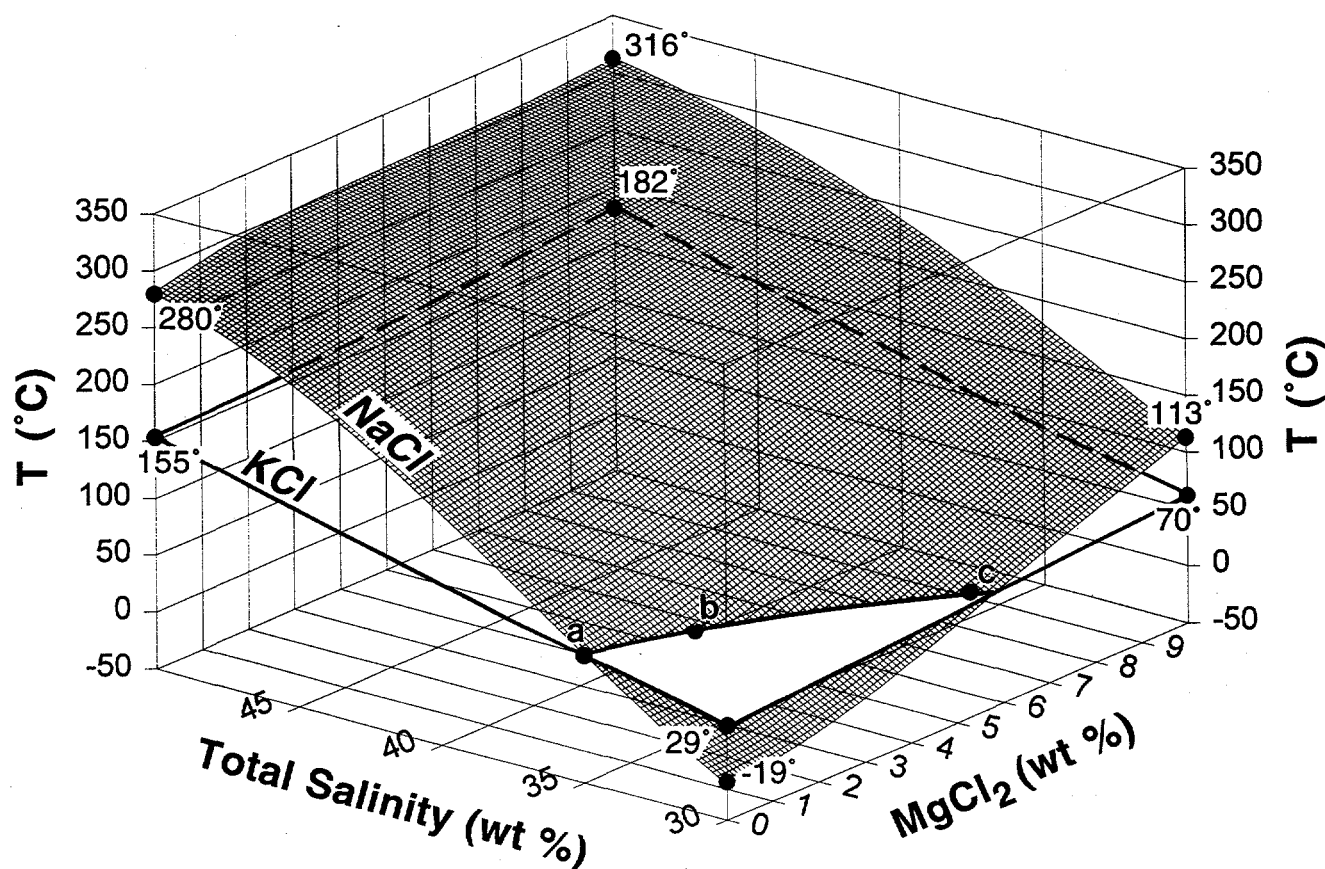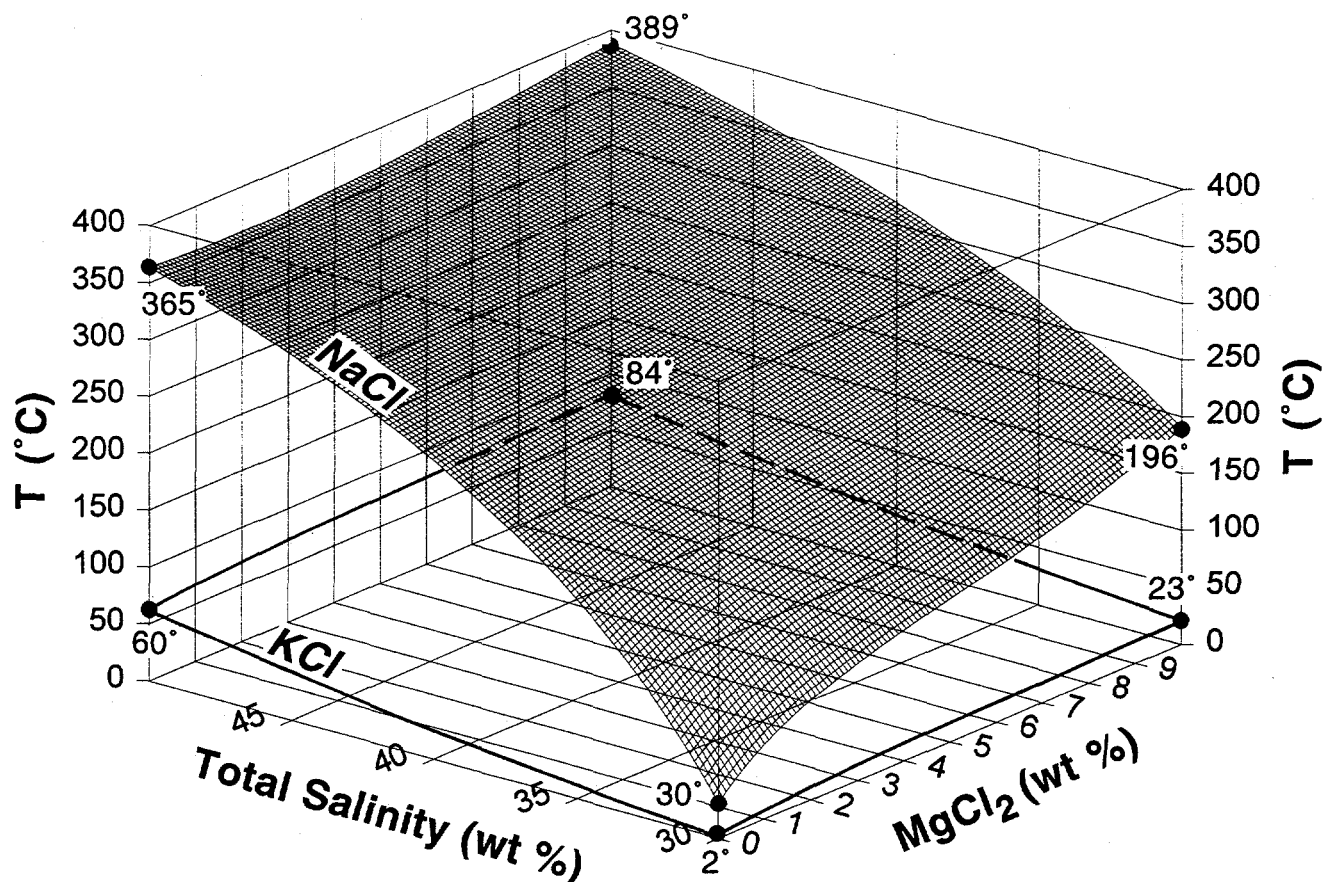
Figure 4. Halite (top shaded surface) and sylvite (bottom surface) vapor-saturated solubility surfaces in the NaCl-KCl-MgCl₂-H₂O quaternary system for NaCl:KCl = 3:1, calculated using equations (3) and (4). The halite surface describes NaCl solubility between 30° and 389°C. The sylvite surface describes KCl solubility from 2° to 84°C. Temperatures corresponding to the points on the 0 and 10 wt.% MgCl₂ projections represent the dissolution temperatures of halite and sylvite obtained from synthetic fluid inclusions.

The halite solubility surface in the NaCl-KCl-MgCl₂-H₂O quaternary system with NaCl:KCl = 3:1 is given by:

$$S = \frac{(a + bM + cM^2 + dM^3 + eT + fT^2)}{(1 + gM + hM^2 + iM^3 + jT)} \quad (3)$$

where S = total salinity (wt.% NaCl + KCl); M = wt.% MgCl₂; and T = dissolution temperature of halite. Values of the coefficients (a - j) are listed in Table 2. Equation (3) is valid for total salinities from 30 to 50 wt.%, temperatures from 30° to 389°C, and MgCl₂ concentrations from 0 to 10 wt.%. Equation (3) predicts total salinities with an average residual of ±0.23 wt.% and a maximum residual of 0.63 wt.% at 360°C.

The sylvite solubility surface in the NaCl-KCl-MgCl₂-H₂O quaternary system with NaCl:KCl = 3:1 is given by:

$$S = a + bM^{0.5} + cT^{0.5}\ln T \quad (4)$$

where S = total salinity (wt.% NaCl + KCl); M = concentration of MgCl₂ (wt.%); and T = dissolution temperature of sylvite. Values of the coefficients (a - c) are listed in Table 2. Equation (4) is valid over the salinity range 30 - 50 wt.%, for temperatures from 2° to 84°C, and for MgCl₂ concentrations from 0 to 10 wt.%. Equation (4) predicts total salinities with an average residual of ±0.91 wt.% and a maximum residual of 2.9 wt.% at 48°C.

Halite and sylvite solubility surfaces as a function of temperature, total salinity, and MgCl₂ concentrations are shown on Figures 3 and 4. For solutions with NaCl:KCl = 1:1 (Figure 3), the halite-sylvite cotectic (a - b - c on Figure 3) defines the locus of temperature, total salinity, and MgCl₂ concentrations at which the solution is

saturated in both halite and sylvite. As shown on Figure 3, the cotectic for solutions with NaCl:KCl = 1 moves to progressively lower total salinities as the $MgCl_2$ concentration increases. For solutions with NaCl:KCl = 3:1 (Figure 4), the halite-sylvite cotectic is not intersected over the range of temperatures and compositions studied here.

For both the NaCl:KCl = 1:1 and 3:1 solutions, the temperature of dissolution of halite along an isopleth increases with increasing $MgCl_2$ concentration, although the effect is much more pronounced at 30 wt.% total salinity than at 50 wt.% total salinity. The increase in sylvite dissolution temperature along an isopleth is much less than for halite although, as with halite, the effect is more pronounced at lower salinities than at higher salinities.

Summary

Experiments have been conducted to determine the effect of $MgCl_2$ on the solubilities of halite and sylvite in the quaternary system H_2O-NaCl-KCl-$MgCl_2$. The data indicate that solubilities of both NaCl and KCl decrease as $MgCl_2$ is added to the system, although the solubility of NaCl is affected more than that of KCl. For both NaCl and KCl, the effect of $MgCl_2$ on solubility is greater in low-salinity (30 wt.% total salt) than in higher-salinity (50 wt.% total salt) solutions. Solubilities of three industrial salt cakes were found to be adequately represented by the H_2O-NaCl-KCl-$MgCl_2$ system.

Acknowledgment

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