Part 2 Calcium Chloride

GEOLOGY

Calcium is one of the most common elements found in nature, occurring most frequently in gypsum or anhydrite, and also in many other rocks and minerals and as one of the common ions in water and many brines. However, calcium in the form of calcium chloride is relatively uncommon. The only calcium chloride mineral that is found in massive quantities is the double salt tachyhydrite ($CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$), occurring in three large potash deposits and as isolated crystals in a few other locations. Only one other mineral is known, antarcticite ($CaCl_2 \cdot 6H_2O$), which is exceedingly rare and only crystallizes in relatively small quantities in one Antarctic pond and in one desert lake (Dunning and Cooper, 1969; Torii and Ossaka, 1965). It has been speculated to be present as isolated crystals in a few other locations such as in the occlusions of some minerals, and small amounts of calcium chloride tetrahydrate ($CaCl_2 \cdot 4H_2O$; sergipite?) may possibly occur in the Sergipe tachyhydrite deposit (Sonnenfeld and Kuehn, 1993). Calcium chloride brines on the earth's surface are almost as rare, only being found in one pond and two dry lakes as a strong $CaCl_2$ brine, but there are several lakes with dilute $CaCl_2$ brines, several with $CaCl_2-MgCl_2$ brines, and a modest number of dilute $CaCl_2$ springs (Stankevich *et al.*, 1992; Shearer, 1978).

In contrast to this scarcity on the earth's surface, calcium chloride brines are frequently found in several types of underground, and one type of undersea formations. Most potash and some halite formations are associated with strong calcium chloride brines. They are found in porous strata either below, adjacent to, or above the deposits, gradually becoming more dilute if they approach the surface, and modified somewhat in proportion to their distance from the potash or salt deposit. They were formed by a "dolomitization reaction" with calcite and the high-magnesium chloride end liquor (or carnallite [$KCl \cdot MgCl_2 \cdot 6H_2O$] decomposition brine) from the potash (or other highly evaporated brine) deposits (Garrett, 1996).

Dilute calcium chloride brines are also occasionally found in coastal aquifers, and some oil or gas formation waters that have been formed from seawater by the same dolomitization reaction supplemented by the leaching of certain types of rocks. In addition, many deep sea geothermal vents contain calcium chloride that appears to have been formed by both the dolomitization process and extremely hot seawater or brine reacting with basalt or other rocks. Because of the acidic nature of the calcium chloride brines, they usually have been modified by the products of various other brine–rock reactions, and occasionally from Na/K-for-Ca ion exchange with clays or zeolites (Sanford *et al.*, 1992; Lebedev, 1969). The occlusion or fracture waters in some hard-rock mineral deposits (and some other geologic formations) also contain a calcium chloride solution that may have been formed by the same reactions, or have been an original magmatic fluid. These various calcium chloride occurrences will be discussed in more detail in the following sections.

Calcium Chloride Dolomitization Brine

As seawater (and many non-marine waters) evaporate, calcium carbonate is the first major mineral deposited, and it thus is present in large quantities under or adjacent to any halite and potash deposit. In addition, since fresh seawater periodically flooded into the evaporating halite or potash basins, some calcite is present in, and usually over the deposit. Gypsum and then salt crystallize next in the seawater evaporation sequence, and finally potash, which theoretically crystallizes first as leonite ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$), then schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), kainite ($KCl \cdot MgSO_4 \cdot 2.75H_2O$) and finally as carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). The first two potash salts are either minor occurrences, or do not form at all, and the first three are usually converted by stronger brines (from continued evaporation) into carnallite. It, in turn is usually converted to sylvite (KCl) by later being leached with a slightly more dilute brine ($H_2O + KCl \cdot MgCl_2 \cdot 6H_2O$[carnallite] → KCl[sylvite] + [$MgCl_2 + 7H_2O$][brine]). Both the evaporation and carnallite conversion produce a strong magnesium chloride end liquor that could be flushed away, but usually slowly seeped through the deposit. During this seepage, high-calcium chloride brines were then formed by the partial-to-complete dolomitization reaction of the end liquors with the basins' abundant calcite:

$$MgCl_2(\text{in brine}) + 2CaCO_3(\text{calcite}) \rightarrow CaCl_2(\text{brine}) + CaCO_3 \cdot MgCO_3(\text{dolomite}).$$

If there was a large excess of magnesium chloride, or the brine was very hot, the final product could be magnesite ($MgCO_3$). Much of the impurities in the calcite (if any) such as strontium, barium and manganese would also be reacted (Ayora *et al.*, 2001; Vlasova and Valyashko, 1980). To a much lesser extent, calcium chloride may also be formed by reactions to produce other seawater salts, polyhalite or glauberite:

$$\begin{aligned}&(\mathrm{MgCl_2} + 2\mathrm{KCl} + 2\mathrm{H_2O})(\text{brine}) + 4\mathrm{CaSO_4}(\text{anhydrite})\\&\quad\rightarrow \mathrm{K_2SO_4{\cdot}MgSO_4{\cdot}2CaSO_4{\cdot}2H_2O}(\text{polyhalite}) + 2\mathrm{CaCl_2}(\text{brine}),\end{aligned}$$

and

$$\begin{aligned}&(\mathrm{Na_2SO_4} + 2\mathrm{NaCl})(\text{brine}) + 3\mathrm{CaSO_4{\cdot}2H_2O}(\text{gypsum})\\&\quad\rightarrow 2\mathrm{Na_2SO_4{\cdot}CaSO_4}(\text{glauberite}) + (\mathrm{CaCl_2} + 4\mathrm{H_2O})(\text{brine}).\end{aligned}$$

The extent of each reaction gives the converted brine a variable calcium chloride concentration, depending upon the amount of calcite (or gypsum) contacted. In addition, both the high-$MgCl_2$ and high-$CaCl_2$ brines are acidic, and they usually react to some extent with the surrounding rocks. They may also be diluted by groundwater, and if they encounter a high-sulfate water gypsum (or anhydrite) would precipitate (Poroshin, 1981).

Seawater contains 4.4 times as much $MgCl_2$ as KCl, and most of the $MgCl_2$ does not remain with the potash or halite deposits. Epsomite ($MgSO_4{\cdot}7H_2O$) is the first of the magnesium salts to crystallize, (it deposits with the late-stage halite) and it is almost always leached, or later converted to gypsum or anhydrite. Kainite ($KCl{\cdot}MgSO_4{\cdot}2.75H_2O$) is only a major component in very few potash deposits, but carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) is much more common. However, in both cases the amount of magnesium that is present in most deposits is far less than the seawater ratio of magnesium to potassium or halite. It is likely that only at the end of deposition could much of the magnesium chloride be flushed away from the depositing salts, so consequently in almost all of the deposits most of the magnesium must have been removed from the formation as an end liquor which seeped away, and thus formed these massive dolomitization brine aquifers.

As noted above, this type of brine is by far the most common calcium chloride occurrence, and it accompanies most of the world's potash, and some of the late-stage halite deposits that contain up to ~200 ppm bromine (indicating that the seawater evaporation extended to the point of forming a strong [$>16\%$ $MgCl_2$] end-liquor and almost producing potash; Table 2.1). This end liquor often accumulated in porous strata below or adjacent to the deposit, and perhaps was later forced into strata in and above the potash or halite as the sediments were compacted. Typical analyses of seawater at various stages of evaporation are listed in Tables 2.1 and 2.2, and compared with the formation fluids and occlusions actually found in a halite deposit adjacent to potash. The formation fluids are usually somewhat of an average of the end liquor formed between halite's initial crystallization and the first kainite that deposited. However, as with most formation waters, there has been some dilution, and in some cases, such as the Carlsbad example of Table 2.2, it apparently came from a geothermal source supplying additional boron and iodine. The adjacent Carlsbad potash deposit

Table 2.1

The Composition of Sea Water End Liquor at Various Stages of Evaporation (wt.%) (Garrett, 1996)

	Data from small experimental ponds					Brine in Carlsbad, New Mexico Halite[a,b]	
				Carnallite			
	First NaCl	First $MgSO_4$	First kainite	First	Last	Average	Range
Na	8.68	6.10	1.65	0.59	0.24	8.10	5.08–9.87
K	0.31	0.79	2.00	1.70	0.52	1.76	1.51–2.27
Mg	1.04	2.64	5.90	6.90	7.80	2.25	1.62–4.43
Cl	15.60	15.10	15.20	17.70	20.50	18.98	17.30–20.20
SO_4	1.53	3.70	6.20	4.70	3.60	1.94	1.52–3.31
Br[c]	535	1350	3460	4580	5520	1547	1280–2410
B[c]	38	96	244	326	392	1716	1420–1888
I[c]	0.49	1.3	3.2	4.2	5.1	16.7	12.2–21.0
Ca[c]	338	166	—	—	—	310	260–381
Sr[c]	6.7[d]	3.3[d]	—	—	—	2.35	0.87–6.90
TDS	27.26	28.56	32.90	33.10	33.30	30.57	27.30–31.90
Density	1.219	1.245	1.313	1.326	1.340	1.223	1.21–1.25
pH	—	—	—	—	—	6.04	5.6–6.4
Concentration ratios[e]	8.1	20.6	52.5	70	84	23.7	20–37

(*continues*)

Table 2.1

(continued)

				Carnallite			
	First NaCl	First $MgSO_4$	First kainite	First	Last		
Bromine in the crystals of:[c]						*In actual deposits*	
Halite	29	85	190	250	300	35–100[b]	20–450[f]
Sylvite	—	—	2500	3300	4000	—	250–4000
Carnallite	—	—	—	2400	2900		340–3460
Rubidium in the crystals of:							
Kainite			—	—	—	20	10–60
Sylvite			—	—	—	50	10–480
Carnallite			—	—	—	430	60–1900

[a] Abitz *et al.* (1990).

[b] Deposits with no potash.

[c] In ppm.

[d] Estimate.

[e] Concentration factor based upon bromine (multiple of the original sea water concentration).

[f] Deposits with potash.

Table 2.2

Examples of Potash Deposit Dolomitization Brine (Garrett, 1996)

(A) Average brine analyses in the Starobin Deposit's overlying formations (mg/liter) (Zatenatskaya *et al.*, 1968)

Depth (m)	SO_4	Cl	HCO_3	Ca	Mg	Salinity (g/liter)	pH
170.8[a]–203	65	88	164	60	14	0.45	7.0
220.5[a]–236	616	562	101	156	86	1.88	7.0
260[a]–335	3900	3180	91	482	284	10.9	6.8
344.4[a]–386	7130	7890	251	740	469	23.5	7.2
412[a]	9590	83,500	110	1430	966	151.5	7.1
428.5[b]–517.5	5720	178,000	0	2100	1110	301	6.0
542.2[b,c]–781	860	257,000	455	95,300	17,600	408	—

(B) Brine analyses in clays within and near the Stebnik deposit (g/kg) (Valyashko *et al.*, 1973)

Ca	SO_4	Cl	Br	Mg	Na	K	Total salts	Density (g/ml)
(1) Brines within the Deposit (Sea water end liquor)								
Tr.	3.37	192.1	2.86	47.1	21.8	26.2	293.5	1.25
Tr.	14.23	181.7	2.50	46.8	22.2	23.8	291.2	1.25
0	25.78	200.8	2.82	65.0	17.9	10.1	322.3	1.277
(2) Brines near the Deposit (dolomitization brine)								
51.3	0.40	192.6	3.83	20.1	18.7	18.5	305.7	1.273
62.0	0.10	189.0	4.40	15.90	17.2	9.3	298.1	1.258

(C) Brine analyses in clays within the Prypat and lrkutsk deposits (g/kg) (Azizov, 1974)

Deposit	SO_4	Cl	Br	Ca	Mg	Na	I (in ppm)	K	Sr	Total salts	Density (g/ml)	pH
Pripyat	0.08	171.2	2.32	49.5	5.3	39.6	46	66.7	1.48	284	1.24	6.4
lrkutsk	0.71	264.7	5.73	118.1	11.4	7.9	2	15.2	4.24	425	1.41	4.6

(*continues*)

(D) Analyses of a brine pocket in Zechstein A-1 anhydrite (adjacent to Ca2 dolomite; 408 m depth; Norwegian–Danish Basin) (wt.%) (Fabricus, 1983)

NaCl	KCl	$CaCl_2$	$MgCl_2$	Salinity	pH
3.95	3.55	15.15	8.10	31	3.18

(E) Brine analyses near the Paradox Basin potash deposit (ppm) (Mayhew and Heylmun, 1966)

Mississippian Formation

	Ca	Na	Mg	Cl	SO_4	Br	Fe	TDS	pH
Average	4560	120,100	2870	191,600	5090	240	550	319,300	5.5
Range	240–12000	110,000–140,000	270–7500	153,000–220,000	1800–7400	—	90–1000	252,000–374,000	4.6–6.7

Paradox Formation

	Ca	Na	Mg	K	Li	Cl	Br	SO_4	HCO_3	B	TDS	pH
Low average	5030	22,200	4300	21,400	66	120,900	1320	255	208	702	274,668	4.9
High average	42,700	99,900	32,900	52,500	173	217,200	2660	4390	1260	1630	38,2651	6.2

Also present in some samples

Sr	PO_4	NH_4	Fe	F	I	Mn	Rb	Al	Zn	Cs	Cu	Pb	Ba
1300	1010	850	750	280	264	260	95	66	60	16	6	6	0

(F) Salt Range, Dhariala, Pakistan (Gill and Akhtar, 1982). Well at 1200 m depth, flowing at 1,500 bbls/hr at 721 psi. Similar brine at 1347 m and 2439 m depth

	$CaCl_2$	$MgCl_2$	KCl	NaCl
Average (wt.%)	4.6	16.5	6.7	5.7

[a] Siltstone.

[b] Argillaceous marl.

[c] Halite with seams of marl and sylvite from 525–1262 m (bottom of drill hole).

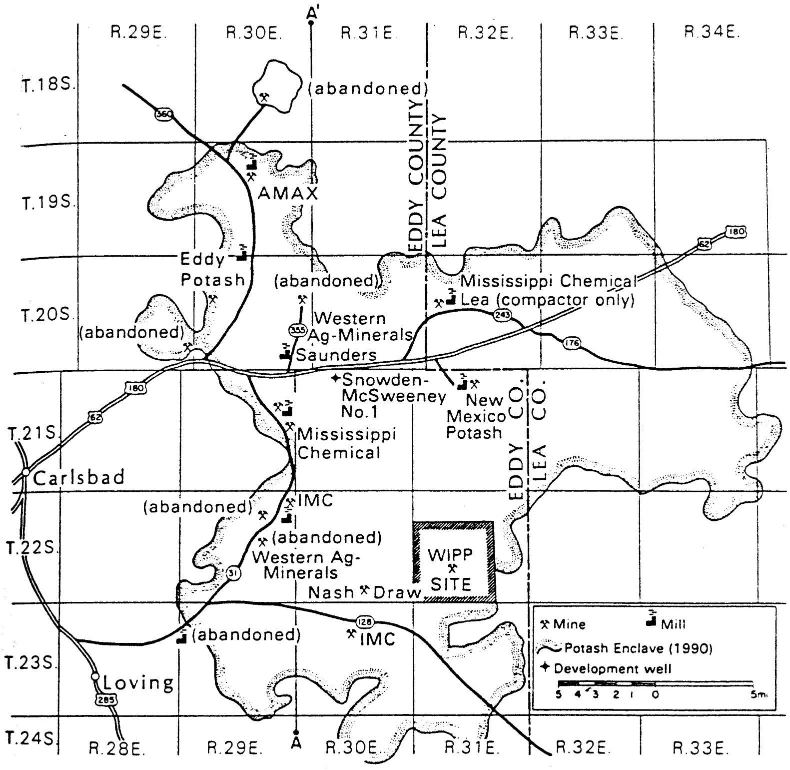


Figure 2.1 Map of the Carlsbad, New Mexico potash deposit (Austin and Barker, 1990; reprinted by permission of the Society of Economic Geologists).

(Fig. 2.1) is known to have had a geothermal input because of its high-temperature minerals (such as langbeinite, $K_2SO_4{\cdot}2MgSO_4$), and various heavy metal impurities. Similar formation and occlusion brine analyses in Carlsbad halite have been given by Stein and Krumhansl (1988) and others, in halite near the Stebnik (Table 2.2) and in the Pripyat Deep, Russian potash deposits by Valyashko *et al.* (1973) and Poroshin (1981), respectively, and in other deposits by many authors. The diluted dolomitization brine may also have later dissolved varying amounts of halite, potash or other soluble salts that it encountered.

Several examples of the dolomitization brines that have been formed from these end liquors are listed in Tables 2.2 and 2.3. In some areas, such as the Michigan (Figs. 2.2–2.4) and Paradox Basins (Fig. 2.5) in the United States, most of this brine appears to still be very near the potash/halite deposits, while in others its former presence is well documented (e.g., in Saskatchewan; Fig. 2.6; Table 2.3) but much of it has migrated some distance away or has escaped.

Table 2.3

Average Brine Analyses Encountered in Saskatchewan Potash Mines, (mg/liter)[a] (Garrett, 1996)

Mine, sample location	Depth (m)	δD	$\delta^{18}O$	Cl	Na	K	Ca	Mg	Br	I	SO_4[b]	HCO_3	pH	Density
Recent glacial drift	61–73	−147	−19.1	888	1300	84	28	10	6.5	18.5	1460	311	7.4	0.997
Upper section of shafts	250 (122–378)	−128	−16.1	2430	3950	44	145	41	54	59	5350	151	7.65	1.001
Average	220	−138	−17.6	1660	2630	64	137	26	30	39	3410	231	7.5	0.999
Rocanville Shaft	486–572	−126	−14.8	29,300	16,800	256	1089	647	110	23	—	100	7.0	1.032
Cory Shaft	524–673	−127	−15.4	30,900	19,600	958	2177	681	175 (1 at 12.900)	16	—	151	7.1	1.036
Allan Shaft	610–774	−138	−17.5	41,900	27,800	1406	2200	448	223	18 (1 at 155)	—	100	7.4	1.050
Average	630	−130	−15.9	34,000	21,400	873	1820	592	169	19	6220	117	7.2	1.039
Rocanville Shaft	604–890	−70	−4.1	159,000	108,000	1830	4320	1530	1250	74	—	64	6.7	1.166
Allan Shaft	823–860	−116	−13.5	171,000	122,000	1990	5210	2420	1670	112	—	(18)	6.2	1.194
Cory Shaft	647–975	−103	−9.0	182,000	88,600	1590 (1 at 16,300)	(21,930)	4680 (1 at 28,400)	1820 (1 at 21,700)	108 (1 at 508)	(4000)	160 (1 at 1464)	6.7 (1 at 5.7)	1.158
Average	790	−96	−8.7	171,000	106,000	1800	4770	2880	1580	98		81	6.8	1.173
Cory Shaft	930	−98	−8.8	218,000	55,500	6700	59,600	11,000	4080	302	—	128	5.8	1.229
Rocanville Shaft	1200	−94	−6.5	222,000	84,600	48,800	7090 (1 at 18,900)	9770	4650	82		63	5.2	1.232
Average	1065	−96	−7.7	220,000	70,000	27,800	33,300	10,400	4370	192	250	96	5.5	1.231

(*continues*)

Table 2.3

(*continued*)

Mine, sample location	Depth (m)	δD	$\delta^{18}O$	Cl	Na	K	Ca	Mg	Br	I	SO_4[b]	HCO_3	pH	Density
Lanigan Mine	1200	− 88	− 7.8	274,000	11,100	12,300	6110	85,600	8920	65	(1200)	(73)	4.6	1.257
Allan Mine	1200	− 60.5	− 3.15	293,000	11,900	31,300	37,000	113,000	4070	—	(750)		4.3	1.280
Average	1200	− 74	− 5.5	284,000	11,500	21,800	21,600	99,300	6500	65		(73)	4.45	1.269
Lanigan Mine	1200	− 62	− 3.9	325,000	2750	7100	141,000	782	20,500	782	—	—	4.4	1.286
Cory Mine	1200	− 62	− 1.85	338,000	4620	15,700	152,100	21,400	19,400	406	—	138	4.4	1.351
Average	1200	− 62	− 2.9	332,000	3690	11,400	147,000	11,100	20,000	594	(300)	138	4.4	1.319

Values in parenthesis imply limited number of analyses or data; not considered in the average. Reproduced from Potash; Deposits, Processing, Properties and Uses, Table 1–7, pages 51–52, ©1996 with kind permission of Kluwer Academic Publishers.

[a] Wittrup and Kyser (1990).

[b] Calculated by ion balance difference.

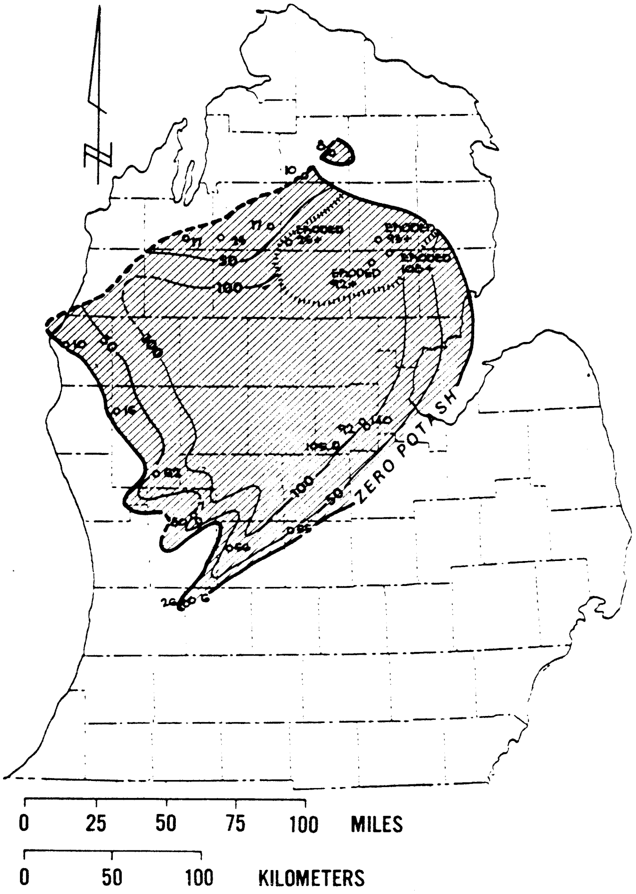


Figure 2.2 Estimated area and thickness of the Michigan Basin potash deposit (Matthews and Eagleson, 1974, courtesy of the Northern Ohio Geological Society).

The dolomitization reaction had been observed to take place relatively rapidly and completely in modern evaporating seawater tidal flats when calcite sand or mud is present, the brine had evaporated to a fairly high strength, and the brine pool was quite warm (Levy, 1977; Kinsman, 1966; others). Normally, however, for seawater or similar low-concentration brines, the dolomitization reaction appears to take place only at very high temperatures (e.g., deep sea vents), or with exceedingly long residence times and some temperature elevation (e.g., in some coastal aquifers or oil field brines).

For the more concentrated calcium chloride brines associated with potash or late-stage halite deposits, there is also usually a very direct correlation between dolomite formations and the calcium chloride brine. An example of this is with

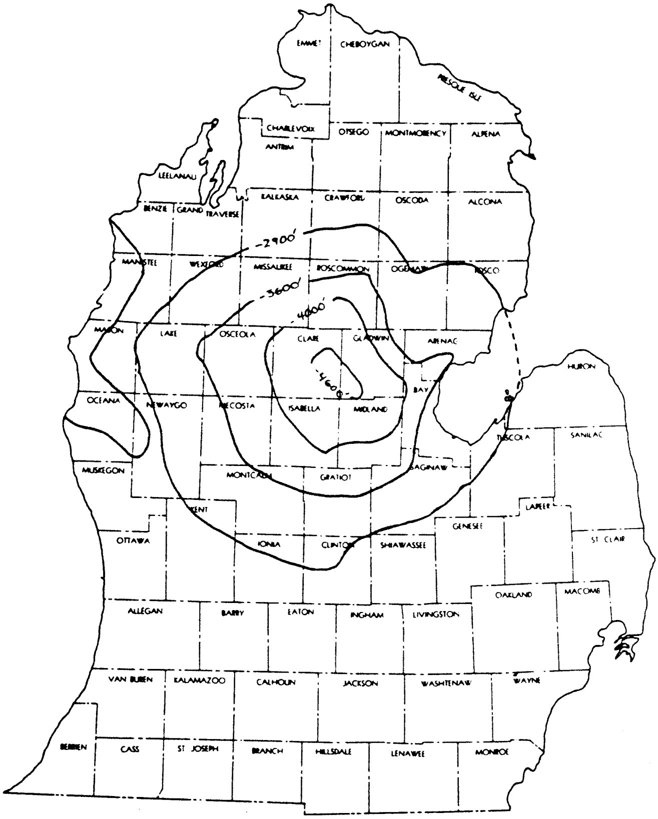


Figure 2.3 Area of the Detroit River brine aquifers, and depth to the top of the formation (Sorensen and Segall, 1974, courtesy of the Northern Ohio Geological Society).

the very large Paradox Basin halite and potash deposits in the south-central section of the United States (Fig. 2.5; Utah, Colorado and New Mexico), where most of the original calcite layers in the deposit have been converted to dolomite. In addition, the brine occlusions in secondary halite is of the calcium chloride type (Hite, 1983). This very large deposit generated massive amounts of calcium chloride brine, found primarily in various porous strata under or near the deposit, but some of the high-$CaCl_2$ aquifers are scattered over a great distance. The brine's concentration and composition vary widely, depending upon the extent of dolomitization, its mixing with other waters, and the leaching of other minerals. As with most other calcium chloride brines, there are a large number of minor elements present (Table 2.2).

It is also not uncommon for the dolomitization brine to have been forced into porous formations in or above the potash or halite deposits, as indicated by

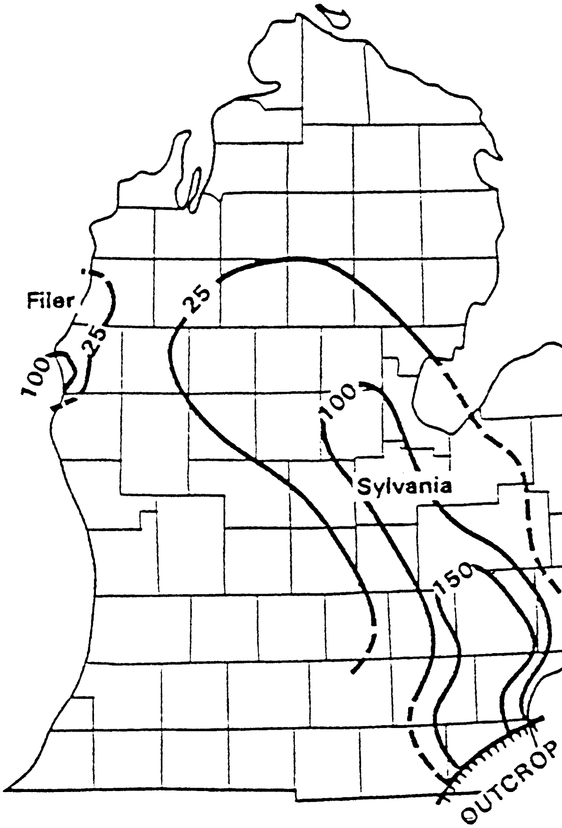


Figure 2.4 Area of the Sylvania and Filer Sandstone aquifers, and their thickness (Pavlick, 1984).

the Michigan Basin in the United States (Table 2.4), the Starobin deposit in Russia (Table 2.2), and the gigantic Saskatchewan potash deposit in Canada (Table 2.3). In these cases, there is almost always a progressive dilution of the brine with meteoric water as it is found in shallower aquifers, and the sulfate content in near-surface water is greatly diminished because of increased reaction with the brine's calcium ions. Also, the isotopic signature of the water and various ions gradually changes from being predominately of a marine to a meteoric source. When the dolomitization brine is found in halite or sylvite occlusions, these minerals are always secondary, and have been recrystallized after the dolomitization brine was forced back up through the deposit. In a similar manner, when it is found within the deposit's void spaces, there also always is a progressively more dilute dolomitization brine at the higher elevations.

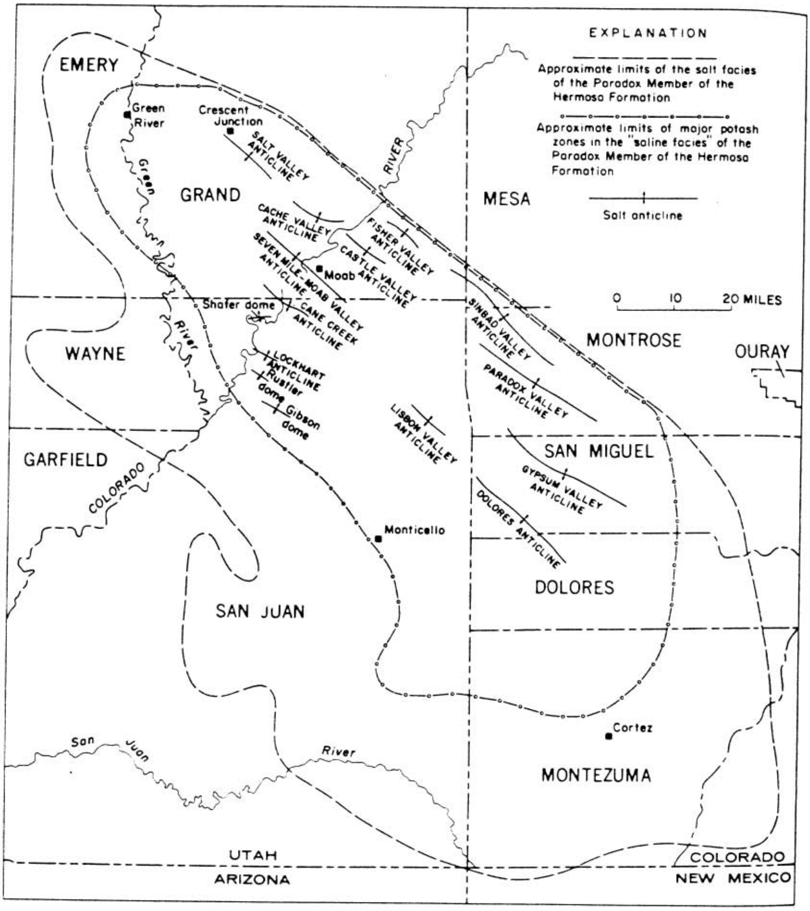


Figure 2.5 Map of the Potash and Halite Deposits in the Paradox Basin (Hite, 1961; reprinted by permission of the United Nations Economic and Social Commission for Asia and the Pacific).

Michigan, USA Brines

This very large halite/potash deposit has many aquifers that contain a high-calcium chloride brine (Table 2.4; Figs. 2.3 and 2.4) both above and below the Silurian Salina Group's halite (NaCl) and 33,700 km^2 (13,000 mi^2) potash (sylvinite, a mixture of NaCl and KCl) deposits. The major aquifers are the overlying Devonian carbonate and sandstone beds, but there are also many lesser aquifers (Fig. 2.7). There is an extensive area of strong calcium chloride brine directly over the potash deposit and extending to the south southeast (Fig. 2.4) in the first porous bed above the potash (the Sylvania Sandstone Formation) that is at

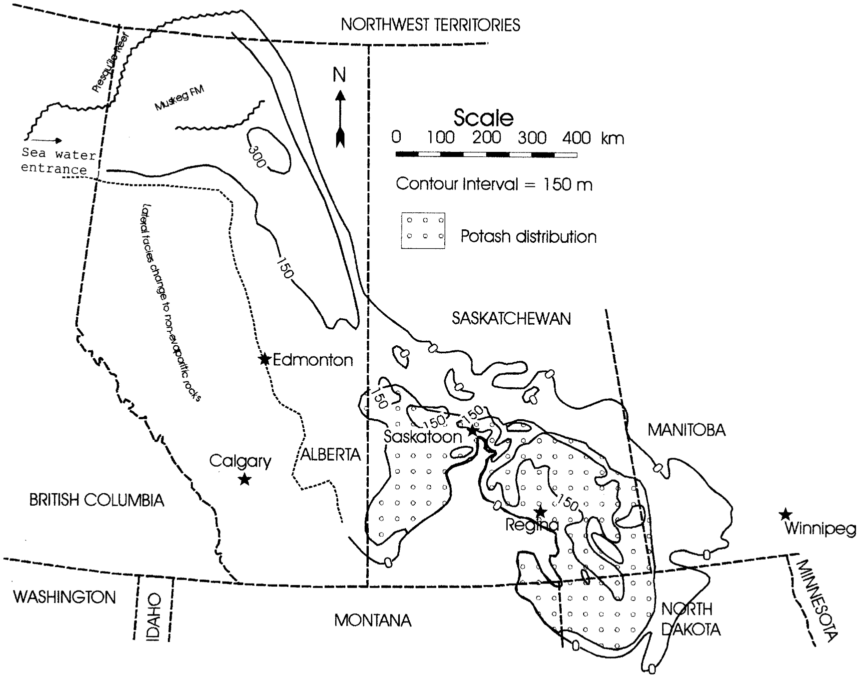


Figure 2.6 Map of the Prairie Evaporite Formation and the Saskatchewan Potash Deposit (After Fuzesy, 1982; reprinted courtesy of the Saskatchewan Department of Energy and Mines).

nearly the same concentration as potash end liquor. The small Filer Formation of sandstone to the northwest contains a similar, but slightly more dilute brine. Several thinner and less abundant aquifers also occur under the potash beds with equally strong, or stronger calcium chloride brines (Table 2.4).

Each of the aquifers have roughly the same ratio of salts, but as they approach the surface become progressively more dilute. It would thus appear that in this basin, the potash end liquor that originally seeped through and under the potash deposit (and reacted with calcite) was much later forced from its original sediments as they were compressed by deep burial (perhaps aided by the thick glacial ice that formed over this basin) into the overlying porous strata. Their variable mineral content, as seen in Table 2.4, resulted from their considerably different migration history and variable dilution by meteoric or other groundwater (as is strongly indicated by the brine's deuterium and ^{18}O analyses), precipitation (such as gypsum), and their different contact with rocks that they could partially leach or react with. However, in this basin these reactions were limited, since the porous (average ~20%) carbonate strata contains fairly pure carbonates, and the sandstone strata fairly pure silica (quartz arenites) cemented by dolomite

Table 2.4

Brine Analyses in Various Michigan Aquifer Formations

(A) The major calcium chloride formations (wt.%) (Pavlick, 1984)

	Formation (increasing depth →)						
	Parma	Marshall	Berea	Traverse	Dundee	Sylvania	Filer
NaCl	15	13	20	10	13	5	2
$CaCl_2$	0.5	10	4	15	9	19	17
$MgCl_2$	0.5	3.5	2	3	2.6	3.6	10
Br	0.05	0.15	0.1	0.2	0.1	0.26	0.25
I (ppm)	nil	nil	3	20	5	30	nil

(B) Range of concentrations, wt.% (McKetta and Cunningham, 1975)

$CaCl_2$	NaCl	$MgCl_2$	KCl	Br_2
2–23	2–20	2–4	1–2	0.1–0.3

(C) Sylvania Formation (wt.%)

(1) Egleson and Querio (1969)

							ppm							
	$CaCl_2$	NaCl	$MgCl_2$	KCl	$SrCl_2$	Br	NH_3	LiCl	B	SO_4	I	Rb	TDS	Density
Average	20.09	5.33	3.61	1.52	0.56	0.281	398	351	273	44	34	15	31.50	1.2914
Range	19.88–20.75	4.82–5.65	3.40–3.83	1.08–1.80	0.52–0.64	0.259–0.293	250–488	220–440	236–410	36–54	18–46	10–19	30.6–33.1	1.2788–1.2959

(2) Sylvania and Filer Formations (Wilson and Long, 1992)

						ppm			
	Ca	Na	Mg (in ppm)	K (in ppm)	Cl	Br	HCO_3	SO_4	TDS
Average 25 samples	6.10	2.50	9440	7820	17.20	2070	73	48	27.75

(*continues*)

As compounds	$CaCl_2$	NaCl	$MgCl_2$	KCl	Br	Density
	16.90	6.36	3.69	1.49	0.207	1.25 (assumed)

(D) Various minor formations (wt.%) (ppm; Martini, 1997)[a]

	Ca	Na	Mg	K (in ppm)	Sr (in ppm)	Ba (in ppm)	Cl	Br (in ppm)	pH
Berea Sandstone	4.78	7.14	1.08	1790	1860	1910	21.31	1770	4.55
Niagara Limestone	9.75	2.49	1.13	4030	4030	901	26.55	2850	4.53
St. Peter Sandstone	7.43	3.35	0.62	3070	3150	16,140	21.34	2180	5.3

(E) Some of the Devonian Aquifers (Wilson and Long, 1993)[b] (ppm)

Formation	Ca	Na	Mg	K	Sr	NH_4	Li	Rb	Cs	Cl	Br
Berea	37,200	57,800	5780	528	1640	66	6.6	3.0	2.4	160,000	1200
Traverse	26,500	53,900	4980	1356	981	130	28	4.4	2.4	143,600	1030
Dundee	22,600	62,950	4770	1410	757	103	24	3.5	1.8	146,100	901
DetroitR.	63,800	28,270	9270	9790	1820	453	65	30	2.7	167,000	2470
Richfield	51,800	32,400	6810	5570	1930	202	38	9.6	4.2	162,200	1570

	SO_4	HCO_3	I	B	Si	TDS	pH	Depth	°C	No.	δD	$\delta^{18}O$	$^{87}Sr/^{86}Sr$
Berea	54	16	19	–	2.8	259,290	4.9	755	26.4	3	-17	0.7	0.70912
Traverse	143	33	17	46	3.7	232,070	5.3	805	27.8	11	-37	-2.1	0.70898
Dundee	187	34	12	27	2.5	236,530	5.0	960	31.4	28	-39	-2.5	0.70845
DetroitR.	0.55	140	30	207	1.6	282,530	4.5	1057	33.8	3	-34	3.5	0.70782
Richfield	69	138	17	111	2.3	245,390	4.7	1277	38.7	10	-40	2.9	0.70814

[a] The analyses appear to be in error since the anions far exceed the cations. The Berea Sandstone is gas-bearing. The Niagara Limestone is below the halite-potash deposit; the St. Peter Sandstone is much deeper.

[b] No. is the number of samples averaged together; depth is in meters; DetroitR. is Detroit River.

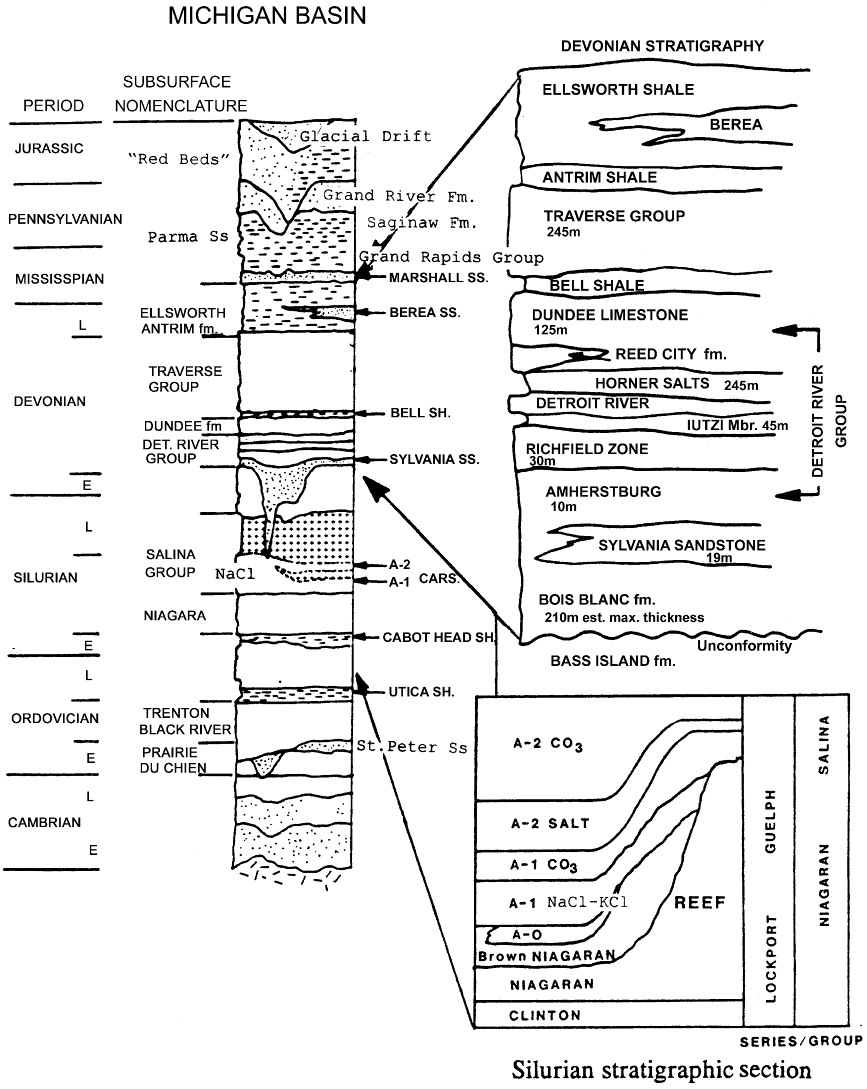


Figure 2.7 Stratigraphy of the Michigan Basin (After Wilson and Long, 1993, 1992; reprinted from Water–Rock Interaction by permission from Swets & Zeitlinger publishers; reprinted from Applied Geochemistry, Vol. 8, p. 83, Fig. 2, ©1993, with permission from Elsevier).

or quartz (Martini, 1997). The variability in dolomitization brine composition seen here is also typical of the world's other dolomitization brine formations. There is a general synclinal structure to the strata under the Michigan Basin, and examples of the specific stratigraphy to the southeast of the center of the basin at Midland are shown in Fig. 2.7 (Egleson and Querio, 1969).

The Detroit River Group consists of 0–350 m of variable porosity carbonates, and at its base there is 0–90 m of porous sandstone called the Sylvania Formation. Each of these formations cover about 40% or more of the Michigan Basin, and contain strong calcium chloride brines at depths of 300–1400 m. Their brines have been commercially recovered in the past, and were generally only considered to be economic below about 880 m. The brines' total dissolved solids (TDS) and the amount of $CaCl_2$ increases fairly consistently with depth from 3 to 23% $CaCl_2$, and the NaCl and $MgCl_2$ concentrations vary inversely with the $CaCl_2$. In the Sylvania Formation, the $CaCl_2$ usually ranges from 14 to 22%. Additional information on the brine in other aquifers and the various reactions and changes that have occurred with them has been given by Martini and Wilson (1997) and Wilson and Long (1993, 1992).

The Michigan Basin brines' very low pH helps to explain their ability to leach and react with other rocks, as is indicated by their high contents of strontium, barium and other metals, although much of the Sr and Ba probably came from the reaction with calcite. Geothermal water also probably mixed with some of the formations, as indicated by the variable presence of iodine, boron, lithium, cesium, rubidium and other rare metals. With most of the brines, the calcium concentration is somewhat higher than its magnesium equivalent in seawater end liquor from a potash deposit, and the potassium a little lower. Wilson and Long (1993) speculated that this occurred by the conversion of the clays kaolinite and smectite to illite:

$$\begin{aligned}&2K^+ + CaCO_3 + 3Al_2Si_2O_5(OH)_4(\text{kaolinite})\\ &\quad\rightarrow 2KAl_2(AlSi_3)O_{10}(OH)_2(\text{illite}) + Ca^{2+} + 4H_2O + CO_2,\\ &\text{or}:\\ &3[Ca_{0.33}(Mg_{0.33}Al_{1.66})Si_4O_{10}(OH)_2\cdot nH_2O](\text{smectite}) + 2K^+ + Al^{3+} + CaCO_3\\ &\quad\rightarrow 2KAl_2(AlSi_3)O_{10}(OH)_2(\text{illite}) + 2Ca^{2+} + Mg^{2+} + (n+1)H_2O + CO_2\\ &\qquad + 6SiO_2.\end{aligned}$$

Small amounts of glauberite ($CaSO_4\cdot Na_2SO_4$) and polyhalite ($2CaSO_4\cdot K_2SO_4\cdot MgSO_4$; both of which can also produce some calcium chloride) have also been found in the basin. Finally, some of the calcium chloride aquifers have a slightly elevated ratio of $^{87}Sr/^{86}Sr$ (they vary from 0.7080 to 0.7105; seawater is 0.70919, further indicating that there was some rock leaching [Martini, 1997]).

Various Other Dolomitization Brines

Even though most of the world's many potash deposits, as well as some of the even more common halite deposits, have formed dolomitization brine, in many cases the brine has migrated away, or has not been examined and reported. Consequently, only a few examples of the more well-known brines will be discussed. In Canada, studies have been made on the dolomitization brine found in the potash mines of south-central Saskatchewan (Fig. 2.6), and at higher elevations in their mine shafts (Table 2.3). Later Bernatsky (1998) reviewed the sampling of various aquifers in southern Saskatchewan, and found that most of them contained a seawater, calcium chloride-type brine that correlated well with the Prairie Evaporate Formation brine of the potash deposits. In both the mines and aquifers, the shallower brines were progressively diluted with meteoric water, and some of the calcium was precipitated by the surface water's sulfate content. All of the brine contained ions from the leaching of other rocks, some of the deeper brine showed signs of having leached halite, and occasionally it appeared to have increased in strength by shale adsorption or other means. In what is perhaps an unrelated study, Bottomley *et al.* (1999) noted what appears to be strong seawater dolomitization brine in the Canadian Shield (at a gold mine) far to the north in the Northwest Territories toward the presumed seawater entrance of the potash deposits. The Canadian Shield brine had similar calcium chloride, bromine, strontium and lithium concentrations, as well as $\delta^{34}S$, $\delta^{6}Li$ and deuterium values as in the potash deposits. Since very little of the Saskatchewan potash deposit end liquor dolomitization brine is now directly under, above or adjacent to the deposits, it would appear that most of it became diluted in the area's aquifers, or traveled long distances from its origin.

The *Zechstein Formation* is a series of massive halite–potash deposits extending from England, through Norway, France, Germany, and ending in Poland. It had 4 major periods of potash deposition, each of which have supported a number of potash mines (Garrett, 1996). In the last (youngest), or Zechstein 4 period in North Yorkshire (Boulby), England, a high-calcium chloride dolomitization brine oozes from cuts in the Boulby halite that underlies the potash deposit (that is being mined; Talbot *et al.*, 1982). In this area of England, there are also high-calcium chloride brines (up to 16.1% salts) in several aquifers such as the upper Carboniferous Coal Measures, often in the lower Carboniferous, and occasionally in the Devonian Old Red Sandstone (Anderson, 1945).

In the *German Zechstein* potash deposits (Fig. 2.8), Herrmann (1980) has examined over 190 brine samples from mine water or aquifers in 6 mining districts. Of these samples, 14 contained 5–25%, and 2 contained 40–50% $CaCl_2$ (of the total salts present), each with a typical dolomitization composition, but differing degrees of conversion and dilution. The other samples had the composition of seawater end liquor or of having leached various minerals in the formations. Many authors have also noted dolomitization brine in the occlusions of secondary halite in the Zechstein (Wolfgramm and Schmidt, 2000; Zwart and Touret, 1994 [7–15% $CaCl_2$]; Fabricus, 1983). The Zechstein dolomitization brine has found its way into some of the country's deeper aquifers such as in southern Bavaria (Udluft, 1976), and also formed a number of calcium chloride springs.

Figure 2.8 Map of the German Potash Deposits (Garrett, 1996; reproduced from Potash; Deposits, Processing, Properties and Uses, Fig. 2.16, p. 112, ©1996 with kind permission of Kluwer Academic Publishers).

At Stecklenberg in the Harz mountains, a dilute calcium chloride brine rises from underlying aquifers through a network of fissures to the surface (Haller and Mestwerdt, 1938; Harrassowitz, 1935).

Two other probable Zechstein formation dolomitization brines are the strong calcium chloride subsurface waters of the Permian and Triassic *Sudeten Foreland* monocline in Czechoslovakia (Depowski and Llaszcz, 1968), and the similar brines that occur in occlusions in recrystallized Upper Triassic halite of the *Lorraine Basin* in France (Fanlo and Ayora, 1998). In the *Paris Basin*, the Triassic Keuper halite contains small amounts of trapped seawater dolomitization brine that has been enriched in Li, B and Sr (Fontes and Matray, 1993).

In India, at the eastern end of the *Salt Range* at Dhariala in the Punjab region, typical low-conversion dolomitization brine (Table 2.2) has been found at a depth of 1370 m (Gill and Akhtar, 1982). The Salt Range is a narrow plateau with an average elevation of 610–910 m, extending about 240 km from Jhelum to the Indus river. There is a massive halite deposit under the Salt Range, containing numerous beds of potash (sylvinite and mixed sulfates; Alam and Asrarullah, 1973). Levy (1977) found a similar brine in the coastal sabkhas of the northern Sinai of Israel. It had been formed by the reaction of evaporated seawater with the fine grained calcite in the playa muds.

The former Russian states have a large number of potash and halite deposits (Fig. 2.9), and calcium chloride brines have been associated with many of them. Sturua (1974) has presented a map of various Russian calcium chloride groundwater occurrences, and the majority of them are closely grouped near major potash deposits. In the *Caspian Depression*, Moskovskiy and Anisimov (1991) have reported such brines, and the *Carpathian* group's *Stebnik* potash deposit in south-central Russia (which contains potassium sulfate minerals, and not the normal sylvinite), still has dolomitization brine near the deposit (Valyashko *et al.*, 1973). Similar brines have been found with 80–169 g/liter Ca in the Ukraine's *Dnieper–Donets Basin*, grading to 50, then 6 and finally 1.5 g/liter $CaCl_2$ as the

Figure 2.9 Map of several of the Russian potash deposits (Garrett, 1996; reproduced from Potash; Deposits, Processing, Properties and Uses, Fig. 2.20, p. 123, ©1996 with kind permission of Kluwer Academic Publishers).

brine approaches the surface (Petrichenko and Shaydetska, 1999, 1998; Lyalko and Tereshchenko, 1973). The adjacent Belarus *Pripyat Trough* (or *Deep*; Azizov, 1975, 1972) also contains calcium chloride brines with a total salts content of up to 300 g/kg beneath the area's halite and potash deposits. A detailed study of inclusions in the halite has shown that only typical end liquor is found in originally deposited salt, but that recrystallized salt contains high-calcium chloride brine with a very reduced sulfate content. For the latter salt, there was also evidence of adjacent dolomite formations and an excess of gypsum. They suggested that the reaction:

$$\begin{aligned}&\mathrm{MgSO_4(brine) + 2CaCO_3(calcite)}\\&\quad\rightarrow \mathrm{MgCO_3{\cdot}CaCO_3(dolomite) + CaSO_4(gypsum)}\end{aligned}$$

accompanied the dolomitization reaction, since some $MgSO_4$ is always present in seawater end liquors (Poroshin, 1981). In the *Kama River* area near Perm, the aquifers' salinity increases with depth, and their analyses become more typical of dolomitization brine (Baldina and Sverdlov, 1959).

In the *South Siberian Platform*, the groundwaters appear to be dolomitization brines, but in one occurrence the deuterium content was nearly that of meteoric water (Pinneker *et al.*, 1968). Near numerous intruding basaltic sills the halite has been reported to contain inclusions with the solids $CaCl_2$, $CaCl_2{\cdot}KCl$ and $n\mathrm{CaCl_2}{\cdot}m\mathrm{MgCl_2}$ (Grishina *et al.*, 1992). In the *Tungussky Basin* of the Siberian Platform, dolomitization brines were found with an additional content of leached rock minerals (Shvartsev and Bukaty, 1996). In the *Angara-Lena* artesian basin of the *Irkutsk* oblast in Siberia, the deepest waters are only saturated with salt, but at higher elevations they change to the dolomitization type with up to 25.4% $CaCl_2$ and 37.3% TDS, and then gradually become more dilute as they approach the surface. All of this basin's calcium chloride waters are unusual in containing up to 600–2000 ppm of hydrogen sulfide and 1600–1900 ppm Li (Pinneker, 1967; Ryabtsev *et al.*, 2002). Very strong calcium chloride brines were also found directly under the Irkutsk halite–potash deposit (Azizov, 1972). Under the *cis-Ural* region's halite–potash deposits, both primary seawater end liquor and dolomitization brine (100–150 g/liter $CaCl_2$; 200–280 g/liter total salts) have been found. The amount of dolomite in the region roughly corresponds to the amount of $CaCl_2$ formed, and the reaction has created enough porosity in the dolomite to provide space for a large petroleum reservoir (Popov, 1988).

In the United States, the seawater end liquor in the large *Carlsbad* potash deposit (Fig. 2.1) has been previously noted (Table 2.1), and the brines in the Salado Formation below and adjacent to this deposit have been studied by Jones and Anderholm (1995). Similar studies have been made by Graf *et al.* (1966) on the calcium chloride brines in the *Illinois Basin*, and its adjacent *Michigan Basin* (discussed above). The two basins have a sequence of fresh to calcium chloride brine varying with depth, with several indicators showing that the deep brine had

Table 2.5

Analyses of a Few Oil and Gas Field Brines (wt.% or ppm)[a]

(A) Lane (1927)

Field	Ca	Mg[a]	Na	Cl	SO_4[a]	HCO_3[a]	TDS
England, Apedale well	3.51	120	4.23	13.16	270	0	21.02
Michigan, Freda sandstone	1.60	30	0.76	4.04	—		6.52
England, Renishaw well	1.36	3000	3.74	9.06	450	16	14.50
Texas, Spur; Cisco Fm.[b]	1.03	879	2.10	4.41	155	—	9.45
Oklahoma, Tulsa Co. (2)[b]	0.95	1350	3.39	7.37	440	—	11.95
Texas, Mid-Continent Field	0.74	2900	3.70	7.88	tr.	tr.	12.63
Ventura, Shiells' Canyon (2)[b]	0.70	—	0.24	1.56	144	653	2.57
Ventura, CA So. Mtn. Fld.[b]	0.55	43	0.40	1.61	49	156	2.61
Ventura, CA So. Mtn. Fld.	0.56	190	0.55	1.89	0	0	3.01
Ventura, CA Wiley Canyon[b]	0.53	40	0.46	1.60	315	346	2.66
San Joaquin, CA Midway Fld.	0.29	7	1.05	2.10	31	293	3.48
Appalachian, Penn., Ohio, W. Va(3)[b]	0.26	180	0.50	1.31	42	—	2.13
Fresno, CA Seabord Fld.[c]	0.22	832	1.48	2.90	0	193	4.70
K[a]251, Ba[a]42, NH_4[a]31, Br[a]108, NO_3[a]44, SiO_2[a]36, I[a]21, B[a]8.3, F[a]0.6, pH 6.4							
Texas, Mid-Continent Field	0.18	464	1.11	2.00	2100	313	3.58
Israel (46)[d]	0.166	536	1.936	3.413	186	257	5.66
Br[a]138, Sr[a]63, Si[a]10.4, I[a]12, Li[a]20, δ^6Li − 23.5, 1549 m depth							

(B) Land and Mcpherson (1992) Gulf of Mexico Sedimentary Basin

(1) Cenozoic Formation Waters

	Ca	Na	K[a]	Mg[a]	Li[a]	Sr[a]	Ba[a]	Zn[a]	Fe[a]	Mn[a]	Cl
High-Ca; 3 wells	3.75	2.48	1580	149	33	1770	629	7.8	33	33	10.67
Average; 40 wells	1.78	3.02	911	376	32	1210	492	25	57	14	8.03
Low-Ca; 6 wells	0.84	3.10	505	443	10	564	70	1.2	23	3.5	6.64

(*continues*)

(ppm)	SO_4	Si	Br	I	B	Org.[e]	TDS%	$\delta^{13}C$	$\delta^{18}O$	$\delta^{11}B$	Sr[f]	°C	m[g]
High-Ca	4.7	33	469	86	73	240	17.14	—	4.8	25	0.7088	127	3572
Average	26	33	245	22	73	287	13.21	−6.5	5.6	25	0.7086	132	3565
Low-Ca	9.8	21	123	13	65	240	10.79	−7.2	4.0	27	0.7080	104	2881

(2) Same Area, Shallower, NaCl-type Waters

	Ca	Na	K[a]	Mg[a]	Li[a]	Sr[a]	Ba[a]	Zn[a]	Fe[a]	Mn[a]	Cl
Three Formations[h]	0.21	3.52	180	819	4.1	153	61	0.2	10	0.7	5.87

(ppm)	SO_4	Si	Br	I	B	Org.[e]	TDS%	$\delta^{13}C$	$\delta^{18}O$	$\delta^{11}B$	Sr[2]	°C	m[g]
	4.1	24	92	30	38	855	9.83	−3.3	2.2	36	0.7083	80	2435

(3) Cretaceous Reservoirs, Texas

	Ca	Na	K[a]	Mg[a]	Li[a]	Sr[a]	Ba[a]	Zn[a]	Fe[a]	Mn[a]	Cl
Sixteen wells[i]	1.14	3.90	887	899	132	1852	137	69	95	45	8.48

	SO_4[a]	Si[a]	Br[a]	I[a]	B[a]	TDS%	$\delta^{18}O$	$\delta^{11}B$	Sr[f]	°C	m[g]
	65	49	426	65	197	14.01	−9.5	17	0.7087	146	3689

(C) Oil field brines with a high bromine content, wt.% (evidently mixed with potash or halite end liquor; Collins, 1970)

	Ca	Mg	Na	K[a]	Sr[a]	Li[a]	Cl	Br[a]	SO_4[a]	B[a]	I[a]	TDS	Location in Figs. 2–10
Michigan	7.0	1.5	1.4	8000	1500	60	20.0	2500	1200	300	40	31.15	10
Utah	6.0	1.0	2.8	40	3000	10	17.9	3200	1200	40	40	28.37	1
N.Dakota	4.0	0.5	6.6	1.0%	2000	100	19.8	700	300	—	20	32.29	4
W.Virginia	3.5	0.4	7.2	2000	—	90	18.6	1800	12	—	20	30.09	13
Texas	3.0	0.9	5.5	2500	—	40	16.6	1200	1200	90	25	26.42	3
Louisiana	3.0	0.6	7.3	600	—	15	18.4	200	180	60	20	29.39	8

(*continues*)

Table 2.5

(*continued*)

(C) Oil field brines with a high bromine content, wt.% (evidently mixed with potash or halite end liquor; Collins, 1970)

	Ca	Mg	Na	K[a]	Sr[a]	Li[a]	Cl	Br[a]	SO_4[a]	B	I[a]	TDS	Location in Figs. 2–10
Kentucky	3.0	0.5	7.4	700	900	25	18.2	2000	1800	—	40	32.74	9
Arkansas[j]	3.0	0.5	6.8	4000	—	100	17.5	5000	180	—	10	28.72	7
Kansas	2.0	1.1	0.8	—	—	—	7.9	—	1050	—	—	11.84	5
Pennsylva.	2.0	0.5	5.8	3000	1000	10	14.3	1300	180	—	30	23.14	12
Ohio	1.4	1.1	1.6	9000	800	—	9.0	1500	60	—	40	14.24	11
Oklahoma	1.0	600[a]	5.1	100	1000	5	9.8	600	90	10	1000	16.23	6
Germany, Altmark	3.23	568	4.16	3700	1280	263	12.71	—	100	91	10	20.71	—

Values in parenthesis imply number of wells.

[a] In ppm.

[b] Hudson and Taliaferro (1925); So. Mtn. Fld. K 110 (in ppm), Br 67 (in ppm), I 13 (in ppm); Wiley Canyon B 101 (in ppm), Br, I 0; 40°C; 1515 m depth.

[c] White *et al* (1963).

[d] Bentor (1969), Chan *et al* (2002) (Heletz field).

[e] Organic acids.

[f] $^{87}Sr/^{86}Sr$.

[g] Depth, meters.

[h] Oligocene Frio, Miocene Frio, Pliocene–Pleistocene (the latter also contained 300 ppm HCO_3).

[i] Also 296 ppm HCO_3.

[j] An average of 11 wells in the Smackover Formation, ppm: Ca 29,070, Na 73,400, K 5060, Li 365, Rb 11.2, Cs 6.1, F 4.6, density 1.229 g/cc (Collins, 1976).

[k] Holdorf *et al* (1993). $\rho \sim 1.20$. When evaporated, as wt.%: Ca 12.12, Sr 0.495, Na 0.37, Mg 0.295, K 0.15, Li 0.098.

a seawater source. In the *Paradox Basin's* large halite–potash deposit (Fig. 2.5; with 33 NaCl–potash cycles) the correlation of the amount of dolomite near the deposit with the amount of $CaCl_2$ in the underlying aquifer is also in approximate agreement (Williams-Stroud, 1994).

Calcium Chloride in Oil and Gas Field Brines

Calcium chloride occurs occasionally in oil and gas fields brines since the oil and gas are also of marine origin. The brines vary from being more dilute than seawater to usually not more than 6 times more concentrated. Normally, the calcium content is far greater than the magnesium, and the sulfate content is very low, as seen by some typical examples in Table 2.5. Also, as shown in Fig. 2.10, calcium chloride oil and gas field brines may be found throughout the United States, as well as throughout the world. These waters appear to be typical dolomitization brines, originating from the seawater that was trapped with the petroleum deposit as it formed. Possibly, in the coastal shallows near to the area accumulating the organic debris that later formed the oil and/or gas the seawater would have become somewhat concentrated, and then because of its increased

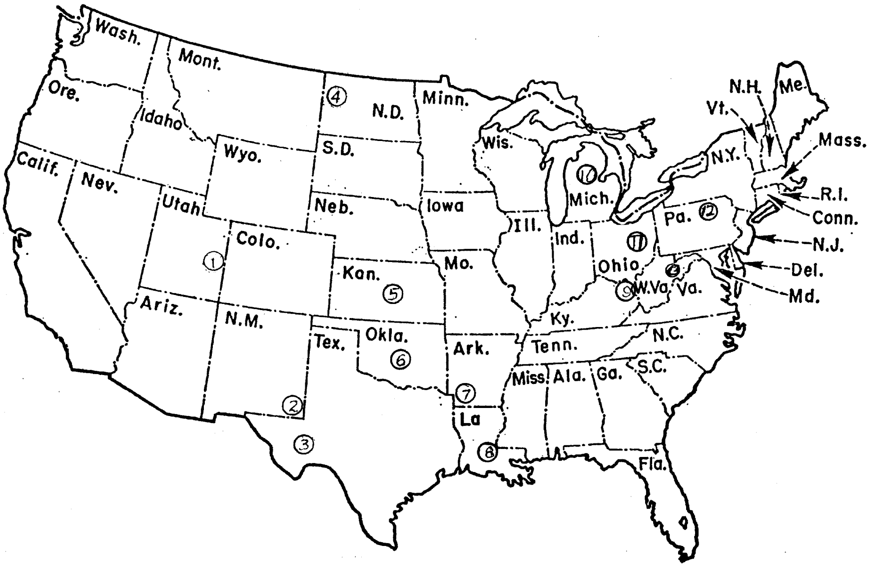


Figure 2.10 Location of some of the United States' oil and gas field calcium chloride brines (Collins, 1970; excerpted by special permission from Chemical Engineering September 21, 1970, copyright ©1970, by Chemical Week Associates, New York, NY 10038). (See Table 2.5 for brine analyses).

density, flowed downward and covered the debris. Its higher concentration may have even helped to preserve the organics from bacterial decomposition. Later, as the organics were converted to oil or gas and the mixture migrated into its final "trapped" formation, the accompanying seawater would have occasionally contacted enough calcite, and been warm enough to nearly complete the dolomitization reaction. Much of its sulfate content would have also precipitated as gypsum (as governed by the $Ca^{+} + SO_4^{2-} \leftrightarrows CaSO_4$ solubility product). Very long residence times would have usually been involved, allowing even seawater that was diluted during its travels to have completed the dolomitization reaction. In the migration, the now-acidic brine would have also reacted with or leached other minerals, adding many minor constituents to it. Most observers believe that the brine's occasionally high-iodine content would have come from the marine organic debris that formed the petroleum deposit. Collins (1975) has reviewed the general geochemistry of these oil field waters, and called attention to a few (in 1970) that definitely appear to be potash or halite end liquor dolomitization brines (Table 2.5(C)). Both bromine (in Arkansas and Michigan) and iodine (in California and Michigan) are or have been commercially recovered from such brines. A few other oil or gasfield brines appear to have contacted geothermal or magmatic brines because of their high boron and/or lithium (and perhaps heavy metal) content.

Land and Macpherson (1992) have made a detailed study of the calcium chloride-containing oil field brines in Texas and the entire U.S. Gulf Coast area (Table 2.5). All of these waters appear to be dolomitization brine that was, on average 2.4–5.5 times more concentrated than seawater, based upon the very similar Na, Cl, K and Br ratios to seawater for each oil or gas field. Some brines had a fairly high iodine content, and comparatively high B, Ba, Fe, Li, Mn, Si, Sr and Zn values. The boron isotope $\delta^{11}B$ numbers were in a range only found in geothermal brines (Garrett, 1998), and were very similar to the boron found in the underlying or nearby Louann Salt mass, which was also known to have had a geothermal component. These geothermal brines probably also contributed the lithium and silica (as silicic acid) to the oilfield waters, as well as some of the other metals.

Land and Macpherson (1992) also postulated that the depth of burial heated these calcium chloride brines sufficiently so that they could leach some components from various rocks that they contacted. When magmatic rocks such as feldspars were present and the brine warm enough, it could do some selective leaching and convert much of the plagioclase (including its anorthite component) into the less soluble albite. The *Gulf Coast Basin* has sandstone units that are feldspar-rich (e.g., the Frio sandstone contains up to 30% feldspars, of which 70% are plagioclase, having an average content of 20% anorthite), and widespread albitization in these aquifers is well documented. When such reactions take place, they can produce additional calcium chloride and liberate strontium, barium (in addition to that from the calcite) and other metals from the plagioclase:

$$\begin{aligned} &CaAl_2Si_2O_8(\text{anorthite}) + 4H_4SiO_4(\text{silicic acid}) + 2NaCl \\ &\quad \rightarrow 2NaAlSi_3O_8(\text{albite}) + CaCl_2 + H_2O \end{aligned}$$

(where other metals sometimes substitute for the Ca. The silicic acid is perhaps hypothetical, but dissolved silica is present in many of these waters). This type of reaction would help explain the higher amounts of equivalent magnesium (now as calcium and other divalent metals) in the oilfield brine to that accounted for by the dolomitization reaction with calcite (and other carbonates) and seawater. The $^{87}Sr/^{86}Sr$ ratios in the brines are indicative of both seawater and volcanic rocks, while the $\delta^{18}O$ and $\delta^{13}C$ values are similar to seawater that has undergone some dilution with meteoric or geothermal water.

Many other articles have been written on the calcium chloride in oil and gas field brines, such as the general articles on calcium chloride brine–rock leaching chemistry by Martini (1997), Rankin (1990), Liu (1982), Collins (1975) and Lane (1927), on the fluorine and boron content of such brines (Tageeva, 1942), and the mechanism of sulfate removal from ground or seawater by calcium chloride brines (Gavriell *et al.*, 1995; Hite, 1983; Rotkin *et al.*, 1973; Valyashko *et al.*, 1973). Other articles have discussed calcium chloride brines in specific oil and/or gas fields. In the *Presqu'ile* dolomite barrier reef gas fields of British Columbia, Canada, there is a close correlation between the reservoir's dolomitic cement and the calcium content of the gas field brines. In the shallow fields, the dolomitization reaction is speculated to have occurred at about 50°C, and in deeper fields at 150°C (Morrow *et al.*, 2002). The *Heletz–Kokhav* oilfield in Israel is an example where the brine in the Heletz field only averages 2.15 times the concentration of seawater (based upon the very consistent average of Na, Cl and Br), and dolomitization has only slightly taken place. The concentration of Ca (0.15%) is about twice the seawater ratio even after reacting with about 97% of the sulfate, and the Mg (.06%) is about half of the seawater ratio. The adjacent Kokhav field's brine has only concentrated 1.38-fold, but the Ca enhancement (0.09% Ca) and Mg and SO_4 depletion are about the same. Both fields have about 5 times more lithium than would be found in seawater (2.0 and 1.5 ppm, respectively; seawater is 0.17%), and δ^6Li values of -23.5 and -19.7 compared to seawater's -32.3. This would appear to indicate some dilution of the oilfield brine with geothermal water (or perhaps some unusual rock-leaching), but other indicators such as temperature, boron, fluorine and heavy metals were not analyzed to help make this determination (Chan *et al.*, 2002).

Holdorf *et al.* (1993) reported on high-calcium (38.8 g/liter), and unusually high-lithium (0.315 g/liter) brines in the *Altmark* gas field in Germany (also containing 110 mg/liter B and 12 mg/liter I). Aren and Depowski (1965) noted the calcium chloride brines in the *Podlasie Basin* gas field of Poland. Evans (1991) reviewed the hydrocarbon formation and Ca-brine migration in the *Appalachian*

Basin, USA, while Hudson and Taliaferro (1925) considered the calcium chloride brines of the *Ventura, California* oil fields. With these brines, there was only a very rough correlation of the calcium content with depth, and the brines varied widely in their calcium content and degree of dolomitization over relatively short distances within the field (see two examples of this with the South Mountain Field in Table 2.5). A strong calcium chloride and calcium fluoride brine has been reported in the *Mobile Bay* gasfield (Schutz *et al.*, 2000). Klosterman (1981) studied the strong calcium chloride brine inclusions in calcite of the *Smackover Formation* in the *Walker Creek and Mount Vernon* oil fields of southern Arkansas, USA.

Dodonov *et al.* (1948) considered the order of crystallization from calcium chloride brines in the Carboniferous gas-bearing formation of the *Saratov District* in Russia, while Romanyuk *et al.* (1973) discussed the calcium chloride brine anomalies in the Paleogene gas condensate deposits in *Rassolnaya and Kosmach*, Russia. Chochia (1972) noted the calcium chloride formation waters and speculated on the amount of oil and gas occurring in the *Zyryanka Basin*, Russia. Shtogrin (1971) discussed the chemistry of the calcium chloride brines in both the gas-bearing and non-productive structures of the eastern part of the *North Crimean Trough* (in Russia), while Kolodiy and Dobrov (1969) noted that the *Turkmenian* calcium chloride oil and gas field brines contained less deuterium than the near-surface waters. Krotova (1959) discussed the relationship of deep, strong calcium chloride brines with the amount of oil and gas in *Siberia.*

Calcium Chloride in Geothermal Brines

Deep Sea Vents

A third well-documented occurrence of calcium chloride is in the brine being emitted from a number of deep sea vents in rift or subduction zones. There are also a few inland geothermal springs containing calcium chloride, and in one location, the Salton Sea Trough in California and Mexico (also a rift zone) there is a massive deep, very hot, concentrated calcium chloride brine formation. The composition of these brines is quite complex, although all have either a known seawater origin (the deep sea vents) or a possible seawater connection. The exact reactions between the seawater and the rocks that they contacted is not known, but as with the oil field brines, in most cases it may be assumed that there was an initial contact with calcite. The resulting acidic and very hot brine probably then went through reactions such as the plagioclase (including its anorthite component) conversion into the less soluble albite, and the leaching of feldspar and other rocks (Shemiakin and Korotkov, 1979).

Among the specific reactions that might occur, Von Damm *et al.* (1985) have suggested the following for the liberation or removal of several ions.

(1) Liberating calcium:

(a) (as noted above)

$$CaAl_2Si_2O_8\text{(anorthite)} + Na^+ + Si(OH)_4$$
$$\rightarrow NaAlSi_3O_8\text{(albite)} + Ca^{2+} + Al(OH)_4^-.$$

(b) $Ca_2Al_2Si_3O_{12}(OH)\text{(epidote)} + 3Mg^{2+} + 2Fe^{2+} + 9H_2O$

$$\rightarrow Mg_2Fe_3Al_2Si_3O_{10}(OH)_8\text{(chlorite)} + 2Ca^{2+} + Al(OH)_4^- + 7H^+$$

(2) Freeing Na:

$$NaAlSi_3O_8\text{(albite)} + 3Mg^{2+} + 2Fe^{2+} + Al(OH)_4^- + 6H_2O$$
$$\rightarrow Mg_3Fe_2Al_2Si_3O_{10}(OH)_8\text{(chlorite)} + Na^+ + 8H^+$$

(3) Removing Ca:

$$Ca^{2+} + CaAl_2Si_2O_8\text{(anorthite)} + Al(OH)_4^- + Si(OH)_4$$
$$\rightarrow Ca_2Al_2Si_3O_{12}(OH)\text{(epidote)} + H^+ + 3H_2O$$

(each of the above minerals are members of the greenschist group).

Pastushenko (1967) has proposed a more elaborate series of reactions that might produce calcium chloride:

1. Clinozoisite and epidote can replace plagioclase in vitreous tuffs and volcanic ash, forming sericite scales and calcite grains:

$$6CaAl_2Si_2O_8\text{(anorthite)} + KCl + H_2O + CO_2$$
$$\rightarrow 2Ca_2Al_3Si_3O_{12}(OH) + 2KH_2Al_3Si_3O_{12} + CaCl_2 + CaCO_3$$

2. Plagioclase (anorthite) is replaced by sericite, albite and kaolin:

$$3CaAl_2Si_2O_8\text{(anorthite)} + 4NaCl + H_2O + CO_2 + 8SiO_2$$
$$\rightarrow 4NaAlSi_3O_8 + H_4Al_2Si_2O_9 + CaCl_2 + CaCO_3,$$

or :

$$5CaAl_2Si_2O_8\text{(anorthite)} + 2KCl + 4NaCl + 4H_2O + 2CO_2 + 6SiO_2$$
$$\rightarrow 2NaAlSi_3O_8 + 2KAl_3Si_3O_{10} + 2NaAlSi_2O_6{\cdot}H_2O + 3CaCl_2 + 2CaCO_3$$

3. Reactions with analcite to form hydrous glass:

$$\begin{aligned}&CaAl_2Si_2O_8(\text{anorthite}) + NaAlSi_3O_8 + SiO_2 + 2NaCl + 3H_2O\\&\quad \rightarrow 3NaAlSi_2O_6{\cdot}H_2O + CaCl_2\end{aligned}$$

4. The conversion of amesite and chlorite into pennine and clinochlore:

$$\begin{gathered}CaAl_2Si_2O_8(\text{anorthite}) + NaAlSi_3O_8 + H_4Mg_2Al_2SiO_9 + H_4Fe_2Al_2SiO_9\\+ 4NaCl + 4H_2O \rightarrow 3Na_2Al_2Si_3O_{10}{\cdot}2H_2O + H_4(MgFe)Al_2SiO_9\\+ CaCl_2 + MgCl_2 + FeO\end{gathered}$$

5. Stronger calcium chloride solutions to form silica:

$$2NaAlSi_3O_8 + 2H_2O \rightarrow Na_2Al_2Si_3O_{10}{\cdot}2H_2O + 3SiO_2,$$

or :

$$\begin{aligned}&4CaAl_2Si_2O_8(\text{anorthite}) + 6NaAlSi_3O_8 + 8NaCl + 14H_2O\\&\quad \rightarrow 7Na_2Al_2Si_3O_{10}{\cdot}2H_2O + 4CaCl_2 + 5SiO_2\end{aligned}$$

6. Reactions accompanied by the adsorption of silica:

$$\begin{aligned}&CaAl_2Si_2O_8(\text{anorthite}) + 2NaCl + 2H_2O + SiO_2\\&\quad \rightarrow Na_2Al_2Si_3O_{10}{\cdot}2H_2O + CaCl_2,\end{aligned}$$

or :

$$\begin{aligned}&6CaAl_2Si_2O_8(\text{anorthite}) + NaAlSi_3O_8 + 2SiO_2 + 6NaCl + 15H_2O\\&\quad \rightarrow 3Na_2Al_2Si_3O_{10}{\cdot}2H_2O + NaCa_2Al_5Si_5O_{20}{\cdot}6H_2O\\&\qquad + CaAl_2Si_3O_{10}{\cdot}3H_2O + 3CaCl_2.\end{aligned}$$

Many authors have also proposed different reactions for the contact of very hot seawater in the rocks of deep sea vents, including Hardie (1990) who considered the primary reaction to be with basalt to form spilitic greenstone. With vents and various other hot calcium chloride brines Shvartsev and Bukaty (1996), Stura (1977, 1974), Azizov (1975), Kissin and Pakhomov (1969), and Pastushenko (1967) have proposed reactions with a wide variety of other rocks. Several authors have also discussed rock leaching, adsorption, precipitation or ion exchange to add or remove components in the dolomitization brine.

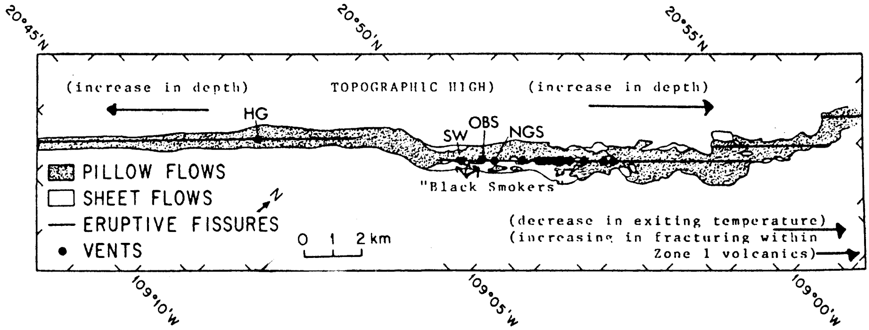


Figure 2.11 Lava flows and vents in a portion of the East Pacific Rise (Von Damm *et al.*, 1985; reprinted from Geochimica et Cosmochimica Acta, vol. 49, ©1985, with permission from Elsevier).

Deep sea vents have been found in many locations where the earth's crustal plates are rifting apart, or one is being subducted under the other, as shown in Fig. 2.11. Table 2.6 lists the analyses of several of these vents, including deep wells in Iceland that are in a continuation of East Pacific Rise rift system (Fig. 2.12). In all cases, it is quite certain that the vents emit seawater that has seeped deep into the earth's interior through cracks in the active zone, been heated to very high temperatures, and then forced back up through other fissures to form the vents. For instance, the deep temperatures in an Indonesian vent's cores varied from 220 to 348°C, and the $NaCl + CaCl_2$ content of the deep brine from 2 to 25 g/liter (Moore *et al.*, 2000). The vent's composition is that of a seawater dolomitization brine, and based upon the analysis of some of the crustal material (e.g., in Iceland or from drill cores), probably most of the seawater has contacted calcite in its travel path. However, the deep basalt and fissured rocks in the vents have also been considerably altered, thus indicating that there was considerable leaching and reaction with the rock in the conduit by the very hot seawater, and probably its acidic dolomitization brine. This would also be consistent with the brines containing more calcium than indicated by the seawater's original magnesium content, and the presence of many other constituents (including metals) in the brine. This latter factor is so significant that many of the vents are actively forming metal deposits in the surrounding areas, and it has been speculated that many of the world's lead–zinc and other metal deposits may have formed in this manner. The analyses of deep cores have shown that the rocks are leached of their calcium, lithium and some other minerals at depth, but that there is considerable re-precipitation of various minerals in the upper sections of the vents. The vent brines usually have a total salt content nearly that of seawater, but may also have been diluted by other waters, or concentrated by evaporation.

Table 2.6

Composition of some Ocean-Vent and Geothermal Brines (wt.%)

(A) Deep Sea Hydrothermal Vents

	Ca (in ppm)	Na	K (in ppm)	Mg (in ppm)	Mn (in ppm)	Fe (in ppm)	Sr (in ppm)	Ba (in ppm)	Zn (in ppm)	Pb (in ppm)	Li (in ppm)
Sea water[a]	413	1.08	393	1294	—	—	8.2	—	—	—	0.17
Galapagos[b]	427	0.602	400	1261	—	—	—	86	—	—	0.30
East Pacific Rise[c]	648	1.048	939	0	49	80	7.1	1.4	5.5	0.54	7.2
Mid Ocean Ridge[a]	1611	1.12	731	0	63	—	—	6	—	—	—
Reykjanes (Wells36)[d]	1630	1.01	1340	18	—	0.49	—	—	—	—	—
Red Sea[e]	5150	9.29	1870	764	82	81	48	0.9	5.4	0.63	0.30

	Cl	SO_4 (in ppm)	SiO_2 (in ppm)	HCO_3 (in ppm)	Br (in ppm)	B (in ppm)	TDS	°C	pH
Sea water[a]	1.935	2711	—	144	65.4	4.7	3.419	—	~7.6
Galapagos[b]	1.210	2687	13.2	—	—	—	2.438	8	—
East Pacific Rise[c]	1.826	0	1050	—	—	—	3.16	357	3.5
Mid Ocean Ridge[a]	2.110	214	21.9	—	—	—	3.35	—	—
Reykjanes, Iceland[d]	1.965	59	510	2290[f]	—	12	3.31	246	5.7
Red Sea[e]	15.550	840	59.1	142	128	7.8	25.80	56	—

(B) Geothermal Springs

	Ca (in ppm)	Na	K (in ppm)	Mg (in ppm)	Fe (in ppm)	Mn (in ppm)	Ba (in ppm)	Li (in ppm)	Cl	SO_4 (in ppm)
Dead Sea Springs[g]	9450	2.11	2650	17,000	—	—	—	—	10.34	1140
Asal,Spg.NE Cor.[h]	5920	2.11	1440	1520	—	—	—	—	5.63	204
Qarhan Spg.China[i]	5200	8.40	510	4700	—	—	—	—	15.20	1450
Tiberias Spring[j]	3930	0.691	77[k]	825	7.8	—	—	—	1.92	891
Reykjanes, Iceland[d]	2260	1.43	1670	123	0.192	—	—	7.4	2.91	206
Utah Hot Spring[l]	1140	0.703	904	70	0.4	1.9	—	—	1.33	189

(*continues*)

Table 2.6

(continued)

(B) Geothermal Springs

	Ca (in ppm)	Na	K (in ppm)	Mg (in ppm)	Fe (in ppm)	Mn (in ppm)	Ba (in ppm)	Li (in ppm)	Cl	SO_4 (in ppm)
Stinking Spring[l]	946	1.26	571	297	—	—	4.1	—	2.16	111
Guilietti Springs[m]	386	803 (in ppm)	61	35	—	—	—	—	1880 (in ppm)	173

	SiO_2 (in ppm)	HCO_3 (in ppm)	Br (in ppm)	H_2S (in ppm)	B (in ppm)	I (in ppm)	F (in ppm)	TDS	°C	pH
Dead Sea Springs[g]	—	118	2250	42	—	—	—	16.64	42	—
Asal,Spg.NE Cor.[h]	—	38	—	—	—	—	—	8.755	60	6.8
Qarhan Spg.China[i]	—	—	—	—	—	—	—	24.80	—	—
Tiberias “Spring[j]	23	366	1.4[k]	77	—	—	—	3.23	61.9	7.3
Reykjanes, Iceland[d]	544	5	98	0.2	12	7.4	0.5	5.216	99	6.2
Utah Hot Spring[l]	38	192	8.2	—	—	—	—	2.28	57	6.7
Stinking “Spring[l]	48	324	15	60	—	—	—	3.65	48	—
Guilietti Springs[m]	79	63	–	–	1	—	—	3400 (in ppm)	44.6	7.5

[a] Garrett (1996).

[b] Galapagos Spreading Center, Edmond *et al.* (1979); also as ppm F 1.39, Rb 0.14.

[c] Von Damm *et al.* (1985); 4 vents; also as ppm: H_2S 202, Rb 2.54, Cu 1.41, NH_4 and As 0.18, Al 0.12, Cd 0.10, Co 0.08, Ag 0.03, $^{87}Sr/^{86}Sr$ 0.70314.

[d] Bjornsson *et al.* (1972) (36 well analyses; average 1027 m deep; also as ppb Mo 8.5, Ge 5.8, Ti 5.7, Ga 5.1, V 1.6).

[e] Also 0.1–0.5 ppm As, Co, Cu, Ni, Se, U; Manheim (1974).

[f] Reported as CO_2.

[g] Vengosh and Rosenthal (1994); Average of Zohar and Yeha springs, west edge of the Dead Sea.

[h] Lake Asal, southern end of the Danakil Depression; Valette (1975).

[i] Lowenstein *et al.* (1989).

[j] Northern Israel.

[k] Vengosh and Rosenthal (1994) list K at 341, Br 244 ppm.

[l] Near the Great Salt Lake, Utah.

[m] Edge of Guilietti Lake in the Danakil Depression, Ethiopia; 10 samples; Martini (1969).

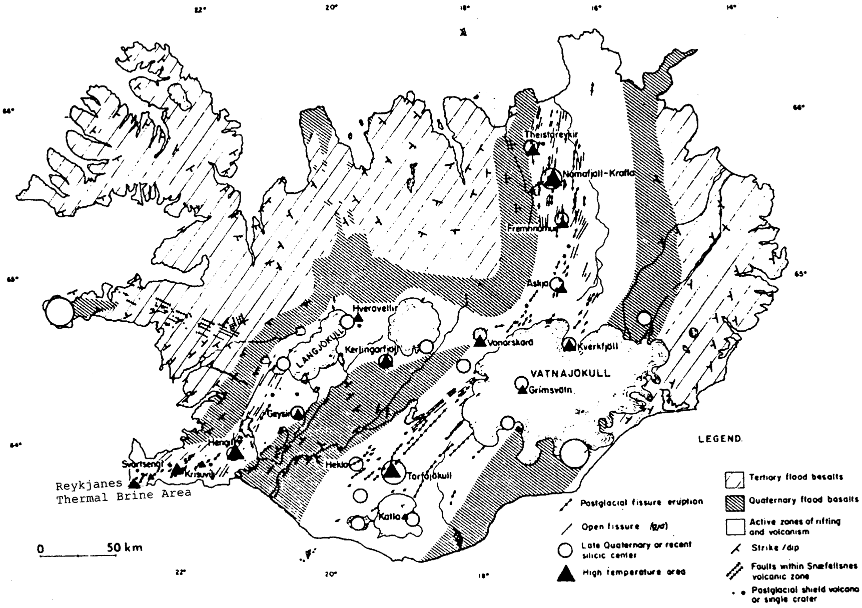


Figure 2.12 Location Map for the Reykjanes Thermal Brine Area, Iceland (Bjornsson *et al.*, 1972; reprinted from the AAPG Bulletin. AAPG© 1972, reprinted by permission of the American Association of Petroleum Geologists, whose permission is required for further use).

In some deep-sea vents, the brines have not undergone the dolomitization reaction, and/or have such massive circulation rates near the ocean floor that they have only moderately increased calcium and fairly normal seawater magnesium contents, augmented by other constituents. Examples of this are the vents at the Galapagos spreading center (Edmond *et al.*, 1979), and many wells and thermal springs in Iceland (Bjornsson *et al.*, 1972). The fairly large number of seawater vents in the world has given rise to the rather surprising speculation by some authors that their calcium content could precipitate enough of the sulfate in the world's oceans to have periodically made them essentially sulfate free (Hardie, 2000). This conclusion was reached despite the tremendous amount of high-sulfate river water that constantly enters the oceans, and the relatively small volume of the thermal vents. Also, studies such as by Ayora *et al.* (2001) and many others have demonstrated that the sulfate content in occlusions within the same formation in individual marine basins varies widely, thus indicating the presence of either dolomitization brine or seawater, and not a change in seawater's composition.

As seen in Tables 2.6 and 2.7 the *Red Sea vent brine of Egypt and Saudi Arabia* is somewhat different from the brine in most other deep sea vents. It appears to be slightly concentrated seawater that has dissolved additional halite (the Br, B and Li concentration ratios are similar to each other, and average 1.73 times seawater; the Na and Cl ratios are similar to each other, but average 8.34 times seawater). Presumably, as the seawater in the bottom of the Red Sea sank through the rift zone sediments it dissolved additional halite that underlies much of the Red Sea. It then was heated, underwent the dolomitization reaction as it contacted calcite, and finally leached some of the fissure's rocks as it was forced back to the sea floor by convection flow or steam eduction. Massive halite outcrops from under the Red Sea to the south near Jizan, Saudi Arabia, and to the north on the coastal plain at Safga, Egypt. Limited potash (sylvinite) beds have also been found in some locations with the very thick halite deposits (Notholt, 1983), and elsewhere langbeinite has been indicated by gamma ray logs (Hite and Wassef, 1985).

The Red Sea vent's metal content is similar to many other deep ocean vents, with quite high strontium values. Pushkina *et al.* (1982) also commented on the amounts of Ba, Cu, Fe, Mn, Ni, Pb and Zn in the brine, while Manheim (1974) in addition noted the presence of elevated amounts of As, Co, Se, U and perhaps F. Older vents in the same rift area appear to have formed Fe–Mn–Ba, Pb–Zn, and Pb–Zn–Cu–Ba deposits along the Red Sea far to the north and south of the current vents (Figs. 2.13 and 2.14). The sea floor Late Miocene shale-anhydrite breccia just south of the vents contains about 5% Zn. At the vents, the rocks contain 14–21% Fe, 0.8% Zn, 0.6–0.8% Cu and 0.5–0.7% Pb. Based upon marine sediments and the presence of several deposits of this type, it appears that the Red Sea once filled the adjacent Afar (Danakil) Depression clear to the Ethiopian Plateau (Fig. 2.13; Manheim, 1974; Bonatti *et al.*, 1972).

In addition to the dilute vent brine, there are also indications that hot potash end-liquor and its dolomitization brine have been formed under the Red Sea in other areas. It has been speculated that both of these brine types have migrated separately and formed springs and groundwater along the Red Sea fault line many hundreds of kilometers to the north in Israel (Tables 2.6 and 2.8; Fig. 2.16).

Inland Geothermal Brines

There are also a very limited number of calcium chloride-containing geothermal springs in inland locations (Table 2.6B), since most geothermal springs are of a sodium carbonate-type and/or low in calcium (Garrett, 1992). Most of the $CaCl_2$ thermal springs appear to be seawater dolomitization brines because of their very similar concentration and composition, but their connection to the ocean or potash/halite deposits is uncertain. As previously noted, the Reykjanes, Iceland spring is near the ocean and in a highly fractured volcanic belt (containing considerable calcite) that is a continuation of the Mid-Atlantic Ridge (Bjornsson *et al.*, 1972; Fig. 2.12). The *Danakil Depression* in the Northern Afar Rift zone (Fig. 2.14) has springs that are in an active volcanic area near the Red

Table 2.7

Geothermal Brines from the Salton See, Red Sea and Cerro Prieto, Mexico, ppm except as noted (Garrett, 1996)

	Cerro Prieto Brine				
	Power plant discharge	From pre-conc. pond	From salt pond	Typical Salton Sea brine[a]	Red Sea geothermal brine[b]
Cl (ppm)	—	—	—	142,000–209,000	155,500
NaCl (wt.%)	2.20	22.2	17.83	12.7–17.8	23.6
KCl (wt.%)	0.32	3.23	6.87	2.48–6.53	0.357
$CaCl_2$ (wt.%)	0.12	1.22	2.59	6.26–10.81	1.426
$MgCl_2$ (wt.%)	—	0.06–0.19	—	0.27–2.23	0.292
LiCl (ppm)	100	1100	2400	1340–1950	1.6
Br	20.5[c]	—	—	200	128
Rb	9.4[c]	—	—	25–100	—
Cs	3.5[c]	—	—	24	—
Sr	15.7[c]	—	—	540–2000	48
B	12[c]	—	—	400–500	7.8
Ba	9.73[c]	12.4[d]	17.0[d]	200	0.9
U	—	7.0[d]	31.0[d]	—	—
As	1.20[c]	7.1[d]	6.5[d]	312	—
Pb	—	3[d]	6.7[d]	90–210	0.63
Te	—	2.2[d]	4.0[d]	520	—

(*continues*)

Table 2.7

(*continued*)

	Cerro Prieto Brine				
	Power plant discharge	From pre-conc. pond	From salt pond	Typical Salton Sea brine[a]	Red Sea geothermal brine[b]
Fe	0.94[d]	3.3[d]	0.4[d]	1200–3700	81
Si	—	2.4[d]	2.1[d]	40	27.6
Sb	—	1.8[d]	3.3[d]	—	—
Mn	0.64[c]	0.6[d]	1.8[d]	1000–2000	82
Zn	0.2[c]	—	1.7[d]	500–700	5.4
Cu	0.12[c]	0.4[d]	0.6[d]	6–20	0.26
Ag	—	0.6[d]	0.8[d]	1–2	—
NH_4	—	—	—	650	NO_3 0.044
$S^{=}$	—	—	—	15–30	SO_4 840
Density	—	1.207[d]	1.250[d]	1.18–1.26	—
pH	—	—	—	4.6–5.5	—

Reproduced from Potash; Deposits, Processing, Properties and Uses, Table 2-12, pages 184–185, ©1996 with kind permission of Kluwer Academic Publishers.

[a] Various sources.

[b] Craig (1969, 1966).

[c] Average of original well brine (Mercado, 1976); Other Cerro Prieto analyses (Galinzoga, 1981).

[d] Vazquez (1981).

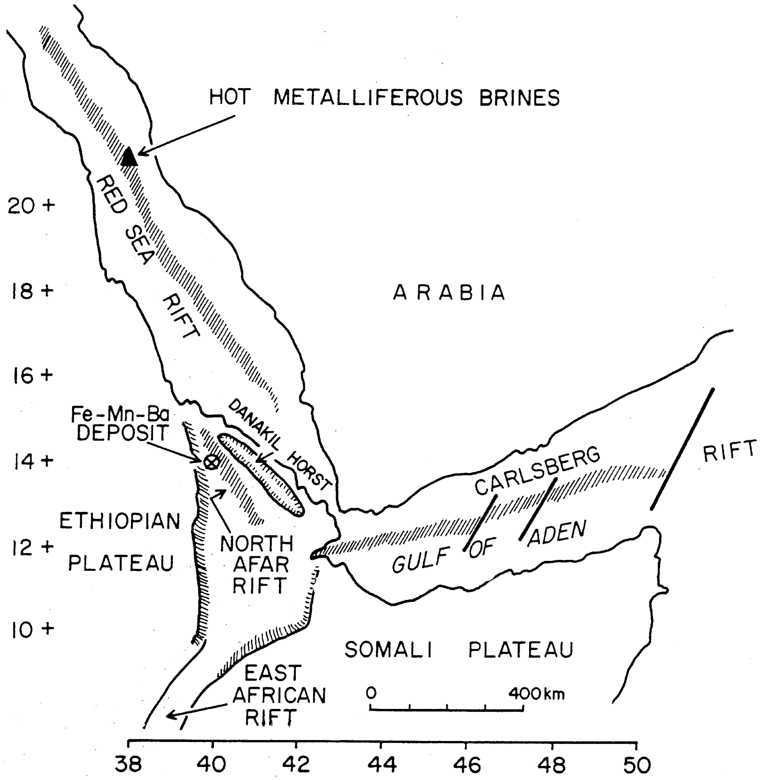


Figure 2.13 Location of the Red Sea Thermal Brines, Metal Deposit, and the Danakil Depression (Bonatti *et al.*, 1972; reprinted with permission from Economic Geology, vol. 67:6, p. 718, Fig. 1, Bonatti, E., Fisher, D. E.; Joensu, O., Rydell, H.S. and Beyth, M., 1972).

Sea coastal plain. They are below sea level and they are also adjacent to a large inland potash deposit. Also as noted above, the Israeli high-calcium chloride springs are presumed to have originated in the Red Sea fault system, with its large halite–potash deposits. Both the Icelandic and Ethiopian springs have a composition very similar to seawater, and they are in areas with recent volcanic activity. They also contain many metals that appear to be derived from rock-dolomitization brine reactions. There are also $CaCl_2$-thermal springs in a thermal zone in Utah, USA near the *Great Salt Lake*, which has a brine composition very similar to seawater. Some geothermal calcium chloride waters have also been reported in the *Cascade Range* in Washington (Mariner *et al.*, 1994).

Several hot springs in Japan contain calcium chloride, such as the *Tsurumaki Spa* (Oyama *et al.*, 1987), the *Togo-Matsuzaki hot springs* in Totturi prefecture (Umemoto *et al.*, 1958) and the *Komumi* and *Ishibu-Iwachi* springs on the Izu

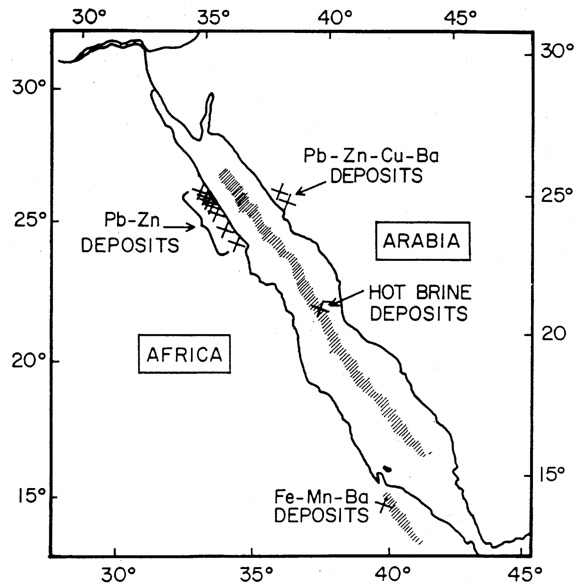


Figure 2.14 Metal deposits from ancient or current Red Sea thermal vents (Bonatti *et al.*, 1972; reprinted with permission from Economic Geology, vol. 67:6, p. 727, Fig. 2.8, Bonatti, E., Fisher, D. E.; Joensu, O., Rydell, H. S. and Beyth, M., 1972).

Peninsula. The latter springs appear to be of the seawater-type, containing 3.1–15.8 g/liter salts with a high bromine and low K, Mg, Na and SO_4 content (Kanroji and Tanaka, 1980). Also, in the *Matsushiro* area, short-lived calcium chloride springs were formed as a result of an earthquake swarm (Yoshioka *et al.*, 1970). All of the Japanese springs are near the ocean and rift zones, and have a seawater dolomitization-type brine. The numerous calcium chloride geothermal springs in Israel have previously been mentioned (Fig. 2.16). In *Turkmenia*, Lebedev (1972) has described a few calcium chloride geothermal springs in *Cheleken*, near Ashkhabad (and also near a potash deposit).

Miscellaneous Springs

Various other cool-to-warm calcium chloride springs have been reported. Low volume and dilute calcium chloride springs feed into one section of the *Qarhan Lake* in China (Fig. 2.15), and some other dilute $CaCl_2$ thermal springs have been reported in China (Xu, 2000). In England, there are extensive areas of high-calcium chloride ground water and springs that may have been derived from England's Zechstein Formation halite and potash deposits (Anderson, 1945). There are calcium chloride springs in the *Harz Mountains* at Stecklenberg, Germany

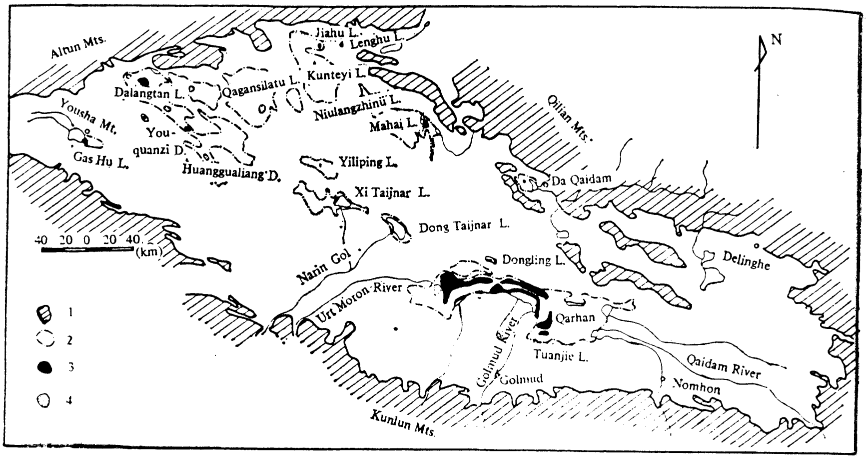


Figure 2.15 Structure of Qaidam Basin, China (Sun and Lock, 1990). Legend: 1. mountains; 2. Playa surface; 3. major potash deposits; 4. smaller potash deposits; ---. outline of Qarhan Playa; Q. Qarhan Salt Lake; D. Dabuxun Saline Lake. Reprinted by permission of Science Press (China). (See Fig. 1.19.)

where the brine probably originated in the Zechstein beds and then rose through a network of fissures (Haller and Mestwerdt, 1938; Harrassowitz, 1935). In the United States in the *Trans-Pecos region* of Texas, the deeper Permian and lower Cretaceous aquifers contain calcium chloride brines, and their mixing with shallower aquifers results in some quite dilute calcium chloride springs (i.e., the *San Solomon, Griffin and Phantom Lake springs*; Hart, 1992). Similar waters have been observed in the *Texas Panhandle* (Bein and Land, 1982), and both appear to have originated from the large Carlsbad potash deposit or perhaps from oil field brines.

Salton Sea Geothermal Brine

A very large pool of extremely hot high-calcium chloride brine occurs in the Salton Sea trough, south of the Salton Sea, California and extending further south to Cerro Prieto and the Gulf of California in Mexico (Table 2.7). The highest brine concentrations and temperatures are found near the Salton Sea, and the temperatures rise again at Cerro Prieto, but with much more dilute brine (about 1/10th the concentration). The northern geothermal area covers about 50 km^2, and the southern area is somewhat smaller. In the north, 300°C brine is found at about a 900 m depth, and 360°C brine at 2100 m (White, 1968). At Cerro Prieto, there are power-production wells drawing 250–344°C brine from a depth of 780–1450 m (Dominguez and Vital, 1976). The brines are very complex, variable and have an unusual heavy metal content. The basin containing these brines is an extension of the Gulf of California rift-fault system, and filled with at least 4300 m of deltaic sediments from the Colorado River emptying into the Gulf of California. The basement rocks are at a depth of about 6100 m. Various major faults of the San Andreas system extend from the north into the trough, and no data have been published on the source of the heat anomaly in the area. The northern zone is estimated to contain over 300 million tons of calcium chloride.

Originally the brine, as with the somewhat similar brine under the Red Sea, was thought to be a pure magmatic ore fluid with a deep thermal source. However, as numerous isotopic studies were made on the water in the brine it was indicated that much of it was of local meteoric origin. White (1968) suggests that rain falling on the Chocolate Mountains several kilometers to the east of the Salton Sea seeped through fault zones to depths of 3000 m or more. As it descended, it was heated, and perhaps it dissolved small potash (mostly carnallite [$KCl \cdot MgCl_2 \cdot 6H_2O$] with some kainite [$KCl \cdot MgSO_4 \cdot 2.75H_2O$]) deposits that had been formed in this gulf area's ancient tidal basins (as are now present near the Gulf). It also may have mixed with some magmatic brine, and most of the magnesium ions from the potash (and magmatic) brine then reacted with calcite in the formation to form calcium chloride. As the resultant high-strength brine circulated through the upper porous strata, its heat and acidic nature (because of its high-$CaCl_2$ and $MgCl_2$ content) allowed it to dissolve a wide range of other elements. The thermal currents that were formed caused some circulation throughout the basin, but the brine still maintained a variable temperature, dilution and mineral content. A model for the convective mixing in the brine, as driven by thermal and concentration (density) differences has been proposed by Oldenburg and Pruess (1997). They suggest that this mixing is still occurring.

The deuterium content of the geothermal brine, thermal springs in the area, and the springs at the base of the Chocolate Mountains are all very similar, and far different from ocean, Salton Sea or Colorado River water. The brine also has a very large ^{18}O "shift" (increase), which is proportional to its temperature, and typical of very hot water reacting with rocks much higher in ^{18}O. It is assumed that the deuterium content of a magmatic water would not be as high as the geothermal brine (although no examples of magmatic fluids are known; Craig, 1966), and that at best 25% magmatic water could be present based upon the isotopic and deuterium data (White, 1968). However, the ^{34}S values are very similar to that assumed to be present in magmatic fluid. The ratios of NaCl and KCl to Br, and KCl to Rb and Cs are similar to what would be obtained by leaching a carnallite deposit, and the low bromine concentrations would appear to rule out the presence of normal seawater dolomitization brine. Also, there are no large potash or halite deposits in the area to have supplied such a brine.

A probably related dilute calcium chloride brine source occurs in the flow from an artesian well on Mullet Island in the Salton Sea near Niland, California. The brine only contains 3.01% salts, distributed as: 0.56% Ca, 0.54% Na, 0.02%

Mg and 1.89% Cl. For a short period, this brine was the feed for a salt works, and the by-product calcium chloride end liquor was sold as a dust-control road salt (Ver Planck, 1957).

Calcium Chloride Lakes

The Dead Sea, Israel and Jordan

As with calcium chloride geothermal springs, there are also only a few calcium chloride lakes in the world. Most of them contain considerable (or even predominantly) $MgCl_2$ as well as $CaCl_2$, are fairly dilute and relatively small, with the exception of one gigantic concentrated lake, the Dead Sea (Tables 2.8 and 2.12). It is located in both Israel and Jordan, being split in half in a north–south direction between the two countries (Fig. 2.16). It is extremely large, containing an estimated 6.8 billion tons of $CaCl_2$ in the complex brine that is commercially processed for potassium chloride, magnesia, bromine and salt. The Dead Sea is the low point in a long, narrow valley, which extends northward from the Gulf of Aqaba to beyond the Sea of Galilee (also called Lake Tiberias). It is the lowest natural lake on earth, about 66 km long and 10–20 km wide, with a surface area of about 930 km^2, and a mean depth of 396 m. It is within the Jordan Rift Valley, an active slip strike fault with high, steep-sided escarpments on both its east and west boundaries. This trough is a branch off of the Red Sea, and an extension of the massive Rift Valley system to the south in Africa.

A thick mass of evaporites, shales and conglomerates of the Dead Sea Group of Plio-Pleistocene to Recent Age fill the rift trough. The lower, or Sedom Formation consists predominately of marine halite, while the upper, or Dead Sea sediments and the Lisan Formation are of terrestrial origin. The bromine content of the lower halite averages a little over 100 ppm, while that of the upper two formations are quite different, averaging 209 in the Lisan, and 292 in the Dead Sea halite. This indicates a much higher bromine content in the terrestrial basins' waters than seawater. The Lisan Formation contains abundant diatoms, fish and plant remains, typical of hyper saline inland lakes. It would thus appear that the last seawater incursion into the Jordan Valley occurred during the Amara period, and that during the latter three depositional periods, the basin has been closed to the sea, concentrating inland (and in the last phase, geothermal) waters of a quite different composition than seawater. Following the marine period a freshwater lake (Samara Lake) was first formed, then the brackish-to-saline Lisan Lake, and finally the Dead Sea (which may have started to form before the Lisan Lake totally evaporated). The oldest sediments within the Dead Sea, based upon carbon dating are about 25,000 years old (Zak, 1974, 12,000 years; Bentor, 1961).

The source of the Dead Sea's mineral content, and especially the calcium chloride, is somewhat uncertain. Its composition (Table 2.8) is very similar to a seawater dolomitization brine (from potash end liquor) that has had only limited

Table 2.8

Analyses of the Dead Sea and Adjacent or Related Springs and Waters (wt.% or ppm)[a]

	Dead Sea		Sdom Well	Mt. Sdom Springs		Near Lake Tiberias[a,b]	
	Kenat (1966)	Bentor (1969)	Bentor (1969)	Bentor (1969)	Jordan River[a,b]	Tiberias Hot Springs	Tannur Springs
Ca	1.2–1.6	1.58	3.99	8.29	129	3930	364
Mg	2.8–4.2	4.20	4.27	1.98	95	825	105
Na	2.7–3.5	3.49	2.22	3.49	224	6910	978
K	0.5–0.8	0.76	1.57	2.87	32	77	27
Cl	15–21	20.80	24.97	26.52	762	19,200	2230
Br	0.3–0.6	0.59	0.29	0.30	9	1.4	20.5
SO_4[b]	550–660	540	95	108	97	891	173
HCO_3[b]	200–230	240	127	0	181	366	240
SiO_2[b]	8–10	—	—	—	—	0.2	—
TDS	25–32	31.50	37.33	42.01	1529	32,300	41,390
pH	6.2–6.4	—	—	—	—	—	—
°C	19–40	—	—	—	—	—	—
Density	1.18–1.22	—	—	—	—	—	—

[a] Amira (1992), Hardie (1990).

[b] In ppm.

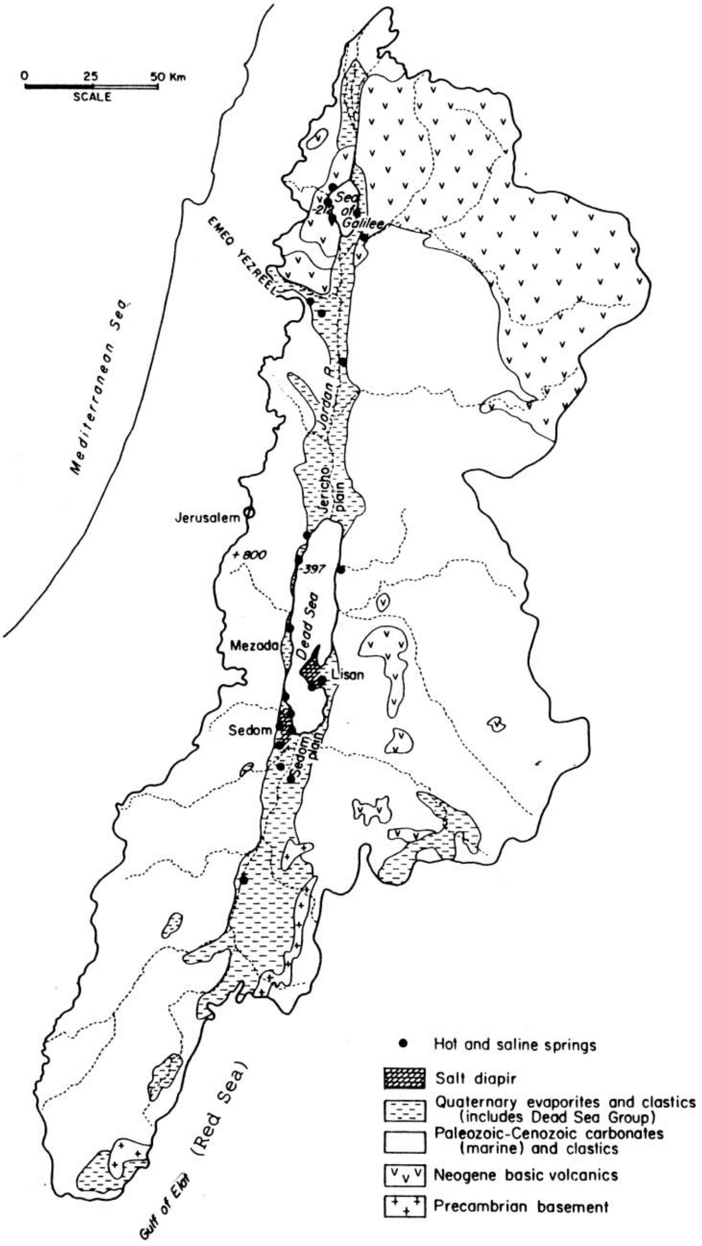


Figure 2.16 Dead Sea basin drainage area and general geology (Zak, 1974, courtesy of the Northern Ohio Geological Society).

contact with calcite, but there are no potash deposits in the area. The underlying marine halite contains only minor amounts of potash, and its average bromine content is only half that required for the beginning of potash crystallization (see Table 2.1). There are, however, potash deposits along the fault line under the Red Sea to the south and west, but that area's present brine (the geothermal springs in the Red Sea, which are perhaps related to the similar ones far to the north at Lake Tiberias in Israel) is low in bromine. However, the ground water in the Dead Sea area, as represented by the nearby Sdom well and the Mt. Sdom, Zohar, Yeha and several other hot springs do contain a high bromine content, but are indicative of a higher dolomitization conversion (i.e., less magnesium) than found in the Dead Sea. If they, or brines like them, were the primary mineral source for the Dead Sea, the blending of Jordan River water (which contains the Lake Tiberias spring water, and has more magnesium) over the years could easily account for the Dead Sea brine's composition. Bentor (1961) calculated a one-third Jordan River, two-third groundwater mixture as the Dead Sea source. This would assume that the strong calcium chloride Dead Sea geothermal wells and springs contain brine from a different aquifer than the Red Sea–Lake Tiberias source, and that it was a more conventional potash end-liquor dolomitization brine. It could have come from the Red Sea potash deposits, or even been residual from much older, now extinct deposits. A similar differentiation of brines with different compositions following separate fault lines is occurring at Lake Assal in Ethiopia at the present time.

In the past, before the present extensive irrigation and other uses, the Jordan River carried up to one million tons of salts per year to the Dead Sea, and brought about 75% of its yearly water supply. It had a fairly high calcium, magnesium, sulfate and bicarbonate content, and in the Dead Sea all of the calcium soon precipitated as calcite (and in some periods gypsum). Despite the Dead Sea's high magnesium chloride content, this calcite probably was not later converted to dolomite, since it would have been deposited with suspended sediments in the dilute end of the Dead Sea. The resultant excess of river water's magnesium would then change the Dead Sea's Mg/Ca ratio, and perhaps resulted in the present high magnesium chloride content compared to that in the Dead Sea wells' or springs' brine. At present, it is assumed that the Sdom and other springs near or under the Dead Sea supply 70% of its yearly mineral input (Zak, 1980), and if all of this input had a composition similar to the Sdom well and spring it would help to support this theory.

Bristol and Cadiz Dry Lakes, California

The only strong-$CaCl_2$, low-$MgCl_2$ lakes in the world are the very small Don Juan Pond, Antarctica and Bristol Lake. Cadiz Lake (adjacent to Bristol Lake) has a somewhat more dilute, higher magnesium brine. Bristol and Cadiz Lakes are relatively small late Quaternary dry playas in the Bristol–Danby Trough of the south-central area of California's Mojave Desert, which is also in the western United States' Basin and Range province. They are located about 360 km east of Los Angeles and 135 km west of Needles, California. Bristol Lake lies just south of the main line of the Santa Fe Railroad and the small town and rail station of Amboy (Figs. 2.17 and 2.19). Its elevation is 180 m, it has an area of about 130 km^2 (155 km^2; Rosen, 1992), and its lacustrian sediments are very deep ($>$500 m, of which 260 m are halite; $>$1000 m, Jachens and Howard, 1992). The lake is in a broad closed basin with a 2000 km^2 drainage area (before a fairly recent lava flow it had been 4000 km^2) formed by the Bristol and Marble Mountains to the north and northeast. The mountains are composed of Jurassic granite, metamorphosed Paleozoic sedimentary rocks and some Precambrian granite. On the south and southeast of Bristol Lake are the Bullion, Sheephole and Coxcomb Mountains

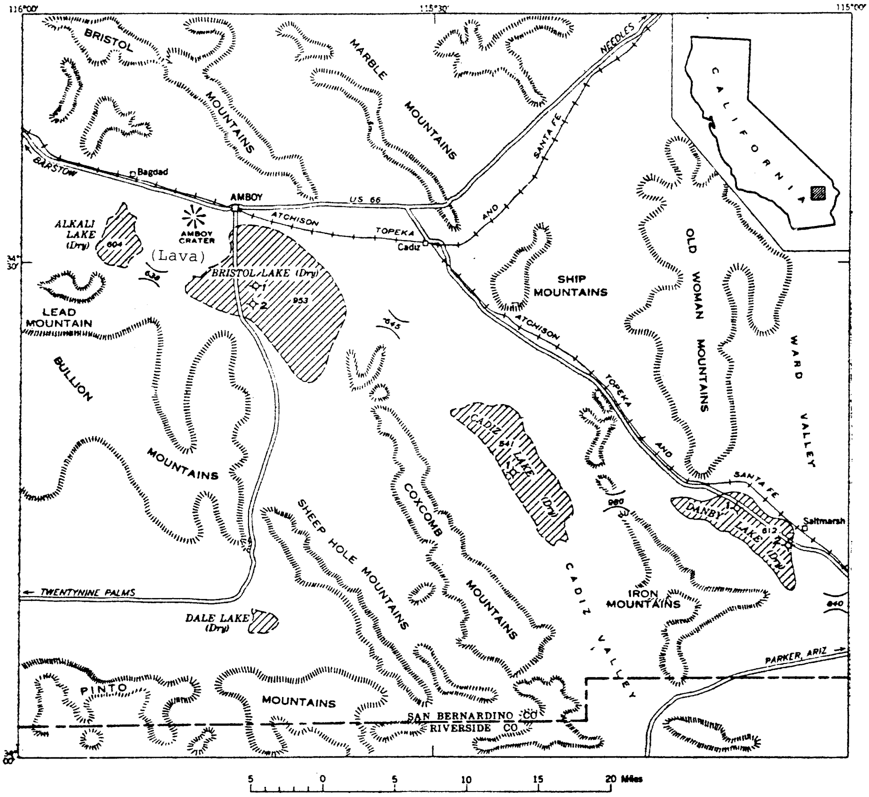


Figure 2.17 Location map for Bristol and Cadiz Dry Lakes, showing elevations and adjacent lakes (Bassett *et al.*, 1959).

with relatively steep alluvial slopes, and to the east southeast there are low ridges that are mostly buried by drifting sand. They separate the adjacent, smaller and 31.7 m lower Cadiz Lake to the southeast by only a 15.8 m ridge, although it has been theorized that Cadiz Lake may still drain into Bristol Lake at considerable depth through a subterranean channel.

On the west and northwest edges of Bristol Lake there is a 62 km^2, <2 m thick, roughly circular and level black basaltic lava flow on top of the playa surface that originated at the same time as the Amboy Crater (also called the Bagdad Crater or Bagdad Cinder Cone; Fig. 2.18) in its northeast corner. There are no lake sediments or shoreline markings on the lava, indicating that it was formed since the last time the lake was full, presumably since the last ice age ended ~10,000 years ago (Recent to Late Pleistocene). Most of the basins in the Mojave Desert were filled with water at times during the ice age periods from 50,000 to 10,000 years ago, and were actively depositing lacustrine sediments (Smith, 1976, 1979). Bristol Lake could have also been filled during the milder Tioga period 6000 years ago, but few of the Mojave basins were, so the lava's age more likely could be as much as 10,000 years. This still makes it the youngest lava formation in Southern California. The lava field is so uniformly thin and flat that it appears to have been formed rapidly (such as within a few weeks) by a relatively hot and thin fluid. It has a low silica and high-potassium content, which would reduce the lava's viscosity, and its lack of large crystals indicates that it was very hot when erupted, and then cooled rapidly. The 76 m high and 472 m diameter cinder cone 3 miles southwest of Amboy appeared to have formed at the same time and from the same lava by gas escaping from at least three closely connected vents, making it an unusually broad, low, nearly circular and flat-topped crater of cinders and larger ejecta (Hazlett, 1992).

Figure 2.18 The Amboy Crater and lava field viewed across the desert northwest of Bristol Lake.

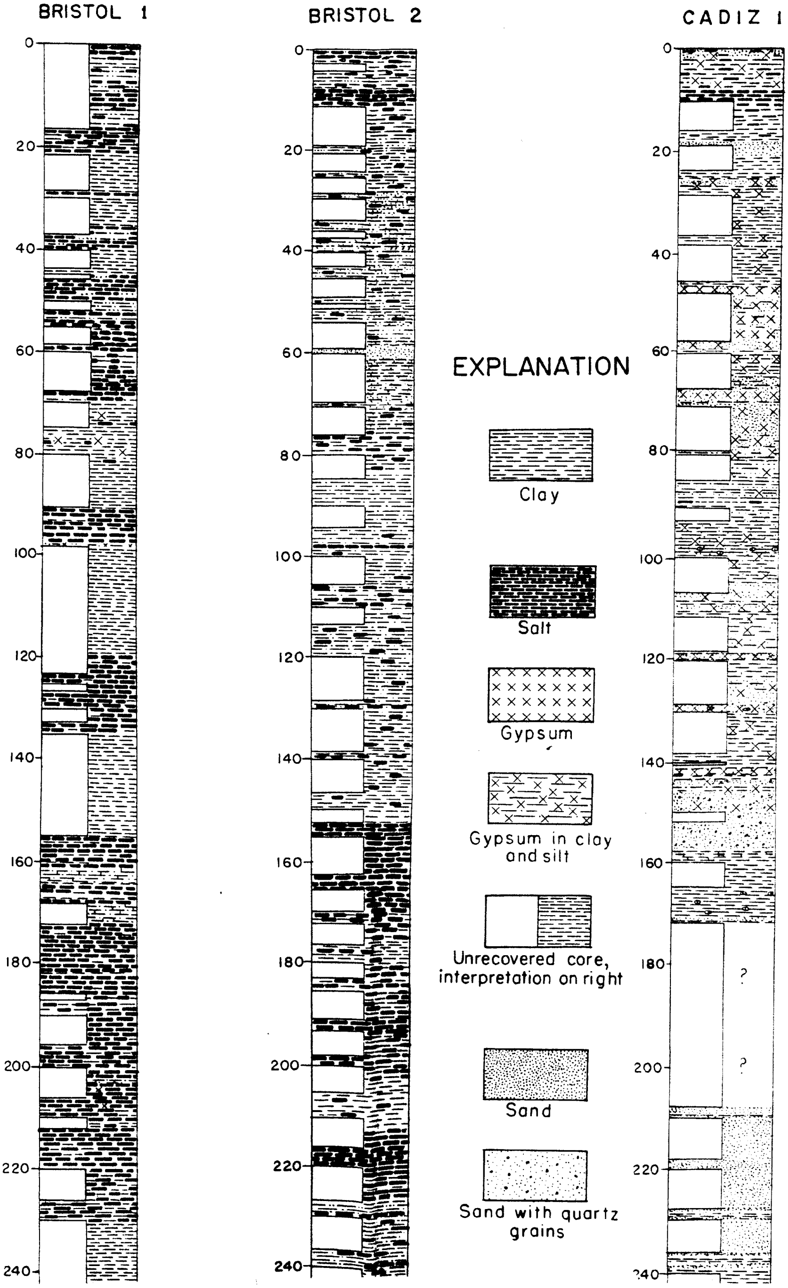


Figure 2.19 Stratigraphy of Bristol and Cadiz Lake Sediments (Bassett *et al.*, 1959).

The lava divided the original Bristol Lake into two sections, forming the smaller Alkali Dry Lake to the northwest.

The area is one of the most arid in the United States with a mean annual rainfall of <100 mm, and there are 2–3 year periods with no rain at all. The evaporation rate in the area is very high, and even though the lakes are the terminus for fairly large drainage basins, they only occasionally flood to a shallow depth after heavy storms, and then evaporate rapidly (Rosen, 1992; Bassett *et al.*, 1959; Gale, 1951). Both Bristol and Cadiz Lakes have three types of surfaces, with the principal one being "puffy (and) efflorescent, called *self-rising ground*, caused by the evaporation of (fairly shallow) capillary(-flow) brine, (and the crystallization of the brine's halite [primarily] and calcite content)." There are also some areas of hard-packed clay where the water table is lower, and other areas (generally at the lakes' lowest levels) where there is salt on, or just below the surface (Bassett *et al.*, 1959). These areas become smooth and sparkling white after the rare lake flooding. The outer periphery of the playa is filled with alluvial deposits of rock, sand and clay washed down from the surrounding mountains, with the average particle size being considerably graded as it approaches the lake. In many areas, these porous sediments are filled with a dilute calcium chloride brine containing roughly the same ratio of salts as in the lake. A ring of gypsum-containing sediments surrounds the lake where the sulfate ions of entering groundwater have precipitated with the lake's calcium chloride brine.

The *Bristol Lake Basin* was initially drilled with two holes to a depth of 307 m (1007 ft), finding salt, silt and clay in both mixtures and alternating beds (averaging about 40% halite; Fig. 2.19) throughout the depth of the drill holes. Some of the more than 40 massive and relatively pure halite beds were in excess of 3.6 m thick (totaling 160 m of halite). Later four other very similar-appearing holes were drilled up to 537 m in depth, with 260 m of halite, and the sediments near the bottom of the holes indicated an age of 3.65 mybp (million years before the present; Rosen, 1992). In the southwest area of the lake there is a 13 km^2 zone called the *Salt Lake*, which began to be mined for salt in 1909. In 1951, it contained an average 1.5 m (0.9–2.1 m) thick salt bed under a roughly equal thickness of surface clay and salts, and the salt was pure enough to have been sold without further processing. Fairly large amounts of this salt were mined, such as 220,000 st in 1942 and 120,000 st in 1951, but more recently salt production is obtained from some of the calcium chloride solar ponds, and it is then drained and washed to an even higher purity. Beginning in 1982, a second salt area formed to the south of the lake, growing by 1988 to about a 0.4 m thickness.

Gypsum that was used to produce plaster was also recovered from the lake from 1907 to 1924. In one area near the lava flow, small grains of gypsum had been deposited as dunes that could be excavated to a depth of 1.8–2.4 m. The cleanest gypsum consisted of a "spongy white mass, granular to coarsely crystalline, that was easily broken into blocks or crushed." A final mineral in the

Table 2.9

Examples of the Calcium Chloride Brine in Bristol and Cadiz Lakes

	Bristol Lake		Cadiz Lake
	Sample 1	Sample 2	Sample 3
(A) as ppm (Smith, 1966)			
Na	46,070	57,370	22,600
Ca	17,190	43,000	4500
K	1479	3303	1040
Mg	598	1074	410
Sr	—	—	—
Cl	104,600	172,900	44,760
SO_4	1048	210	280
B_4O_7 (B)	88(25)	30(8.4)	—
TDS	171,000	279,000	73,600
$CaCl_2$	4.14	12.02	1.22
(B) % of total salts (Ver Planck, 1957)			
Na	26.86	20.55	30.71
Ca	10.02	15.52	6.12
K	0.86	1.18	1.41
Mg	0.35	0.38	0.56
Sr	0.23	0.34	—
Cl	60.99	61.95	60.82
SO_4	0.61	0.08	0.38
B_4O_7(B)	0.05	0.01	—
TDS	171,000	279,000	73,600
$CaCl_2$	24.2	43.1	16.53

(C) Maximum solar evaporation, Bristol Lake (wt.%) (Gale, 1951, 1940 data)

	Original % of TDS	Concentrated	
Na	23.6	$CaCl_2$	48.70
Ca	25.3	Na (and K)Cl	0.49
Mg	1.1	$MgCl_2$	0.30
		Total	49.49
Cl	49.91		
SO_4	0.04		
HCO_3	0.05		

(D) Lithium and chloride in various brines (Vine, 1980)

Bristol Lake	Li 68–108 ppm,	18–21.6% Cl
Cadiz Lake	Li 20–67 ppm,	8–18% Cl

(*continues*)

Table 2.9

(*continued*)

(E) Typical Bristol Lake product, 40.6°Be (1.39 g/cc)

	wt.%		ppm
$CaCl_2$	36.0	Sr	2400
NaCl	1.0	B	48
KCl	0.4	Ba	9
$MgCl_2$	0.9	HCO_3	150
pH	4.1	SO_4	120
		F	2

Samples (1) Drainage canal brine from National Chloride in 1953. (2) Solar concentrated brine in 1953. (3) Brine from 11 m depth in 1920.

Lake that once had a very limited commercial value was celestite (strontium sulfate). It is found on or near the surface in muds, particularly along the southern border. It occurs as nodules with a potato-like shape composed of milky white, minute crystals, and "two cars" of these nodules were gathered in 1942 for sale (Gundry, 1992; Gale, 1951).

Bristol Lake is unique in the world in containing a fairly strong calcium chloride, low-magnesium chloride brine in its near-surface sediments. Only a few other lakes in the world are of the calcium chloride type, but most of them are much more dilute and/or contain a higher proportion of magnesium. Drilling has indicated that the calcium chloride brine (Table 2.9) is found throughout the lake, but only in the upper 9.75 m (32 ft) of its sediments. Its source is unknown, but the fact that it only occurs at shallow depths might indicate that during the recent lava flow and formation of the Bagdad Crater (over a dry playa) the brine near the surface was heated to temperatures high enough to react with calcite in the lake's sediments. Based upon the brine-type in many nearby and adjacent basins (i.e., Dale Lake, Danby Lake, etc.) the residual brine from the crystallization of Bristol Lake's massive halite deposits would have almost certainly been of the strong magnesium chloride type, and the lake sediments do contain large amounts of calcite. The heat from the lava flow would have been sufficient to initiate the dolomitization reaction, and then both thermal and brine concentration (density) effects would have caused a circulation of the lake's brine. This would have allowed all of the lake's brine to be reacted, and the $MgCl_2$ to be almost totally converted to $CaCl_2$. The heat and the acidic nature of the brine would have also resulted in some rock leaching. After a little overflow to Cadiz Lake, the remaining brine would have then been trapped in the near-surface sediments by the lake's frequent layers of low-permeability clay.

Alternately, the calcium chloride might have originated from waters that accompanied the lava, but no similar lava (or magma)-flow calcium chloride brines are known. Similar basalt flows in the West African Rift Valley are accompanied by high-carbonate brine, in the Andes by high-boron and lithium brines, and in some pegmatites by high-metal content brines. Calcium chloride appears to only accompany lava flows when seawater (or seawater-type lacustrine brine) is present to have its magnesium converted by the dolomitization reaction, or to assist in very hot rock leaching. Possibly an ion exchange reaction may have been initiated by the lava's heat between clays and the lake's brine to liberate calcium, but most clays are naturally in the sodium form (because of the predominance of salt in the clay-forming basins), calcium is more strongly adsorbed than sodium, and heat is usually not a significant factor in this exchange. Possibly the heat may have caused gypsum to react with salt to form glauberite and calcium chloride, but this has never been known to occur at any temperature, glauberite is much more soluble than gypsum, and no glauberite is present in the lake's sediments. Finally, the heat from the lava may have resulted in sufficient rock leaching to form the calcium chloride. However, if this were the case the lake's original $MgCl_2$ should still be present, there should be many other metals in the brine, and there should be massive evidence of altered minerals.

Many articles have been written about Bristol Lake, including one noting that most of the gypsum in the lake is near the edges, and thus apparently formed by groundwater seepage into the lake (Rosen and Warren, 1990) Handford (1982) examined the lake's sediments, and the general geology of the region was noted by Miller *et al.* (1982). A number of other articles have been written on more specific aspects of the area's geology.

Cadiz Lake is located just to the southeast of Bristol Lake at an elevation of 165 m, and also contains a calcium chloride brine in its near-surface sediments. The brine is similar but more dilute than at Bristol Lake, and has a higher ratio of sodium to calcium chloride. However, in other features the two lakes are quite different, and do not appear to have ever been joined as a single lake in a deeper basin. A 152 m core hole (Fig. 2.19) showed that its sediments contain no halite except for one 0.3 m thick bed 2.7 m below the surface, and that its strata are quite different from that at Bristol Lake. The Cadiz basin contains much more gypsum, sand, silt, and even many fresh and saline water fossils. Near the center of the lake, there is a low area with the above-noted halite close to the surface, surrounded by large areas with an efflorescent surface. However, the northeastern and southern parts of the playa have a fresh water aquifer, and there are some large expanses of dry clay flats which are now utilized for agricultural production. The differences in the lake's sediments would indicate that after the calcium chloride was formed at Bristol Lake, there was a limited period of overflow of sodium and calcium chloride brine into Cadiz Lake, but that during their prior long period of basin filling there was no connection between the basins. If there was some occasional overflow into Cadiz Lake, then the salts must have been quickly diluted (there are frequent fresh-water fossils) and rapidly flushed from the basin. Alternately, Danby and Cadiz Lakes may have been pre-settling and pre-evaporation basins for a then-lower Bristol Lake, but the current relative elevations make this unlikely, and there should have been occasional zones of similar sediments (or marker beds) in each lake, which there is not. Finally, Danby and Cadiz Lakes contain some fairly old sediments from the Gulf of California, which Bristol Lake does not have (Brown, 1992). Among other articles on Cadiz Lake there have been gravity and magnetic studies (Mickus *et al.*, 1988), and a geologic map prepared (Howard *et al.*, 1989).

Danby Lake is southeast of Cadiz Lake, and is the last member in the Bristol–Danby Trough. It is 3.2–4.8 km wide by 22.5 km long, at an elevation of 189 m, and the divide between it and Bristol Lake is 152 m high (Fig. 2.17). Its sediments are somewhat similar to Cadiz Lake, but it does not contain any calcium chloride. Its brine and salts are predominately of the sodium chloride–sulfate type (Calzia, 1992), which would have precipitated any calcium chloride that may have overflowed from the other lakes. Danby Lake has had limited commercial production of sodium sulfate, and considerable production of salt (Garrett, 2001).

Lake Giulietti, Dallol Salt Pan, Lake Asal, Ethiopia

The Danakil (Afar) Depression is a former branch off the Red Sea that extends to the northwest from the Gulf of Tadjoura and closed about 40,000 years ago. Metal deposits such as may now be forming from the deep Red Sea vents are located in its northern section, and there are coral ridges along its borders (Fig. 2.14). The Depression is roughly parallel and about 45 km from the Red Sea, and below sea level, with an elevation down to − 120 m. It lies between the Danakil Alps near the Red Sea coast and the Ethiopian Plateau in the interior (Figs. 2.13, 2.20 and 2.21; Table 2.10). Lake Asal is located at the southern end of the Danakil Depression, while Lake Giulietti is near its middle-west in a mountain valley that drains into the Depression. The Dallol Salt Pan is in its northern section. Also in its northern end in the Masli area there is a large Pleistocene–Quaternary potash deposit.

Lake Giuletti is 70 m below sea level, has an area of about 70 km^2 and a depth of over 100 m. It is in an actively rifting area in a valley formed by volcanic peaks in the center of the Danakil Depression. The active volcano Alid lies southeast of the lake in the Danakil Alps (Erta'Ale) range, and there are other active volcanoes in the central range further north and to the south. A number of calcium chloride-containing hot springs flow into the southwest edge of Lake Giulietti, and the lake appears to occasionally drain into the nearby Dallol Salt Pan (playa). The dilute calcium chloride spring water is similar to slightly diluted

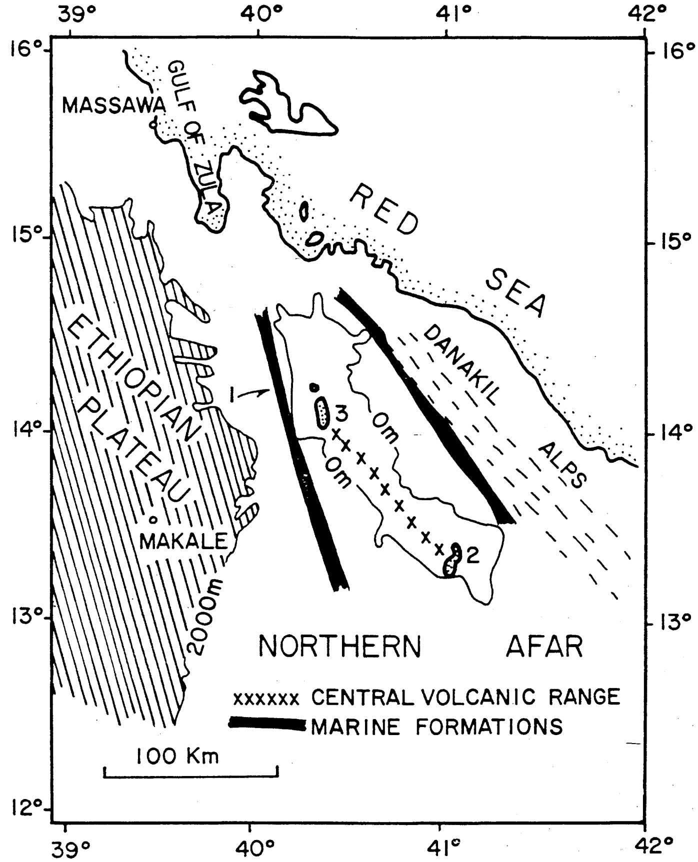


Figure 2.20 Map of the Northern Afar Rift in relation to the Red Sea. 1. Assumed vent metals deposit. 2. Lake Giulietti. 3. Salt playa. (Bonatti *et al.*, 1972; reprinted with permission from Economic Geology, vol. 67:6, p. 719, Fig. 2, Bonatti, E., Fisher, D. E., Joensu, O., Rydell, H. S. and Beyth, M., 1972).

dolomitized seawater (Table 2.6; Fig. 2.22; Barberi *et al.*, 1970). There are marine formations containing calcite and coral between the lake and the Red Sea, and since the lake is below sea level in a rift valley connected to the Red Sea, it would appear that seawater flows into the hot, volcanic strata to form the hot springs. Some intermittent streams also flow into the lake, but they are quite dilute and do not contain calcium chloride. The lake's mineral content is similar to the calcium chloride springs (Bonatti *et al.*, 1972; Martini, 1969).

Lake Asal is at the southern end of the Afar Depression and even closer to seawater, being only 9 km from the Goubet el Kharab bay, which connects to the Gulf of Tadjoura off of the Red Sea (Fig. 2.23). The lake is 155 m below sea

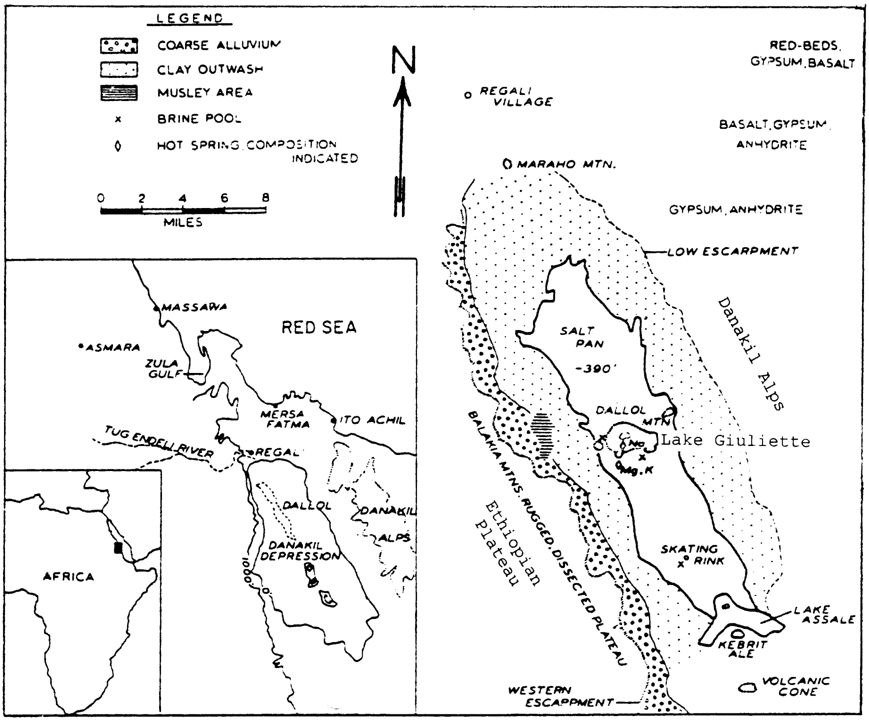


Figure 2.21 Location map of the Danakil Depression, showing Lake Giuliette, Lake Asal and the Dallol Salt Pan. (Reprinted with permission from Economic Geology, vol. 63:2, p. 125, Fig. 1, Holwerda, J. G. and Hutchinson, R. W. 1968).

level, about 8 km wide and 14 km long, up to 35 m deep, and has a brine-covered area of 54 km^2 and a salt–gypsum–clay area of 61 km^2. The lake receives about 200 mm/yr of rain, and the average air temperature is 30°C. There are a large number of springs surrounding the lake, with many in the east and northeast being hot (40–80°C), having a low flow rate and being high in calcium chloride. Those to the south and southeast are warm (30–40°C) with a high flow rate ($>$100 liter/s) and a composition similar to seawater. The springs to the southwest are similar to those in the northeast but hotter (80°C) and with a lower flow rate (1–100 liter/s). There are only a few cold springs (30°C) flowing into the lake in the north and west.

The average analyses of seven high-calcium chloride springs to the northeast are listed in Tables 2.6 and 2.10, with the composition of the lake's brine in Table 2.10 (which remains fairly constant throughout the year). It is seen that the seawater-type brine entering from the south results in the precipitation of

Table 2.10

Composition of Some Calcium Chloride Lakes (ppm)

Lakes[a]	Ca	Na	K	Mg	Cl	SO_4	SiO_2
Don Juan Pond[b]	121,800	3470	157	1850	136,100	7.4	—
Don Juan Pond[c]	83,700	1180	100	—	148,900	63	—
Deep ground water[b]	64,200	6190	84	902	128,000	90	—
Kzakhstan a[d]	39,700	45,870	1340	11,190	173,800	797	—
Namib Desert[e]	27,500	75,200	8000	15,900	200,000	568	46
Dallol Salt Pan[f]	23,290	46,020	8860	16,570	168,600	0	—
Vanda[c]	21,500	6410	685	—	68,040	630	—
Guilietti[f]	13,600	39,300	2450	805	83,400	1020	66
Guilietti Spring[f]	386	803	61	35	1880	173	79
Red Lake, Crimea[g]	6030	59,700	—	33,400	200,900	—	—
Asal, Spg. NE Cor.[h]	5920	21,090	1440	1520	56,290	204	—
Ushtagan[d]	3380	55,090	73	5330	103,880	3930	—
Kzakhstan b[d]	556	2930	—	504	5135	578	—
Asal, Average[h]	2000	103,600	5000	11,900	200,000	2500	—

	HCO_3	CO_3	NO_3	B	F	TDS	pH	°C	Density
Don Juan Pond[b]	—	—	—	—	—	363,400	4.1	0–8	1.355
Don Juan Pond[c]	36	—	—	4.7	223	385,100	5.57	3.0	1.276
Deep ground water[b]	—	—	—	—	—	199,500	6.55	−16	1.164
Kzakhstan a[d]	690	—	—	—	—	273,500	—	21.5	—
Namib Desert[e]	340	100	22,500	157	55	350,000	8.4	—	—
Dallol Salt Pan[f]	—	—	—	—	—	263,300	—	—	—
Vanda[c]	375	—	—	4.2	84	165,900	5.67	21.0	1.092

(*continues*)

Table 2.10

(continued)

	HCO_3	CO_3	NO_3	B	F	TDS	pH	°C	Density
Guilietti[f]	115	—	—	20	5	140,600	6.6	—	1.13est.
Guilietti Spg.[f]	63	—	—	1	6	3400	7.5	44.6	—
Red Lake, Crimea[g]	—	—	—	—	—	300,100	—	—	—
Asal, Spg. NE Cor.[h]	38	—	250	—	—	87,550	6.8	60	—
Ushtagan[d]	256	—	—	—	—	171,140	—	25	—
Kzakhstan b[d]	211	8	—	—	—	9922	—	—	—
Asal, Average[h]	131	—	307	—	—	325,730	7.0	—	—

	Sr	Li	Mn	Ba	Fe[i]	Zn[i]	Cu[i]	Ni[i]	Pb[i]	Co[i]	H_2S	Eh/V
Don Juan Pond[c]	862	235	0.90	1.18	42	118	1.7	2.7	102	.34	<0.01	0.63
Vanda[c]	73	27	2.24	.58	256	2.7	.71	.53	.38	.19	10.3	-1.00

[a] Also, a small section of Qarhan Lake, China has 0.6–8.0% Ca in the near-surface sediments (Bihao *et al.*, 1986).

[b] Harris and Cartwright (1981).

[c] Wright Valley, Antarctica; the Lake Vanda data are at 70 m depth; also <0.045 ppm I; the Don Juan Pond is late in the summer evaporation period (Goguel and Webster, 1990; Webster and Goguel, 1988).

[d] Central Kazakhstan lakes, Russia; b = average of four other lakes; Posokhov (1949).

[e] A coastal salt pan in Namibia; also 0.22 ppm Fe (Cagle and Cruft, 1970).

[f] Danakil Depression, Ethiopia; 10 samples; Martini (1969).

[g] Russia; Hudson and Taliaferro (1925).

[h] Afars–Issas area, Ethopia; Valette (1975).

[i] In ppb.

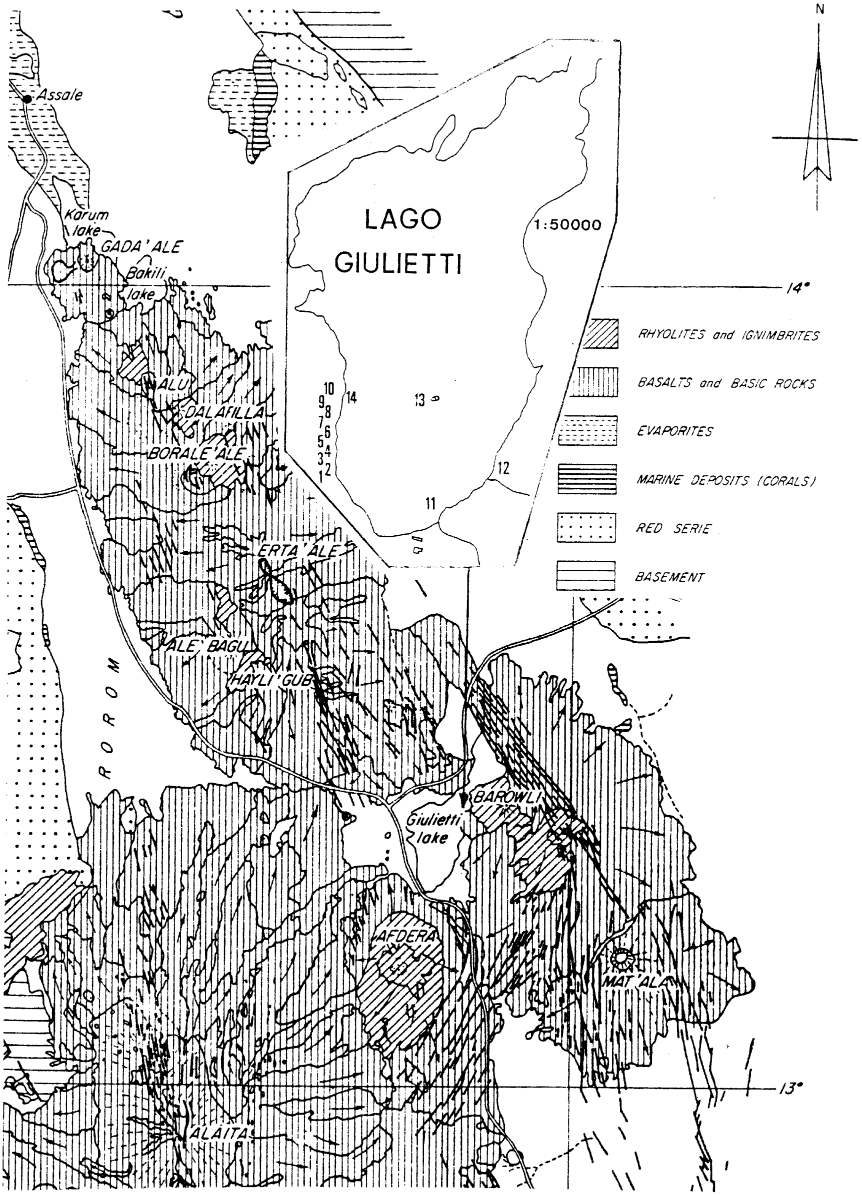


Figure 2.22 Location of Lake Giulietti, its thermal springs and adjacent volcanoes (Martini, 1969; Barberi *et al.*, 1970 [Numbers 1–10 are hot springs; other numbers are sampling locations.]; reprinted from their Philosophical Transactions, 1970, vol. 267, p. 67 by permission from the Royal Society of London).

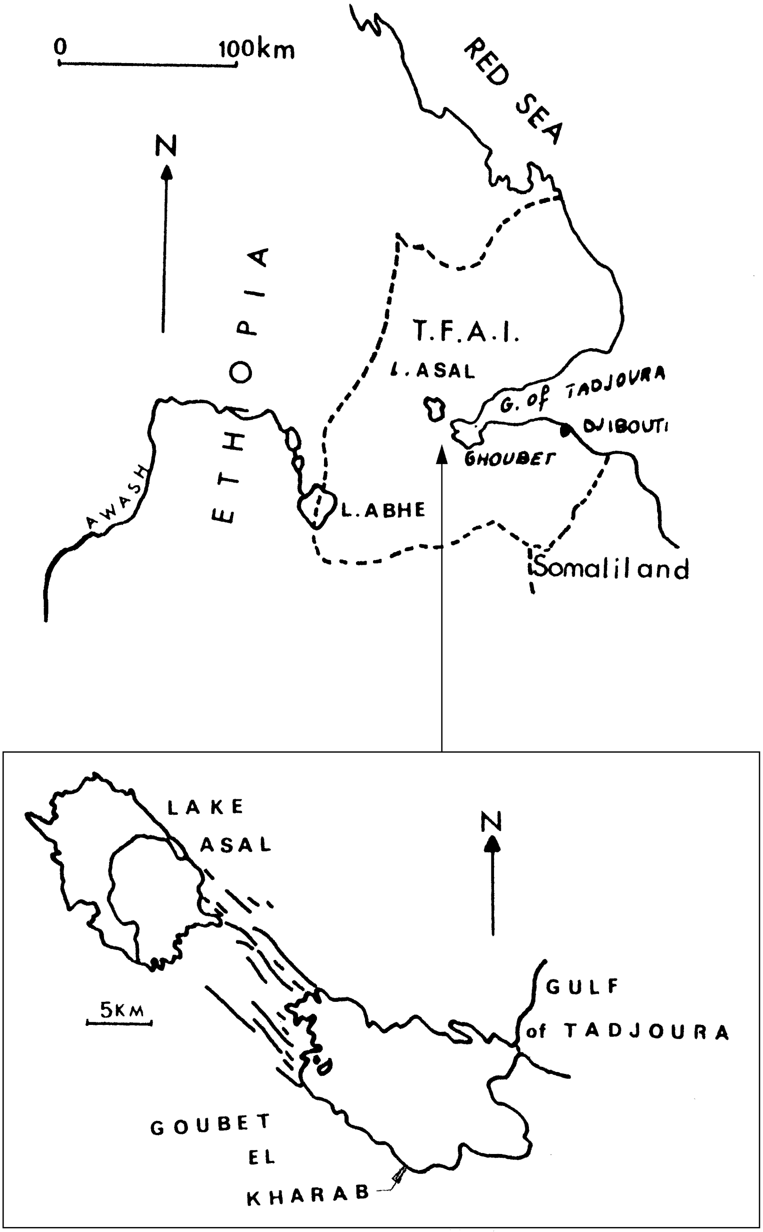


Figure 2.23 Location map of Lake Asal (Valette, 1975, courtesy of the International Union of Geodesy and Geodynamics).

much of the lake's calcium, leaving the average lake water only slightly enriched in calcium chloride. The calcium chloride springs from the northeast contain a modest concentration of manganese and lead, while those from the southwest contain SiO_2, Sr, Fe, Ni and Co. The seawater-type springs have a slightly elevated fluorine content. The sediments in the lake bottom are primarily gypsum, while in the northeast and southwest there are also traces of many metals, and elsewhere there is some calcite, dolomite, fluorite, plagioclase, pyroxenes, halyte, kaolinite and montmorillonite (Valette, 1975). There is considerable limestone in the sediments between the lake and sea, and many fault lines. Since the lake is below sea level, it appears that dolomitization brine is the source of the calcium chloride. The hotter springs with the greater content of calcium chloride appear to contain brine that traveled through a somewhat different path than the seawater brine, and through some of the recent hot volcanic rocks of the Afar rift zone's mountains. Lopoukhine (1974) has also reported on the chemistry of the lake's hot springs.

Qarhan Lake, China; Kazakhstan Lakes

Several springs and a small area of the Qarhan Lake, China (into which the springs flow by means of the Golmud River; Fig. 2.15) contain a modest content of calcium chloride (Table 2.6 for the springs; some lake brine has 0.6–8% $CaCl_2$). The remainder of the lake contains a seawater-type brine, and gypsum precipitates in the zone between the high-calcium and high-sulfate sections. The lake is in the Qaidam Basin, and in 2001 was being prepared for large-scale potash production. There is no indication of the source of the calcium chloride, although the majority of the water entering the lake evaporates to form a strong magnesium chloride brine. As this heavy liquor seeps into the underlying calcite-containing sediments, it should form a dolomitization brine. Some of this brine that has penetrated semi-impermeable zones might then be forced to the surface as springs by the slowly building compaction pressure of the lakes sediments. In the lake, some tachyhydrite has been reported in small isolated pools in the limited calcium chloride zone (Spencer *et al.*, 1991).

In Kazakhstan, Russia there are a group of six somewhat similar lakes (listed as "a" in Table 2.10), with Lake Ushtagan containing a fairly strong calcium chloride brine, and the others having only a modest calcium chloride content. They were all formed by dilute calcium chloride springs (Posokhov, 1949), which almost certainly originated from dolomitization brine formed by the area's extensive potash deposits.

Lake Vanda and the Don Juan Pond, Antarctica

One of the most unusual of the world's calcium chloride lakes is Lake Vanda and the nearby Don Juan Pond in Antarctica. The lake is covered with ice, there is nearly fresh water under the ice, and below that a stratified strong calcium chloride brine. It is located in the Wright Valley of Southern Victoria Land on Antarctica's southeastern side, the "Dry Valley Area" that includes the Soya Coast and Vestfold Hills (Fig. 2.24). In this area, there are more than 90 saline-to-fresh water lakes, and all but Lake Vanda (and the nearby Lake Bonney) contain a seawater-type brine and/or snow or glacial melt water. Lake Vanda is totally different from the others in containing a high-calcium chloride, medium-magnesium, almost no-bromine (a seawater indicator) brine. It, along with the small nearby Don Juan Pond with an even stronger calcium chloride brine, are also the only highly concentrated lakes in Antarctica, except for Lake Bonney in the adjacent Taylor Valley. Lake Bonney (Fig. 2.24) contains an ice-covered, stratified strong sodium–magnesium chloride brine with medium-low calcium and an unknown bromine content (Table 2.11). Tachyhydrite has been reported in soils near Lake Bonney (Pastor and Bockheim, 1980), but this is unlikely, since tachyhydrite only forms at temperatures above 22.8°C, and it is acidic, while the soil was stated to be very alkaline.

Lake Vanda has no outlet, and is fed by the Onyx River for brief periods in the summer. There is a permanent 3.6 m layer of ice covering it, then fairly dilute water, and below about 50 m depth the brine rapidly becomes quite strong, warmer and contains many heavy metals (Tables 2.10 and 2.11; Fig. 2.25). There is some suspended halite (NaCl) in the lower brine, and the floor of the lake consists primarily of calcite and gypsum (the latter with + 18.9–20.9 $\delta^{34}S$ values, or the same as seawater's ~ + 20; Matsubaya *et al.*, 1979). Lake Vanda is about 8.5 km long, 2.5 km wide, 70–74 m deep, and its surface elevation is at about 89 m. The Don Juan Pond's elevation is 116 m, 8 km to the west southwest in the same valley. The Onyx River flowing into Lake Vanda contains almost pure water, which is not of the calcium chloride type. Sulfate-reducing bacteria appear to be present in the bottom of the lake, forming hydrogen sulfide that partially precipitates some of the dissolved metals. In the shallow waters at the margin of the lake there are thick microbial mats, dominated by cyanobacteria (Webster *et al.*, 1996).

If the lowest, most concentrated brine in Lake Vanda was its original mineral source, and it slowly became diluted following an incursion of fresh water, then diffusion calculations would indicate an age of about 12,000 years since that event (Wilson, 1964; Webster and Goguel, 1988). This later flooding might be further indicated by the essentially constant values for both δD and $\delta^{18}O$ between 5 and 60 m depth, indicating a uniform original water supply, since it was not further isotopically fractionated (by evaporation or freezing) with depth, even though the concentration of salts greatly increased.

However, if the data of Matsubaya *et al.* (1979) and Webster and Goguel (1988) are both correct, then it would appear that there has been about an 18% additional dilution of the lower brine during the 15-year period between their two samplings (January 1973–1988; average of the 70 m Cl, Ca, Na and K ratios; compare the two investigator's Cl versus depth plots in Fig. 2.25). These data

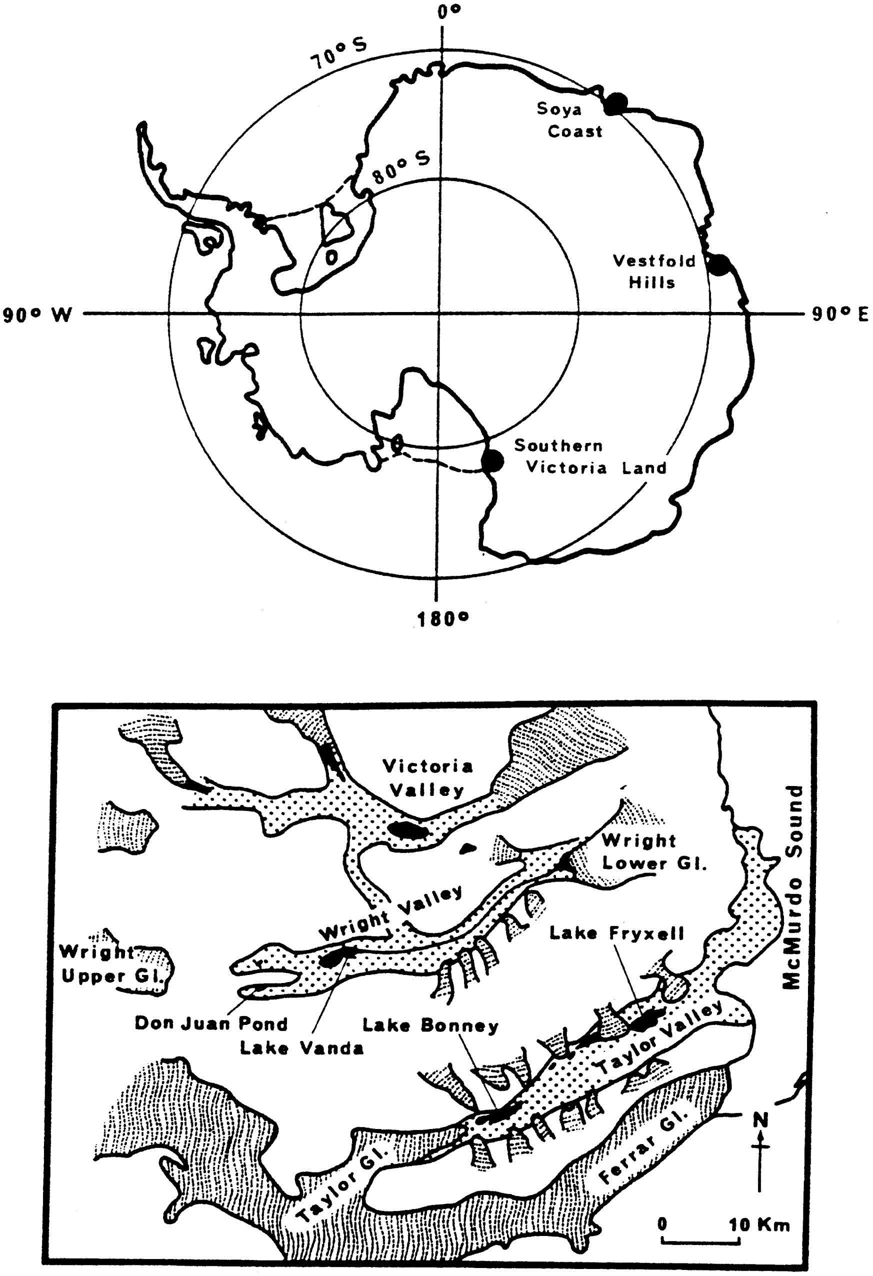


Figure 2.24 Location map of Lake Vanda, the Don Juan Pond and Lake Bonney in the Dry Valley Area of Southern Victoria Land, Antarctica (Matsubaya *et al.*, 1979; reprinted from Geochimica et Cosmochimica Acta, vol. 43, ©1979, with permission from Elsevier).

Table 2.11

Analyses of the Brines of Lake Vanda and the Don Juan Pond, Antarctica (g/kg) (Matsubaya *et al.*, 1979; data from January 1973)

Depth (m)	Cl	Ca	Mg	Na	K	$-\delta D$	$-\delta^{18}O$	Density	Br[a]	SO_4[a]
Lake Vanda										
4 m[a]	240	52	14	39	8.3	244	31.2	—		
8[a]	200	61	15	44	9.2	245	31.3	—		
14[a]	300	96	22	59	11	246	31.5	—		
16[a]	500	165	34	90	19	245	31.8	—		
20[a]	500	180	42	97	19	245	32.0	—		
30[a]	600	174	45	98	19	248	32.0	—		
40[a]	600	195	43	150	19	247	31.7	—		
44[a]	900	276	66	127	19	252	31.9	—		
45[a]	1100	314	88	151	26	246	31.9	—		
48[a]	1600	496	132	192	29	256	31.7	—		
50[a]	5300	702	472	554	67	248	31.8	—		
55	28.4	10.7	3.02	2.39	0.247	246	31.5	1.039		
56	33.3	14.8	4.19	3.46	0.351	248	33.3	1.046		
60	53.8	19.7	5.56	4.33	0.385	244	30.5	1.069		
Average						247	31.5			
64	60.9	19.2	5.81	5.12	0.402	237	29.7	1.075		
65	70.0	24.5	7.05	6.34	0.551	246	29.5	1.094		
65.5	74.1	33.1	8.70	7.96	0.604	248	29.2	1.096		
68	73.5	25.6	—	6.98	0.586	244	29.4	1.095		
Average						246	29.5			
71.3[b]	73.7	—	—	—	—	239	29.3	1.093		
72.2	93.2	28.9	9.03	7.82	0.980	236	28.2	1.122	25	463
76.2	109	33.2	10.5	9.75	1.09	240	27.0	1.142	28	284
80.2	114	—	—	—	—	242	26.8	1.150		

(*continues*)

Table 2.11

(continued)

Date or Depth (m)	Cl	Ca	Mg	Na	K	$-\delta D$	$-\delta^{18}O$	Density	Br[a]	SO_4[a]
Don Juan Pond[c]										
Stream[a,d]	140	28	22	42	2	—	—	1.000	—	60
4–74	158	81.1	1.1	—	—	206	19.5	1.224	—	0
7–74	148	74.1	1.1	—	—	206	20.2	1.208	—	30
12–74	163	—	—	—	—	183	13.6	1.233	—	30
12–74	176	—	—	—	—	180	12.4	1.255	—	10
1–75	182	—	—	—	—	170	10.3	1.265	—	30
87–88[e]	149	83.7	—	1.18	0.10	—	—	1.276	106	63
1–71	151	76.4	0.45	19.6	—	156	9.4	1.216	—	20
1–71	197	99.3	1.5	16.0	0.14	162	8.3	1.283	—	0
12–71	201	102.5	1.27	—	—	195	14.4	1.288	—	0
11–69	209	107.2	1.6	—	—	214	17.4	1.298	—	0
11–73	216	112.7	1.6	—	—	209	16.6	1.324	—	0
1–76[d]	236	122	1.85	3.47	0.157	—	—	1.355	—	7.4
12–68	236	127.1	1.8	3.51	0.20	183	10.8	1.361	111	0
12–73	244	—	—	—	—	197	11.8	1.370	—	—
12–63	247	132.2	2.6	2.16	0.23	193	13.5	1.380	120	0
1–65	251	137.1	1.8	1.63	0.26	186	13.9	1.386	123	0
3.8 m[b]	139	—	—	—	—	211	21.0	1.203	—	—
6.1	87.3	44.4	0.44	—	—	179	16.1	1.119	—	367
9.4	91.0	46.7	0.46	—	—	176	16.3	1.121	—	353
15[d]	120	61.9	0.86	5.93	78	—	—	1.164	—	86
58[d]	134	65.8	0.93	6.35	89	—	—	1.182	—	85
Lake Bonney, East Lobe, Taylor Valley (a NaCl–$MgCl_2$ lake) (g/kg)										
26 m	143	1.35	27.3	43.9	2.74	251	25.0	1.181	—	2.75
32.5	162	1.22	21.0	56.9	2.30	252	25.2	1.203	—	2.94

(*continues*)

Depth (m)	Cl	Na	K[a]	Li[a]	SO$_4$[a]	HCO$_3$[a]	F[a]	Br[a]	Density	pH	°C
Webster and Goguel (1988); Lake Vanda (g/kg)											
Onyx River	7.0[a]	2.8[a]	1.5	0.001	4.0	23	0.19	0.02	1.00	7.2	3.2
5 m	265[a]	50[a]	13	0.10	18	43	0.29	0.06	1.00	8.3	2.5
15	321[a]	58[a]	15	0.12	18	50	0.50	0.10	1.00	7.9	2.5
25	476[a]	63[a]	17	0.15	20	42	0.67	0.14	1.00	8.1	3.0
35	568[a]	86[a]	23	0.22	28	63	0.86	0.16	1.00	8.1	4.0
40	513[a]	83[a]	23	0.21	25	60	0.89	0.16	1.00	8.0	7.0
45	575[a]	63[a]	16	0.16	26	52	0.91	0.18	1.00	7.5	7.0
50	1.34	142[a]	34	0.51	33	67	2.14	0.47	1.00	7.4	8.5
55	10.0	889[a]	143	4.08	138	99	15.0	3.80	1.01	7.0	12.5
60	31.9	2.54	361	13.8	263	166	43.1	9.19	1.04	6.4	17.0
65	55.9	4.66	557	22.9	519	278	75.9	15.0	1.07	5.9	20.5
70[f]	48.0	6.41	685	27.0	630	375	84.2	19.6	1.092	5.7	21.0
Don Juan Pond (1987–1988 season)[g]											
	148.9	1.18	100	235	63	36	223	106	1.276	5.6	3.3

Other elements (ppm[h]) (1987–1988 season)

	Sr	B	Ba	Mn	Zn	Pb	H$_2$S
Onyx River	0.023	0.005	0.002	0.019	4×10^{-3}	0.3×10^{-3}	<0.01
Lake Vanda	73	4.2	0.58	2.24	3×10^{-3}	0.4×10^{-3}	10.3
Don Juan Pond	862	4.7	1.18	0.90	0.118	0.102	<0.01

[a] in ppm.

[b] Analyses below the line are of groundwater under the Lake (11-1973) or Pond (12-1973), except the first line in Don Juan Pond represents a continuous series of dates.

[c] In the first column, the numbers are dates, not depth, except for the groundwater.

[d] Harris and Cartwright (1981) (1-20-1975 data).

[e] Webster and Goguel (1988) (1987–1988 season).

[f] Also Ca = 21.5 g/kg.

[g] Also Ca = 83.7 g/kg.

[h] Goguel and Webster (1990) (1987–1988 season).

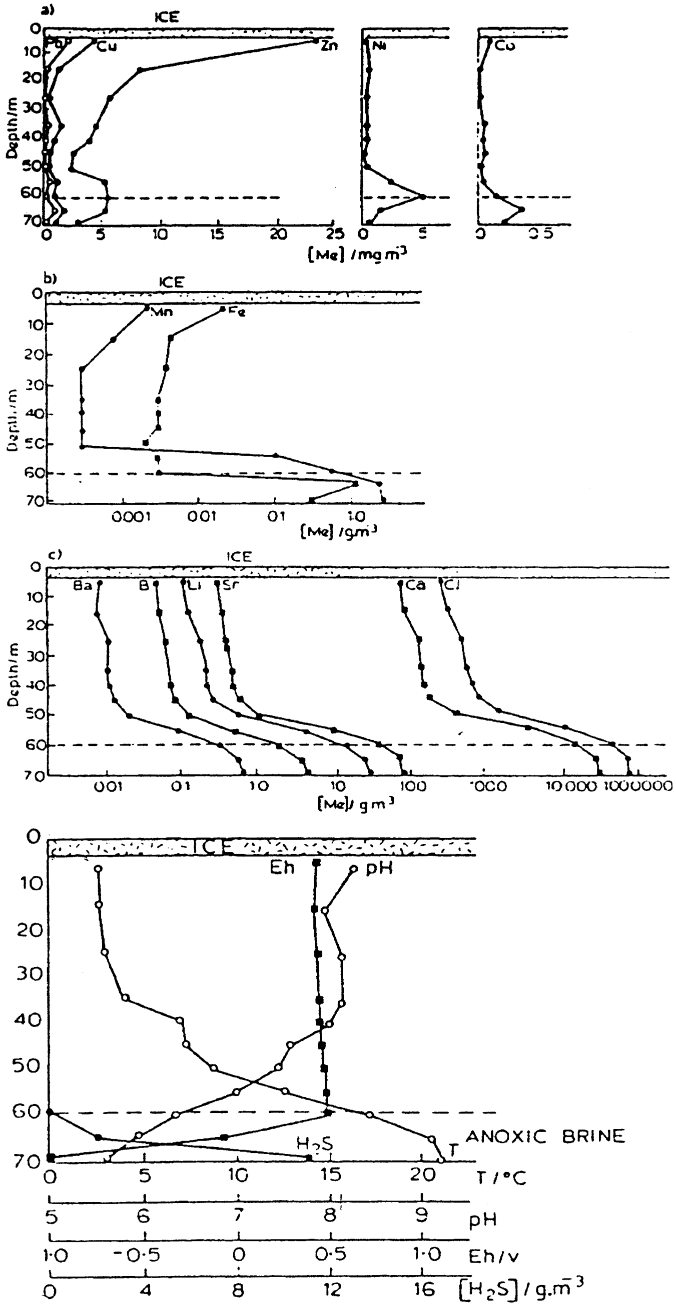


Figure 2.25 Stratification in Lake Vanda, Antarctica (Goguel and Webster, 1990, courtesy of the New Zealand Antarctic Record).

would also indicate that during the same period the lake gained 2 m in depth (from 68 to 70 m). Finally, the temperatures at the base of the lake are far higher than the area's mean-average temperature, and perhaps could be explained by a much more recent "salt gradient effect" (the heating of a lower [light-absorbing] brine by solar radiation passing through a thin and transparent cover layer of water). This effect has been shown to be capable of heating a brine to 40–60°C even in the cold winters of the high Andes, but it is hard to believe that enough radiation could pass through the ice and upper water layer to still heat the lower more concentrated and opaque brine. If this effect is not the cause of the increased temperatures with depth, then the area must posses a much higher than normal thermal gradient.

The *Don Juan Pond* (Figs. 2.26 and 2.27) is a very small basin in the same valley and up slope from Lake Vanda, containing such a concentrated calcium chloride brine that it remains at least partly unfrozen all year, even at −50°C temperatures. During the 1975–1976 season the pond varied in size from $178 \times 595\ \mathrm{m}^2$ ($59{,}500\ \mathrm{m}^2$) to $121 \times 406\ \mathrm{m}^2$ ($40{,}500\ \mathrm{m}^2$ area; $7780–3080\ \mathrm{m}^3$ volume; 7.6–13 cm depth) in its fairly flat 300 × 700 m basin. The valley's sides are quite steep (1000 m rise in less than 1 km; Fig. 2.27), and the valley rises 200 m east of the pond before it slowly drops to Lake Vanda. In some summers, the pond evaporates to dryness, forming crusts of halite, gypsum and the rare mineral antarcticite ($CaCl_2 \cdot 6H_2O$). In late summer a small river flows into the pond containing a low-salt, non-calcium chloride-type water with a pH of 7.7, indicating a considerable HCO_3^- content. Under the pond is 14 m of "silty sand" containing gypsum and calcite that is frozen elsewhere in the valley, but it is not known how deep it remains unfrozen beneath the pond. Under this surface "soil" is 30–40 m of fractured Ferrar dolerite (also called diabase, an intrusive

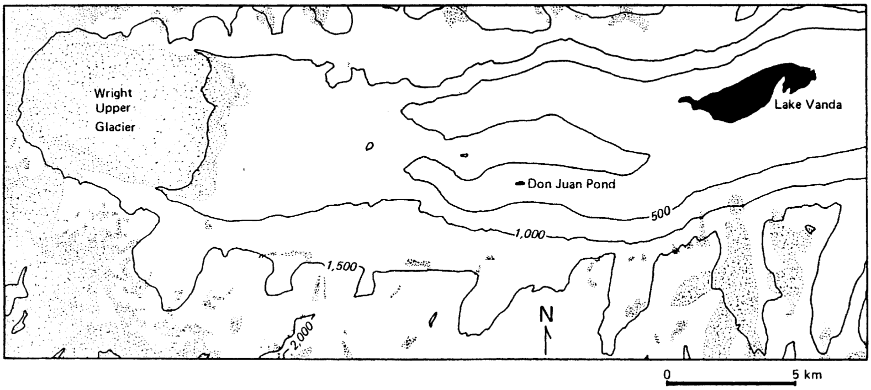


Figure 2.26 Location map of Lake Vanda and the Don Juan Pond, Wright Valley, Antarctica (Harris and Cartwright, 1981; ©1991, American Geophysical Union, reproduced by their permission).

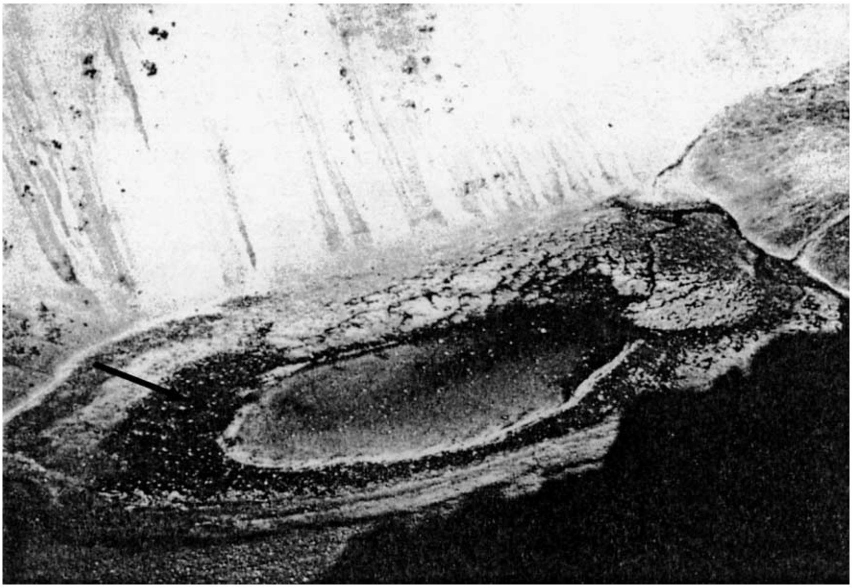


Figure 2.27 Oblique view of the Don Juan Pond (Harris and Cartwright, 1981; ©1991, American Geophysical Union, reproduced by their permission).

mixture of labradorite [feldspar of the plagioclase series containing equal amounts of Na and Ca] and pyroxene). The fractures in the dolerite contain a high-calcium chloride brine that appears to be sealed to form an artesian pressure, and beneath it is the granite basement complex (Fig. 2.28).

The average precipitation (as snow) in the valley is 50–100 mm/yr, and the evaporation rate of the strong brine at the pond in November, 1975 averaged 1.1 mm/day (it increased over 10-fold when there were heavy, cold and dry [$<20\%$ humidity] winds). Brine samples taken at random locations and at different periods before the pond's complete evaporation are listed in Table 2.11, and are notable for their high strontium and various trace metal content. Throughout the valley, there are seawater aerosol-formed mirabilite–thenardite crusts and small deposits, as are common in all of the coastal regions of Antarctica (Garrett, 2001; Harris and Cartwright, 1981; Goguel and Webster, 1990). Gypsum in the Don Juan Pond has a $\delta^{34}S$ value of 30.5, while at the edges of Lake Vanda the values were 39.1–48.8. Both are estimated to have been precipitated from seawater sulfate, and then subjected to considerable sulfate-reducing bacterial action. Glacier melt water gypsum in the Wright Valley has a $\delta^{34}S$ of 9.3–9.6, and snow melt water gypsum 12.6–13.4 (both of the terrestrial [$\delta^{34}S \sim 10$] sulfate-type; Tomiyama and Kitano, 1985).

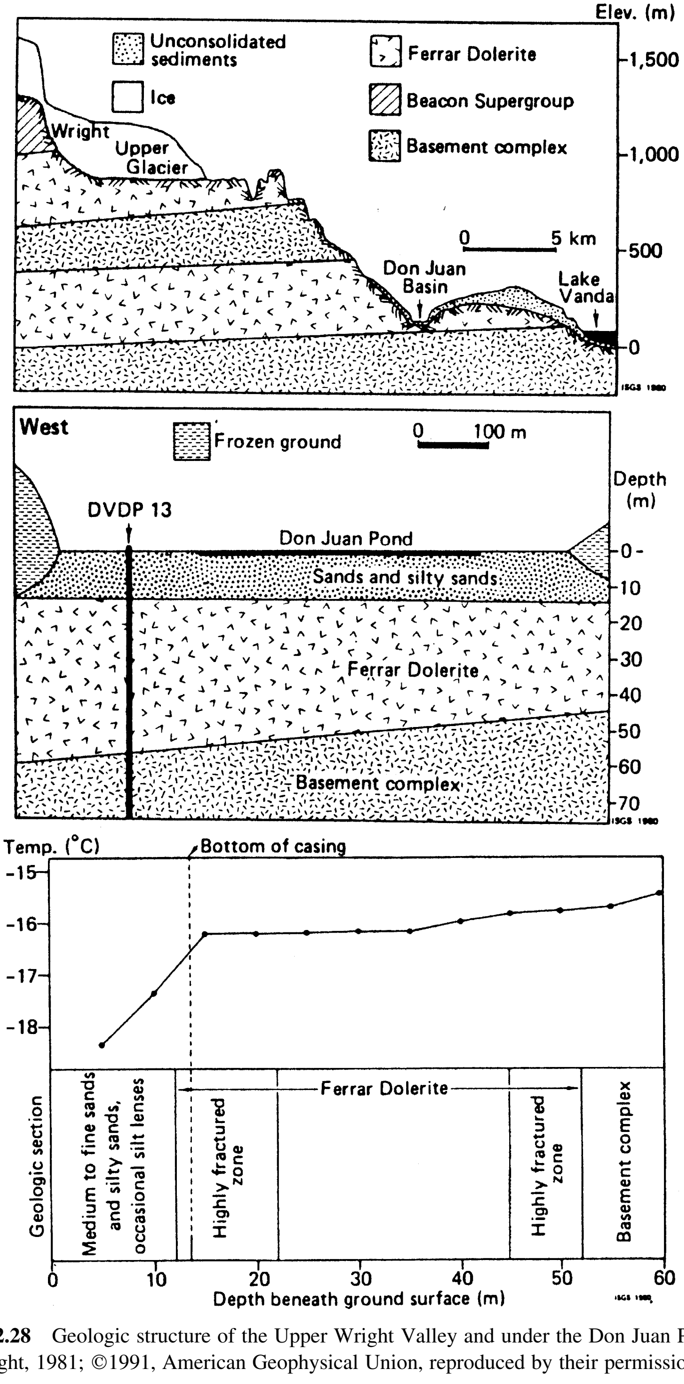


Figure 2.28 Geologic structure of the Upper Wright Valley and under the Don Juan Pond (Harris and Cartwright, 1981; ©1991, American Geophysical Union, reproduced by their permission).

The source of the calcium chloride in these deposits is unknown, but based upon there being no $CaCl_2$ in the analyses of the river, glacial and other surface waters it is very doubtful that local run-off alone could be the source. This is further indicated by Tomiyama and Kitano (1985) who sampled many small pools of water and salts in the valley from the Wright Upper Glacier to the Don Juan Pond. The water compositions varied from 283 mg/liter of a calcium sulfate–sodium sulfate-type to 3.5–104 g/liter of a sodium–magnesium-sulfate–chloride-(seawater) type brine (without considering the dissolved gypsum or calcium bicarbonate, which they did not analyze). The salts found on the ground

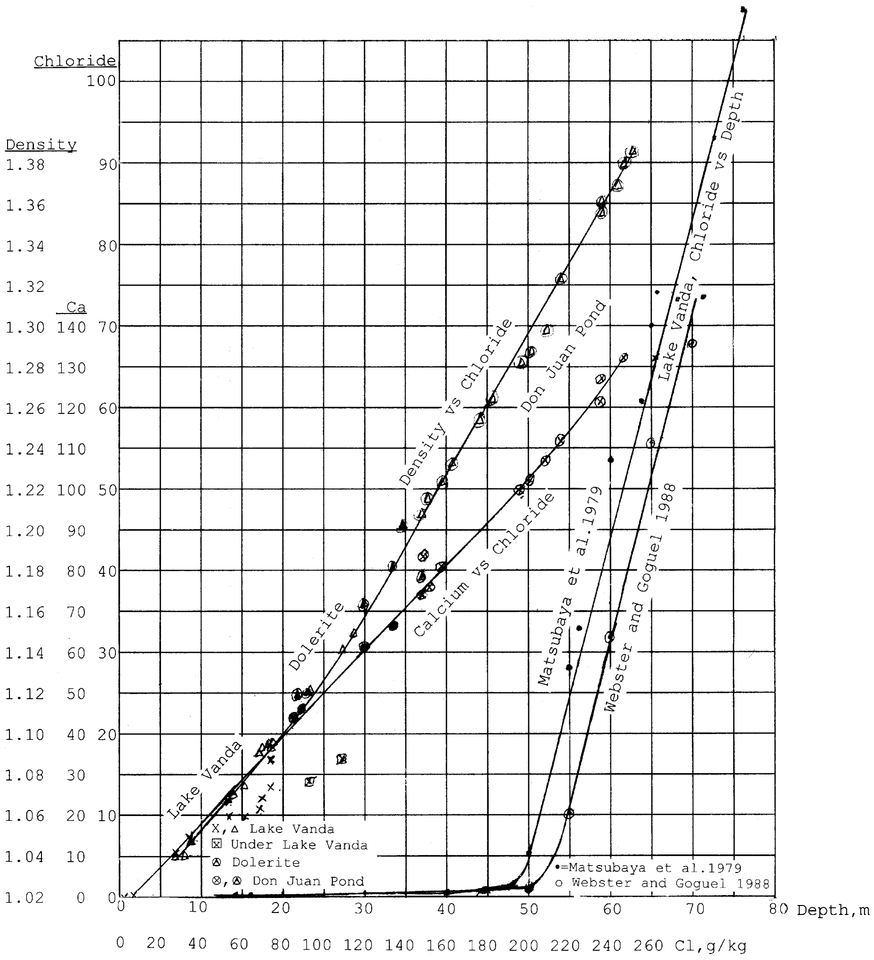


Figure 2.29 Lake Vanda plot of depth versus the brine's chloride concentration; and plots of chloride versus calcium and density.

and near brine pools were predominantly gypsum, sodium sulfate and calcite, with some sodium chloride. Calcium chloride-type water was not found in any sample, although the salts near one small brine pool a short distance from the toe of the glacier, in its central area may have had some bishoffite ($MgCl_2 \cdot 6H_2O$) in one sample and antarcticite in another, although since neither carbonate nor bicarbonate were analyzed these salts were probably merely dolomite and calcite.

By contrast to the river and surface samples, as noted above, Harris and Cartwright (1981) found that under the valley's 14 m of frozen surface soil, the groundwater in the fractured dolerite (resting on granite bedrock) contained an artesian high-calcium chloride brine. This brine appeared to be trapped and to have no pathway for entering the pond or lake, making it possible that each of these three occurrences were older calcium chloride brines that possibly originated from the same source (since their Cl versus Ca [analyses] and density plot consistently, indicating primarily a difference of dilution [Fig. 2.29]). There are some slight differences in the ratio of ions, but these can probably be attributed to their differing flow paths and basins. In Lake Vanda, there is more magnesium and sodium, and less bromine than the Don Juan Pond. The dolerite brine is similar to, but more dilute than the Don Juan Pond, with perhaps a sightly higher sodium and an unknown bromine content. Water balances based upon the river flows to the ponds and lake, and evaporation rates (after the necessary corrections for small pan-to-pond data were made) indicate that no brine leaves the lake or pond, and only a very small input of salts, with no calcium chloride are added to them each year.

Thus, because of the low values for bromine and other indicators none of the brines (Lake Vanda, the Don Juan Pond and the brine in the underneath fractured dolerite) can be considered as concentrated seawater dolomitization brine. In Lake Vanda, for example, the concentration ratios of key ions to seawater at 70–76 m depth are: Br ~ 0.44, Cl 3.5–5.6, Na 0.7–0.9, K 1.5–2.8 and Mg (including its equivalence in Ca) 15–19. However, seawater aerosol also appears to have a quite different ratio of salts than seawater itself. All of the coastal areas of Antarctica receive large amounts of seawater spray each year, with sodium sulfate (as the decahydrate) being the principal mineral crystallized from it. Much less sodium chloride crystallizes, perhaps because of its lower freezing temperature, but more likely there is less sodium chloride in the aerosol. There are no analyses of this spray, but based upon the limited and partial analyses of river and surface water in the area, the sulfate and magnesium contents are proportionally high, and the bromine is very low compared to seawater. Most of the aerosol's sodium sulfate crystallizes, thus perhaps leaving the high-$MgCl_2$, low-Na, K and Br brine found in the surface water (and similar to that found in Lake Bonney in the next valley). It has also been predicted that there were at least four periods of glacial intrusion into the entire valley, scouring it, and almost certainly leaving large amounts of feldspar and plagioclase (from the dolerite and granite) in the layer of glacial till soil (called sands and silty sands) under the lake and pond. The till is also said to contain considerable calcite. Finally, there are bench marks 20–30 m above the Don Juan Pond indicating its depth as a lake in some former wetter period.

To combine these observations, the deposited modified-seawater aerosol end liquor (after $Na_2SO_4 \cdot 10H_2O$ crystallization) would have slowly accumulated in both the Don Juan Pond and Lake Vanda basins, flushed by the glacial and snow melt waters that are currently observed. During dry periods (such as when the ocean ice shelves were greatly reduced 2500–4000 years ago; Perkins, 2001) this water would evaporate and concentrate, eventually crystallizing salt and mirabilite (some of which dehydrates to thenardite), and perhaps forming playas as at present in the Don Juan Pond. Some of the salts on the surface would have slowly been blown away (as now happens with the very fine particles of thenardite and some salt elsewhere in Antarctica), or at times been dissolved and flushed from the basin. The strong magnesium chloride residual brine that was formed would stratify to the bottom of the lakes, and at times been strong enough to melt the ice in the underneath till (snow melting is a current use for $MgCl_2$ and $CaCl_2$), allowing it to react (at its slightly elevated temperatures) with the calcite to form dolomite and exchange the magnesium for calcium (the dolomitization reaction). Its acidic nature would also allow it to react with the plagioclase and feldspar to liberate considerable additional calcium and minor amounts of many other cations, as now occurs with many other $CaCl_2$ brines. However, as the strong magnesium–calcium chloride residual brine melted the underneath ice it would become diluted, lowering its density and causing it to be displaced by stronger brines and forced to the surface. In this manner, the surface brine would slowly contain increasing amounts of calcium chloride, with even more melting power, and the circulation and calcium conversion would continue. After this process had melted all of the frozen soil, it would begin to replace water in the underneath fractured dolerite formation, where the plagioclase reaction would even more completely liberate calcium and replace magnesium with calcium. During wetter periods, both basins would become lakes (as the current Lake Vanda), and store its dilute seawater aerosol run-off waters until the next dry period. Occasionally, the lakes would overflow and flush out the surface salts. Differences in the extent of concentration, dilution, and the calcite and plagioclase content of the underneath soil and dolerite would explain the differences in the present brines.

The reason why there is calcium chloride in these brines, and why it only formed in these locations might thus be due to: (1) their being in the Dry Valley Area (with a very dry, high evaporation rate climate), (2) their nearness to the ocean in order to receive seawater aerosol spray, (3) their presence in impermeable basins (the underneath granite), (4) the presence of calcite and reactive plagioclase in the basins' surface soil, and (5) the slightly elevated rock temperatures to enhance the brine's reactivity. Lake Bonney in the adjacent valley has collected a strong magnesium chloride brine, perhaps in the same manner as assumed here (its low sulfate and potassium contents [Br has not been analyzed] probably imply that it also did not originate from trapped seawater), but apparently the floor of the Taylor Valley does not have sufficient calcite or plagioclase, or higher rock temperatures to convert much of its magnesium chloride into calcium chloride, or liberate as much additional calcium.

Many other articles have been written about Lake Vanda and the Don Juan Pond, such as on the lakes' chemistry (Nakaya *et al.*, 1984; Yamagata *et al.*, 1967), when the stratification occurred (Roberts and Wilson, 1965; Wilson, 1964), organic life in the Don Juan Pond (Siegel *et al.*, 1979), and Lake Vanda's former climate (Perkins, 2001).

Antarcticite

Since the Don Juan Pond forms the world's only substantial deposit of antarcticite, its characteristics will be noted here. Its crystal habit is hexagonal, its density is 1.715 (1.700 is theoretical), and its strongest X-ray diffraction lines are 2.16, 2.80, 2.59, 2.28 and 1.978. Its optical properties are $\omega = 1.550$ and $\epsilon = 1.495$ (Torii and Ossaka, 1965). Small amounts of "divergent groups of colorless, prismatic crystals and compact aggregates (of antarcticite)" have also been found in small isolated pools at Bristol Lake in California (Dunning and Cooper, 1969; Muehle, 1971). Several authors have also reported crystals of antarcticite trapped in other minerals' occlusions, and small amounts have been calculated to be present in the Sergipe, Brazil tachyhydrite deposit, although both sources are unconfirmed.

Calcium Chloride Groundwater

Throughout the world there are a number of calcium chloride groundwater occurrences that often are of an unknown origin. In many cases, they may be seawater dolomitization brines or oil field calcium chloride waters that have traveled great distances, but in some cases they appear to have originated by other means. Many authors have presented a variety of theories as to their formation, with the currently most popular of these being that they resulted from the reaction of seawater (or other water) with plagioclase to form albite. Others have suggested that the reaction was between lava or similar volcanic rocks with sea or other water (Hardie, 1990), the leaching of feldspar or mica, or the reaction of the gases that accompanied volcanoes (H_2S, HCl, CO_2, etc.) with calcite. Many favor the ion exchange of sodium in the original water with calcium in clays, zeolites or other rocks. All of these reactions must have occurred to some extent, but it would appear that by far the most dominant reaction to produce calcium chloride is strong-magnesium chloride brines (seawater or end liquors from extensive inland water evaporation) with calcite. Some of the various calcium chloride groundwater analyses that have been reported are listed in Table 2.12, and their descriptions will be reviewed in the following section.

One of the minor occurrences of calcium chloride groundwater, but one where there has been a study on the source of the calcium chloride is in the

Table 2.12

Examples of Calcium Chloride Groundwater (ppm)

	Ca	Na	K	Mg	Cl	SO_4	SiO_2	NO_3
Namib Desert[a] 1	1823	1620	78	2187	3850	1105	50	200
Namib Desert[b] 2	137	34.3	8.4	86.7	20	18	8.8	0.7
So. High Plains[c]	4430	9700	209	3310	32,000	1470	—	—
England, Av. No–Ba[d]	3500	8580	43	313	20,040	240	—	—
England, Av. Hi–Ba[d]	5020	18,270	26	593	39,280	64	—	—
Israel[e] 1 (5)[f]	1170	6890	177	532	12,790	2025	—	—
Israel[e] Oil (46)[f]	1660	19,360	355	536	34,130	186	—	—
Israel[e] 2 (8)[f]	15,300	22,120	586	1350	64,470	810	—	—
Israel[e] 3 (23)[f]	11,570	34,440	761	1440	77,340	571	—	—
Israel[e] 4 (6)[f]	39,050	29,600	1160	5150	130,100	741	—	—
Israel[e] 5 (4)[f]	39,930	22,210	15,670	42,670	249,670	95	—	—
Israel[e] 6 (2)[f]	82,870	20,520	28,730	19,770	265,150	108	—	—
Israel[e] 7 (1)[f]	15,800	34,940	7560	41,960	208,020	540	—	—
Siberian Plat.[g]	50,100	32,700	9600	7900	170,800	133	—	—
W. Caucasus[h]	63,600	16,300	—	283	138,300	15	—	—
Germany	36,000	45,000	4000	900	142,000	110	—	—

	HCO_3	Br	I	F	TDS	pH	Depth (m)	
Namib Desert[a] 1	476	—	—	3.2	9305	6.85	—	
Namib Desert[b] 2	227	—	—	0.3	305	7.4	—	
So. High Plains[c]	143	—	—	—	52,260	6.35	50	
England, Av. No–Ba[d]	155	29	—	—	32,900	—	—	
England, Av. Hi–Ba[d]	193	39	—	—	65,570	—	—	
Israel[e] 1 (5)[f]	216	55	—	—	23,850	—	1457	
Israel[e] Oil (46)[f]	257	138	12	—	56,630	—	1549	—
Israel[e] 2 (8)[f]	92	727	—	—	107,785	—	2326	—
Israel[e] 3 (23)[f]	164	620	4.1	—	126,920	—	2404	—

(*continues*)

Table 2.12

(continued)

	HCO_3	Br	I	F	TDS	pH	Depth (m)	
Israel[e] 4 (6)[f]	103	2550	—	—	207,463	—	2085	—
Israel[e] 5 (4)[f]	127	2940	—	—	373,310	—	0	—
Israel[e] 6 (2)[f]	0	2990	—	—	420,120	—	0	—
Israel[e] 7 (1)[f]	240	5920	0.1	—	314,980	—	0–400	—
Siberian Platform[g]	382	3100	—	—	274,600	—	2558	ρ 1.264 est.
W. Caucasus[h]	327	3.6	0.5	—	218,800	7.1	1153	1.118 est.

[a] Coastal plain in Namibia; a well in the Swartberg farm (Cagle and Cruft, 1970).

[b] As 1, except the Spes Bona farm.

[c] Southern High Plains of Texas, Kiamichi Formation, Sanford *et al* (1992).

[d] Anderson (1945); The Hi–Ba water (15 samples) also contained, as ppm: Fe 103, Li 64; no-Ba water (17 samples): Fe 13.

[e] Bentor (1969); All are ground waters except "Oil"; No. 1 is found in very near the coast, and more diluted in the central plateau; Jurassic and Lower Cretaceous formations; Oil is oil field brines in the near-coastal Lower Cretaceous formations; No. 2 is in the Negev; Paleozoic; No. 3 is western Negev and deeper Jurassic; No. 4 is Rift Valley Arava 1 and Heimar 1; No. 5 is the Mount Sdom spring (in the Rift Valley); No. 6 is the Sdom 1 artesian well (in the Rift Valley); No. 7 for comparison is the Dead Sea (in the Rift Valley).

[f] Values in parenthesis imply the number of wells in the average.

[g] Bakhta megaexposure, Siberian Platform, Russia; 6 wells; Shvartsev and Bukaty (1996).

[h] Okumi-II well; Bajocian volcanic deposits, Western Caucasus, Russia; Pastushenko (1967).

[i] Holdorf *et al.* (1993). Also 290 ppm Li.

Double Lakes areas of the Kiamichi Formation in the Southern High Plains of Texas (Sanford *et al.*, 1992). Samples were taken of the Na, Ca and Mg content of wellwater with depth, and corresponding samples were taken of the exchangeable cations in the soil. The surface water in the area has a high content of calcium/magnesium bicarbonate, while the upper formation (the Ogallala) originally contained a high-sodium/magnesium sulfate/chloride water. In areas of the High Plains where current or ancient dry lakes have formed, such as the Double Lakes, the high-sulfate water has been concentrated, and many lakes have deposits of mirabilite (sodium sulfate decahydrate), and some of them halite. In the Double Lakes basin, the Ogallala Formation contains this strong sodium chloride–sulfate brine (as wt.%: Na 2.7, Cl 4.5, SO_4 1.7, Mg 0.338, K 0.337; as ppm: Ca 655, HCO_3 141; pH 7.08). With increasing depth (in the underlying Kiamichi Formation) the sodium, potassium and magnesium decreases, the calcium increases, and much of the sulfate has been precipitated. This formation consists of a marine smectite clay shale that after it had been uplifted was converted to the calcium and magnesium ion exchange form (as indicated by soil samples taken some distance from the lakes). However, under the Double Lakes the soil contained considerable more exchangeable sodium (Fig. 2.30; potassium was not measured). The authors concluded that ion exchange had occurred in the soil, and that considerable sodium and potassium from the descending strong lake basin water had replaced some of the soil's calcium, forming a $CaCl_2$ brine (Table 2.12).

This theory appears to be at least partly correct because of the low potassium in the calcium chloride aquifer, but dolomitization could have also formed this water. When the Ogallala waters evaporate to deposit mirabilite and perhaps halite (as is found in many of these lakes) a high-magnesium chloride end liquor is formed. Being heavier, it would seep into the Kiamichi Formation and have undergone the dolomitization reaction in the playa sediments to form a brine such as is now present. Later the typical Ogallala (less concentrated) water would have migrated back into the upper formation, as it now does in lakes that have commercial sodium sulfate production. In either case, gypsum would have precipitated as the change in the soil took place, forming gypsum with the low ^{34}S content ($+7-+10$) that it now has, rather than the original marine value of $\sim +20$. The change observed in the ion exchange capacity in the Kiamichi Formation would have also occurred as the strong sodium–magnesium chloride/sulfate end liquor passed through it.

In northwest Queensland, Australia strong calcium chloride brines have been reported in the Proterozoic Cloncurry District, (Williams, 1994) with no indication of their source. In Yellowknife, in the North West Territories of Canada (Fig. 2.6) a very strong calcium chloride brine has been found in a gold mine and throughout the Canadian Shield area. Isotopic studies and a high bromine content in the brine strongly indicate that it is of seawater origin, and it is strong enough

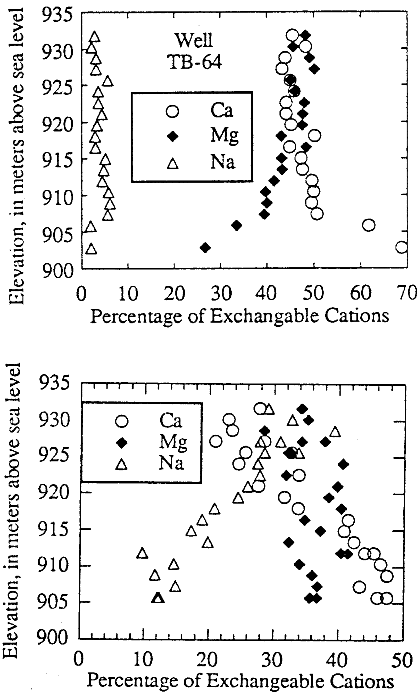


Figure 2.30 Cation exchange capacity of the Kiamichi Formation adjacent to (top figure) and under (bottom figure) Double Lakes, Texas (Sanford *et al.*, 1992; reprinted from Water–Rock Interaction by permission from Swets & Zeitlinger Publishers).

to have been a potash deposit dolomitization brine, possibly from the Saskatchewan deposit (Bottomley *et al.*, 1999).

In the Variscan foreland of southern Belgium, calcium chloride ground waters have been reported (Muchez and Sintubin, 1997) that very likely are related the area's Zechstein Formation halite and potash deposits. In England, there are also extensive areas of high-calcium chloride ground water and springs that may have also been derived from England's Zechstein Formation. Anderson (1945) reported on a number of these occurrences, and especially those in the North East Coalfields. Many of the waters have a high barium, iron and lithium analysis (Table 2.12), and their total salt content varies considerably from 0.12 to 4.6 times that of seawater. In Cyprus, the Ophiolite formation contains calcium chloride brine that appears to be related to a seawater incursion, as evidenced by carbon and oxygen isotope determinations (Kerrich and Vibetti, 1985). A similar situation exists in Greece with the northern aquifer of the Filiatra limestone (Tavitian and Sabatakakis, 1994), in the soil around the Ennur coastal tract in Madras,

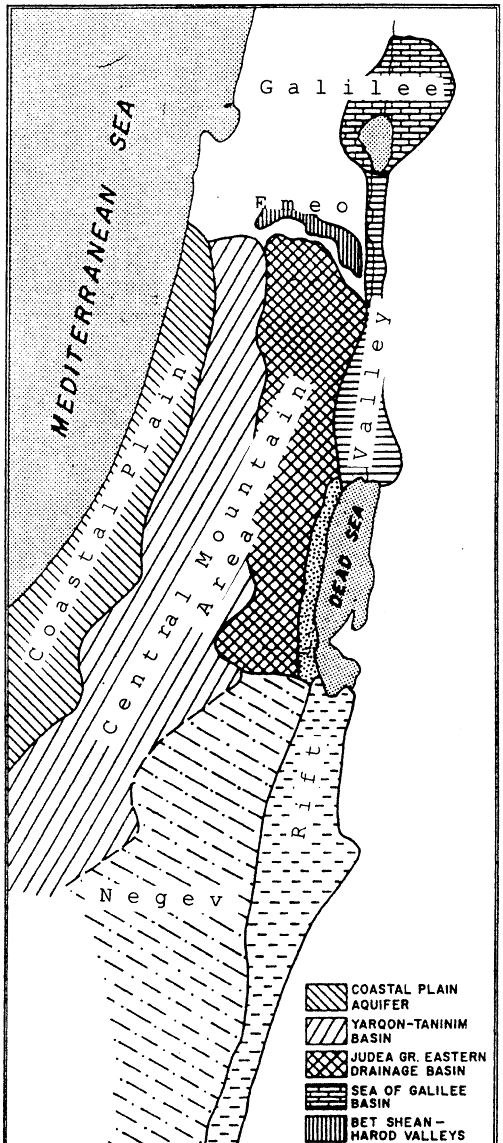


Figure 2.31 Major Groundwater Basins of Israel (Vengosh and Rosenthal, 1994; Bentor, 1969; reprinted from the Journal of Hydrology, Vol. 156, p. 391, Fig. 1, ©1994, with permission from Elsevier. Reprinted from Chemical Geology, Vol. 4, p. 85, Fig. 1, ©1969, with permission from Elsevier).

Tamil Nadu, India (Shepherd *et al.*, 1994), and in the sediments of Lake Veli near the southwest coast of India (Anirudhan *et al.*, 1991).

The calcium chloride groundwater in Israel is a rather special case, since its source might have been any or all of: the Dead Sea or brine in the fault system that formed the Dead Sea; other (perhaps Red Sea-derived) calcium chloride springs in the country; from oil and gas formations; and seawater intruding into the coastal plains. However, even with such well-known potential sources, the exact nature and origin of the calcium chloride aquifers in various parts of the country are still in doubt, and many articles have been written about them. General discussions of the subject have been presented by Vengosh and Rosenthal (1994), Rosenthal (1988, 1985) and Sass and Starinsky (1979) (strontium in the brines), and Bentor (1969).

The latter author tabulated many analyses of calcium chloride groundwater in various aquifers of the country (Fig. 2.31 and Table 2.12), with all of them appearing to be different forms of dolomitization brine. Those very near the coast (the first three of Israel 1 in Table 2.12) were almost pure seawater with much of the magnesium replaced by calcium, and very little of the sulfate yet precipitated. The other two samples of Israel 1 were from the central plateau, and of the same composition but considerably diluted with meteoric water. The oil field and Negev aquifers (Israel Oil and 2, 3) are slightly more concentrated seawater dolomitization brines, but the Rift Valley aquifers, springs and the Dead Sea represent considerably altered potash deposit dolomitization brine that appears to have traveled along the Red Sea fault system to Israel (Bentor, 1969).

Among other articles on Israel's groundwater, the *Bet Shean–Harod* multiple calcium chloride aquifer system has been reviewed by Rosenthal (1988), and the similar Eocene aquifer of *Alonim Shefara* by Azmon (1993). Several articles have been written about calcium chloride in the *coastal aquifer* (Artzi *et al.*, 1996; Vengosh *et al.*, 1991), and about calcium chloride brine in the *coastal sabkhas* (playas; Levy, 1977).

In the coastal plain of Namibia, there are both very dilute and more concentrated calcium chloride ground waters (Table 2.12), and in one basin the evaporation of similar water to produce salt also forms a quite concentrated calcium chloride brine (Table 2.12; [1]). This area is similar to northern Chile in that the morning coastal fogs allow the capturing of catalytically formed nitric oxides, which in turn produce nitrates (Garrett, 1985), giving the groundwater and brines a high nitrate content (Cagle and Cruft, 1970). The source of the calcium chloride in the aquifer is unknown, but it likely has resulted from a seawater dolomitization brine–meteoric water mixture in this coastal area (i.e., the salt pan is only 32 km from the ocean).

Russia has a number of calcium chloride ground waters, just as it has many marine halite and potash deposits (Fig. 2.9) and oil and gas fields. However, even though there are potash deposits in the general area of most of the following calcium chloride occurrences, it is not known whether this is their source, and many alternate theories for their origin have been suggested. Poroshin (1981) reviewed the strong calcium chloride brines found in various locations, and Shvartsev (1973) discussed several possible sources for the calcium, strontium and barium in these brines. Samarina *et al.* (1971) suggested ion exchange and rock leaching as the calcium chloride source in arid regions such as south central Russia. Seletskiy *et al.* (1973) discussed the supersaturated calcium chloride brines in the *Angara-Lensk* basin, while Pastushenko (1967) theorized that the alteration of volcanic rocks to form zeolites liberated calcium chloride for the brines in the middle Jurassic volcanic deposits of the western *Caucasus* region. In the eastern and central area of the Caucasian foreland, Nikanorov and Volobuyev (1968) discussed the calcium chloride brines in the Mesozoic–Cenozoic aquifers, and Volobuyev (1967) noted their increasing concentration with depth. Ovcharenko and Kurishko (1971) reviewed the characteristics of the calcium chloride brines found in the Melovyy Uplift in the *Crimean Steppe*. Gamalsky (1956) noted that in the *Russian Platform* calcium chloride brines are found in all of the deep formations, and that the different circulation patterns in the brine resulted in changes in the mineralization. In the Khapchagay uplift in the Vilyuysk area of Siberia, the deep ground water is of the calcium chloride type (Shabalin and Grubov, 1969), as are the aquifers in the *Siberian Platform* (Shvartsev and Bukaty, 1996). In the *Volga region*, certain areas have soils with a high-calcium chloride content, which is similar to some sediments in the bottom of the Caspian Sea (Slavnyy, 1966).

In Saudi Arabia, the Umm Er Radhuma limestone in the eastern part of the country contains calcium chloride (Sen and Al-Dakheel, 1986), possibly either of oil field or direct seawater origin. Various calcium chloride groundwater observations have also been made in the United States. A late Alleghanian migration of such waters has been noted in the central *Appalachian mountains* (Evans and Battles, 1996), while in Massachusetts some calcium chloride has been found in the groundwater of Middlesex county (Toler and Pollock, 1974). The *Waste Gate* Formation in Maryland contains a $CaCl_2$ water with about 6.5% TDS (Hansen, 1982). In the Trans-Pecos region of Texas, the deeper Permian and lower Cretaceous aquifers contain calcium chloride brines, and their mixing with shallower aquifers results in some quite dilute calcium chloride springs (i.e., the San Solomon, Griffin and Phantom Lake springs; Hart, 1992). Similar waters have been observed in the Texas Panhandle (Bein and Land, 1982), and both almost certainly originated from the large Carlsbad potash deposit (Fig. 2.1). In Zimbabwe, aquifers in the southern Zimbabwe Craton and northern margin of the Limpopo Belt contain calcium chloride waters (Schmidt Mumm, 1997).

Tachyhydrite Deposits

There are three massive tachyhydrite ($CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$) deposits in the world, with two of them probably having once been joined and then split by a continent-forming rift system (Fig. 2.32). The deposits in Brazil and the Congo appear to be positioned exactly next to each other before the South American and African continents drifted apart. Both areas contain potash deposits of Lower Cretaceous

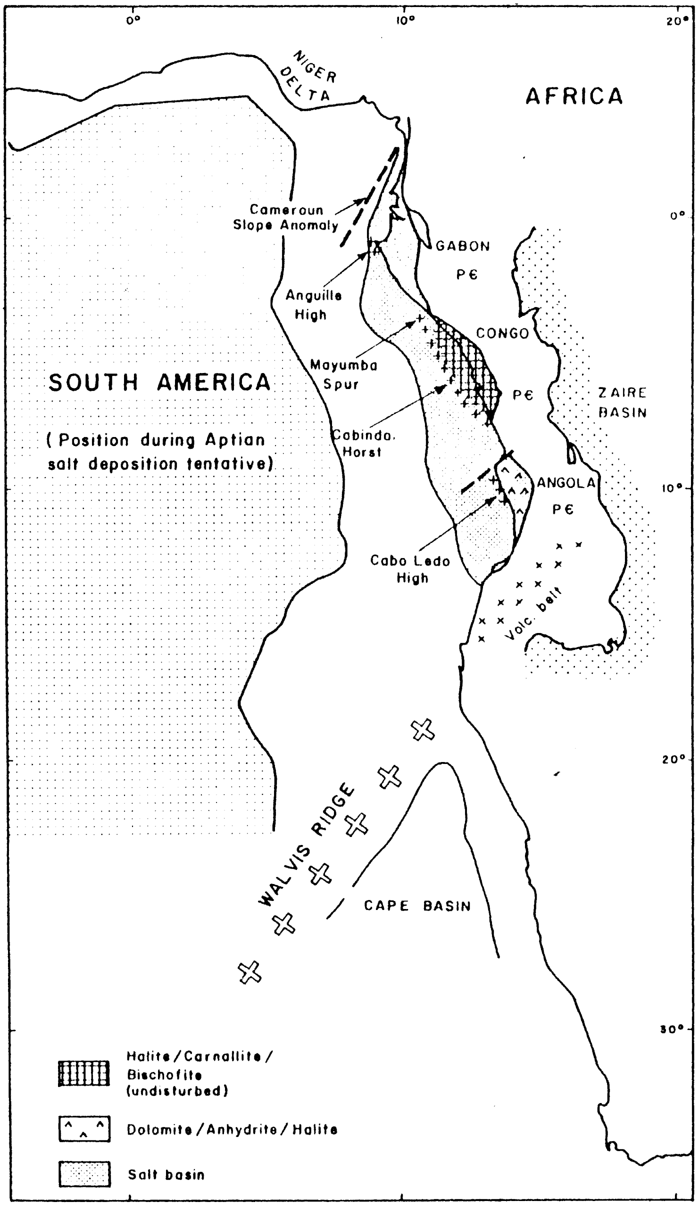


Figure 2.32 Location of the Congo salt–potash basin, and presumed pre-rift location of South America (DeRuiter, 1979; reprinted with permission from Economic Geology, Vol. 74:2, p. 426, Fig. 12, deRuiter, P. A. C., 1979).

Aptian age, with significant and very similar amounts of at least 10 trace elements, most of which are quite different than found in other potash deposits (Wardlaw and Nicholls, 1972). The formations are not of normal marine origin, since there are no underlying or admixed layers of calcite (or dolomite) or gypsum (or anhydrite), and they were crystallized directly on top of continental conglomerates or shale, and tightly bounded by similar rocks (Fig. 2.33). Their bromine and rubidium contents, however, are fairly similar to seawater deposits (Table 2.13).

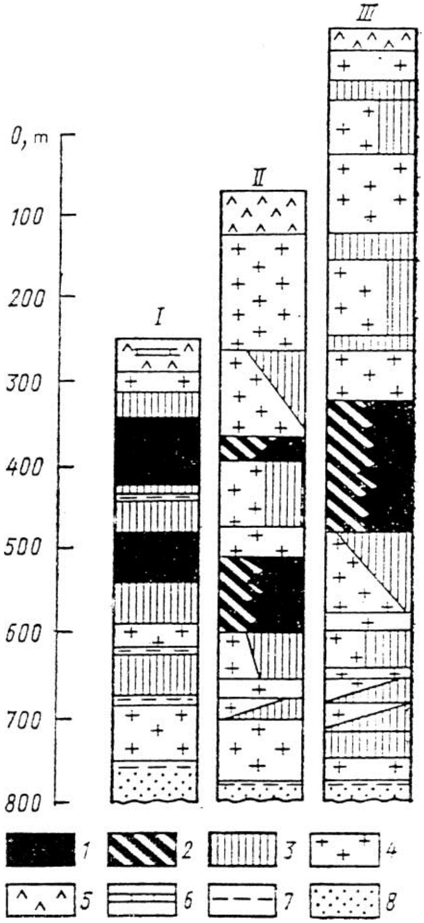


Figure 2.33 Structures in Cretaceous tachyhydrite-bearing evaporite formations: (1) tachyhydrite; (2) bischofite; (3) carnalite rock and sylvinite; (4) halite; (5) anhydrite; (6) carbonates; (7) clays and argillites; (8) sandstones, siltstones, and conglomerates; (I) Sergipe–Alagoas Basin; (II) Gabon Depression; (III) Congo Depression (Vysotskiy, 1988; reprinted with permission from International Geology Review, Vol. 30, No. 1. pp. 31–35, ©vol. H. Winston & Sons, Inc., 360 South Ocean Boulevard, Palm Beach, FL 33480. All rights reserved).

Table 2.13

Bromine and Rubidium Analyses in Sergipe, Brazil Minerals (ppm) (Wardlaw, 1972)

				Marine deposits[a]	
Mineral	No. of Anal.	Range	Average	Range	Average
(A) Bromine					
Halite	63	93–643	360	20–450	320
Sylvite	6	830–1340	1140	250–3900	1850
Carnallite	30	1960–8150	4730	350–4000	3000
Tachyhydrite	43	3050–4730	3670	2000–4400	3500
(B) Rubidium					
Sylvite	6	18–55	38	7–480	50
Carnallite	29	55–126	74	60–500	200

[a] Garrett (1996).

In considering the origin of the calcium chloride in these deposits, if seawater dolomitization brine from other potash or halite deposits were the source it could have provided the tachyhydrite's seawater-type bromine and rubidium values. However, there is almost no possibility of there having been predecessor potash or halite deposits in the area, so this source is quite unlikely. It is much more probable that the deposits were formed by a brine similar to that found in some of the modern rift systems (i.e., the deep sea vents and various hot springs as in the Afar Depression, Iceland and Japan; Vysotskiy, 1988). They are also derived from seawater, but much of the magnesium has been replaced by calcium, additional calcium and many trace metals have been added by rock-leaching, and most of the bicarbonate and sulfate has been precipitated. Consequently, if during Cretaceous times such rift brines flowed into a closed, shallow inland playa-type lake in a subsiding basin, with a hot, arid climate, and did so for sufficient time, they would have formed these deposits without crystallizing the normal seawater companion masses of calcite and gypsum. This type of brine source for the deposits would also appear to be indicated by the analysis of brine in fluid inclusions found in halite in all three of the deposits. They contain 23.1–24.6% Ca, 4.8–5.9% Mg and 0.42–0.49% K, with no detectable sulfate (Timofeeff *et al.*, 1998).

The geothermal nature of these brines would have also been a necessity in forming the deposits, since at present even in the harshest of deserts and hottest conditions (i.e., such as at the Dead sea, Bristol Lake and the Salton Sea [experimental] solar ponds) bischoffite ($MgCl_2 \cdot 6H_2O$, a companion and predecessor mineral in the deposits) rarely forms except for small amounts in isolated locations, and tachyhydrite essentially never is crystallized except as an occasional rare mineral. It could form in low-humidity areas such as the high-Andes or Antarctica, but the tachyhydrite deposits are in more tropical zones and near oceans. Thus, it would appear that only a geothermal brine could evaporate at high enough temperatures to form such massive tachyhydrite deposits. As an example of such present-day evaporation, in the nearby African Rift Valley at Lake Magadi, Kenya geothermal brine pools evaporate at temperatures of 45–85°C, and have formed a several billion ton trona deposit. Deep sea vent-type springs might well have been available in inland, near-rift basins to form the tachyhydrite deposits in Brazil and the Congo, and the similar Lake Giulietti-type brine might have been present at the non-rift basin in Thailand. The latter deposit is fairly near to the ocean, and has had magma intrusions such as have formed the Danakil Basin's Lakes Asal and Giulietti calcium chloride hot springs. As a further indication of this, the potash deposits in both the Congo and Brazil still have abnormally high temperatures, such as 44°C at 500 m depth in the Sergipe mine (Mraz *et al.*, 1996).

The phase chemistry of the rift-type seawater rock-leaching, dolomitization brines would have allowed deposits like each of these tachyhydrite occurrences to have been formed. However, in each of the three deposits it is also quite certain that they were formed in a non-marine basin with some terrestrial water and sediments in addition to the geothermal calcium chloride brine input. As an alternate source for the calcium chloride, it possibly could have been a magmatic fluid that originated with the molten rocks of the rifts, but based upon data from the present-day rifts and the deposit's low boron and lithium content, this would appear to be quite unlikely. Stankevich *et al.* (1992) have discussed the mineralogy (including the major and minor minerals) of such deposits, while Vysotskiy (1992, 1988), and Valyashko (1975) have also speculated on the possible geochemical conditions that formed these deposits.

Sergipe, Brazil

This deposit occurs in three separate sub-basins of the Ibura member of the Muribeca formation in what appears to be fault bounded troughs, although the presence of 18 similar marker beds in all three basins implies that they were connected as the deposit formed, or that the evaporating conditions were very similar in each basin (Fig. 2.34; Borchert, 1977). The potash and other salts extend to the very edge of the basins, instead of the usual seawater deposits merging into halite, anhydrite or dolomite over a much wider area. A common sequence (from the bottom to the top) of the 10–800 m thickness of soluble salts is halite, carnallite and then tachyhydrite, although in some cases carnallite (or its sylvinite replacement) lies on top of the tachyhydrite (Fig. 2.35). The tachyhydrite is usually very coarse-grained, pure and with a transparent-to-slightly milky color (Wardlaw, 1972). These characteristics could be explained by the crystallization

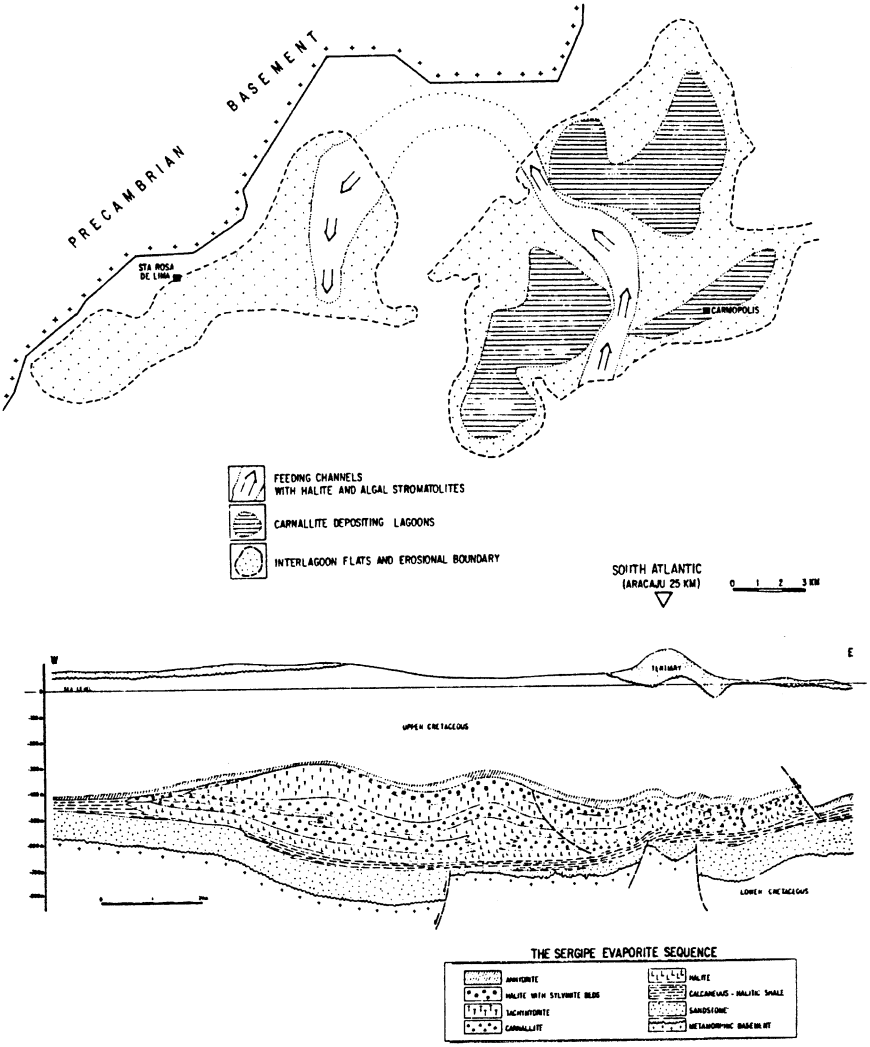


Figure 2.34 Map of the Sergipe Potash Deposit Sub-Basins and their Generalized Structure (Szatmari *et al.*, 1979; reprinted with permission from Economic Geology, Vol. 74:2, p. 444, 445 Fig. 9, 11, Szatmari, P., Carvalho, R. S. and Simoes, I. A. 1979).

being primarily from evening cooling, followed by considerable daytime redissolving and then evening recrystallization to form large, clear crystals.

There are sylvinite beds within the carnallite zones, or sometimes they occur alone. An example of the latter case is the commercial potash mine at Taquari–Vassouras, which covers an area of 85 km^2. The deposit's depth varies

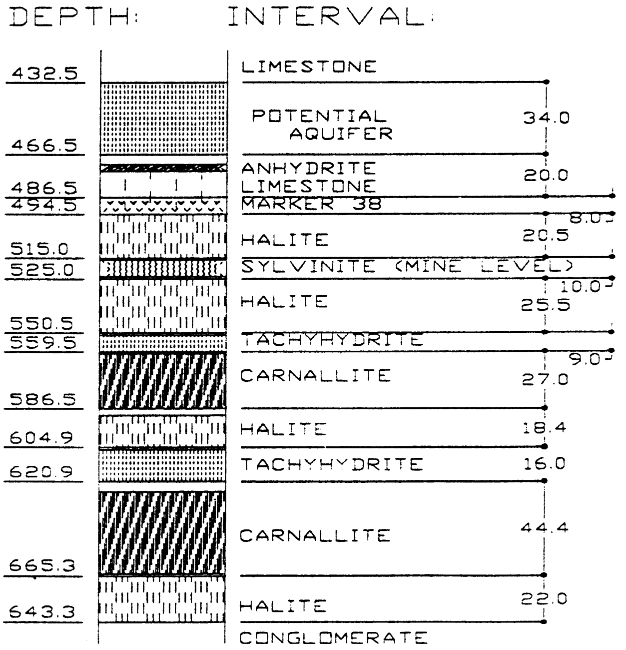


Figure 2.35 The Formation Stratigraphy at the Sergipe Potash Mine (Mraz *et al.*, 1996; reprinted from Rock Mechanics by permission from Swets & Zeitlinger Publishers).

from 500 to 850 m, and in the initial mining area fine grained halite overlay the sylvinite (which contained some carnallite), and tachyhydrite was underneath. The tachyhydrite had a low mechanical strength, high creep tendencies and was very hygroscopic, all of which contributed to mining difficulties (Garrett, 1996). More recently, the mining area has been moved, the new mine has a depth of about 500 m, and the sylvinite is between two halite beds (Fig. 2.35). In this area, there are nine evaporite cycles, with the lower six having a sequence of halite, carnallite and then tachyhydrite. Above that the sequence is carnallite, sylvinite, halite, and limestone with shale (Mraz *et al.*, 1996; Zharkova, 1985).

Fernandes (1976) has prepared contour maps of the carnallite and tachyhydrite (Fig. 2.36) ore in one area of the deposit, and tabulated the total reserves of magnesium. In the current mining area there appeared to be 533 million tons of $CaCl_2$ (and 387 MMmt of MgO) in massive and easily solution-minable tachyhydrite. Andrade (1984) analyzed various trace metals in the run-of-mine (impure) minerals of the deposit, and these values are compared with fairly pure minerals in Table 2.14. The values are very similar to those in the Congo deposit, and many of the world's calcium chloride brines. They are particularly high in strontium, and relatively high in some of the heavy metals. In Sonnenfeld and Kuehn's (1993)

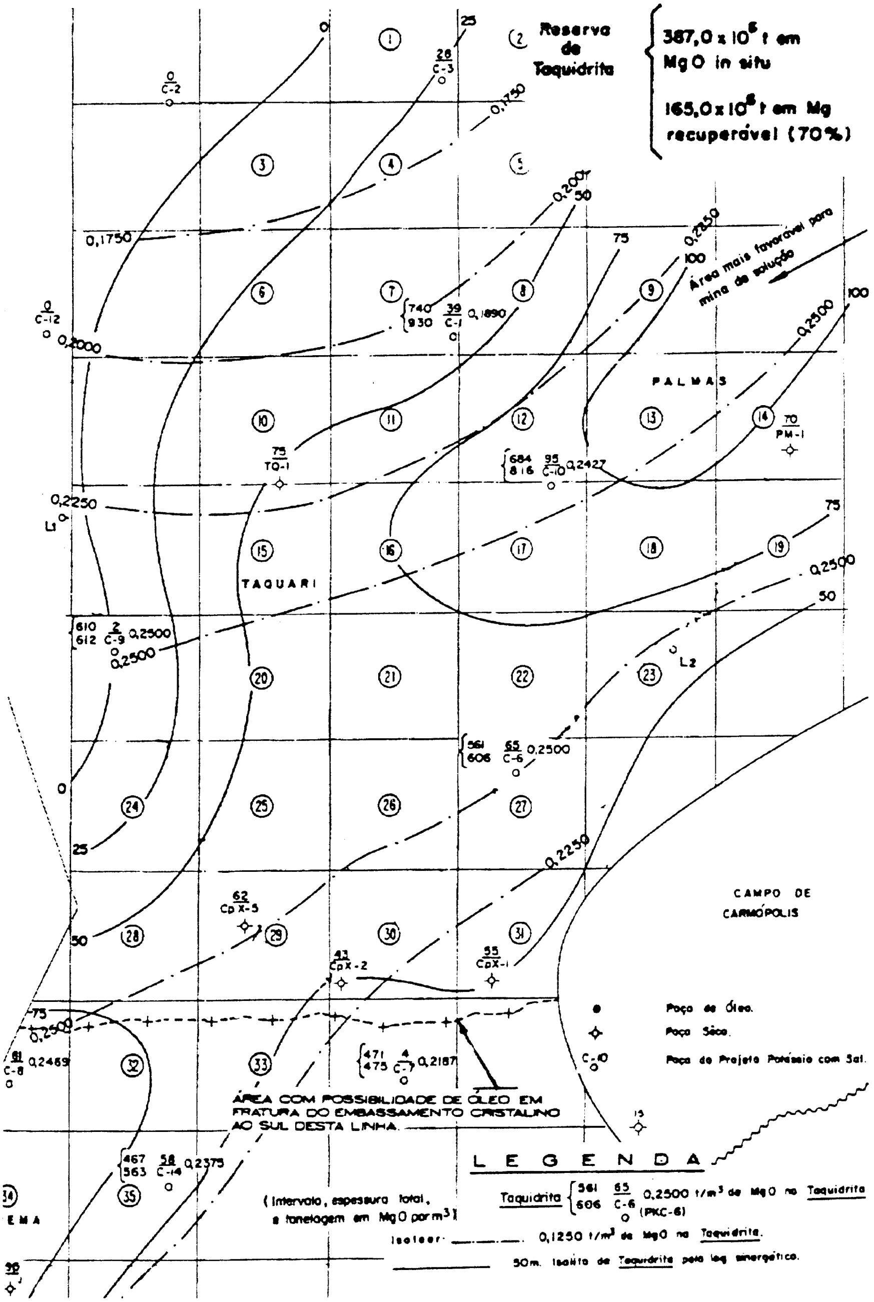


Figure 2.36 Thickness isopachs of tachyhydrite in the Sergipe mining area (Fernandes, 1976, courtesy of Minerals and Metallurgy [Brazil]).

Table 2.14

Various Analyses of the Sergipe Deposit (ppm)

	Halite		Carnalite		Sylvinite		Tachyhydrite	
	And.	W&N	And.	W&N	And.	W&N^a	And.	W&N
Ca, %Pure^b	—	—	—	—	—	—	—	7.74
		1.60		0.04	—	0.04	6.8	7.37
Mg, %Pure^b	—	—	—	8.75	2.5	—	—	9.39
		0.04		8.38	—	0.08	6.3	9.46
Na, %Pure^b	—	39.35	—	—	—	—	—	—
		35.08		1.95	—	4.28	—	0.08
K, %Pure^b	—	—		14.08	—	52.45	—	—
		0.20	—	12.55	—	42.50	—	0.15
Cl, %Pure^b	—	60.65	—	38.28	—	47.55	—	41.00
	—	59.81		38.73	—	48.42	—	40.44
Sr	1070	—	750	—	180	—	1930	1820
	—	—	—	—	—	—	—	1360^c
Ba	1600	3.2	930	1.9	360	—	1300	7.2
Mn	700	0.6	125	0.6	180	—	130	0.4
Zn	—	1.5	—	6.2	—	—	125	1.5
Cr	130	—	150	—	72	—	100	—
V	48	—	54	—	70	—	71	—
Cu	190	—	30	4.0	170	—	63	2.5
Fe	—	—	—	—	—	—	—	50^c
Ni	21	—	22	—	25	—	34	—
Pb	100	—	54	—	92	—	27	7.5
Mo	24	—	40	—	50	—	13	—
Co	14	—	9	—	11	—	6	—
F	—	5.2	—	7.2	—	—	—	3.3
Ag	0.5	—	1.6	—	0.8	—	1.7	—
Be	0.6	—	0.5	—	0.6	—	1.0	—
B	—	1.4	—	2.4	—	—	—	0.4

And. = Andrade (1984) (apparently a run-of-mine sample). W&N = Wardlaw and Nichols (1972) (apparently fairly pure crystals).

[a] Sylvite.

[b] As wt.%; Pure means pure crystals (theoretical analysis); the second line is that of actual samples.

[c] Sonnenfeld and Kuehn (1993). They also listed for tachyhydrite 440 ppm K, and 240 ppm Na (also presumably fairly pure crystals).

chemical analysis of tachyhydrite, they indicated a very slight excess of Ca in the sample. This caused them to speculate that perhaps as much as 3.5% antarcticite ($CaCl_2 \cdot 6H_2O$; or $CaCl_2 \cdot 4H_2O$, sergipite?) might be present, but neither sulfate nor carbonate were analyzed, so the excess Ca could have been gypsum or calcite. Mraz *et al.* (1996) have given a detailed analysis of the amount of closure (creep) occurring in a previously mined sylvinite panel, while Trummel (1974) examined the laboratory creep characteristics of sylvinite, halite, carnallite and tachyhydrite from the mine. Many other articles have been written about the deposit, such as by Hite (1973).

Congo

The Lower Cretaceous salt deposits of the adjacent Gabon and Congo basins (Fig. 2.37) are very similar to those at Sergipe, Brazil. They appear to have been formed as interconnected terrestrial lakes whose depositional period ended with seawater encroachment, perhaps as the period of rifting, or continent separation and drifting became more severe. There are only terrestrial fossils under the deposits, but marine fossils begin to appear in the overlying gypsum bed that caps the deposits (which probably formed by the calcium chloride brine reacting with intruding seawater). In the Congo area, the Douala (in Cameroun), Gabon, Congo (in Congo, Zaire and Angola) and Cuanza (in Angola) basins appear to have been

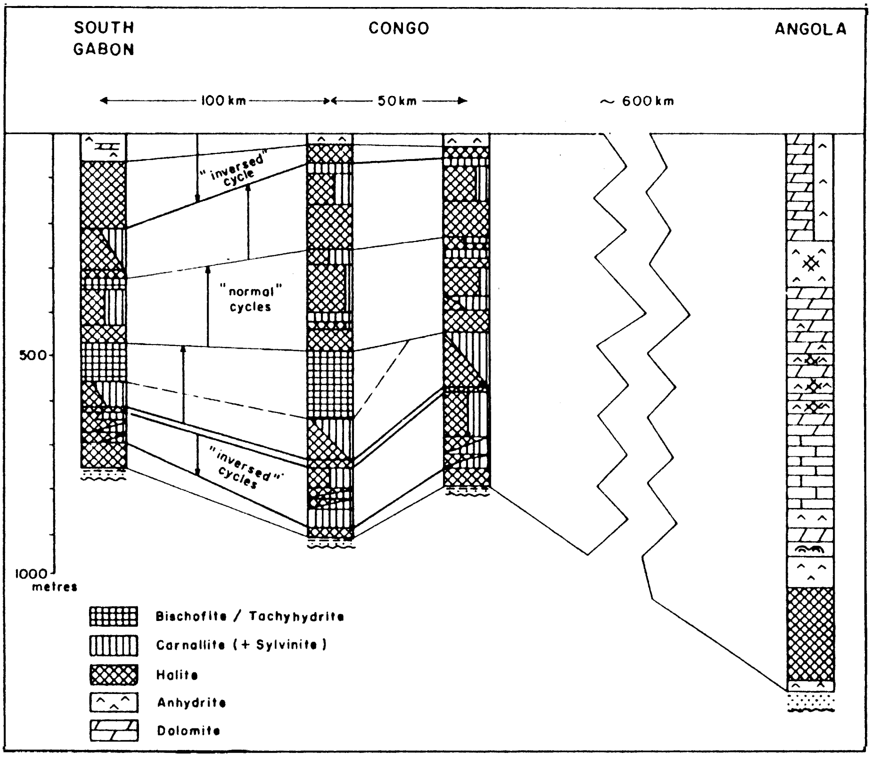


Figure 2.37 Typical depositional cycle of the Congo potash deposit (DeRuiter, 1979; reprinted with permission from Economic Geology, Vol. 74:2, p. 425, Fig. 11, deRuiter, P. A. C., 1979).

connected during the time that the potash–tachyhydrite deposit was forming. Their lower depths are filled with fresh water “rift sediments” and fossils, and the section immediately below the salts has a high organic content that has formed oil shale. The deposits began to form apparently just as the subsidence and rifting started.

Even though the salts in the Congo deposit are very similar to those in Brazil, as seen in Fig. 2.33, the detailed stratigraphy is somewhat varied. The Congo area contains less sylvinite, about the same amount of carnallite (estimated to be about 15–20% of the deposit) and more bischoffite. In the central part of the deposit,

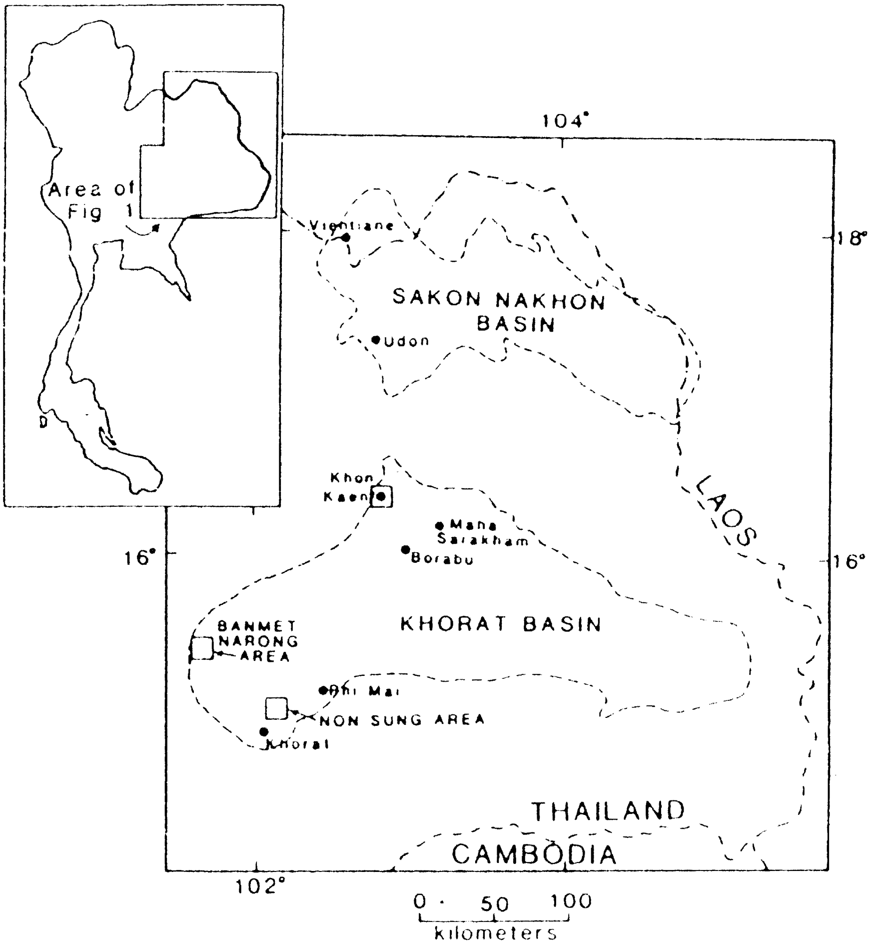


Figure 2.38 Location map of the Khorat Plateau, Thailand (Hite, 1986; reprinted by permission of the United Nations Economic and Social Commission for Asia and the Pacific).

the normal depositional sequence is a thin black layer of shale followed by halite, then carnallite and halite (with some of the carnallite converted to sylvinite), and finally up to 150 m of tachyhydrite and bischoffite. In the lower and upper sections of the basin sometimes there are relatively thin "inverse cycles" where the carnallite is followed by increasingly pure halite. The tachyhydrite beds are often lenticular, and sometimes occur as 1–6 m intercalated beds of tachyhydrite or bischoffite–tachyhydrite with carnallite or carnallite–halite. There are very few insolubles in the soluble salt beds (i.e., 2–5%; Vysotskiy, 1988). The Gabon and Congo basins' deposits are similar to each other, and the strata correlate well, but they are totally different than the adjacent basins. The others began with similar sediments, but as the rifting started they were apparently filled with seawater, and became marine formations (Garrett, 1996). Zharkova (1985) has provided an additional review of the stratigraphy and lithology of this deposit's Congo Basin. Some of the impurities in one sample of tachyhydrite are listed in Table 2.14.

Thailand

The Khorat Plateau of Thailand and part of Laos contains a large (~170,000 km^2) evaporite basin from Cretaceous to early Tertiary age (Fig. 2.38). In its Maha Sarakham Formation, there is a massive halite, carnallite (with local zones of sylvinite), tachyhydrite and bischoffite formation. The deposit is divided into two sections: the northern Udon–Sakhon Nakhon (21,000 km^2) and southern Khorat–Ubol (4000–5000 km^2) basins. As with the tachyhydrite deposits in Congo and Brazil, it lies directly on terrestrial sediments, with very little anhydrite and essentially no dolomite in or near the deposit. It differs from the other deposits in having three intrusive basaltic flows in or adjacent to it, and being interbedded and overlain with terrestrial red bed sediments (with little anhydrite and dolomite, and considerable clay). Essentially the only insoluble impurity in the salts is boracite ($MgClB_7O_{11}$, a high-temperature borate salt, usually of geothermal origin), which averaged 3.7% in one drill core section. The bromine content in the different salts is variable but similar to the other tachyhydrite deposits. A typical stratigraphic section of the formation is shown in Fig. 2.39.

The deposit's thickness averages 250 m, but reaches 1.1 km in some areas. The character of the salts are similar in both basins, indicating that they were connected as they formed. The small amount of anhydrite in the occasional interbeds of clay have $\delta^{34}S$ values of 6.4–10.9, indicative of lacustrine water (the $\delta^{34}S$ in seawater is ~20). Also, some of the thin interbeds of anhydrite in the halite had a sieve-like structure and ^{34}S values of 14.3–17.0 (El Tabakh *et al.*, 1999), which are typical of non-marine sulfate that remains behind after considerable sulfate-reducing bacterial attack. Since seawater vent or hot basalt brine has such a low-sulfate content, most of the sulfate would have entered

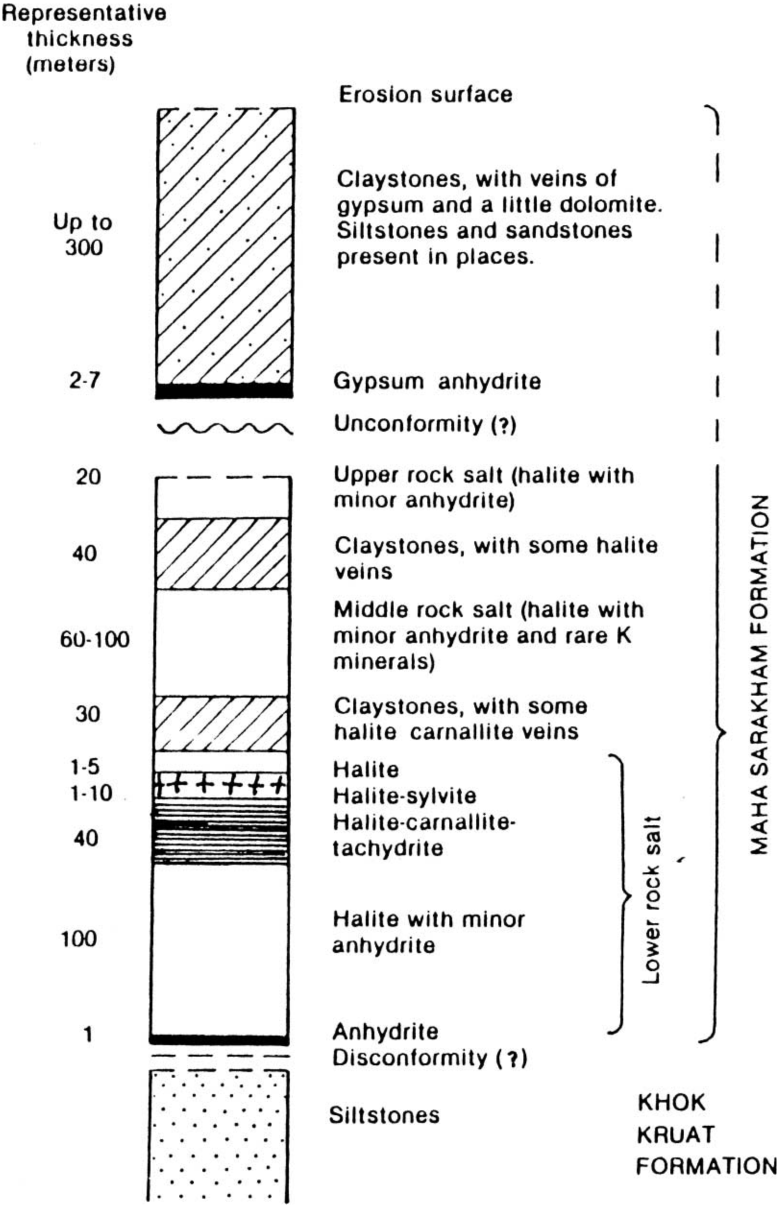


Figure 2.39 General stratigraphy of the Khorat Plateau, Thailand (Japakasetr and Workman, 1981; reprinted from the AAPG Studies in Geology. AAPG© 1981, reprinted by permission of the American Association of Petroleum Geologists, whose permission is required for further use).

the basin from terrestrial sources, as with the "red clay" marker beds. The lack of massive amounts of gypsum and dolomite in the basin preclude there having been a direct seawater input.

The tachyhydrite in the deposit is yellow to honey colored, and it is always found in alternating bands with carnallite, primarily in the central and western part of the basin in beds 1–95 m thick. More than half of the beds are 20–50 m thick, and the average is 39 m. Smaller amounts of tachyhydrite are sometimes found with carnallite as the basement halite slowly grades into the other salts. The sylvinite appears to be a replacement product of the carnallite (as is always the case) and overlying it, and the sylvinite is never accompanied by tachyhydrite (Garrett, 1996). Many other articles have been written about this deposit, such as by Japakasetr and Workman (1981).

Other Tachyhydrite Occurrences

Small amounts of tachyhydrite have been observed in several other potash deposits, and appear to have been formed by some form of sub-surface concentration process. It has been deposited on the collars of drill holes into the very strong dolomitization brine near the Irkutsk potash deposit. Small amounts have also been found in the German Zechstein potash deposits (along with some baeumlerite, $KCl{\cdot}CaCl_2$), and there are many Zechstein references such as by Heide and Kuehn (1965) and Marr (1959). Turkmenian potash deposits composed of mixed potassium–magnesium salts with a small amount of tachyhydrite have also been reported (Azizov, 1972). In each case, geothermal formations have been indicated near the deposits.

Tachyhydrite Characteristics

Tachyhydrite has a rhombohedral crystal structure, with a density of 1.673 and Z of 3. Its bonding structure can be represented by $[CaCl_6][MgCl_2(H_2O)_6]_2$, and its interatomic distances have been estimated by Clark *et al.* (1980). Erd *et al.* (1979) have determined its X-Ray diffraction pattern. It does not crystallize at temperatures below 22.8°C (Charykova *et al.*, 1992). Sinclair *et al.* (1996) studied its phase transitions, while Horita (1989) determined the fractionation of deuterium and ^{18}O in the water of hydration as tachyhydrite was being crystallized. As would be expected, it was indicated that deuterium was depleted in the water of hydration, but surprisingly ^{18}O was enriched.

Many articles or patents have also been presented claiming methods for the formation, recovery or processing of tachyhydrite. Metallic magnesium of $>99\%$ purity has been claimed after the dehydration, fusion and electrolysis of tachyhydrite. Dehydration was claimed to be achieved to 0.5–1.0% H_2O by heating for 4 hr at 260°C and then 8 hr at 725°C with a chlorine partial (vapor) pressure of 0.1–0.95 atm, or under vacuum in the presence of HCl, H_2O or N_2. It could be recovered by solution mining, or separated (dry) from carnallite by free-falling electrostatic separators. It could also be recovered from the wastewater of iodine–bromine production. It is said to be formed in some oil deposits in dolomite formations, and in natural gas pipe lines under certain conditions. It was also formed as one of the trace constituents when salt from an ion exchange process was dried (Niino *et al.*, 1993). Finally, it could be used as a chloridizing agent to solubilize spodumene by heating to 1150°C.

Calcium Chloride Brine in Mineral Deposits

Since microscopes with temperature-controlled specimen holders, and analytical instruments that can focus on small occlusions in other rocks became commonly available, calcium chloride brine has been inferred to have been present in the formation of many minerals and rocks. Occlusions with a freezing (initial crystallization) point (T_f) or melting (solubilization) temperatures [T_m] from below about -15 to -30°C (even with the two temperatures far different from each other, such as by 20–80°C; Davis *et al.*, 1990) have been assumed to be calcium chloride solutions. Also, several micro-instrumental (analytical) methods (Sampson and Walker, 2000) have frequently indicated $CaCl_2$ in both the occlusion crystals and brine. Its presence has been explained by: (1) having been one of the reactants in the solution from which the mineral was crystallized, (2) being formed at a later time by the original brine in the occlusion reacting with the mineral, (3) being present as an inert material as the deposit was forming, or (4) high-$CaCl_2$ brine penetrated, leached and recrystallized the rocks or deposit at a later time. However, very reproducible data can also be obtained from very large supersaturation (metastable equilibrium, or crystallization-point lowering) when crystallizing solutions of $MgCl_2$, NaCl, potassium double salts and many others. This is exemplified by the frequent large differences obtained between T_f and then T_m on the just-crystallized solids, when the values should be the same. Such supersaturation is especially common with inclusions, as illustrated by the extensive work done on halite and potash deposits (see Fabricus (1983)). For instance each of the values for T_h (homogenization of vapor and liquid), $T_{f\ (or\ c)}$ and T_m with primary halite and sylvite crystals have indicated that the massive Zechstein Formation crystallized at temperatures of 97–157°C, or near or far above seawater's boiling point, which of course is impossible (Garrett, 1996). Instrumental methods on these small samples enclosed in other minerals can also be misleading, and unfortunately, very few positive identifications have been made on these calcium chloride occlusions by chemical analyses.

As examples of the literally hundreds of reported calcium chloride occlusions, $CaCl_2$ has been inferred in occlusions in the West Gore *antimony–gold* deposit in Nova Scotia (Kontak *et al.*, 1996), and in *barite* deposits in the western Jebilet of Morocco. It was speculated that the latter deposit contains fluids that may have been related to central Atlantic rifting (Valenza *et al.*, 2000). Similar inclusions have been found in the Long Lake *calcite–fluorite* vein, central Adirondacks, USA (Bird and Darling, 1996) and the calcite cement in the Smackover Formation of southern Arkansas, USA. In the latter deposit, the T_h values indicated formation temperatures of 58–158°C, with the $CaCl_2$ inferred from T_f values from −51 to −68°C, and T_ms from −15 to −32°C (Klosterman, 1981). The Mount Isa, Australia *copper ore* was also indicated to contain $CaCl_2$ inclusions (Heinrich *et al.*, 1989, 1991). Other copper deposits that have reported calcium chloride inclusions are the Little Stobie deposit at Sudbury, Canada (with precious metals; Molnar *et al.*, 1999), the Granisle *porphyry copper* deposit in British Columbia, Canada (Quan *et al.*, 1987), and the Aquas Claras deposit in the Carajas region, Para, Brazil (Gaia da Silva and Villas, 1998).

Small amounts of a calcium chloride brine have been found in a strike-slip *fault system* in Belgium (Muchez and Sintubin, 1997), and Parry (1998) has noted that solutions with up to 19% $CaCl_2$ have been found in a few other *fault zones*. Microscopic observations on these (and many other occlusions) indicate that they were formed at elevated temperatures and pressures, which the authors suggested initiated rock-brine reactions that formed the calcium chloride. The South Platte *fluorite-REE* pegmatites, Colorado, USA occlusions when crystallized were indicated to contain ice, hydrohalite and antarcticite by cryogenic laser spectroscopy (Walker, 1998). Raman spectra of occlusions in *garnet, apatite and quartz* in the Austroalpine Otzal Basement complex indicated that when cooled they contained hydrohalite and antarcticite (Kaindl *et al.*, 1999). The *gold and copper* deposits of the Cloncurry district, Queensland, Australia was inferred to contain a calcium chloride solution that formed the deposit at 220–360°C (Williams *et al.*, 2001), and a similar deposit in the Mallery Lake area, Nunavut, Canada also recorded strong calcium chloride in lower temperature (90–150°C) occlusions (Turner *et al.*, 2001). A strong-calcium chloride brine was interpreted to be in fluid inclusions in the Leinster *granite and quartz* veins of SE England (Moran *et al.*, 1997). Calcium chloride brine has also been indicated in the Soultz-sous-Forets, France *granite* alteration zone (Savary *et al.*, 1997), and in a *granitic* pegmatite in Colorado a cryogenic Raman spectroscope indicated hydrohalite and antarcticite (with a T_m from −50 to −70°C; Samson and Walker, 2000). Calcium chloride was also indicated in a shear zone of the Harare *greenstone* belt in Zimbabwe (Mutemeri *et al.*, 1997), and in the greenstone of the southern Zimbabwe Craton and the northern margin of the Limpopo Belt (Schmidt Mumm, 1997). The Abitibi greenstone belt in Canada has also reported calcium chloride in its *gold-bearing quartz* veins, with some indications that the deposit was formed from ancient sea floor hydrothermal vents (Neumayr and Hagemann, 2002; Kerrich and Ludden, 2000). As noted in previous sections, the occurrence of strong calcium chloride dolomitization brine in secondary halite is quite common (Zimmermann, 2000; Grishina *et al.*, 1992).

The *lead–zinc–barium* district at Thunder Bay, Ontario, Canada appears to contain calcium chloride brine (Haynes, 1988), as does the Largentiere *lead–zinc* deposit in France (Leost, 1999). The *migmatites* of the Tatra Mountains, western Carpathia have occlusions with a strong calcium chloride brine (along with pure nitrogen; Hurai *et al.*, 2000), and *molybdenum–bismuth* mineralization in the Cadillac deposit Quebec, Canada has indicated antarcticite in frozen occlusions by SEM–EDS analysis (Taner *et al.*, 1998). The *Ni–Cu–Pt* deposit at Lindsley, Sudsbury, Canada (Molnar *et al.*, 1997) is said to contain calcium chloride, as is the *PGE* mineralization at the New Rambler deposit in SE Wyoming (Nyman *et al.*, 1990). Numerous authors have reported calcium chloride brine in quartz vein inclusions, such as in the Batum Salt Dome, N. Jutland, Denmark (Fabricus, 1984), the Sandia Pluton contact (Pletsch-Rivera *et al.*, 1998), the Valles caldera, New Mexico (Sasada, 1988), the Strzegom pegmatites, Poland (Kozlowski, 1994), the Spanish Central System (Martin *et al.*, 1997), the Bushveld Complex, South Africa (both $CaCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 4H_2O$ crystals were indicated in the quartz occlusions by Raman spectra, implying a $>42\%$ $CaCl_2$, boiling formation brine; Schiffries, 1990), boreholes in northern Switzerland (Mullis and Stalder, 1987; and the Mori geothermal field in Hokhaido, Japan [Muramatsu and Komatsu, 1999]).

Calcium chloride was indicated in *rare earth* deposits (Shmulovich *et al.*, 2002), and the Puebla de Lillo, Spain *talc* deposits (formed with 0–25% $CaCl_2$ at 280–405°C; Tornos and Spiro, 2000). There were calcium chloride occlusions in the San Rafael Lode *tin* deposit in Peru (up to 40% $CaCl_2$; Kontak and Clark, 2002), a *tin skarn* in the Yukon Territory (Layne and Spooner, 1991), and the *tin–polymetallic* ore field in Guangxi, China, which is said to contain daughter crystals of antarcticite (Fu *et al.*, 1993). The Kombolgie *uranium* deposits in the Northern Territory, Australia (Brisset, 2000, Derome *et al.*, 2000) and the Gays River and Jubilee, Nova Scotia, Canada *zinc* and *zinc–lead* deposits are also reported to contain fluid inclusions of $CaCl_2$ (Kontak, 1998; Savard and Chi, 1998), as is the Mascot-Jefferson City zinc district, Tennessee, USA, using SEM and "energy dispersive" analysis of occlusion "decrepitates" (Haynes *et al.*, 1989). The Balmat-Edwards District *zinc (sphalerite)* deposit, northwest Adirondacks, NY, USA is also reported to contain $CaCl_2$ occlusions (Hill and Darling, 1997), along with the Lyonsdale area of northern New York ("a fossil shield $CaCl_2$ brine"; Garside and Darling, 1993).

Occlusions in the King Island *scheelite skarn* deposit may contain $CaCl_2 \cdot 6H_2O$ crystals as well as a $CaCl_2$ brine, and it is felt that the calcium chloride was formed during deposition by reactions of the type: (1) $Fe^{2+} + CaCO_3\text{(calcite)} + 2SiO_{2(aq)} + 2H_2O \rightarrow CaFeSi_2O_6\text{(hedenbergite)} + HCO_3^- + 3H^+$, or (2) $2Fe^{3+} + 3CaCO_3\text{(calcite)} + 3SiO_{2(aq)} + 3H_2O \rightarrow Ca_3Fe_2Si_3O_{12}\text{(andradite)} + 3CO_2^* + 6H^+$, and (3) $6H^+ + 3CaCO_3\text{(calcite)} \rightarrow 3Ca^{2+} + 3CO_2^* + 3H_2O +$ *pore space* (*the CO_2 would probably be in the form of $CaCO_3$). In zones where there was no calcite there was no calcium chloride, and in other zones the $CaCl_2$ concentration was proportional to the amount of Fe-calc-silicate crystallized (Kwak and Tan, 1981).

Reactions of Calcium Chloride with Minerals

The leaching (partial solubility) of a number of minerals in calcium chloride solutions has been discussed in previous sections, and reviewed by Korzhinskii and Shmulovich (1988) and Vakulenko and Razina (1992). The solubility of *anhydrite* at temperatures of 250–325°C was studied by Templeton and Rodgers (1967), being unexpectedly high, which they attributed to the formation of $Ca_2SO_4^{2+}$ and $Ca(SO_4)_2^{2-}$ ions. The solubility of *anorthite* in supercritical calcium chloride solutions was studied by Roselle (1993) at temperatures of 400–600°C, a pressure of 2 kbar, concentrations of 0.005–6 M and pH values of 0.06–6.2. The amount of calcium liberated, and the formation of albite was appreciable. In the studies it was assumed that aqueous SiO_2 and $Al(OH)_3$ would always be present, and that the calcium chloride occurred in the forms of $CaCl_3^-$, $CaCl^+$, $Ca(OH)^+$ and $CaCl_2$ under these conditions. Phase relationships in the reaction of calcium chloride with *apatite* to produce chlorapatite at temperatures of 600–1150°C have been studied by Morton (1961), as were the kinetics of the $CaCl_2$–hydroxyapatite reaction. The rate of calcium chloride solutions' conversion of *aragonite* to calcite at 100°C was investigated by Berndt and Seyfried (1999), while determinations were made on *calcite's* solubility in calcium chloride solutions by Nagy and Morse (1986), its precipitation rate (Tomiyama and Kitano, 1984), its speciation in supercritical $CaCl_2$ solutions (Baumgartner, 1991), and inhibiting agents for its precipitation (Akagi and Kono, 1995). X-ray studies of $CaCl_2$–*chabazite* and dehydrated $CaCl_2$–*natrolite* were made by Fang (1961). When *clinoptillite* was treated with $CaCl_2$, the cations were exchanged, and upon heating the Ca–clinoptillite inverted (Shepard and Starkey, 1966). The solubility of *fluorite* in cool-to-supercritical solutions of calcium chloride was determined by Malinin and Kurovskaya (1999, 1994) and Ryzhenko *et al.* (1999). At low temperatures, the $CaCl_2$ appeared to be disassociated into Ca^{2+} and $2Cl^-$ ions, but at higher temperatures a wide variety of other ions and complexes were formed. The surface properties of *mica* in $CaCl_2$ solutions was studied by Kjellander *et al.* (1990).

Liquid occlusion analyses, $\delta^{18}O$ data and drill core analyses have indicated that portions of the Troodos *ophiolite (basalt-gabbro)* formation in Cyprus has been converted by marine dolomitization brine at high temperatures into actinolite, anorthite, epidote, albite and quartz, and at temperatures below 100°C into laumontite and calcite (Kerrich and Vibetti, 1985). Kalinin (1966) studied the reaction of *plagioclase* with calcium chloride solutions, producing garnet of the grossularite–andradite series along with anorthite. Dujon and Lagache (1986) considered the influence of fluid mixing on the cation exchange of $CaCl_2$ solutions and *plagioclase* at 700°C. The solubilities and thermodynamic properties of solutions of calcium chloride and *silica* were determined by Popp and Frantz (1979), and their electrokinetic potential by Jichova and Havlica (1999). The solubility of amorphous silica in calcium chloride-type geothermal waters was investigated by

Gallup (1989), while the change of *stishovite* to a denser phase by $CaCl_2$ was examined by Shu *et al.* (1996). Winkler and Luettge (1999, 1997) studied the reaction of *tremolite* with calcite and quartz to form diopside, CO_2 and H_2O, with and without the presence of $CaCl_2$. The temperatures ranged from 630 to 720°C (the equilibrium temperature was 617°C), the pressure was 5 kbar, the concentration 0–5.5 wt.% $CaCl_2$, and the reaction time up to 34 days. The presence of the calcium chloride increased the reaction's rates more than 10-fold to values that were much higher than expected. Zimmerman *et al.* (1996) performed the opposite type of reaction, and studied the formation of tremolite from calcium chloride solutions.

Studies on the *vermiculite* mine at Libby, Montana have been made concerning the origin of the deposit. The ore lies in an augite pyroxenite that has been altered to biotite, hydrobiotite and vermiculite, with numerous syenite dikes in the pyroxenite. Ion exchange tests have shown that biotite alters to vermiculite at room temperatures in solutions with >0.1 wt.% $CaCl_2$, and it was theorized that the augite was altered to biotite by the intruding syenite dikes. Later some of the biotite was altered to hydrobiotite and vermiculite by descending calcium chloride-containing near-surface waters (Bassett, 1959).

In a different type of reaction, potassium chloride solutions can be reacted with gypsum to form the mineral *syngenite* and calcium chloride, and the syngenite in turn can be dissolved in water to form potassium sulfate. This reaction has been used commercially in several operations, but was only economically successful as a means of lowering the end liquor loss at a K_2SO_4 plant. Orlova *et al.* (2000) have recently noted that the presence of carbamide greatly improves the reaction.

Clay Minerals

Bentonite and the other clay minerals have considerable ion exchange capability, and their physical characteristics change dramatically depending upon the content of the salt solution in their pore space, and whether the clay is in the calcium or sodium form. As examples of publications considering the influence of calcium chloride on clays Sjoblom *et al.* (1999) noted the slowness of water to penetrate compacted bentonite (*Na–montmorillonite* is its major constituent), but that a calcium chloride solution could rapidly penetrate the bentonite and allow it to be washed away. Fresh water causes compacted bentonite to swell and to produce free-surface particles by exfoliation. These particles form a gel which further closes the pores to water uptake, while the $CaCl_2$ solution causes the exfoliated material to shrink (or at least swell less). This allows more solution to enter the pores, causing differential expansion and a lower gel strength so that the clay may be more easily washed away.

Di Malo (1996) also studied the osmotic and mechanical effects of calcium chloride solutions upon bentonite. Water-saturated bentonite when exposed to $CaCl_2$ solutions became more consolidated, had a large decrease in deformability, and an equally large increase in shear strength. These effects could not be changed by water washing, and X-ray diffraction analysis showed that calcium had ion exchanged for the sodium in the bentonite. The osmotic effects became almost negligible. Anson and Hawkins (1998) also noted the increase in shear strength with *bentonite and kaolinite* when treated with solutions as dilute as 80 mg/liter of Ca^{2+}, and Ahmad *et al.* (2000) found that a 50:50% mixture of bentonite and kaolinite had about the same coefficient of consolidation and permeability as bentonite alone, and could form effective pond liners for strong acidic or alkaline solutions, but not when calcium chloride was present. Wang *et al.* (1996) studied the effect of $CaCl_2$ solutions on the dehydration of Ca-exchanged *montmorillonite*. Haydon (1983) noted that as a calcium chloride brine passed through compressed *smectite* at elevated temperatures and pressure ion filtration and stable oxygen isotopic fractionation occurred. Dennis (1991) studied the compaction and swelling of *Ca–smectite* in calcium chloride solutions.

Soils

Many articles have been written about the interaction of calcium chloride with soils, as indicated by the following examples. Ernani and Barber (1993) have studied the effect of *cation leaching* (*ion exchange*) of acid soils by treatment with $CaCl_2$ solutions, while Chen and Shao (2001) noted that the presence of calcium chloride greatly aided in the *coagulation* of suspended sediments in aqueous solutions. Dakshinamwite and Chandool (1966) examined the *conductivity* and ion exchange capacity of soils and clays. They found ion exchange capacities of 10–105 meq/100 g, and a relationship between the soil conductivity in a $CaCl_2$ electrolyte and the ion exchange capacity. Baudracco and Tardy (1988) studied the *dispersion and flocculation* of clays in unconsolidated sandstone reservoirs by percolating $CaCl_2$ solutions. Murashko *et al.* (1970) examined the *penetration coefficients* of various salt solutions on clay soils, finding that $CaCl_2$ solutions ranked much higher than NaCl and pure water. White *et al.* (1964a) noted the improved *permeability* of oil and gas formations if first flushed with a $CaCl_2$ rather than NaCl brine, due to the reduced swelling of clays in the structure. Stern and Shackelford (1998) studied calcium chloride solutions' *permeability* in sand–clay mixtures, while Aoubouazza and Baudracco (1992) did similar studies on clayey sandstones. Little (1992) determined the relationship between soil *pH* measurements in water and $CaCl_2$ suspensions. Alsharari (1999) studied the *reclamation* of highly alkaline soil with gypsum, langbeinite and calcium chloride, while Mukhtar *et al.* (1974) studied the effect of $CaCl_2$ solutions on the *structural stability* of two Vertisols: Gezira clay from Sudan, and Houston Black clay from Texas.

PROCESSING

The processing of calcium chloride brines can be either a very simple or a complex series of operations, depending upon the purity required, the desire to produce solid as well as liquid products, and whether other by-products are also recovered from the brine. A general article on the subject has been presented by Kotsupalo *et al.* (1999), and descriptions of the current actual production processes are reviewed below. Other information on processing is included in the commodity reviews by the U.S. Bureau of Mines (1992–1982), articles in Chemical & Engineering News (2001) and in chemical engineering encyclopedias.

Michigan Dolomitization Brines

Dow Chemical Company

The Michigan calcium chloride brines have the distinction of playing a very important role in the early development of the United State's chemical industry. By 1897, Dr. Herbert Dow had investigated these unique brines and raised capital to commence the recovery of some of the components in one of the fairly shallow brines at Midland, Michigan. The basic chemicals were then converted into a series of much more valuable products, and the total facility became a highly diversified chemicals complex. The operation was successful from the beginning, and soon was one of the major facilities in the country's fledgling chemical industry. It still remains as one of Dow Chemical Company's basic operations, and since 1914 calcium chloride has been one of the major products recovered from the Michigan brines. Figure 2.40 shows the major steps involved in the original process.

The first operation was with brine from the relatively shallow and dilute Marshall formation (Table 2.4), and began by passing the brine through an electrolytic cell (Dr. Dow was an electrochemist). The current was carefully controlled in order to oxidize the bromide ions to elemental bromine, which could

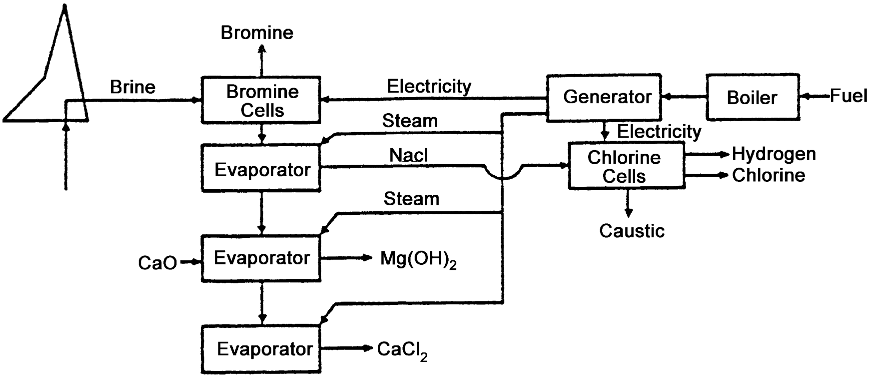


Figure 2.40 Flowsheet for the original (1914) Dow Chemical Brine Recovery Process (Pavlick, 1984).

then be blown out of the cell with air, condensed and converted into various compounds. The brine was next sent to a triple effect evaporator where the solution was concentrated and much of the sodium chloride crystallized. The sodium chloride was removed, dissolved, and sent to electrolytic cells to be converted into chlorine and caustic soda (along with small amounts of hydrogen). Evaporation was then continued to crystallize some magnesium chloride (with the salt), and it was separated and converted into magnesium oxychloride, a material popular at that time for producing floor tile. The brine was next reacted with slaked lime ($Ca[OH]_2$) to precipitate almost all of the remaining magnesium, and the magnesium hydroxide was filtered, washed, and converted into a variety of magnesium compounds (such as magnesium sulfate heptahydrate, epsom salts). The remaining brine was again sent to evaporators to be concentrated to a 38% $CaCl_2$ solution as the final step in the operation, and the sodium chloride that crystallized during evaporation was also removed and sent to the chlorine–caustic plant. This brine was adequately pure for most calcium chloride sales, and could be marketed directly or further evaporated to form various solid products.

Later brine from the deeper and stronger Sylvania Formation (Table 2.4) was utilized, and since it also contained iodine, it and many of its derivatives were also produced (Fig. 2.41). The brine was first acidified and treated with just enough chlorine to react with the iodide ions and covert them into elemental iodine. The iodine was then blown from the brine with air in a packed tower, and re-absorbed for separate processing in a smaller tower. The residual brine was next heated, passed through a second large packed tower, and blown with steam and chlorine. The bromide ions were converted to bromine by the chlorine and carried by the steam from the tower. As much water as possible was separated from the bromine, and the bromine was further dried with sulfuric acid and re-distilled in a separate tower. Magnesium chloride and calcium chloride were then recovered from the brine (Pavlick, 1984).

Figure 2.42 shows how the operation, and the chemicals derived from processing the Michigan brines has changed over the years. In 2002, brine was only extracted (Fig. 2.43) from the comparatively shallow and rich Filer Formation near Ludington at a 910 m (3000 ft) depth. This ~130 km (80 mi) long sandstone formation is about 30 m (100 ft) thick and has a 10–15% porosity. The Filer brine contained 17.1–17.4% $CaCl_2$, 9.2–9.9% $MgCl_2$, 2.0–4.0% NaCl, 0.8–0.9% KCl and 0.232–0.241% Br. Its specific gravity varied from 1.277 to 1.287 g/cc at 25°C, its viscosity was 2.1 cp, specific heat 0.69 cal/g/°C, pH 4.4–4.8, and its boiling point 111.6°C. To recover the brine, Dow utilized 17 wells, with about 10 normally in service at any given time, pumping 100–150 gpm/well, or a total of 850–1200 gpm. To maintain a vigorous flow rate, it was necessary to re-inject a similar amount of wash, dissolved salt and other water near the periphery of the well field.

Since the Filer brine does not contain iodine, bromine was the first product recovered from it by the “steaming” process as described above. The brine was

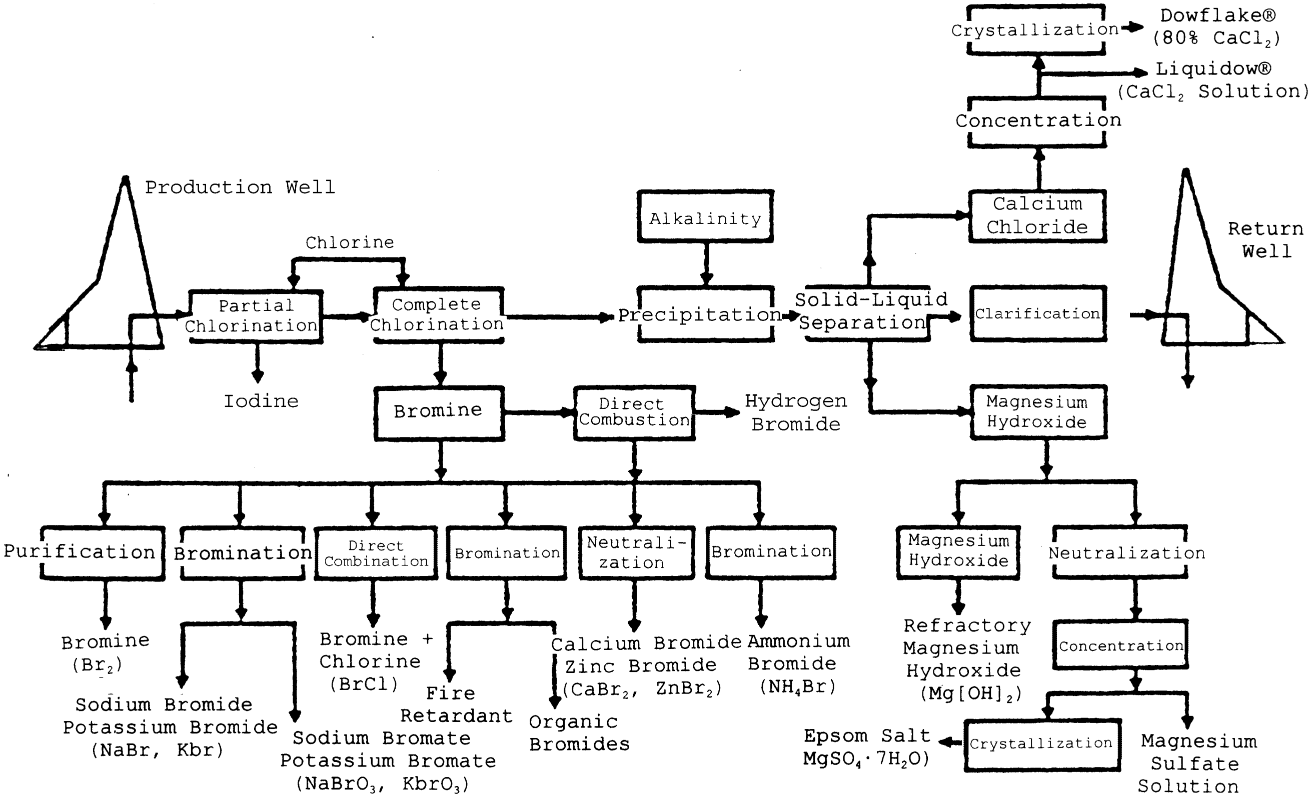


Figure 2.41 Some of the products previously produced from the Sylvania Formation by the Dow Chemical Co. (Pavlick, 1984).

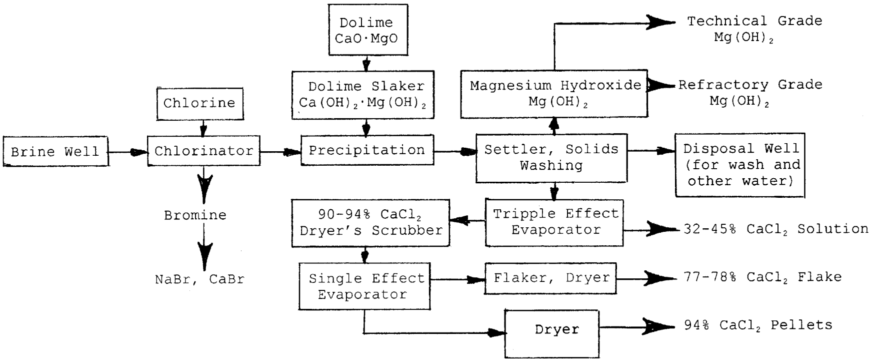


Figure 2.42 Dow Chemicals process for recovering calcium chloride and other products from Michigan Brine in 2002 (after Pavlick, 1984).

next reacted with slaked dolime ($CaMg[OH]_2$) to precipitate magnesium hydroxide. The dolime (CaO·MgO) had been purchased from Ohio and delivered to the plant by rail, and then reacted with water (slaked) in the plant's previously used dolime roasting–slaking facilities. The precipitated magnesium hydroxide trihydrate was then settled, filtered, washed and finally re-pulped, with about 67% of it pumped to a nearby company that converted it to dead burned magnesia, and the remainder was sold for water treating or other uses.

The residual brine had a pH of 8–9, contained 24–25% $CaCl_2$, and was next sent to triple effect evaporators to be concentrated to 32–45% $CaCl_2$. The first effect (installed in 1978) was of a forced circulation type with an external heat exchanger. The second and third effects were of the calandria type (dating from 1942), with an agitator to increase the flow rate through its internal heat exchanger tubes. This greatly reduced the scaling problem, and re-tubing was only required on about a 10-year schedule. The salt that crystallized during the evaporation process was settled and then removed from the brine in solid bowl centrifuges, to be re-dissolved and added to the re-injection water into the Filer Formation. The centrifuges were rebuilt every 2–3 years. Steam for the evaporators was purchased from an adjacent cogeneration power plant, and cooling water for the third stage barometric condenser was withdrawn from an estuary of Lake Michigan next to the plant. However, Zebra mussels tended to grow prolifically in the cooling water, and had to be periodically killed with chlorine and removed from the system. A vacuum pump was used for the second stage non-condensables.

Part of the concentrated solution was sold directly, and part was further concentrated to 77–78 $CaCl_2$ flakes or 90–94% pellets (Table 2.21(A) and (B)). The 42–45% $CaCl_2$ brine contained about 2.5% NaCl (with the KCl expressed as equivalent NaCl) and 1% other salts. To make solid products, this solution was

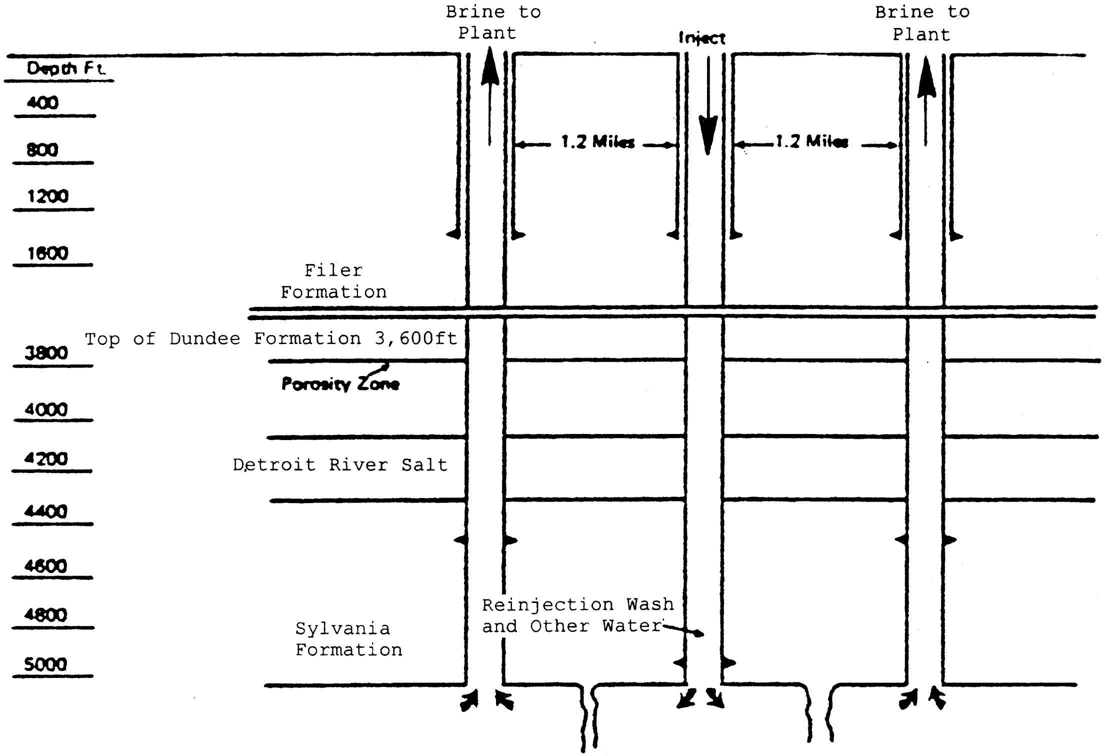


Figure 2.43 Schematic drawing of the brine recovery and reinjection wells in the Michigan Sylvania and Filer Formations (after Pavlick, 1984).

first further concentrated in a single-stage forced circulation evaporator using high-pressure steam. For the production of 74–78% $CaCl_2$ flakes, some of this concentrated solution was sent to heated pans below large rotary drums. The cooled drums were dipped into the hot solution, causing some of the calcium chloride to cool and freeze on the drums' outer surface as the drums rotated. These approximately calcium chloride dihydrate solids were then scraped off on the other side before the drum dipped into the pan again. The thin flakes that were formed (about 0.5–2 mm thick by 6–12 mm wide; Fig. 2.44) dropped into the top of a very large multi-tray dryer. In the top two-thirds of the dryer the flakes were contacted by hot flue gas, and in the lower third they were cooled by air. The cooled product was then bagged, put into bulk bags or shipped to the customers in bulk.

To produce the 90–94% $CaCl_2$ solid product, a portion of the concentrated liquid was sprayed into a dryer and directly heated by very hot flue gas. Solids were removed from the dryer, cooled and screened to the desired particle size, while the exhaust gas was scrubbed and then vented. The oversize was crushed and returned to the screen, while the fines were recycled to the 45% feed solution, or compacted into almond-shaped pellets. The 90–94% $CaCl_2$ pellets were also shipped in either bulk or bags.

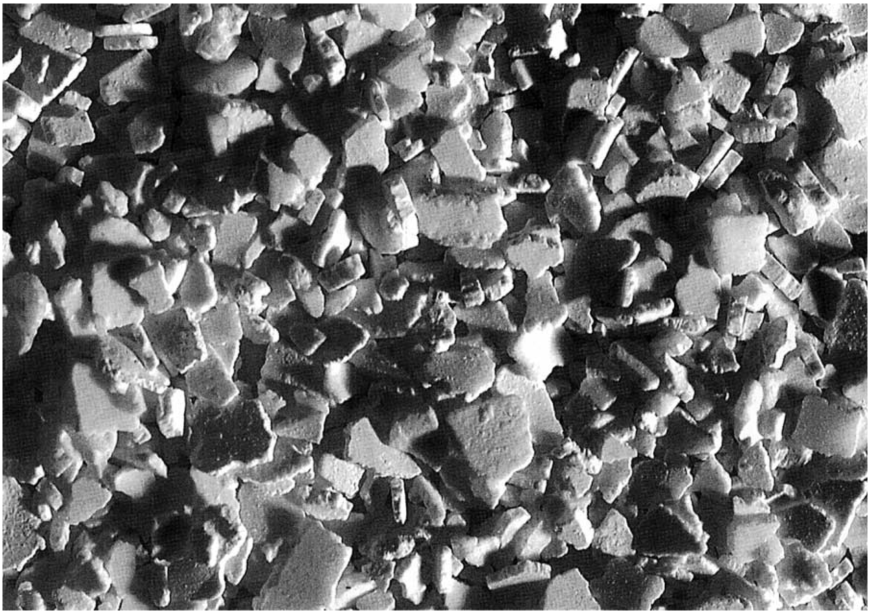


Figure 2.44 Typical flaked calcium chloride (Dow, 2001, courtesy of The Dow Chemical Company).

Figure 2.45 The Dow Chemical Calcium Chloride Plant at Ludington.

In 2002 the 600,000 st/yr capacity (of equivalent 100% $CaCl_2$ product) Ludington plant (Fig. 2.45 shows the entire plant, and Fig. 2.46 the solids plant) had 225 employees. Its products were bromine, sodium bromide, calcium bromide, magnesium hydroxide, and the calcium chloride in liquid, flake, pellets or a food grade made by filtering the final 45% $CaCl_2$ solution. The products were shipped by pipeline, truck, rail or by barge through the Great Lakes, and a large inventory was maintained for the seasonal demand. In early 2003, it was announced that within about 1 year the plant would stop manufacturing magnesium hydroxide, and close their brine-gathering wells. They would instead purchase a magnesium-depleted 24% $CaCl_2$ brine from Martin Marietta Magnesia Specialties Co. in Manistee, Michigan (their former primary magnesium hydroxide customer), and deliver it by pipeline to their plant. This would cause a reduction in their staff of about 30 people (Busch, 2003, 2002; Dunklow, 2002; Chemical Market Reporter, 2002; Pavlick, 1984).

Other Companies

The General Chemicals Group in Manistee and the Wilkinson Co. in Mayville also produced calcium chloride from Michigan brines in 2002. However, in late 2002 the General Chemical Group announced that they had closed their Manistee plant with a capacity of 450,000 st equivalent flake/yr. None of the world's other

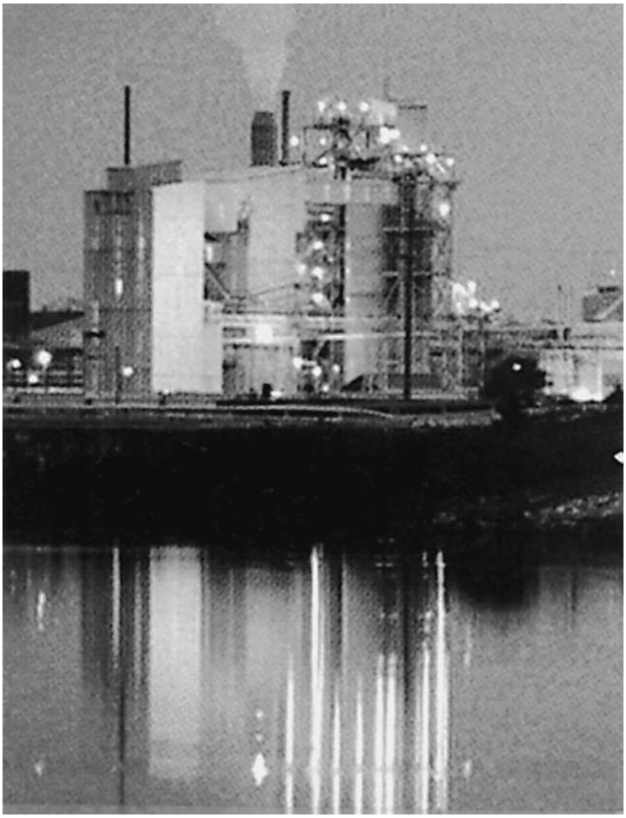


Figure 2.46 Evening Picture of Dow Chemical Company's Solid Calcium Chloride Plant at Ludington, Michigan (Van Savage, 2002; reproduced by permission of the Chemical Market Reporter).

dolomitization brines are or have been worked on a large-scale to produce calcium chloride, but the Cory potash mine near Saskatoon, Saskatchewan for a period recovered its very strong calcium chloride mine water brine (Table 2.3), and sold it, as is. However, the quantity of mine seepage gradually decreased with time until the operation no longer remained profitable.

Bristol and Cadiz Lakes

The high-calcium chloride brine of Bristol Lake has been continuously recovered on a commercial basis since 1910 (Jachens and Howard, 1992). The brine permeates the uppermost 9.75 m section of the playa sediments, and appears to be present throughout the entire lake. However, the permeability of the sediments varies widely, being the greatest in the halite layers, less in the sandy silt beds, and much less in the high-clay beds. The seepage of brine through the sediments thus varies considerably throughout the lake, and appears to be the greatest in the lowest areas (called the Salt Lake zones) where there is more salt near the surface. In the commercial operations, the brine (Table 2.9) is gathered by seepage trenches or pits, and a brackish calcium chloride water is evaporated from wells adjacent to the lake. By 1951, some of the trenches had been extended up to 8 km in length, and by 1992 there were 43.5 km of canals, pits and solar evaporation ponds (Gundry, 1992). The initial brine has a density of about 19°Be (1.15 g/cc), and it is usually concentrated to about 40°Be (1.38 g/cc), or about 32–36% $CaCl_2$ (Table 2.9). The solubility of the sodium chloride in the brine decreases during the solar evaporation process to a steady value of about 1% NaCl at 35% $CaCl_2$. During the evaporation, salt thus crystallizes (starting at about 25°Be [1.21 g/cc]) in the trenches, pits and ponds, and must be periodically removed from them.

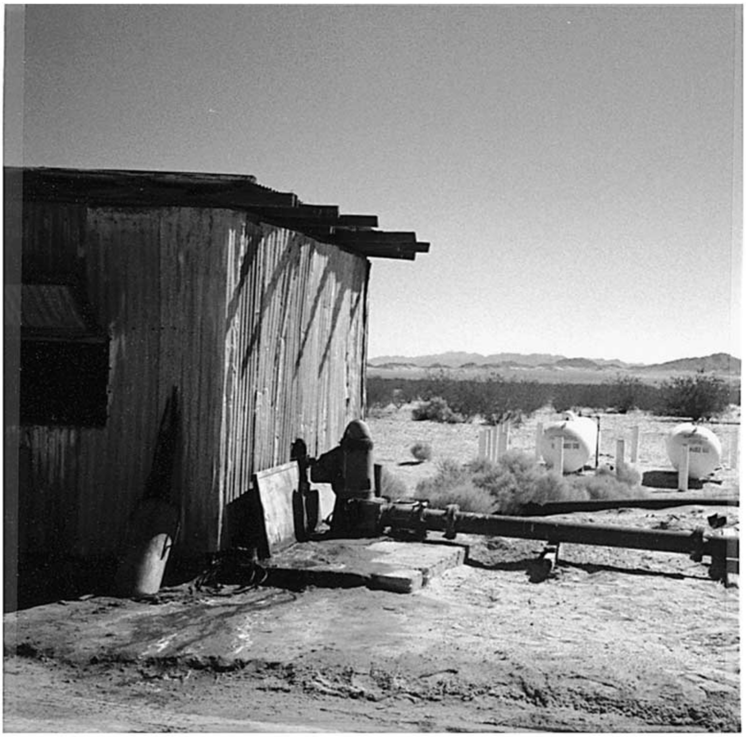
Because of the area's very high summer temperatures and low humidity, the dilute brine from the playa can be evaporated (with pond temperatures reaching 59°C) to a commercially saleable strength in as little as 2 weeks or up to 1–2 months. However, during storms, cool evenings or in the winter (humid periods) the brine will actively absorb moisture from the air. Since most of the uses for calcium chloride do not require a very high purity, the evaporated product is normally sold without further treatment. When processed into the solid form, or if the magnesium concentration is too high the solution becomes quite corrosive, and its pH must be adjusted to 7.5–8.5 with caustic soda. A corrosion inhibitor such as sodium chromate or dichromate (or a less toxic salt) may also be added (Gale, 1951).

As an example of the production of calcium chloride on Bristol Lake, the National Chloride Company of America started large-scale production in 1950. They own some of the land on which they operate, and have placer mining claims from the U.S. Bureau of Land Management on other areas (some dating from 1908). Most of their land is in the southern part of the lake, including much of the lowest section, the Salt Lake areas. Over the years, they have excavated a large number of drainage canals, (Fig. 2.47) with the longest extending for 10 km (6 mi) and another for 4.8 km (3 mi). Many of the trenches drain to a central gathering area, and portable diesel pumps (Fig. 2.48) move the brine from others to the central canals or the ponds. The early trenches were made with a Northwestern 80 dragline, while the newer ones are excavated about 4.3 m (14 ft) deep and wide by a large backhoe (Fig. 2.49). Some deep pits (Fig. 2.50) are also utilized as brine collectors, with one dug to a 23 m (75 ft) depth, but the extra depth was not found to be beneficial. As a final method of brine collection, brackish water from aquifers just outside the lake is pumped (Fig. 2.48) to trenches to be evaporated and join the other brine. This large aquifer of a dilute calcium chloride brine (~ 10,000 ppm) in some of the alluvial fan sediments next

Figure 2.47 A typical brine seepage trench at Bristol Lake (Courtesy of National Chloride Company of America).

to the lake appears to have migrated from the lake and been diluted by entering groundwater.

By the time brine in the collection trenches has reached at least 27–28°Be it is transferred to holding ponds (Fig. 2.51) to be further concentrated to the product strength of 40°Be. It is then sent to deep ponds (Fig. 2.52) to be held until it is shipped in stainless steel tank trucks by their customers (one customer also re-ships some brine by rail from Amboy). The principal evaporation period for brine production is generally from April/May through September. Salt is periodically removed from the trenches by the back hoe, and from the ponds by a 613C Catapiller scraper-carrier. The seepage of brine into the trenches and pits is very much a function of the weather, with wet years greatly increasing the amount of brine gathered, and in dry periods (such as during the 1960s and in 2002) reducing the flow. During rainy periods (perhaps every 2–3 years), some water briefly floods onto the low section of the lake, causing the salt surface to become very smooth and white. There can also be occasional flash floods in limited areas of the lake, and some of the surface water may get into the canals. To minimize the damage from such isolated rainfall and surface flooding, the 10 km trench has been dammed in the middle. As a rare 25–50 year event, in 1983 the entire lake flooded, filling the ditches with a dilute brine, and necessitating raising the access roads across the lake (Beeghly, 2002).



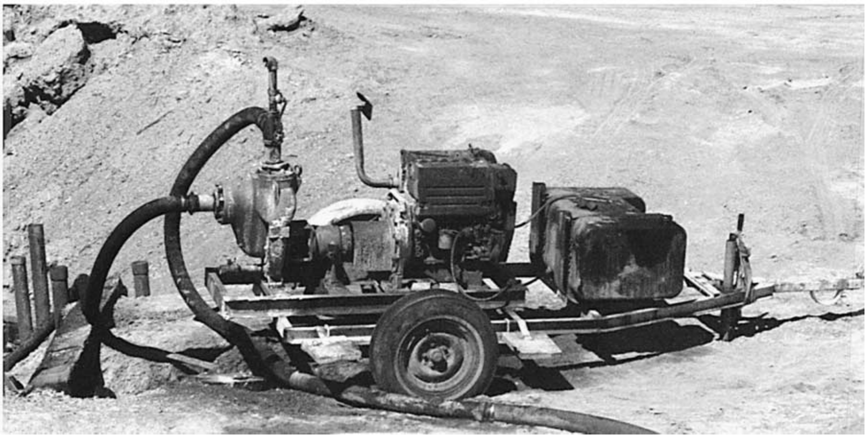


Figure 2.48 Typical brine pumps utilized at Bristol Lake. Top, brackish well at the edge of the lake. Bottom, portable transfer pump for the trenches, pits and ponds. (Courtesy of National Chloride Company of America).

Figure 2.49 Backhoe cleaning salt from a seepage trench at Bristol Lake. (Courtesy of National Chloride Company of America).

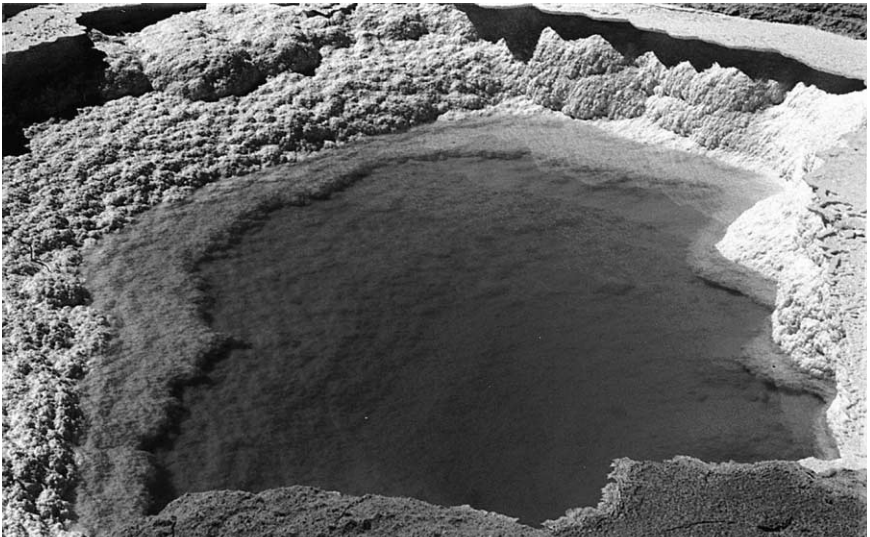


Figure 2.50 A typical brine seepage pit at Bristol Lake. (Courtesy of National Chloride Company of America).

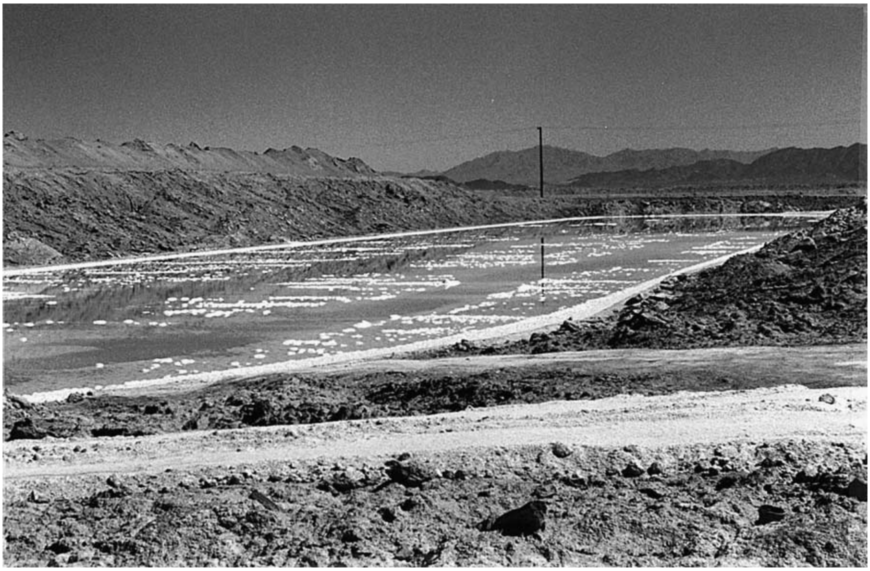


Figure 2.51 A typical brine holding (evaporation) pond at Bristol Lake. (Courtesy of National Chloride Company of America).

The Tetra Technologies operation on Bristol Lake relies more on seepage pits than trenches, and utilizes considerable solar ponding of dilute brine pumped from the edge of the lake. Brine is pumped from the seepage pits into tank trucks, and then hauled to the evaporation ponds. Their operation on Cadiz Lake is entirely based upon dilute brine pumped to solar ponds. In both operations, salt is harvested from the solar ponds, washed and then drained for sale. It is shipped by truck, or rail from the siding at Saltus (near Amboy) where the Bristol Lake salt is washed (Morrow, 2002).

In prior years, some of the Bristol Lake calcium chloride product was converted at Amboy to a 75–78% $CaCl_2$ flake by the Hill Brothers Chemical Co. The concentrated brine from the ponds was sent to open-pan evaporators where it was first heated to 132°C and then evaporated at 171–177°C to the desired concentration (Fig. 2.53). This very viscous solution was next spread on chilled rolls to be cooled and solidified into thin sheets, which were scraped from the rolls and ground to the desired particle size. The flaked product was then sent to turbo dryers, from there cooled and packaged in plastic-lined, air-tight bags, and shipped to their customers.

Some of the early operators on Bristol Lake were the Calcium Chloride Group, The Desert Properties Co., the National Chloride Co. and the California Salt Co. (Gundry, 1992). The latter company at first only mined salt from the lake, but later also produced calcium chloride as a by-product. The company was sold to the Leslie Salt Co., who continued the production of calcium chloride, and eventually

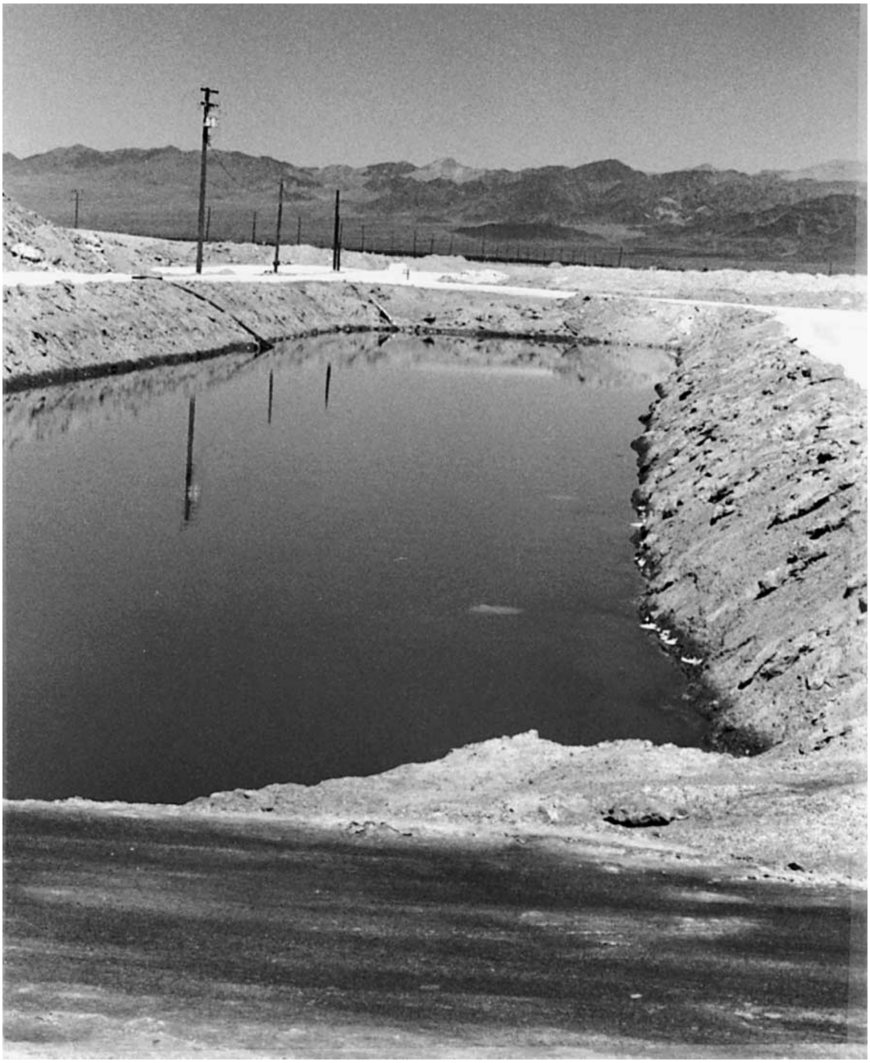


Figure 2.52 A typical brine product shipping pond at Bristol Lake. (Courtesy of National Chloride Company of America).

recovered all of their salt from the calcium chloride ponds. However, they in turn sold their 324 ha (800 acre) of solar pond land, and 450 placer claims in 1978 to the Cargill Co., and Cargill sold to Tetra Technologies on August 2, 1998. Cargill continued to market the operation's by-product salt, and Tetra also later purchased the similar calcium chloride producer, the Lee Chemical Co. on Cadiz Lake. Lee Chemical had started calcium chloride production in 1960, and was soon followed

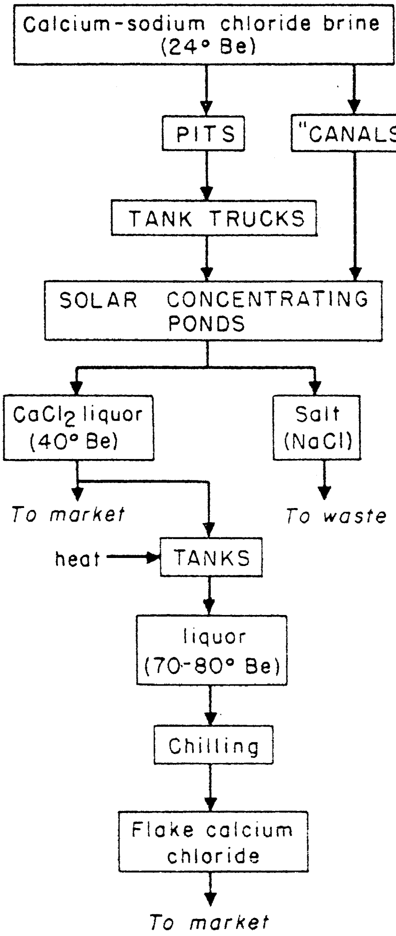


Figure 2.53 Flow chart showing method of recovering calcium chloride from Bristol Lake brine. (Ver Planck, 1957, courtesy of the California Division of Mines and Geology).

by the Delta Chemical Co. They later combined their operations as Lee Chemical. In 2002, Hill Brothers Chemical Co. was a brine sales agent for National Chloride, and ground some Tetra flake (from other locations) to a powder in their very low-humidity Amboy plant (Chemical Market Reporter, 1999; Chemical Week, 2001).

General Processing Technology

Various literature articles have discussed the general subject of producing calcium chloride (Kotsupalo *et al.*, 1999), and others have focused upon the specific operations involved. Wang (1998) and Postoronko *et al.* (1985) reviewed the problem of calcium sulfate scaling in *evaporators* used to concentrate calcium chloride brine, and suggested means of preventing its formation or removing the scale. The solubility of calcium sulfate in $CaCl_2$ solutions was studied by Li and Demopoulos (2002). Bunikowska and Synowiec (2002) noted that sulfate impurities in pH 2.2 calcium chloride brine could be removed by hydrated zirconium oxide ion-exchange pellets. The sulfate could then be removed from the pellets by a 90°C water wash so that they could be re-used. Alternately, the sulfate could be precipitated as barium sulfate. Babkina *et al.* (1981) suggested the use of titanium heat exchanger tubes in the evaporators, while Semke *et al.* (1975) discussed an automatic control system, and later (1977) a mathematical simulation of the evaporation process. Makabe *et al.* (2002) discussed automating the evaporators by means of an attenuated total-reflectance IR spectrometry instrument that continuously analyzed the concentration of all components in the brine. Kotsarenko *et al.* (1975) proposed an automatic condensate control and removal system for the evaporators, while Zhukov *et al.* (1981) noted some of the problems occurring due to the hygroscopic nature of the sodium chloride by-product crystallized in the calcium chloride evaporators. Ross and Sloyer (1953) suggested a purification process when a higher purity $CaCl_2$ brine was required for the preparation of other calcium salts or for food use. They suggest diluting the $CaCl_2$ to about 22%, and then acidifying with dilute phosphoric acid to a pH of 6.5. The filtered solution would contain very little magnesium and less than 0.0001% Fe and $< 0.0005\%$ heavy metals. Niino *et al.* (2002) also suggested the removal of heavy metals by their adsorption on activated carbon. Wheeler (1999) described the precipitation of magnesium from calcium chloride brines with lime, and the analytical monitoring methods.

To produce solid calcium chloride, the starting brine is usually first evaporated to 40–50% $CaCl_2$ in triple effect evaporators (Hedley, 1951). Above this concentration, the large boiling point rise of the liquor, and its high viscosity make multiple-stage vacuum evaporation difficult, so after the crystallized salts (NaCl, $CaSO_4$, etc.) have been removed the brine may be sent to single-effect evaporators to concentrate it to 55–65% $CaCl_2$. In prior years, and smaller operations it could be sent to open-pan evaporators to be concentrated to 70–72% $CaCl_2$, with the temperature rising to about 170°C. At this point, the liquid can be cooled and solidified (such as on rolls), with the solids that are produced being in nearly the dihydrate form (the dihydrate contains 75.5% $CaCl_2$). The solids can then have additional water removed to 76–78%, or even 94% $CaCl_2$ in conventional dryers or kilns. It has also been suggested that evaporators operating under 5–25 psig pressure can take the brine concentration to up to 85.5% $CaCl_2$ (near the monohydrate composition), and operate at temperatures below the solidification point of about 235°C (Graves, 1958).

The most common of the solidification methods is to form *flaked* calcium chloride by having a cooling roll dip into a tray of the hot liquid, as noted above, or spreading the hot solution onto the top of the cooling roll. The solidified sheet

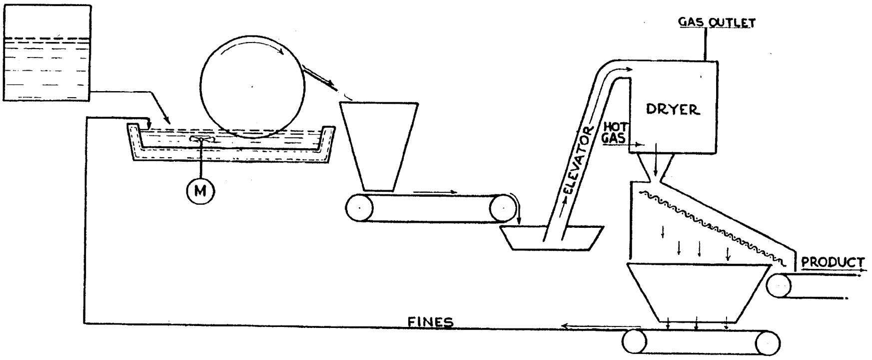


Figure 2.54 Typical Flaked Calcium Chloride Process. (Pittsburgh Plate Glass Co. [Allen] 1963).

of calcium chloride can then be scraped off of the roll and sent to a dryer to reach the desired 76–78% $CaCl_2$ concentration (Fig. 2.54). The flakes are screened and the oversize crushed to form a product with the desired particle size range (Table 2.21(A) and (B); Fig. 2.44). A number of articles and patents have been issued on the production of calcium chloride in the flaked form. Allen and Walton (1963; Pittsburgh Plate Glass) recommended adding low-value fines (−20 mesh) from the product screens back to the (171–182°C) melt tank, so that the water-cooled rotating drum picked up an 8–12% slurry instead of the normal 70–76% $CaCl_2$ solution. The product scraped from the drum was 0.76–2.54 mm thick, and after being broken and dried in a multi-tray dryer it was screened to the desired flaked particle size (20 mesh–9.53 mm [3/8 in.]). The ~122°C flakes were heated in the upper hearths with ~316°C air, and cooled in the lower hearths with ~16°C air. If a 74% $CaCl_2$ solution were in the melt tank, a 78% $CaCl_2$ product would be formed. The Asahi Glass Co. (1982) patented a method for reducing the corrosion problem when producing flake calcium chloride. They stated that it was most effective to treat a 35% $CaCl_2$ solution from the primary evaporators with either 60–1800 ppm of sodium silicate, 60–900 ppm sodium silicate with 500–1000 ppm of $Ca(OH)_2$, or 1000–1500 ppm $Ca(OH)_2$ and 100–200 ppm of gypsum. On the flaking rolls, they suggested 60 ppm SiO_2 (as sodium silicate) and 1500 ppm of $Ca(OH)_2$. This produced a white product with only 60 ppm Fe, in contrast to untreated material having a slightly brown color and up to 400 ppm Fe. Zaikin and Stankevich (1981) recommended cooling the flaked product from its normal 70–122°C temperature to 36–40°C before grinding by using a water-cooled rotating drum augmented with a countercurrent flow of air preheated to 38–41°C to prevent the flakes from sticking together or on the drum walls. Other articles, such as by Markelov *et al.* (1972) discussed a means of level control in the drum feeder to provide a more uniform product thickness.

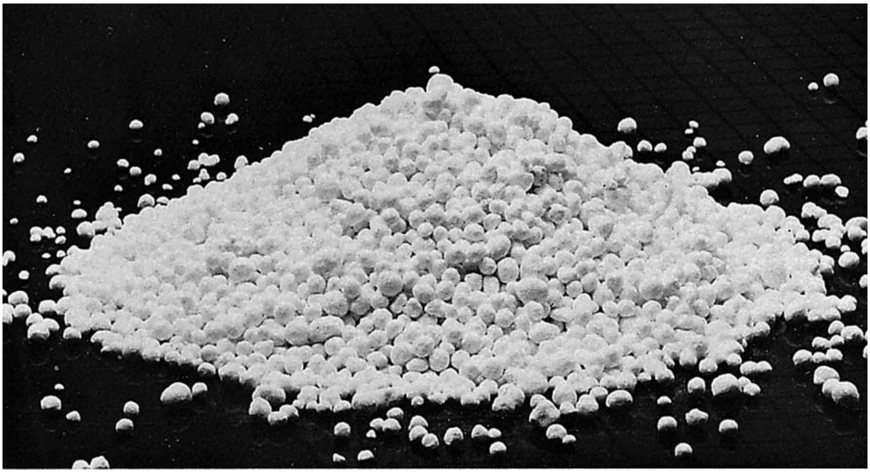


Figure 2.55 Typical granular calcium chloride (Dow, 1980, courtesy of The Dow Chemical Company).

The preparation of *granular calcium chloride* (as shown in Fig. 2.55) can be accomplished by several different means, with perhaps the most common being fluidized bed dryer-granulators such as described by Schwalm *et al.* (1986), and mathematically analyzed by Sulg *et al.* (1973). In the former article, it was suggested to spray a neutralized 55–60% $CaCl_2$ solution into a gas-fired fluidized bed of granules, and to constantly withdraw the desired amount of product. The production rate from 8.5 t/hr of a 56.4% $CaCl_2$ solution would be about 2.3 t/hr of a dry 76% $CaCl_2$ product, and 2.5 t/hr of dust to be recycled by being redissolved in a more dilute (i.e., such as 30% $CaCl_2$) feed solution. A 94% $CaCl_2$ product could be obtained with higher gas temperatures or feed concentrations. Safrygin *et al.* (2002) suggested having the gas velocity in the fluid bed at 1.5–3.5 m/s, and that the fines from the product screens be mixed with the entering feed solution. Scherzberg *et al.* (1985a,b) suggested that the final product could be made less dusty by treating it with 0.7–3% of a more dilute $CaCl_2$ solution, or 0.2–0.7% of oil. For example, 1000 g of 92.5% $CaCl_2$ granules with >5 g of dust were cooled from 170°C in a fluidized bed cooler, and sprayed with 2.5 g of a 30% $CaCl_2$ solution. The resulting product analyzed 90.7% $CaCl_2$ and contained < 1 g of dust.

Other types of granulators include prilling towers where a more concentrated $CaCl_2$ solution is sprayed into the top of a tall, open tower with a counterflow of hot, dry flue gas (James, 1994). Hedley (1951) noted that spraying a 70–72% $CaCl_2$ solution at 170–175°C into a tower maintained under a vacuum of 100–400 mm of mercury could allow the solution to evaporate to 76% $CaCl_2$ without any additional heat, but that a countercurrent flow of hot (180°C) air rising past the granules would allow the process to be more flexible. He also noted that the heat of crystallization of the dihydrate can supply much of the heat needed for the evaporation. Moore (1978) and Misumi and Asagao (1974) suggested spraying a hot (225–285°C) 74–78% $CaCl_2$ solution into a refrigerant (such as CCl_3F) or solvent (such as CH_3CCl_3 at 25–67°C and 25–120 psig pressure to produce a -4 to $+20$ mesh, or 3–5 mm product.

Drum granulators have also been employed, such as in the procedure suggested by Bennett and Carmouche (1953). They sprayed a calcium chloride solution onto a bed of recycled ground semi-dry particles (13% moisture) in a rotary kiln being heated by 250–500°F flue gas. The solution contained >50% $CaCl_2$, was at a temperature within 25°C of its boiling point, and the solids in the kiln were at a temperature between 150 and 190°C. The rate of recycled dust and small particles to the kiln was from 8 to 30 times the amount of the $CaCl_2$ in the sprayed solution. The particles from the drum granulator were sent in succession through a low, and then high-temperature shelf dryer, with two stages of screening. The product was rounded, hard, dense (55–65 lb/ft^3), dust free 3–20 mesh pellets of nearly anhydrous calcium chloride (94% $CaCl_2$). In a subsequent patent, (Wilcox and Speer, 1966) the temperature in the drum granulator was increased to 500–1760°F, which reduced the recycle load to 2–8 times the sprayed amount of $CaCl_2$ solution, and increased the production rate by 30–90%. The hot gas entered the granulator in a concurrent manner, and was regulated in amount so as to not cause melting, puffing or to allow the solids to rise above their previously specified temperature. Lebedenko *et al.* (1982) also described a drum granulator where hot concentrated $CaCl_2$ solution was sprayed into an inclined rotating drum of granules in counterflow to hot flue gas. The still moist granules that were formed were then sent to a conventional dryer. A model was made of the granule's growth.

In a similar manner with a disk granulator, as described by Novotny and Kadavy (1975), the hot, concentrated $CaCl_2$ solution was sprayed onto a bed of granules on an inclined rotating disk. The moist granules overflowed from the bottom of the disk, and were conveyed to a conventional counterflow dryer. The disk could be operated at ambient temperatures, or heated by steam or flue gas. A horizontal disk granulator was suggested by Comstock (1954) to prepare large particles 6.4–19.1 mm in diameter, with a density of 1.32–1.64 g/cc. A 45–60% $CaCl_2$ solution was sprayed inside a thick bed of heated granules, and the granules were then circulated to the surface. For larger particles, a pug mill could also be employed, and be able to process solutions as dilute as 60% $CaCl_2$ and at temperatures of 120–150°C. The hot liquid would be fed into the mill at one end with recycled fines or off-size particles, and be slowly conveyed with mixing to the discharge end. Heat could be applied through the mill's walls, or by a hot air stream blowing over the top. The discharged calcium chloride would be of a mixed size and need to be screened, with the oversize ground to produce the final product (Hedley, 1951). Small granules may be prepared by the use of a high-temperature (400°C inlet flue gas) spray evaporator-dryer feeding 30–40% $CaCl_2$, as suggested by Gleason and Sui (1982). Other forms of solid calcium chloride can also be produced for special uses, such as pelletizing grains or powders, the crystallization of $CaCl_2 \cdot 2H_2O$ (Trypuc and Buczkowski, 1991), pouring ~72% $CaCl_2$ into small molds (Tokuyama Soda Co., 1982), or forming solid calcium chloride tubes (Korolev, 1974).

Articles on the *drying* of calcium chloride flake or granules have also been presented, including the patent on a multiple hearth dryer by Iwamoto *et al.* (1979). With a 70% $CaCl_2$ solid feed material in a three-hearth unit the bed thickness in the first hearth was kept at 40 mm, the second hearth had 92 mm of product, and the third hearth 151 mm. With a 160°C flue gas, the feed material dried to 98% $CaCl_2$, and it did not agglomerate or form a large amount of dust.

Other Sources of Calcium Chloride

As a quite different source of calcium chloride to the natural brines discussed above, it is also produced on a large scale from the waste liquors of Solvey soda ash plants. However, this process is beyond the scope of this book, and its production is quite different from that required in most natural calcium chloride processes. The Solvey end liquor from producing soda ash is normally a fairly dilute solution, such as containing about 9–10.5% $CaCl_2$, 5.5–7% NaCl, 0.3–0.7% SO_4 and ~3% other salts. It is usually first carbonated to remove any free ammonia or $Ca(OH)_2$, treated with an oxidizing agent to remove some of the organics, then with $CaSO_4$ to precipitate some of the sodium sulfate (as glauberite), and finally evaporated to crystallize much of the NaCl and other salts (Novotny, 1968; Shitov *et al.*, 1981). Commercial calcium chloride is also manufactured by reacting by-product or waste hydrochloric acid with limestone. The limestone and HCl are agitated to produce an approximately 37% $CaCl_2$ solution with a pH of about 9. It is then pressure filtered and the pH adjusted to 8 before the solution is evaporated to its desired concentration (Gomes, 1997).

Calcium chloride can also be produced from some waste solutions, and various of them have been discussed in the literature. Coal or other flue gas lime-scrubbing liquors remove SO_2 and lesser amounts of volatile chlorides, and calcium chloride will accumulate in the scrubbing liquor. After gypsum is precipitated and removed from a slip stream, the liquor can be evaporated and spray dried. Riedel *et al.* (1999) have studied the corrosion problems encountered with the evaporator heat exchanger tubes in this application. In laboratory tests, they found that in the first effect with < 100 g/liter $CaCl_2$ and < 85°C that Alloy 31 (X1NiCrMoCu32-28-7) was satisfactory, but that in the last effect with < 300 g/liter $CaCl_2$ and 85°C Alloy 59 (NiCr23Mo16Al) or Alloy C-276 (NiMo16Cr15SW) were required. These results were confirmed in a 9 month plant test, where Alloy 59 had the lowest crevice corrosion in both effects. Alloy tubes were recommended over the competitive graphite tubes because of graphite's susceptibility to mechanical damage.

Other proposed sources of calcium chloride include the thermal decomposition (at 270–280°C) of scrap PVC, with the flue gas being absorbed in a lime or limestone scrubber (Aoki *et al.*, 2002). Others have suggested the washing of incinerator or fly ashes to recover calcium chloride, or the leaching of blast furnace slag with acids. Dust from scrap steel shredders could also yield calcium chloride in the absorbed incinerator flue gas.

USES OF CALCIUM CHLORIDE

Calcium Chloride has a wide range of uses, but the major ones are for deicing, dust control, road stabilization, concrete curing, oil well drilling, tire ballasting and various industrial and miscellaneous uses. The percentages of the total sales as divided into these categories are shown in Table 2.15. There are many excellent discussions of these uses, such as publications by the major manufactures that give detailed instructions on each of their applications, product handling and environmental factors. There are also a few general articles in the literature on calcium chloride uses, such as by Kotsupalo *et al.* (1999).

Deicing

Calcium chloride's usefulness in reducing or eliminating ice and snow on roads, or in preventing bulk commodities (such as coal in open rail cars) from freezing solid (or to thaw them when frozen) is because pure solutions at a concentration of 30.22% $CaCl_2$ have a freezing point as low as −49.8°C (−57.6°F). When ice is contacted by $CaCl_2$, it is rapidly melted by both the freezing point-lowering effect and the heat of dilution, and it also appears to weaken the inter-crystalline bonds of ice to make it more friable and easily broken or removed. In actual practice, calcium chloride is considered to be most useful when the temperatures are below −17°C (1.4°F), and to be quite efficient from −29.4 to −31.6°C (−21 to −25°F). This compares with salt being most effective from above −2 to −4°C (25–28°F, although it can melt ice to −21.2°C [−6.2°F] at a concentration of 23.2% NaCl), while magnesium chloride is most effective to −15°C (5°F), although at a concentration of 21.38% $MgCl_2$ it can melt ice to −33.6°C (−28.5°F). Thus, calcium chloride is the only material inexpensively available for deicing in very cold climates, or for very cold storms. Dow Chemical recommends an application rate of 15–30 gal per lane mile of roadway for their 30% $CaCl_2$ corrosion-inhibited Liquidow © Armor © solution (Dow, 2002). They also note that the solution meets the PNS bulk storage test of less than 1% crystallizing after 7 days at −29°C (−20°F). Magnesium chloride deicers can only pass this test at −18°C (0°F).

When calcium chloride is applied with salt, the freezing point can be lowered to any desired intermediate temperature between their two limits or practical

Table 2.15

Calcium Chloride Use Pattern in the United States (Per Cent of Total Consumption)

Year	Deicing	Dust control[a]	Industrial processing	Concrete additive[b]	Oil and gas drilling	Tire ballast	Other
2001	22	20	20	12	17	5	4
1999	21	25	13	11	22	—	8
1998	35	20	20	10	10	—	5
1998	30	20	20	12	10	4	4
1997	38	18	20	12	4	4	4
1996							
1995	40	20	20	5	10	—	5
1994	35	20	20	5	12	4	4
1993							
1992	40	20	20	5	5	3	7
1991							
1990							
1989	35	22	21	5	10	—	7
1988							
1987							
1986	40	22	20	5	5	4	4
1985							

(*continues*)

Table 2.15

(continued)

Year	Deicing	Dust control[a]	Industrial processing	Concrete additive[b]	Oil and gas drilling	Tire ballast	Other
1984							
1983	35	20	20	5	12	4	4
1982							
1981							
1980	28	23	20	5	15	3	6
1974	25	30	20	10	7	3	5
1972	55[d]		20	10	—	2[c]	8
1969	63[d]		14	11	—	5[c]	10
1966	55[d]		10	13	—	5[c]	17
1965	30	25	—	13	—	5[c]	—
1963	55[d]		10	13	—	5[c]	17
1957	15	30	17	13	—	—	25
Average	31	22	18	9	11	4	5

C&EN (2000), Chemical Market Reporter, Chemical Week; US Bureau of Mines.

[a] And road stabilization.

[b] Cement manufacture and concrete accelerating.

[c] Refrigeration brine.

[d] Combined deicing and dust control.

ranges, and thus the use of salt "pre-wetted" with calcium chloride (Dow recommends 8–10 gal of their Liquidow © Armor © per ton of salt; Dow, 2001; Fig. 2.56) is more economical for less severe temperatures. For temperatures from 0 to −2°C (16–32°F), the ratio of flake calcium chloride to salt in $CaCl_2$–NaCl mixtures should be from about 1 to 3, from −9 to −18°C (0–15°F) 1 to 2, and from −18 to −23°C (−1 to −10°F) the ratio should be 1 to 1 (Dow, 1998). Calcium chloride works much faster than salt, and is most effective if applied before the low-temperature period to prevent ice from bonding to the roadway. However, once the ice has formed the calcium chloride can still be applied in either the liquid, flake or pellet form, and will rapidly melt the ice and break the bond between the ice and road surface. Its ability to then adhere to the road

Figure 2.56 Trucks removing loose snow and ice, and spreading salt pre-mixed with calcium chloride (Allied, 1980).

surface often reduces the frequency of plowing and repeated applications, thus compensating for being more expensive than salt. For the same reasons, abrasives such as sand or cinders scattered onto the ice-covered road can also benefit from being pre-treated with calcium chloride, or mixed with it (Tetra, 2002).

There is considerable literature on deicing, with perhaps the most useful sources being the excellent brochures issued by the calcium chloride producing companies. Among the general studies on deicing are a series of articles (in Japanese) by Sugawara *et al.* (1986–1999). They considered the mechanisms involved by both the heat of solution and the concentration factor on ice melting, and have developed a numerical model for deicing. Kirchner (1992) studied the comparative effectiveness of $CaCl_2$, KCl, urea and Ca–Mg acetate on the salts ability to undercut ice and spread at the road-ice interface. Hahn (1988) compared the advantages of deicing with $CaCl_2$ solutions rather than solids, and Burtwell (2001) noted a large-scale test in England comparing the merits of $CaCl_2$-pre-wetted salt compared to ordinary salt. Boley (1984) discussed coal-thawing with $CaCl_2$, and several papers have suggested quick analytical methods for determining the quantity of ice-melting chemicals on a road surface (Della Faille d'Huysse, 1981; Salins du Midi, 1978; Martinek and Beranek, 1975).

There is also a considerable literature on possible corrosion inhibitors to be added to deicing $CaCl_2$. The suggested chemicals include $Na_2B_4O_7 \cdot 10H_2O$ (borax), 2-butyne-1,4 diol, ammonium carbamate, carboxylic acid with an amine containing alkyl or alkylbenzyl groups, Na_2PO_3F, sodium hexametaphosphate $(NaPO_3)_6$, hexamethylenetetramine, lanthanum or a rare earth salt plus a soluble gluconate, sodium metasilicate, organic acid salts (acetate, ascorbate, formate, lactate, saccharate or tartarate), di and mono orthophosphate, calcium phosphate or calcium hydrogen phosphate, sodium or potassium silicate, a phosphonic acid derivative $(R_nR^1N(CH_2PO_3M_2)_{2-n}$ (where R and R^1 are alkyl aminoalkyl or hydroxyalkyls), sodium tripolyphosphate $(Na_5P_3O_{10})$, urea, and zinc chloride or sulfate. The effectiveness of one of the commercial corrosion inhibitors is illustrated in Fig. 2.57.

The literature on suggestions for making deicing mixtures with calcium chloride is also surprisingly large. As noted above, pre-wetting ordinary salt with $CaCl_2$ solutions, or mixtures of salt with calcium chloride solids are commonly employed, but in addition suggestions for a suspension of fine NaCl crystals in a $CaCl_2$ solution and forming a solid $CaCl_2$ layer around an inner NaCl mass have also been made. There have been suggestions to combine calcium chloride with various other salts, including: the fertilizers potash or urea (perhaps coating the fertilizers with $CaCl_2$), sodium tripolyphosphate $(Na_5P_3O_{10})$, magnesium chloride or sulfate, ammonium chloride or phosphate, and sodium, calcium and zirconium silicates (the latter is a far-IR absorber). Suggested mixtures with minerals or inert substances include: calcite, diatomaceous earth, kieselguhr, pozzolan, pumice, sand or gravel, calcined and expanded shale, and small particles of asphalt or concrete, cinders, lava and sandstone. Many organic agents have also

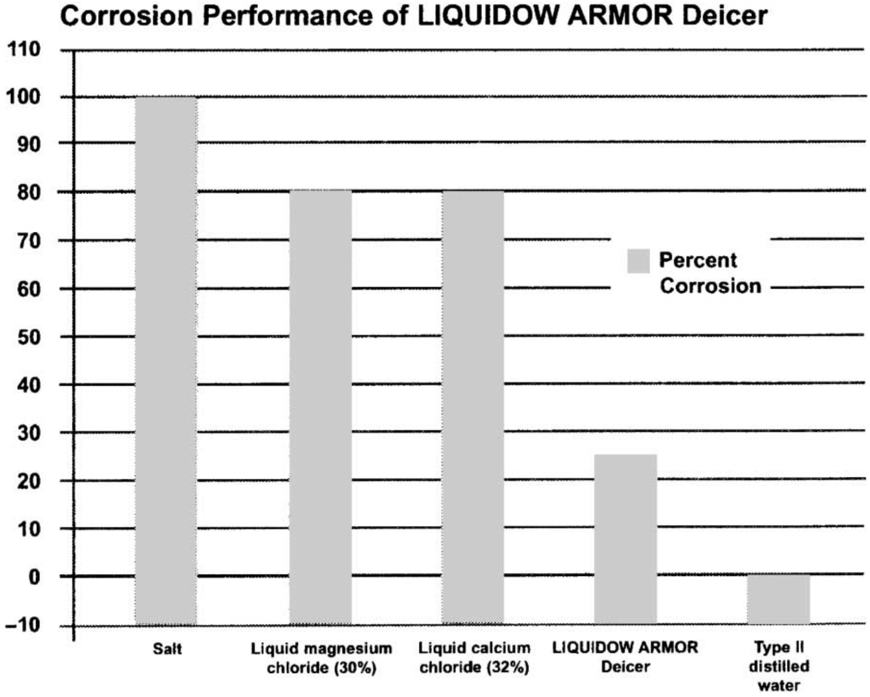


Figure 2.57 (Dow, 2001, courtesy of the Dow Chemical Company).

been suggested to be used with calcium chloride, often with other inert fillers. These include: polymers of methylacrylate, oxyethylene, oxypropylene, urethane, and vinyl acetate; carbohydrates (molecular weight 180–1000), coal tar, ethyl and methyl alcohols, glycerin, glycol, 1-hexadecanol, metal lactates, 1,2-propylene, propylenediamine dioleate, polyglycol, thioacids, solvents, and surface-active agents Ossian and Steinhauser (2000).

Many waste products have also been suggested to be used with calcium chloride, such as wastes from: the alcohol industry (including from molasses, sugar beets and sugar cane), ashes, biofuels, bark mulch, cheese (from milk or whey), magnesium processing, pulp and paper sludge, saccharinic acid (from the alkali treatment of bagasse, corn stalks, molasses, paper pulp, saw dust, straw, sunflower stalks or waste paper), tofu processing, whey, wine (from grapes and other fruit), and zinc.

The environmental problems with calcium chloride in its deicing application, as with salt, are that when used in excess it can harm roadside vegetation and contaminate water supplies. Howard and Beck (1993) have studied the effect of road deicing chemicals upon the springs, wells, groundwater and aquifers near highways in southern Ontario, Canada, and found that a small, rather minimal change occurred compared to background values. Mayer *et al.* (1999) noted that the Canadian environmental agency was studying road salts, finding that the salts' greatest effect on surface water was to small road-side ponds, or streams draining large urban areas. In Italy Canovi (1987) reported that there had been no visible damage to the vegetation near heavily traveled roads, nor an appreciable change in the adjacent soil composition. Rich and Murray (1990) observed that in central Connecticut roads in drainage basins with drinking water reservoirs only used calcium chloride, and not sodium chloride for deicing. Bubeck and Burton (1989) discussed the effect of deicing chemicals on underground aquifers, and Werner and Dipretoro (1998) reviewed road salts' effect upon water-supply springs. Kjensmo (1997) found that a small thermally stratified lake near a highway in Norway was becoming less stratified due to the slow increase of road salts in its upper section.

Bowers and Hesterberg (1976) studied the effect of deicing salts upon white pine near roadways in Michigan. They found that salt spray was a problem, but not $CaCl_2$ with spray or root take-up. Similar observations on Scots pine in Finland were noted by Viskari and Karenlampi (2000) and Hautala *et al.* (1992), where NaCl damage only occurred within 20–30 m of the road, and the seasonal moisture greatly effected the extent of damage. Other tree species (*Sorbus aucuparia* L., *Acer pseudoplatanus* L., *Tilia platyphyllos* Scop., and *Platanus acerifolia* W.) were studied with only $CaCl_2$ deicing in Belgium. It was found that there was little damage, but *Tilia* was the most, and *Platanus* the least effected by the $CaCl_2$. *Platanus* also became somewhat more sensitive to infection by *Gnomonia venata* (Paul *et al.*, 1987). Utosawa (1995) found that deicing $CaCl_2$ that entered a sewage system enhanced the removal of phosphates from the water.

Calcium chloride can also be quite corrosive to concrete, automobiles and other structures that it contacts. However, the addition of corrosion inhibitors to the $CaCl_2$ can reduce its corrosion problems compared to salt by more than 70% (Fig. 2.47), and each of the major producers markets an inhibited product (Dow: Liquidow Armour or Plus; General Chemical: Corguard; Tetra: Winter Thaw-DI; and Reilly Industries for magnesium chloride: Ice-Stop CI2000). Gillott (1978) has discussed the effect of deicing calcium chloride on the corrosion of concrete roadways and adjacent structures. Ludwig and Balters (1994) compared the damage to concrete from various deicers when the temperature fluctuated from -20 to $+10$°C. The damage decreased in the order of NaCl, urea, $CaCl_2$ and water. Tsukinaga *et al.* (1994) found the same order of deterioration based upon the amount of concrete scaled-off under standard test conditions. Balazs *et al.* (1990) reviewed the freeze–thaw corrosion problem, and Frey and Funk (1985) studied the loss of concrete's compressive strength by deicing chemicals. Under the worst conditionsm, there could be a 70–75% loss, but in actual practice the loss was found to be quite small (Pagliolico *et al.*, 1997). Sayward (1984) noted that the mechanism of freeze–thaw deterioration of concrete by deicing chemicals was by the initial formation of micro cracks that facilitated access of salt and water for freeze-cracking, which in turn allowed CO_2, water and salt to corrode the reinforcing rods, and spall the concrete. Hudec *et al.* (1992, 1994) suggested that potassium acetate had equal deicing properties to $CaCl_2$, and was not a corrosive agent.

Dust Control

Since calcium chloride is hygroscopic and deliquescent (it absorbs and retains water) under a wide range of climatic conditions (temperature and humidity), when applied to a dusty or potentially dusty surface (i.e., such as an unpaved country road; Fig. 2.58) it wets and consolidates the dust. It then absorbs more water to help prevent additional dust from forming, and because of its solutions' high-vapor pressure (and high-boiling point), it helps to retain this moisture. This improves safety and the ease of driving, assists in retaining all of the small particles and surfacing material (as well as the dust), aids in producing a dense surface and reduces the amount of blade work that is required for road maintenance. Without the calcium chloride it has been estimated that a car driving one mile per day on a dusty road for a year could cause the loss of 1 t of dust. As these fines are lost (causing vision and health problems), voids are created between the larger particles, and the surface begins to loosen. Then the road begins to degrade, potholes form and "washboarding" occurs, aggregate is pushed to the side, and more frequent blade work is necessary. The application of calcium chloride can reduce the aggregate loss by up to 75%, and the blade work from one-third to one-fifth of that for an un-treated road (Tetra, 2002).

The recommended application rate is $\sim$1.2 liter/m^2 (0.27–0.5 gal/yd^2) of 32–40% liquid calcium chloride (or 1.5 lb of flake/yd^2) in the late spring (preferably after recent blading work and a rain), followed by one-half to one-third of that amount during the summer. When sprayed onto roadways (Fig. 2.59) one company's product is said to be effective with only one application per year, but two to three coatings are usually recommended. Various surface-active additives have been suggested to enhance $CaCl_2$ solutions' ability to penetrate dust, and thus help its control (Dow, 1998, 1980). One of the agents that has been recommended is sodium succinate, which when applied to various strength $CaCl_2$ solutions in the amount of 0.2–0.3% increases their penetration ability by 13–18% (Zhou and Wu, 1999).

Soil Compaction or Stabilization

In a similar manner, calcium chloride is effective in surface consolidation, base stabilization, and compaction during road construction. For the latter use, it is added as either liquid or flake to the aggregate as it is being laid down, or to plant

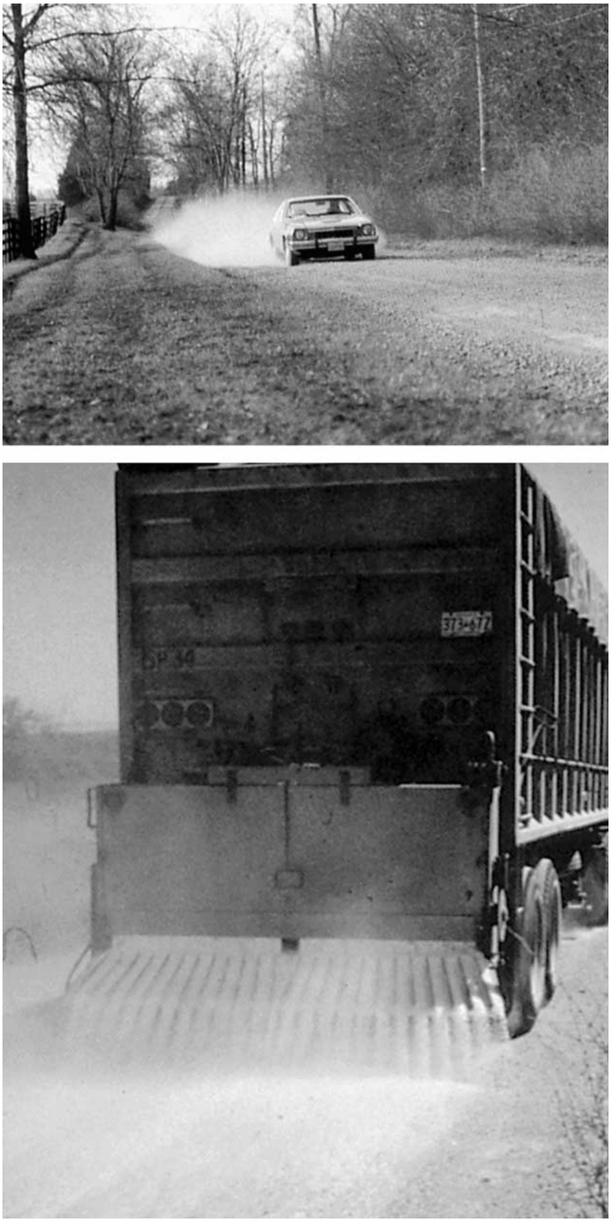


Figure 2.58 Typical dust from an unpaved road, and one type of calcium chloride spreading truck (Dow Chemical, 1980, courtesy of the Dow Chemical Company).

Figure 2.59 Typical liquid calcium chloride spreader for dust control or road stabilization (Dow, 1999, courtesy of The Dow Chemical Company).

mixes. It absorbs water into the base material and later retards the evaporation of this moisture, contributing to the stability of the structure. Studies have shown that a moisture variation of only 1% from optimum may reduce the aggregate's density by over 2 lbs/cuft, and increase void space by as much as 8%. Calcium chloride addition can maintain the moisture level to the desired 7–8% during the road base compaction, which greatly aids in the interlocking process, and is especially important in the summer. Less rolling and grading are required, the load-bearing capacity and stability are improved, and the overall construction costs are reduced (Tetra, 2002). In one test where the top 6.4 cm (2.5 in.) of road-base was graded and then compacted by rolling, with water alone the road was in good condition for 12 weeks and in poor condition for 42 weeks, even with 5 gradings during the year. When flake calcium chloride was mixed with the top 6.4 cm of road base in the amount of 2.2 lbs of flake/yd^3, and then graded and compacted only two additional bladings were required over the 54 week period to keep the road's surface in good condition for 40 weeks and poor condition for 14 weeks. With 4.2 lbs of flake/yd^3 the road stayed in good condition for over 54 weeks with no additional blading (Althouse, 2001).

Some of the literature on soil compaction (also called binding, hardening, increased load-bearing, stabilization or strengthening) include Alkiri *et al.*'s (1975) general article on the subject, and the use of additives with the $CaCl_2$ (Angelova, 1997; Baek, 1997; Fujioka, 1997; Grott, 2000; Shimada *et al.*, 2000; Shirasaka *et al.*, 1998; Sugihara, 1997; Thomas, 1997; Wu, 2000; Zhou and Wu, 1999).

Some of the suggested additives are: CaO, $Ca(OH)_2$, gypsum, NaOH, Na_2SO_4, H_3PO_4, alum, calcium aluminate, cement, blast furnace slag, fly ash, lignosulfonic acid, sulfamic acid, flocculants, polymers and wetting agents. Materials that might be used to increase the penetration of calcium chloride solutions into soil (or dust) include: sodium succinate, sodium silicate, sodium dodecyl sulfonate and sodium dodecyl benzyl sulfonate (Zhou and Wu, 1999; Wu *et al.*, 1998; Wu and Chen, 1998). A number of articles on the effect of calcium chloride on various clay minerals are listed in the Geology chapter.

Concrete

Calcium chloride accelerates the setting time of concrete by as much as 30–50%, with the effect being greater in richer mixtures (with a higher ratio of cement to sand and aggregate) and colder weather. It also provides increased compressive strength, especially at the early stages (i.e., it may be more than doubled after setting one day, and increased by 50% at 7 days). There is also usually an increase in flexural strength of the finished concrete, but this effect is much smaller. Calcium chloride usually reduces the amount of bleeding (water separating from the mixture), settling and subsidence of fresh concrete, and the amount of water required for good workability. Reduced water also helps to densify and waterproof the concrete to minimize later corrosion. Up to 1–2% liquid calcium chloride (as $CaCl_2$) is usually used in concrete formulations, although if solid calcium chloride is preferred at least 5 min of mixing is desirable, with the flaked product dissolving faster than pellets. Increasing the set time and early strength allows earlier finishing of the concrete, which reduces the labor cost and is especially important in colder weather. However, the amount of $CaCl_2$ present is too small to have any appreciable effect on the possible freezing of the water in concrete, but it does cause an earlier liberation of the heat of hydration. Thus, the length of time during which concrete can be damaged by freezing is reduced. Special low-temperature concrete can be prepared with a mixture of calcium chloride, various clays and other additives (Nedra, 1971; Stroitel'stvo, 1971; Go Bocan, 2001). Calcium chloride may also be used as an additive in making cement to lower its alkali content (Jardine *et al.*, 2000; Lackey, 1992).

On the negative side, the presence of $CaCl_2$ can result in increased corrosion to the concrete's reinforcing rods if the steel is not adequately buried (at least 5 cm [2 in.] are recommended) and it is exposed to air and moisture. Since corrosion is enhanced when the steel is stressed, pre-stressed concrete beams should not use calcium chloride. Concrete with $CaCl_2$ is more susceptible to sulfate attack and galvanic corrosion (from stray electrical currents caused by the steel reinforcing rods contacting other buried metals, etc.), and it is more corrosive to any other buried metals (aluminum, copper, etc. pipes or conduit). Calcium chloride does not decrease the deicer freeze–thaw scaling resistance of properly designed and placed concrete, but it can increase winter deterioration with poor concrete, or mixtures that did not have a proper drying period (3–6 months are recommended before freezing). Maintaining a high pH in the concrete (it is normally ~12.5), adding some pozzolans or fly ash to densify the concrete, or even the addition of latex (which is especially advantageous for highway patching; Nagi *et al.*, 1994) can reduce these problems (Lackey, 1992). In general, not more than 1 lb of $CaCl_2$/100 lbs concrete should be used when the temperature is above 32°C (90°F), 1–1.5 lbs at 21–32°C (70–90°F), and 2 lbs/100 lbs concrete below 21°C (70°F; Dow, 1998).

There is considerable literature on the use of calcium chloride in concrete, such as the general article by Anon. (1971), and Foster's (1929) discussion of the effect of $CaCl_2$ on the hydration of the cement minerals. Akhverdov and Batyanovskii (1986) noted that for dry molded, rapidly hardening concrete, 1% of calcium chloride also increases the strength of the concrete by 4.1%. As concrete ages, the surface areas slowly carbonate, and this reduces the harmful effect of road deicing salts in forming calcium oxychloride (Pagliolico *et al.*, 1997). Various types of cement and other additives to the concrete (with the $CaCl_2$) can be used for especially corrosive conditions (Epshtain *et al.*, 2000). Many other articles have been written on the use of calcium chloride in preparing the cement for the concrete, such as with other additives, and for special concrete applications.

Oil and Gas

In the oil and gas industry, calcium chloride is used in well drilling muds to increase the fluid's viscosity and density (and thus the weight [and pressure resistance] of the mud column), and as the internal phase (the small droplets in the oil) in an invert emulsion of an oil–water based system. It is also used in specially designed muds to deal with plastic-flow shale (it stiffens the shale and reduces its swelling), and in completion brines to flush-out the drilling mud prior to pumping the oil. The use of $CaCl_2$ instead of NaCl in drilling muds and as a flushing brine can considerably improve the permeability of the formation because of calcium chloride's ability to coagulate clays and prevent their forming into finely divided colloids that would block the flow of oil or gas (White *et al.*, 1964b).

Calcium chloride is also used as an accelerator in cementing the drill casing to the rock formation (Reddy, 2001; Reddy *et al.*, 2000), or upon abandonment filling of the casing. Some of the literature on other applications of calcium chloride to oil and gas production include those by Reed (1968; with water or steam injection), Trebin *et al.* (1968; improving formation porosity), Bagci *et al.* (2001; the effect of $CaCl_2$ on limestone reservoirs), Navarrete *et al.* (2001; with the addition of a polymer to cement casings when there are highly porous zones), Gupta and Santos (2002; a field test method for the compatibility of $CaCl_2$ drilling fluid with the formation rocks), Blackwell *et al.* (1974; with a gelling agent and liquid hydrocarbon to form a hydrofracturing mixture), Kelkar *et al.* (2001; as a perforating brine for hydrofracturing), a well work-over fluid (again to clean the well of solids before maintenance), and in packing fluids (the fluid in the rubber seal between the tubing and the casing), Sabins (2001; a gravel-pack carrier fluid), Ralston and Persinski (1968; inhibiting salt deposition and crystallization), Arshinov *et al.* (1971; $CaCl_2$'s prevention of gas hydrate from forming), and many others.

In the production of natural gas calcium chloride is commonly used as a drying agent to remove water and prevent the formation of methane hydrates (Hodgson and Martinez, 1984; Kolodezni *et al.*, 1977; Musaev, 1972; Arshinov *et al.*, 1971; Hodgson, 1970; others). An example of an absorption column is shown in Fig. 2.60, where the solid pellets are loaded into the upper section of the column, and the gas introduced into the tower's base and first passed through a phase separator to remove any liquid water or hydrocarbons. As the pellets absorb water they slowly dissolve, and this solution then flows to a modified bubble-cap section where it continues to absorb water until it reaches a concentration of about 20–25% $CaCl_2$, and is then discharged. New pellets are added as needed, and the combined solid and liquid-phase dehydration provides very good efficiency and economy (Dow, 1998). Typical water absorption rates and the amount of gas processed per unit of calcium chloride are shown in Fig. 2.61, and as examples, 1 lb of 94% $CaCl_2$ can absorb 17.3 lbs water at 95% relative humidity, but only 2.1 lb H_2O at 60% humidity. If hydrate growth-inhibitor/modifying compounds are used in the system, they may sometimes be recovered from the treating solution by the salting-out effect of calcium chloride (Blytas and Kruka, 2001). When natural gas is absorbed to enrich the helium content of the residue, a calcium chloride solution is added to the absorbent to produce a dry, enriched gas (Kryukov *et al.*, 1971).

In petroleum refineries, calcium chloride is used to dry materials such as distillate, LPG, kerosene and diesel fuel, while in petrochemical plants it can also be used to dry products like chlorinated hydrocarbons. For these applications, large particles of calcium chloride are required, such as Dow Chemical's Peladow DG, almond-shaped briquettes. Some of the specific literature on this subject include the articles by Barnett (1996) on drying distillates, Sweeney (1981) on gasohol, Hu (1995) on diesel fuel, Masini *et al.* (1990) on the hydrocarbons to produce chloromethanes, and Matsushita Electric Industrial Co. (1982) and Murthy (1975) on kerosene. In the latter article, the drying was done in parallel-series columns (Fig. 2.62), with a flow rate of 0.75–1.0 ft/min through the $CaCl_2$ beds. The capacity was 0.93 lb H_2O/lb $CaCl_2$ to go from 95% $CaCl_2$ pellets to the hexahydrate form, and 0.61 to the tetrahydrate. Salt was used in an initial bed to remove physically trapped water, and the calcium chloride removed most of the remaining (including dissolved) water. The beds were dumped after 18–30 days' operation, with a 32–38 bbl kerosene/lb of $CaCl_2$ capacity.

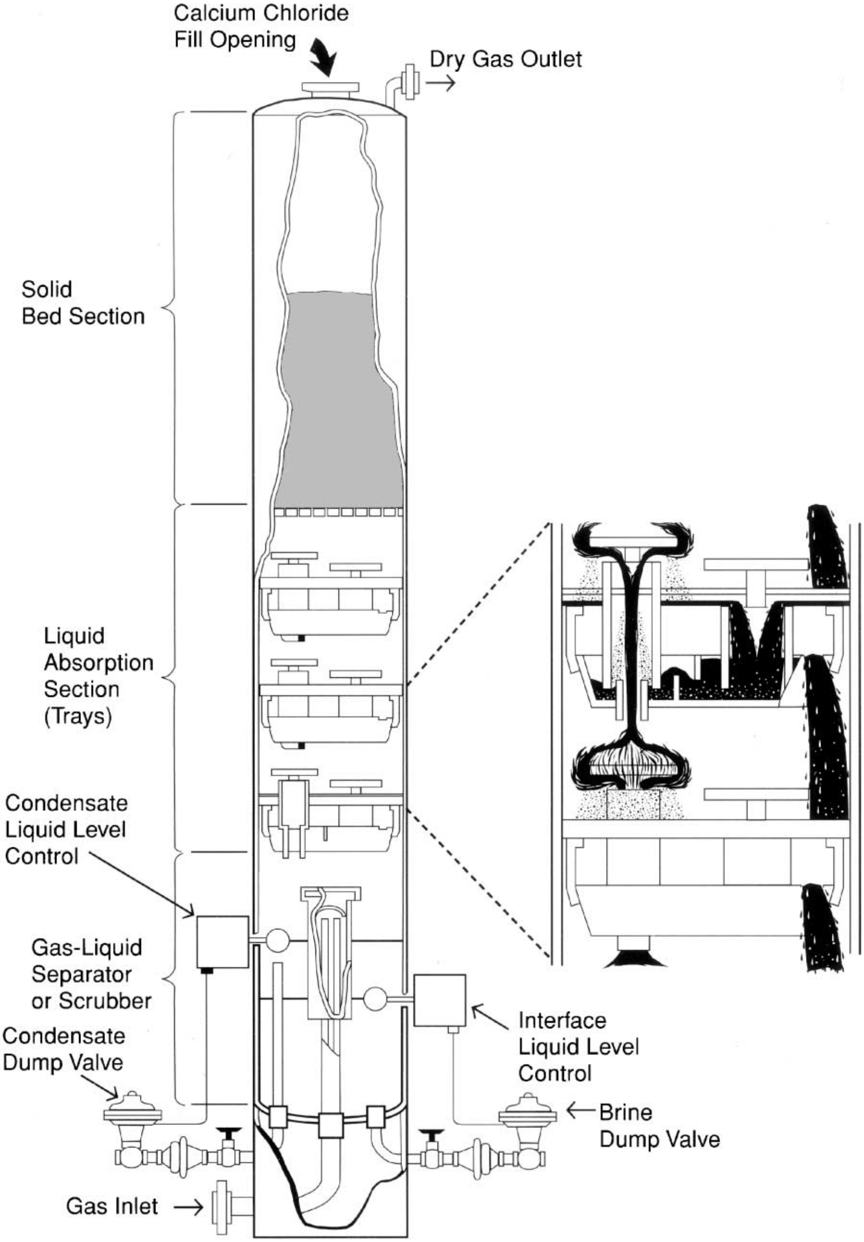


Figure 2.60 An example of a natural gas dryer using calcium chloride briquettes (Dow, 1998, courtesy of The Dow Chemical Company).

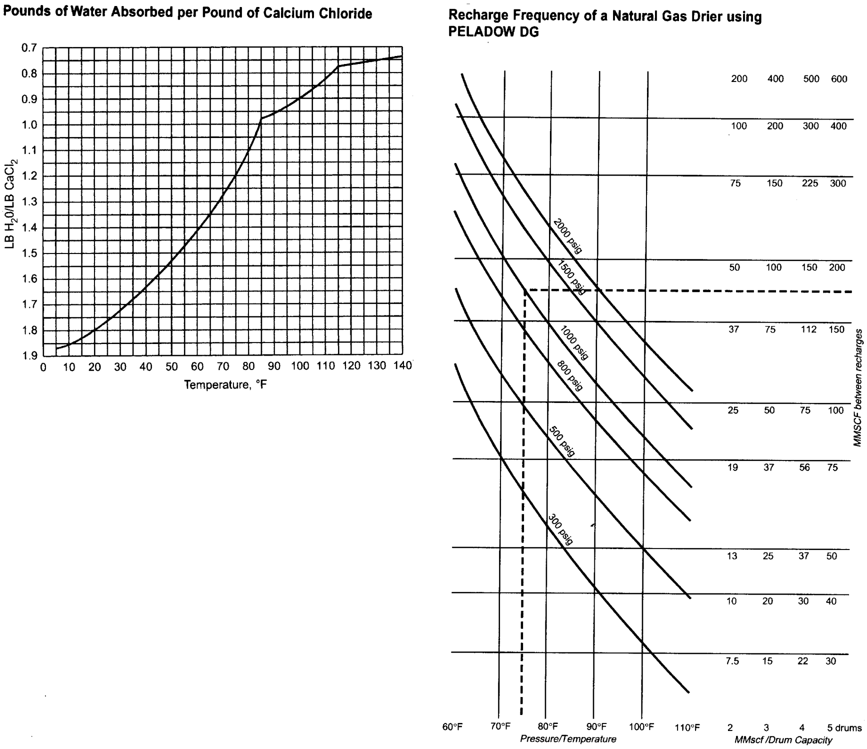


Figure 2.61 Factors in the drying of natural gas with calcium chloride (Dow, 2002, courtesy of the Dow Chemical Company).

Ballasting

Tire weighting is widely used in order to increase the traction of farm and industrial machines under various surface conditions by increasing their weight. A standard (30–40%) calcium chloride solution, with its high density is put into the vehicle's tires, often increasing the machine's weight by as much as 10% without any hindrance to its operability or performance. The axles do not carry any additional weight, and besides improving traction and drawbar pull by as much as 80%, it reduces tire wear and stress on other parts of the vehicle, reduces the vehicle's center of gravity, and helps to prevent the lifting of the front or rear tires with the handling of heavy loads. The calcium chloride solution is pumped or pressured into the tire with its valve stem in the top position, and usually filled to 90% of the tire volume (although 75–100% can be used). Air is then added to the desired pressure. For tractor tires, the amount of solution can be from 16 to 213 gal per tire (Dow, 1998, 1980).

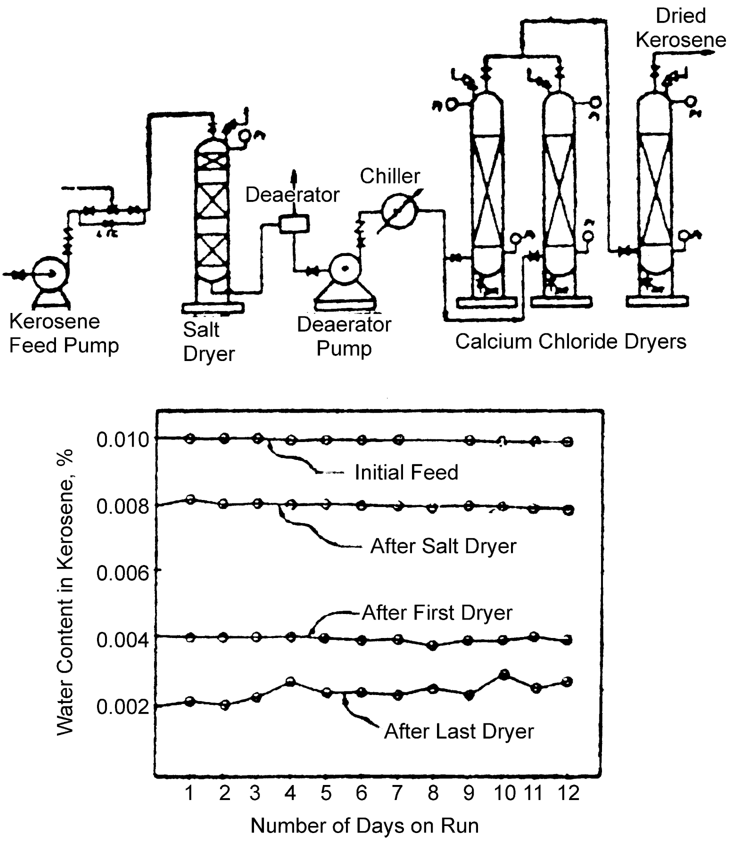


Figure 2.62 The calcium chloride drying of kerosene (Murthy, 1975).

Food Processing

Considerable calcium chloride is used in food processing, but if classified as food-grade it must meet Food and Drug Administration (FCC) standards, and be manufactured under "good manufacturing practices". In 1990 four U.S. companies produced a special anhydrous food grade product, and by 2002 several other companies were marketing both liquid and solid food grade calcium chloride. Calcium chloride is used in canning, pickling ("briner's grade"), water treating for soft drinks or beer, the processing of cheese (it increases the size and strength of curds, and hastens ripening; Guven and Karaca, 2001), to enhance food flavor, for food preservation and packaging, as a nutritional supplement and other food-type objectives. As a few examples of these uses, it can firm the skin of fruits and vegetables. With pasteurized jalapeno pepper rings, it gives the product a firmer, fresh-like, uniform texture (Gu *et al.*, 1999), with macerated fruit or vegetables it enhances the consistency of the product (McCarthy, 1997). Diced fruit and vegetables when treated with 0.5–1.0% $CaCl_2$ in a fruit or vegetable juice provide maximum firmness and improved quality (Hinnergardt and Eichelberger, 1994), and a $CaCl_2$ brine partially dehydrates the outer surface of canned potatoes, thus reducing "sloughing" (Negi and Nathson, 2002). The use of 0.2% $CaCl_2$ in the brine for canned breadnut seeds improved their flavor (Mathews *et al.*, 2001). Beef may also be processed (including being tenderized) with calcium chloride (Moskovskaya, 1996), and fish may be firmed and preserved in a brine with $CaCl_2$ (Cho, 2001; Liberman, 2002). Calcium chloride as a desiccant when shipped with groundnuts reduced the nuts' moisture content to $< 0.8\%$ (compared to 10.2% in a control sample) and prevented mold formation (Navarro *et al.*, 1988).

Industrial

There are many industrial uses for calcium chloride, such as in *chemical manufacturing* where it is one of the common reactants used to produce various calcium compounds. It has also been suggested as a reactant in the production of nitrosyl chloride (Oesterreichische Stickstoffwerke, 1969), and it is often used as a dehydrating agent to help form other chemicals. For instance, in azeotropic distillation its presence can allow the breaking of otherwise inseparable (dilute) azeotropic compositions, such as to form absolute alcohol (Zeitsch, 1989) and acetonitrile (Bala and Botez, 1980). Similar drying of chlorodifluoromethane allows it to be used as a refrigerant (Kwon *et al.*, 1998), and prepares supercritical carbon dioxide (CO_2) for various uses (Diaz and Miller, 1985). Drying a mixture of dipropylene glycol and monopropylene also allows the two products to be separated by distillation (Popescu *et al.*, 1983). In the preparation of ethyl acetate by an esterification reaction, drying the reaction mixture with $CaCl_2$ greatly increases the yield (Terelak *et al.*, 1977), and drying methyl acrylate's raw materials allows an easier separation from the reaction mix (Firsov *et al.*, 1979).

Many products can be made with the addition of calcium chloride, such as an improved xanthan gum (Cahalan *et al.*, 1977), printing inks for embroidery (Chen and Sun, 1990), calligraphic inks (Zhou, 1997), an acrylate flocculent (Katayama Chemical Works, 1984), deodorants (Ogura, 1995), and dry cell paste (Davassy, 1979). Calcium chloride can also be used to help produce certain chemicals, such as recovering aluminum chloride from uranium by-product solutions (Casensky *et al.*, 1999), stabilize chlorine dioxide (Khalaf, 1996), forming cyanuric chloride (Fujimori *et al.*, 1990), and in the low-temperature drying of ceramics made by the lost wax process (Tikhonov and Klinskii, 1974).

It can be used to coagulate latex in the manufacture of rubber, and as a low temperature refrigeration brine. In paper manufacturing, it provides artificial water hardness that increases the web strength of corrugating media. In the steel industry it is an additive to pelletize ore for blast furnaces, and to reduce the alkali content of steel mill furnace feed mixtures. In waste water treatment it can precipitate fluorides, borates and phosphate (Tatsumi *et al.*, 2001; Tano and Tateiwa, 2001, 2002; Kato, 2002, 2003; Koizumi, 2003; Sumita and Oyama, 2002; Kataoka *et al.*, 2002), and help remove organics (COD) in paper industry wastewater (Palitzsch (2002)). It can break emulsions in oily wastes, and remove silicates and various solids by densifying flocs formed by coagulating agents. It has various other environmental uses, such as in reclaiming oilfield soil (Merrill *et al.*, 1990), the remediation of lead, heavy metals and organically contaminated soil (Cline *et al.*, 1993; Dessi *et al.*, 2000), it can be combined with surfactants to remove tetrachloroethylene from contaminated soil (Ramsburg and Pennell, 2000; Schweninger and Falta, 1999) and its addition to other flooding solvents increase their density and penetrability (Myers *et al.*, 2001). It has been added to an aminoalkyl acrylate flocculent to increase its effectiveness (Katayama Chemical Works, 1984).

Calcium chloride has also been used in various *metallurgical operations*, such as flue gas scrubbing as an additive to enhance the lime–SO_2 reaction (Alscher *et al.*, 1979), in the heavy media separation of coal from inadvertently mined rock, and in the high-temperature processing of coal or other fuels (Borkowski, 1976). In other scrubbing applications, it has been used to recover heat from flue gas (Charyev and Malkovskii, 1989), or for energy conservation in vinyl chloride production (Jarosek *et al.*, 1986). It has been used for the leaching of silver and lead from zinc roaster flue gas after the zinc was leached by dilute sulfuric acid (Zheng, 2000), and for the solubilization (chlorination) of Cu, Zn, Pb, Au and Ag by the high-temperature roasting of their sulfides or oxides. Its incorporation into a slag can cause the desulfurization of some iron alloys (Oktay, 2002), and a 40% $CaCl_2$ solution makes a good surface quenching agent for complex steel parts (Liu, 2002).

Drying

Many of the uses noted both above and below result from the ability of calcium chloride to act as a humectant or drying agent, and there is an extensive literature on this subject. Air, gas and hydrocarbon drying are special cases of this ability that have been especially active. Natural gas drying has been previously discussed, but other general articles on gas (any type of gas) drying have been presented by Borkowski (1970), Hodgson (1970), Norton (1968), Popov (1967), Wilcox (1967), and many others. Thurston (1948) studied gas drying by calcium chloride solutions, and developed mass transfer coefficients for the operation of wetted wall and packed towers. Large industrial or commercial air conditioning units, as in Fig. 1.100, commonly employ calcium chloride for both moisture removal, temperature control and sometimes heat recovery (Fujioka *et al.*, 2000; Gultekin *et al.*, 1991; Waldenmaier, 2000).

Air drying equipment and procedures have been described by Balobaev (1987), Drutskij *et al.* (1995), Koyama (1986), Vasseur (1984, 1982), and others. Ullah *et al.* (1988) made experimental studies on air dehumidifying with calcium chloride solutions in packed beds, and established efficiency coefficients. Gandhidasan and Al-Farayedhi (1994) and Lobo and Da Silva (1982) suggested solar evaporation of the absorbing solution. Many solid calcium chloride mixtures have been suggested for drying air, such as by Ehata *et al.* (1986), Mitsui Engineering and Shipbuilding Co. (1985), Suzuki and Hidaka (1977), and many others.

A very large number of calcium chloride drying agents have been described in the literature. This includes suggestions for many types of containers for $CaCl_2$ granules or flake, such as being encapsulated for controlled release, in containers with perforated caps, or being placed in air-permeable plastic bags to be used as disposable dehumidifiers in closed spaces. Even more prolific have been articles on calcium chloride mixtures and different compositions to enhance their dehydrating effectiveness for special conditions, such as reviewed by Lu (1999). This includes mixtures with other chemicals such as forming a double salt with CaO, mixed solutions with LiCl, a mixed slurry with $Mg(NO_3)_2$, and a mixed powder with $MgSO_4$ or sodium silicate. Even more suggestions have been made for mixtures with various minerals, such as with: asbestos; a combination of calcite, talc, magnesia and cement; with activated carbon, fluorite, gypsum, powdered iron or aluminum; untreated or impregnated into foamed or swelled perlite or vermiculite; paper or pumice; sepiolite; silica or silica gel; vermiculite; and zeolite. The largest category, however, is with individual or mixed polymers, including polymers of: acrylamide; acrylic acid; acrylonitrile; alkyleneglycols; cellulose in a large number of forms (alpha starch, bagasse, carrageenan, CM-cellulose, corncob meal, corn starch, Konjak powder, potato starch, Sumikagel, and wheat flour); ethylene; methylcellulose; saccharide; starch (see cellulose); vinyl acetate; vinyl acetamide; and vinyl alcohol. Because of the large number of these patents or articles they will not be listed in the reference section.

Miscellaneous

Other uses for calcium chloride are listed in Table 2.16, including in *mining*, *deinking recycled newspapers*, and in *water treating* for its addition to remove impurities and aid in solids flocculation. In *agriculture* it is a growth-enhancing macro-nutrient fertilizer. Increasing the Ca^{2+}/NH_4^+ ratio in fertilizers has been shown to result in significant growth increases, especially in crops that are roots and tubers (such as onions, beets, etc.) by increasing the rate of photosynthesis (Fenn and Feagley, 1999). It also can be used to treat high-sodium soils (that are “alkaline or salty”; Alsharari, 1999), and a calcium chloride spray has been found useful to control the rain cracking of sweet cherry trees (Fernandez and Flore, 1998; Lang *et al.*, 1998), as well as to thin fruit blossoms (especially apples; Long, 2002). Too much calcium chloride, however, such as may occur with the

Table 2.16

Examples of Some of the Uses for Calcium Chloride

1. Adhesives and antifreeze in poster cements, a raw material in processing natural glue, a starch modifier (it lowers the gel temperature) or humectant.
2. Agriculture. A fertilizer supplying calcium and chlorine, an ingredient in herbicides, liquid feed supplement for cattle, dehydrating agent, tractor tire weighting.
3. Beverages. Precipitant or ingredient in brewing, and to control the water composition in beer and soft drinks.
4. Canned goods. Firming agent for certain fruits and vegetables, gelling agent for low-calorie jellies and preserves, "cold peeling" tomatoes.
5. Cement, concrete and gypsum manufacture. Chemical lowering of high-alkali content in Portland cement, ingredient in water-reducing and set-controlling admixtures for concrete, early-strength accelerator in concrete and mortar, cold weather additive, aerating aid during the calcining of hydrated calcium sulfate.
6. Chemicals. Intermediate chemical in several reactions and various organic synthesis, catalyst, dehydrating agent, manufacture of molecular sieves, manufacture of other calcium salts such as calcium stearate, removal of water from process air.
7. Ceramics. Porosity reducer, lubricant for ceramic bodies and refractory products.
8. Dairy products. Aid in curd formation for making cottage cheese, additive for evaporated milk to increase its calcium content.
9. Dyes. Precipitating agent.
10. Fluxes. Ingredient in many flux compositions, and in some printed circuit boards[1].
11. Gas, Natural. Dehydrating agent, reduces hydrate formation.
12. Highways. Deicing for ice and snow removal, dust control on unpaved surfaces, shoulder and base stabilizing, soil solidification, plant sterilization agent.
13. Hydrocarbons. Desiccant.
14. Electric lamps. Additive to cement used in making electrical insulators, intermediate chemical in producing phosphor powder for fluorescent lamps, refining tungsten ore.
15. Lead. Flux in production of lead–calcium alloys.
16. Mining and metals. Treatment of pelletized iron ore, removes non-ferrous impurities from iron ores, controls alkalies and "scaffolding" in iron blast furnaces, removes non-ferrous impurities from basic oxygen, open hearth and electric furnace waste dust, refining copper and nickel ores, separating copper from auto scrap, production of magnesium metal, production of sodium metal, purifying molybdenite ores, production of calcium molybdate used in alloying molybdenum to steel, production of disposable cores for aluminum die casting, separating shale from coal fines, freeze-proofing and dust-proofing coal, ore and other aggregates for shipment and storage, component in heat-treating salts, fire retardant in brattice cloth (for mine ventilation).
17. Organic compounds. Fire retardant, dehydration agent, azeotrope breaking.
18. Paint, varnish, and lacquer. Manufacture of calcium naphthenates used in various varnishes and lacquers, manufacture of whitewash paints.
19. Petroleum. Drilling mud additive, weighting agent, cement additive to seal wells, completion fluids, flushing agent. In refining as a dehydrating agent, manufacture of lubricant additives.
20. Pharmaceutical and medicinal. Manufacturing processes, hot pack compresses, cold pack dressings, dehydrating agent.
21. Plastics and synthetic resins. Suspending agent to prevent coalescing during polymerization, control particle size development.
22. Printing. Lithographic chemical, etching fluid for aluminum printing plates.

(*continues*)

Table 2.16
(*continued*)

23. Pulp and paper products. Drainage aid, bleach modifier in pulp treatment, increases web strength of corrugating media, improves dye retention.
24. Refrigeration and air conditioning equipment. Heat exchange brine, dehydrating agent.
25. Rubber manufacture, Reclamation. Latex coagulating agent, aid in disintegrating cord and devulcanization.
26. Seed processing. Drying seeds.
27. Vapor degreasing and hard surface cleaning. Desiccant when reprocessing solvents.
28. Waste treatment. Flocculating agent for the treatment of emulsified wastes containing phosphates, oils and paint sludges, removal of fluorides, silicates.
29. Weed killer. Fire retardant and ingredient in certain weed killers.
30. Miscellaneous. Water antifreeze in fire extinguishers, flux for soldering and brazing, hide pickling, kelp processing.

Sources: Allied (1980); C&EN (2000); Chemical Marketing Reporter; Chemical Week; Dow Chemical (1980).

[1] Iwasayama and Oba (1991).

disposal of oil industry high-density brines, can damage vegetation (Vidakovic *et al.*, 2002). Small amounts of calcium chloride are useful in reducing the incidence of milk fever in transition cows by increasing the adsorption of calcium into the blood stream.

Powdered calcium chloride has some uses in *specialized cements* such as metallic, non-shrink grouting cements, pre-mixed dry cement patching and waterproofing compounds, gypsum plaster (as an "aridizing agent"), and special applications of cement acceleration. It can be used in defoaming and humectant formulations, and as a dispersing agent for *textiles*, powdered formulations for paint pigments, "stay soft" salts (as a free-flowing agent), *heat-treating* salts and molten salts *fluxes* (Iwasayama and Oba, 1991). It has also been suggested as a heat-storage agent (Gultekin *et al.*, 1991). In *medical* applications, dilute $CaCl_2$ solutions have been used as an animal purgative, to treat animal tendons, and to soak ligaments for human transplants (Tanaka *et al.*, 2001). It has also been used as a *binding agent* in many applications, such as its addition to refractory clay to reduce the firing temperature and strengthen the product (Volkova *et al.*, 2001). Calcium chloride is said to facilitate the formation of iron ore pellets and to improve both their green and dry crushing strengths (Ivanov *et al.*, 1985; Kawatra *et al.*, 1998). It has even been recommended to aid in the granulation of various halogen-containing polymers (Ueno *et al.*, 1981).

TOXICOLOGY AND SAFETY

Calcium chloride is not a hazardous material, and it even finds many uses in foods and medicines. However, some precautions still must be taken in its handling. Its toxicity upon ingestion, is indicated by the test on rats: oral LD_{50} (rat) is 1.0–1.4 g/kg (the lethal dose for half of the test animals, in this case rats, per kg of animal weight). When applied subcutaneously, the (sc)LD_{50} (rat) is 2.63 g/kg, and for dogs [sc]LD_{LO} [dog] is 274 mg/kg. When contacted intraperitoneally the (ip)LD_{50} (rats) is 264 mg/kg and for mice 280 mg/kg. When applied intravenously, the (iv)LD_{50} (mouse) is 42 mg/kg. The lowest toxic dose for oral consumption by rats over a 20 week period (oral TD_{LO}) in one test was 1.12 g/kg. The acute toxicity when ingested is thus quite low, but still somewhat more toxic than sodium chloride [oral NaCl LD_{50}(rat) is 3.0 g/kg], and it may irritate the gastrointestinal tract if swallowed in large doses. However, the ip and iv toxicity is quite high, so care must be taken for these low-probability exposure routes (Sax, 1979).

Contact of either solid material or strong solutions of calcium chloride in the eyes is likely to produce severe irritation and/or moderate corneal injury. The effects may include a burning sensation, conjunctival irritation with edema, as well as corneal injury. Single exposures to the skin may result in some reddening, while repeated or prolonged contacts may result in an allergic reaction, appreciable irritation and possibly a mild burn. Contact with abraded skin or cuts can cause severe necrosis. Contact with dilute solutions (under 5–10%) usually has only a slight to no harmful effect. Dust inhalation may irritate the nose, throat and lungs, but there are no threshold values (TLVs) or ACGIH dust standards for this material. However, one manufacturer recommends that the dust concentration be kept below 10 mg/ft^3 (Dow, 2002). Calcium chloride's aquatic toxicity for fish, LD_{50} (96 hr) is 100 mg/liter (of anhydrous calcium chloride; Allied, 1980).

Safety goggles or face shields should be used when calcium chloride dust or solution might contact the eyes, and long-sleeved shirts and gloves should be used when handling calcium chloride. Dust masks should also be employed when working with solid calcium chloride in a dusty atmosphere. Contact with leather (such as shoes) should be avoided, since calcium chloride causes dehydration, and will ruin the leather. When dissolving solid calcium chloride add the solids to the water slowly, as there will be a considerable temperature rise, and boiling or splashing may occur. Never add water to the solids because of this effect, and when diluting liquid calcium chloride add it to the water (if possible), and slowly for the same reason.

PRODUCTION STATISTICS

The U.S. Bureau of Mines stopped compiling statistics on U.S. calcium chloride production and consumption in 1991, and the average price and net (price) realization by the producers in 1984. Since they were the principal source for this information, the marketing data for calcium chloride after those years have become much less accurate and quite scattered. Different sources have made quite different estimates for each of the statistical numbers, so average values have often

Table 2.17

United States Production of Calcium Chloride (1000 st of equivalent 77–78% $CaCl_2$)

Total Production

1999[a]	1998	1997	1996	1995	1994	1993	1992	1991	1990	1989	1988	1987
~900	875	—	~800	827	823	746	653	621	682	678	703	657
1986	1985	1984	1983	1982	1981	1980	1979	1978	1977	1976	1975	1974
770	944	—	943	853	917	811	841	1031	868	897	828	—
1973	1972	1971	1970	1969	1968	1967	1966	1965	1964	1963	1962	1961
759	940	995	907	960	970	870	890	995	890	806	741	690
1960	1959	1958	1957	1956	1955	1954	1953	1952	1951	1950	1949	1948
670	740	645	645	650	610	524	490	428	514	420	—	—

Natural Calcium Chloride Only

1984	1983	1982	1981	1980	1979	1978	1959–1963	1945–1950
~838	664	~617	705	581	720	773	437 avg. ($19/t)	~300– ~350

California only (75% basis)

1945	1946	1947	1948	1949	1950	1951	1952	1953
6.8	9.9	7.5	10.0	11.1	13.3	17.0	18.0	17.0

C&EN (2000), Chemical Market Reporter, Chemical Week, Majmundar (1985), Manville Chemical Products Corp. (1993), Smith (1966), U.S. Bureau of Mines (1992–1982), Parker (1978), Ver Planck (1957), other sources.

[a] CMR 3/4/02 indicates 1999 at 1108; 2000 at 1143.

Table 2.18

Some Values for the United States Consumption of Calcium Chloride, 1000 st/yr of equivalent 77–78% $CaCl_2$

1999	1998	1996	1995	1993	1992	1991	1990	1989	1988	1987	1986	1985
~900	875	~800	800	805	827	739	817	818	919	807	828	915
1238[a]	1186[a]	1160[a]	1140[a]	1095[a]								
1983	1982	1981	1980	1975	1970	1965						
1064	916	971	799	790	925	1005						

Chemical Market Reporter, Mannville Chemical Products Corp., U.S. Bureau of Mines (1992–1982), Majmundar (1985).

[a] CMR 3/4/02 values from 1995 to 2000; 2000 1316 Mst; Imports: 2000 252,000, 1999 211,000; Exports: 2000 79,000, 1999 81,000.

been listed in the following tables. The total production rate of calcium chloride in the U.S. since 1950 is estimated in Table 2.17. There are fewer statistics for the natural product, but scattered data from 1945 to 1984 are also listed in this table. Some of the early production rates in California (Bristol Lake) are likewise listed from 1945 to 1953. During 1945–1985 the natural production was about 75% of the total, but in recent years because of the increasing conversion of waste hydrochloric acid with limestone to form calcium chloride, the natural product has dropped to about 50%. In the early period the California production was about 3% of the total.

The United States consumption of calcium chloride is estimated in Table 2.18, indicating that there has been very little increase in the consumption rate over the period from 1965 to 1999. Table 2.19 lists an estimated average sales price for both solid and liquid calcium chloride since 1982, based upon

Table 2.19

United States Average Sales Price of Calcium Chloride, \$/st

77–78% $CaCl_2$ (Flake)[a]											
2001	1999	1996	1994	1993	1991	1990	1990	1989	1987	1984	1982
179[b]	134[b]	159[b]	164[b]	143[b]	137	137	(215[c])	139	125[b]	125[b]	120.57
1981	1980	1979	1978	1974	1973	1972	1971	1970	1969	1968	
120.57	111.90	86.06	79.42	32.8	32.8	44.0	44.0	40.8	37.4	45.0	
1967	1966	1965	1964	1963	1962	1960	1959	1957	1955	1954	1950
35.0	35.0	34.0	32.5	32.5	32.0	32.3	31.0	31.1	26.9	26.9	23.1

(*continues*)

Table 2.19
(*continued*)

40% $CaCl_2$ (Liquid)										
2001	1994	1987	1984	1982	1981	1980	1979	1978	1972	1970
52.8[c]	53.6[c]	38.4[c]	36.3[c]	34.64	34.64	33.22	25.89	31.91	16.5	16.2
1965	1964	1963	1960	1955	1950					
14.0	14.0	12.6	12.6	11.8	9.68					
Natural Product, Average Realization, \$/st, 75% $CaCl_2$ basis										
1984	1983	1982	1981	1980	1979	1978				
110.98	107.43	99.72	87.54	82.53	72.09	69.74				
California Only										
1945	1946	1947	1948	1949	1950	1951	1952	1953		
14.6	17.3	14.9	16.3	18.0	19.9	22.1	21.8	22.6		
Average Realization from all Sales, \$/st, 75% $CaCl_2$ basis										
1992	1991	1990	1989	1988	1987	1986	1985	1984	1983	1982
~86.6	122.9	136.5	129.0	119.4	133.1	145.9	143.9	120.2	118.0	108.7
1981	1980	1979	1978	1964						
96.81	91.35	75.91	72.79	29.05						

[a] CMR 3-4-02 stated that the list price was \$270/st in 2002, and steady at \$250/st from 1995 to 2001. Source: U.S. Burea of Mines, Chemical Market Reporter, other sources.

[b] List price for 100 lb bags times the 1990 ratio of average net realization to the list price (\$137/215).

[c] List price.

an early ratio of the list-to-actual prices. Usually the quoted market prices are much higher than the actual average realized prices, making these numbers very uncertain. The production capacity for calcium chloride by the various United States operators is estimated in Table 2.20, and typical product specifications for the natural calcium chloride products are listed in Tables 2.21(A) and (B).

PHASE DATA AND PHYSICAL PROPERTIES

Phase Data

The solubility of calcium chloride in water is listed in Table 2.22 and plotted in Fig. 2.63. Figure 2.64 shows these same data plotted on a larger scale, and Fig. 2.65 indicates the fields of the various crystalline phases in more detail. There are at least four hydrates of calcium chloride, with 1,2,4 and $6H_2O$ (and perhaps

Table 2.20

United States Production Capacity of Natural Calcium Chloride (1000 st of equivalent 77% $CaCl_2$; Chemical Marketing Reporter)

Company	2002	1999	1993	1990	1987	1984	1981
General Chemical, Manistee, MI[a]	360	300	—	—	—	—	—
Dow Chemical, Ludington, MI.	735	700	700[b]	700	700	991	800
Hill Brothers, Cadiz Lake, CA	—	3(?)	5	—	—	4	—
Lee Chemical, Cadiz Lake, CA	15	15	15[c]	15	15	30	—
Magnesium Corporation of America, Rowley, Utah	45	35	35[d]	35	10	10	—
National Chloride, Amboy, CA	20	15	11	11	11	14	14
Wilkinson, Mayville, MI	55	55	55	24	24	5	8
Tetra Technologies, Amboy, CA	25	25[e]	18	18	18	36	30
Total	1255	1148	834	803	778	1090	852

[a] Started by Ambar September, 1997; closed April 30, 2000; sold to General in late 2000; closed in 2003.

[b] Also listed at 625.

[c] Also listed at 25.

[d] Amax sold the operation in 1993 to Renco, who changed the name to Magnesium Corporation of America.

[e] Purchased from Cargil (Leslie Salt) in August, 1998; includes Cadiz, CA.

a fifth with $0.33H_2O$; Reid and Kust, 1992), with considerable debate as to whether the tetrahydrate has three forms, α, β and γ. The early researchers tabulated these three forms [including Seidell (1958); see Fig. 2.64], but later studies have indicated that they are merely quite reproducible metastable phases. The minimum temperature that can be reached by freezing a pure calcium chloride solution is -49.8°C at 30.22% $CaCl_2$ (Seidell, 1958; Yanateva, 1946; -49.8°C and 30.52% $CaCl_2$; Oakes *et al.*, 1990; -49.95°C and 30.33% $CaCl_2$), although this value is very difficult to determine. Earlier researchers had indicated numbers down to -55°C and 29.8% $CaCl_2$. The more recent data from Oakes *et al.* (1990) for the solubility of $CaCl_2$ when saturated with ice (and also for the $CaCl_2$–NaCl–H_2O system) has been obtained by a rapid, less precise procedure. It attempts to remove clear brine from ice-filled samples as the temperature is slowly falling, and estimates the liquid compositions at each withdrawal temperature by comparing their densities against standards. The method would appear to only obtain approximate data, but surprisingly, the numbers agree quite well with other investigators (Table 2.22; for the $CaCl_2$–NaCl–H_2O system Figs. 2.66 and 2.67). Their data further indicate that the ice freezing point of NaCl and $CaCl_2$ solutions and their mixtures, as a first approximation is only dependent upon the total wt.% of salts in the solution (Fig. 2.67).

Table 2.21(A)

Typical Calcium Chloride Product Specifications[a] (wt.%) (Maximum Limits Unless Otherwise Specified)

	Liquid[b]	Flakes[c]	Pellets[d]	Pellets[e] (almonds)	Inhibited liquid[f]
Chemical analysis					
$CaCl_2$	28–42	77–80	90 (min)	91 (min)	30 (min)
				Briquette:	*ppm*
Alkali metals as NaCl	1.68–2.52	4.3	4.9	Density (g/cc): 1.86–1.88	P 25
				Porosity: 15–20%	Ba 10
Magnesium as $MgCl_2$	0.15–0.23	0.07	0.08	Size: 0.7 in. thick, 1.1 in. long	Zn 10
Other salts	—	0.85	0.98	Bed voids: 45–50%	As 5
$Ca(OH)_2$	—	0.10	0.20	Angle of repose: 28°	Se 5
$CaCO_3$	—	0.07	0.20		Pb 1
SO_4	—	0.04	0.20		Cr 0.5
Fe, ppm	—	50	50		Cd 0.2
Heavy metals as Pb, ppm	—	20	20		Cu 0.2
					Hg 0.05
					LC_{50} 23,452[g]
Bulk density (lbs/ft^3)	—	51–60	58–66	60–68	83.5
Appearance	Colorless to pale yellow	White flakes	White pellets	White	Brown, slight odor
Screen analysis	—				
> 3/8 in.	—	0	0	> 1/2 in. 85%	
> 4 mesh	—	0–20	0–20	> 1/4 in. 94–100%	
> 20 mesh	—	—	90–100		
> 30 mesh	—	95–100	99–100		

[a] All Dow Chemical products (Dow, 2001). The trademark names are:
[b] Liquidow,
[c] Dowflake,
[d] Peladow,
[e] Peladow DG, and
[f] Liquidow Armor (a corrosion-inhibited liquid).
[g] Lowest concentration that is lethal to 50% of Rainbow trout, mg/liter $CaCl_2$.

Table 2.21(B)

General Specifications for Calcium Chloride Products

28–42% $CaCl_2$ Liquid[a]: As 38% $CaCl_2$; $<0.1\%$ NaCl (alkali chlorides), $<0.1\%$ $MgCl_2$, $<1\%$ others, excluding water; pH 7–8; density at 68°F (20°C) 11.48 lbs/gal ($\rho = 1.3785$ g/cc); crystallization temperature 41°F (5°C). Recommended to melt ice to −17°F (−27.2°C).

32–41% $CaCl_2$ Liquid, food grade[a]: Analysis based upon 100% $CaCl_2$: Magnesium and alkali salts $<5\%$ (as NaCl and $MgCl_2$), $<0.3\%$ alkalinity (as $Ca[OH]_2$), fluoride $<0.004\%$, heavy metals <0.002 (as Pb), lead, <5 mg/kg; alkaline.

77% $CaCl_2$ Flake[b]: $<0.2\%$ NaCl, 0.50% $MgCl_2$, $<1.00\%$ others; bulk density 48–51 lbs/cuft; particle size: 0% +5 mesh (3.99 mm), $>24\%$ +10 mesh (2.00 mm), $>25\%$ +16 mesh (1.19 mm), $<15\%$ −30 mesh (0.59 mm)

77–80% $CaCl_2$ flake[c]: $<4.3\%$ NaCl, $<0.07\%$ $MgCl_2$, $<0.85\%$ other, $<0.1\%$ $Ca(OH)_2$, $<0.04\%$ $CaCO_3$, $<0.04\%$ SO_4, $<0.005\%$ Fe, $<0.002\%$ heavy metals (Pb); 51–60 lbs/cuft; 0% +3/8 in., 0–20% +4 mesh, 95–100% >30 mesh

94–97% $CaCl_2$ pellets[a]: $\geq 94\%$ $CaCl_2$, $<2\%$ alkali chlorides (as NaCl), $<0.1\%$ magnesium (as $MgCl_2$), $<1\%$ others (not including water), <20 ppm Fe, <500 ppm Na, <250 ppm SO_4, <2000 ppm alkalinity (as $CaCO_3$); pH 7–10; density ~55 lbs/cuft; screen size: 100% −4 mesh (4.76 mm), 80–100% −8 mesh (2.38 mm), 0–5% −40 mesh (0.42 mm).

94–97% $CaCl_2$ food grade[a]: $>93\%$ $CaCl_2$, $<1\%$ alkali chlorides (as NaCl), $<0.1\%$ magnesium (as $MgCl_2$), $<0.1\%$ others (not including water), <20 ppm Fe, <500 ppm Na, <250 ppm SO_4, <2000 ppm alkalinity (as $CaCO_3$); pH 7–10; density ~55 lbs/cuft; screen size: 100% −4 mesh (4.76 mm), 80–100% −8 mesh (2.38 mm), 0–6% −40 mesh (0.42 mm).

[a] Tetra Chemicals (2002).
[b] Dow Chemical Co. (2001).
[c] Hill Brothers Chemical Co. (2002).

The lowest $CaCl_2$–H_2O temperatures obtained with a commercial product and with a short residence time to reach equilibrium (allowing the potential for considerable supersaturation) are stated to vary from −55°C at 29.6% $CaCl_2$ to −61°C at 29.5% $CaCl_2$. However, the presence of small amounts of $MgCl_2$ and NaCl (less than 2%, as is present in commercial calcium chloride) can actually decrease the freezing point to a minimum of −57°C (Luzhnaya and Vereshchetina, 1946). More extensive data on the $CaCl_2$–H_2O system has been published by Potter and Clynne (1978; to 97°C, also with an approximate method), Brass and Thurmond (1983; low temperatures), Williams-Jones and Seward (1989; 100–360°C), Oakes *et al.* (1994; supercritical, two-Phase; 0.3–3.0 mol/kg), Doherty (1990; supercritical), and Sterner and Felmy (1995; a computer program for Pitzer equation parameters). The solubility of calcium chloride in steam is given by Martynova *et al.* (1966).

Table 2.22

The Solubility of Calcium Chloride in Water (A. Data of Seidell, 1958)

	wt.% $CaCl_2$ solution saturated with the solid phase:						
t (degrees)	Ice	$CaCl_2 \cdot 6H_2O$	$CaCl_2 \cdot 4H_2O\alpha$	$CaCl_2 \cdot 4H_2O\beta$	$CaCl_2 \cdot 4H_2O\gamma$	$CaCl_2 \cdot 2H_2O$	$CaCl_2 \cdot H_2O$
−49.8	30.22(8)	30.22(8)	—	—	—	—	—
−40	28.3	32.1	—	—	—	—	—
−30	25.7	33.4	—	—	—	—	—
−20	21.3	34.7	—	—	—	—	—
−10	14.4	36.0	—	—	—	—	—
0	0.0	37.3	—	—	—	—	—
+10	—	39.3	—	—	—	—	—
15	—	41.2	46.0[a,b]	49.0[c]	—	—	—
20	—	42.7	47.5[a]	50.0[a]	51.1[a]	—	—
25	—	45.3	48.7[a]	51.2[a]	52.1[a]	—	—
27.5	—	47.2	49.3[a]	51.8[a]	52.7[a]	—	—
29.0	—	48.5	49.7[a]	52.1[a]	53.0(1)	—	—
29.5	—	49.1	49.8[a]	52.3(2)	53.2	—	—
30.1	—	50.0(3)	50.0(3)	52.5	53.5	—	—
32.5	—	—	50.7	53.1	54.0	—	—
35.0	—	—	51.5	53.9	54.8	—	—
37.5	—	—	52.4	54.7	55.7	—	—
38.5	—	—	52.7	55.1	56.0(4)	56.0(4)	—
40.0	—	—	53.4	55.9	—	56.2	—
41.0	—	—	53.8	56.3(5)[d]	—	56.3(5)	—
45.1	—	—	56.6(6)[e]	—	—	56.6(6)	—
60	—	—	—	—	—	57.8	—
70	—	—	—	—	—	58.6	—
80	—	—	—	—	—	59.5	—
90	—	—	—	—	—	60.6	—
100	—	—	—	—	—	61.4	—
120	—	—	—	—	—	63.4	—
140	—	—	—	—	—	65.6	—
160	—	—	—	—	—	69.0	—
170	—	—	—	—	—	71.8	—
175.5	—	—	—	—	—	74.8(7)	74.8(7)
180	—	—	—	—	—	—	75.0
200	—	—	—	—	—	—	75.7
235	—	—	—	—	—	—	76.8
200	—	—	—	—	—	—	77.6

(B) Data of Potter and Clynne (1978)

$CaCl_2 \cdot 6H_2O$		$CaCl_2 \cdot 4H_2O$		$CaCl_2 \cdot 2H_2O$	
Temperature (°C)	$CaCl_2$	Temperature (°C)	$CaCl_2$	Temperature (°C)	$CaCl_2$
9.13	38.96	30.08	—	45.13	—
12.75	39.87	33.54	50.37	49.37	56.03
22.28	43.12	35.15	50.94	61.81	56.85
28.16	47.15	38.64	52.23	68.63	57.28
30.08	—	42.62	54.20	85.85	58.69
		44.81	55.47	97.65	59.75
		45.13	—		

Solid Phases: (1) $CaCl_2 \cdot 6H_2O + CaCl_2 \cdot 4H_2O\gamma$; (2) $CaCl_2 \cdot 6H_2O + CaCl_2 \cdot 4H_2O\beta$; (3) $CaCl_2 \cdot 6H_2O + CaCl_2 \cdot 4H_2O\alpha$; (4) $CaCl_2 \cdot 4H_2O\gamma + CaCl_2 \cdot 2H_2O$; (5) $CaCl_2 \cdot 4H_2O\beta + CaCl_2 \cdot 2H_2O$; (6) $CaCl_2 \cdot 4H_2O\alpha + CaCl_2 \cdot 2H_2O$; (7) $CaCl_2 \cdot 2H_2O + CaCl_2 \cdot H_2O$; (8) Ice + $CaCl_2 \cdot 6H_2O$.

[a] Metastable.

[b] At 14°.

[c] At 15.9°.

[d] Others reported 55.8%.

[e] Others reported 55.9%.

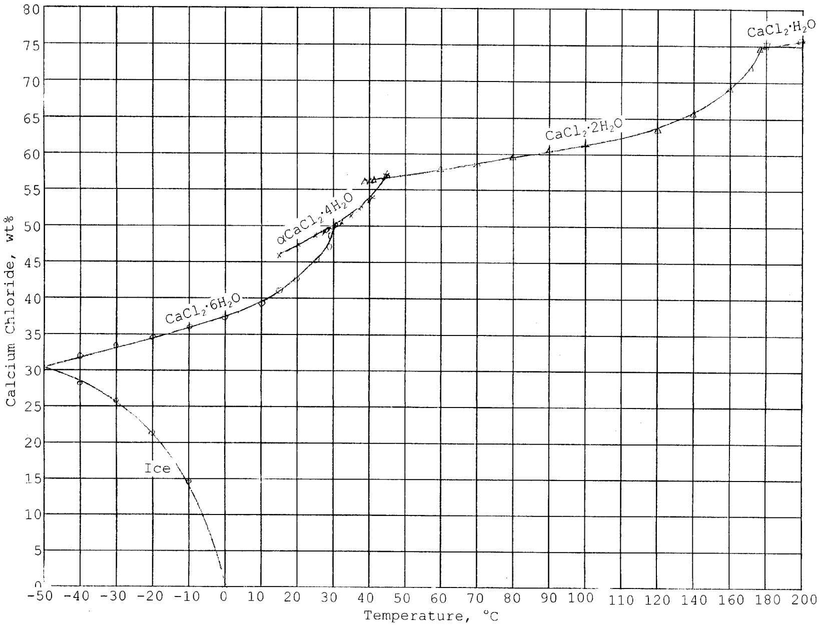


Figure 2.63 The solubility of calcium chloride in water (Seidell, 1958).

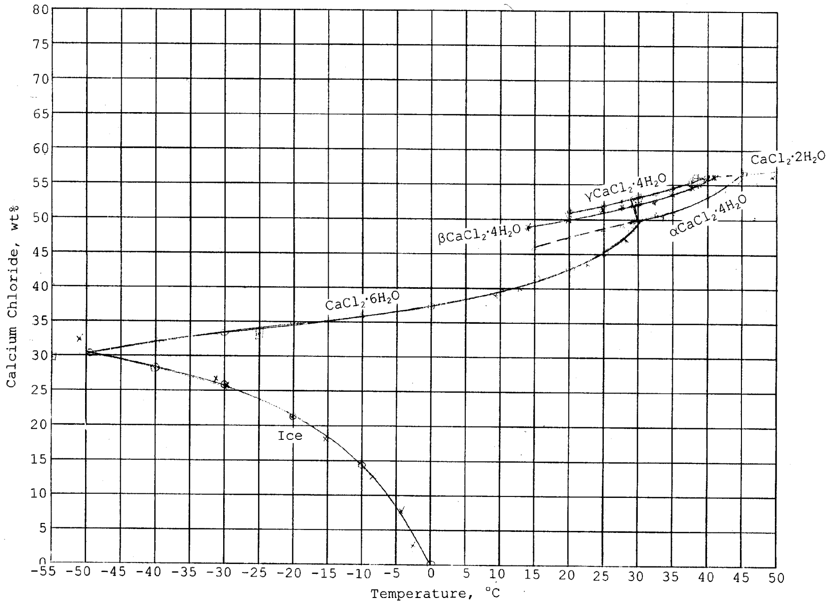


Figure 2.64 Calcium chloride solubility on a larger scale (Seidell, 1958).

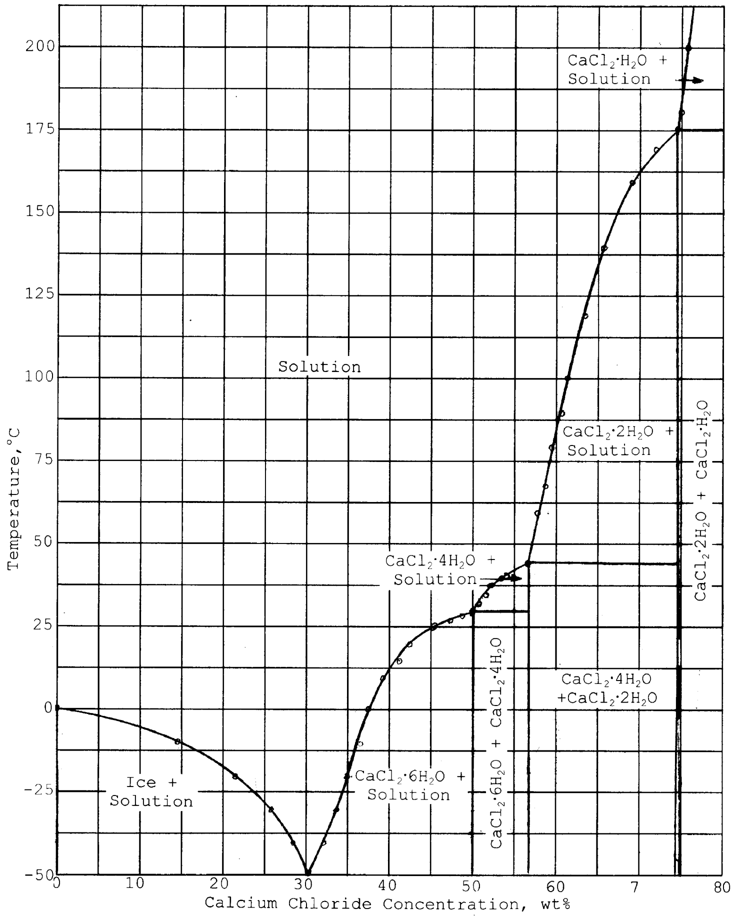


Figure 2.65 Calcium chloride phase diagram showing the phases present (Seidell, 1958).

Tables 2.23–2.25 list solubility data for calcium chloride with sodium chloride, and Figs. 2.66–2.68 plot some of these data. This system has been extensively used to guess at the composition of occlusions in various minerals (because of their observed low freezing temperature and subsequent melting point [ignoring supersaturation and frequently up to a 50°C difference between these two values]), and for the deicing use of calcium chloride. Besides the extensive data of Seidell (1958); including that of Yanateva (1946), there have been publications on this system by Mun and Darar (1956) and more recently by Gibbard and Fong (1975; to −4°C), Oakes (1992) and Oakes *et al.* (1990). Other articles on this system have

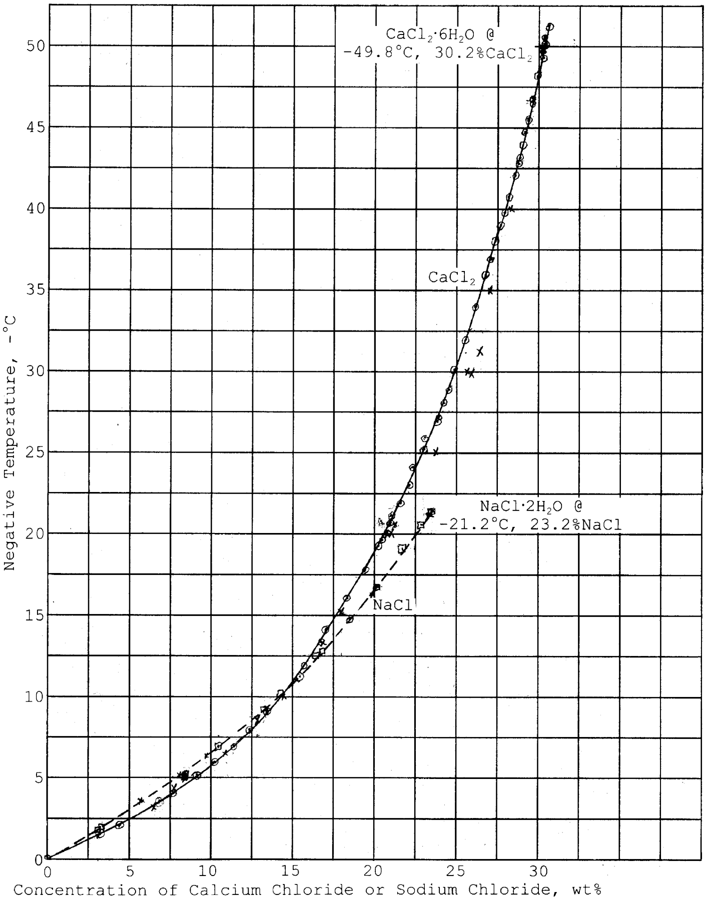
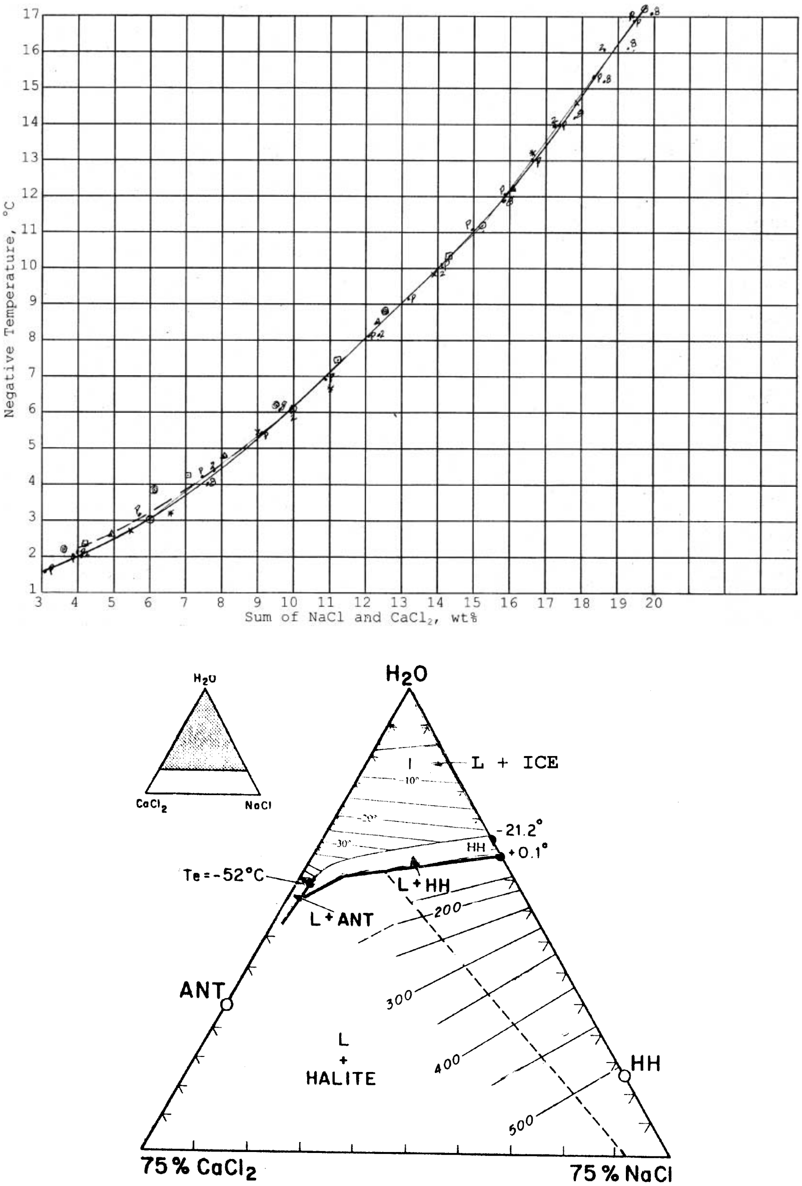


Figure 2.66 The freezing point of ice in $CaCl_2$ or NaCl solutions (Data of: × = Seidell, 1958; Mun and Darar, 1956; ○, □ = Oakes *et al.*, 1990).

been presented by Igelsrud and Thompson (1936; 0°C), Vanko *et al.* (1988; a few points on the ice–$NaCl{\cdot}2H_2O$–solution border), Ivanov (1964; 40°C), Yuan *et al.* (2000a; 25°C; estimated data by the Pitzer equation), Williams-Jones and Samson (1990; theoretical), Naden (1996; a Microsoft Excel 5.0 computer program for $CaCl_2$ solutions), Makarov and Shcharkova (1969) and Kirgintsev and Lukyanov (1965).

There is considerable data available on the calcium chloride–magnesium chloride system, as listed in Table 2.26. Since the solubility of sodium chloride in concentrated calcium or magnesium chloride solutions is quite low, these data



1. L=liquid, Ant=antarcticite, HH=hydrohalite

2. Temperatures in degrees C

Figure 2.67 (a) The freezing point of ice in mixed $CaCl_2$ and NaCl solutions (ratio of NaCl/(NaCl + $CaCl_2$); Data of: Mun and Darar (1956) O = 0.125, × = 0.274, Δ = 460, □ = 0.687; Oakes *et al.*, 1990 P = 0.393, 8 = 0.80, 2 = 0.20). (b) Triangular solubility diagram for the $CaCl_2$–NaCl–H_2O system, with the higher temperature points under 2–4.5 kb pressure (After Oakes *et al.*, 1990; Vanko *et al.*, 1988).

Table 2.23

The System Calcium Chloride–Sodium Chloride–Water (wt.%) (Seidell, 1958)

$CaCl_2$	NaCl	Solid phase	$CaCl_2$	NaCl	Solid phase
Results at −5°			Results at −30°		
8.40	0.0	Ice	24.20	1.00	Ice
7.60	1.20	Ice	23.80	1.80	Ice
4.40	4.60	Ice	22.00	3.80	Ice
0.0	7.40	Ice	19.60	7.00	Ice + $NaCl\cdot 2H_2O$
0.0	25.60	$NaCl\cdot 2H_2O$	24.70	1.20	$NaCl\cdot 2H_2O$
4.80	21.20	$NaCl\cdot 2H_2O$ + NaCl	29.40	2.20	$NaCl\cdot 2H_2O$
13.80	14.80	NaCl	32.00	1.40	$NaCl\cdot 2H_2O$ + $CaCl\cdot 6H_2O$
26.40	4.60	NaCl			
30.80	2.42	NaCl			
33.80	1.40	NaCl			
Results at −10°			Results at −35°		
13.00	2.20	Ice	25.80	1.00	Ice
7.80	8.20	Ice	25.60	1.80	Ice
0.0	13.50	Ice	23.80	4.00	Ice
0.0	25.00	$NaCl\cdot 2H_2O$	23.50	4.50	Ice + $NaCl\cdot 2H_2O$
13.40	14.20	$NaCl\cdot 2H_2O$	24.20	4.20	$NaCl\cdot 2H_2O$
24.00	5.80	$NaCl\cdot 2H_2O$ + NaCl	28.80	2.20	$NaCl\cdot 2H_2O$
26.10	4.30	NaCl	31.60	1.45	$NaCl\cdot 2H_2O$ + $CaCl_2\cdot 6H_2O$
30.70	2.40	NaCl			
33.80	1.20	NaCl + $CaCl_2\cdot 6H_2O$			
Results at −15°			Results at −40°		
16.20	2.60	Ice	27.20	1.00	Ice
10.00	10.50	Ice	26.80	2.00	Ice
0.0	19.00	Ice	26.20	3.10	Ice + $NaCl\cdot 2H_2O$
0.0	24.40	$NaCl\cdot 2H_2O$	28.60	2.10	$NaCl\cdot 2H_2O$
13.00	13.80	$NaCl\cdot 2H_2O$	31.00	1.50	$NaCl\cdot 2H_2O$ + $CaCl_2\cdot 6H_2O$
25.80	4.80	$NaCl\cdot 2H_2O$ + NaCl			
30.65	2.36	NaCl			
33.60	1.40	NaCl			
33.70	1.30	NaCl + $CaCl_2\cdot 6H_2O$			
Results at −20°			Results at −45°		
18.40	3.20	Ice	28.60	1.20	Ice
11.40	12.00	Ice	27.80	2.20	Ice
0.0	22.40	Ice	27.40	2.50	Ice + $NaCl\cdot 2H_2O$
0.0	23.60	$NaCl\cdot 2H_2O$	28.30	2.20	$NaCl\cdot 2H_2O$
12.90	13.60	$NaCl\cdot 2H_2O$	30.30	1.60	$NaCl\cdot 2H_2O$ + $CaCl_2\cdot 6H_2O$
25.40	4.40	$NaCl\cdot 2H_2O$			

(*continues*)

Table 2.23
(*continued*)

Results at −20° (*cont.*)			Results at −45° (*cont.*)		
29.00	3.00	$NaCl \cdot 2H_2O$ + NaCl	30.40	1.20	$CaCl_2 \cdot 6H_2O$
30.60	2.30	NaCl			
33.30	1.30	NaCl			
33.40	1.35	NaCl + $CaCl_2 \cdot 6H_2O$			

Results at −25°		
20.40	3.60	Ice
12.30	12.80	Ice
11.20	13.80	Ice + $NaCl \cdot 2H_2O$
12.80	13.40	$NaCl \cdot 2H_2O$
24.80	4.20	$NaCl \cdot 2H_2O$
29.80	2.20	$NaCl \cdot 2H_2O$
32.60	1.30	$NaCl \cdot 2H_2O$
32.80	1.40	$NaCl \cdot 2H_2O$ + $CaCl_2 \cdot 6H_2O$

Results at 0° (Separate data from two investigators)

$CaCl_2$	NaCl	Solid phase	$CaCl_2$	NaCl	Solid phase
37.55	0.0	$CaCl_2 \cdot 6H_2O$	0.0	26.23	NaCl
37.50	0.31	$CaCl_2 \cdot 6H_2O$ + NaCl	13.80	14.60	NaCl
35.31	0.93	NaCl	26.60	4.60	NaCl
27.14	3.59	NaCl	31.40	2.60	NaCl
20.60	7.78	NaCl	34.40	1.40	NaCl
16.12	11.36	NaCl	37.60	1.10	NaCl + $CaCl_2 \cdot 6H_2O$
9.53	17.28	NaCl			
5.33	21.19	NaCl			
0.0	26.42	$NaCl \cdot 2H_2O$			

Results at 25° (Separate data from two investigators)

d_{25}^{25}	$CaCl_2$	NaCl	Solid phase	$CaCl_2$	NaCl	Solid phase
—	84	0	$CaCl_2 \cdot 6H_2O$	45.60	0.0	$CaCl_2 \cdot 6H_2O$
1.4441	78.49	1.846	$CaCl_2 \cdot 6H_2O$ + NaCl	0.0	26.80	NaCl
1.3651	48.58	1.637	NaCl	27.30	4.70	NaCl
1.3463	53.47	1.799	NaCl	32.40	2.80	NaCl
1.2831	36.80	7.77	NaCl	35.60	1.40	NaCl
1.2653	30.08	10.70	NaCl	43.50	1.00	NaCl + $CaCl_2 \cdot 6H_2O$
1.2367	19.53	18.85	NaCl			
1.2080	3.92	32.48	NaCl			
1.2030	0	35.80	NaCl			

(*continues*)

Table 2.23
(*continued*)

Results at 50°			Results at 94.5°		
g per 100 g sat. sol.			g per 100 g sat. sol.		
$CaCl_2$	NaCl	Solid phase	$CaCl_2$	NaCl	Solid phase
57.0	0.0	$CaCl_2 \cdot 2H_2O$	58.1	0.8	$CaCl_2 \cdot 2H_2O$ + NaCl
56.3	0.9	$CaCl_2 \cdot 2H_2O$ + NaCl	57.4	1.1	NaCl
30.9	3.6	NaCl	45.7	1.3	NaCl
15.1	13.2	NaCl	32.8	4.3	NaCl
3.3	24.4	NaCl	15.3	15.0	NaCl
0.0	26.8	NaCl	11.5	18.1	NaCl

Table 2.24

The System Calcium Chloride–Sodium Chloride–Water at Negative Temperatures with Ice Always Present (wt.%)

Temperature (°C)	$CaCl_2$	NaCl	Temperature (°C)	$CaCl_2$	NaCl
-1^a	0	1.73	− 10	0^a	13.96
	0.36	1.46		0^c	13.90
	0.77	1.15		0^b	13.50
	1.21	0.81		2.80^a	11.18
	1.70	0.42		4.36^c	9.59
	2.22	0		5.60^a	8.40
				7.50^c	6.37
− 5	0^a	7.82		7.80^b	8.20
	0^c	7.73		8.42^a	5.62
	0^b	7.40		10.18^c	3.84
	1.61^a	6.44		11.28^a	2.82
	2.45^c	5.60		12.26^c	1.75
	3.30^a	4.94		13.00^c	2.20
	4.40^b	4.60		14.01^c	0
	4.47^c	3.80		14.06^a	0
	5.07^a	3.38		14.40^b	0
	6.15^c	2.32			
	6.94^a	1.74	− 15	0^a	18.71
	7.50^c	1.07		0^b	19.00
	7.60^b	1.20		3.69^a	14.75
	8.88^a	0		7.30^a	10.96
	8.73^c	0		10.00^b	10.50
	8.40^b	0		10.97^a	7.10

(*continues*)

Table 2.24

(*continued*)

Temperature (°C)	$CaCl_2$	NaCl	Temperature (°C)	$CaCl_2$	NaCl
− 15	14.43[a]	3.49	− 25	9.73[a]	14.60
	16.20[b]	2.60		14.46[a]	9.36
	17.84[a]	0		19.34[a]	3.93
	18.50[b]	0		20.40[c]	3.60
				22.90[a]	0
− 20	0[a]	22.36		23.80[b]	0
	0[b]	22.40			
	4.39[a]	17.58	− 30	15.50[a]	10.33
	8.64[a]	12.96		20.32[a]	5.08
	11.40[b]	12.00		21.03[a]	4.28
	12.74[a]	8.50		22.00[b]	3.80
	16.72[a]	4.18		23.80[b]	1.80
	17.34[a]	3.53		24.20[b]	1.00
	18.40[b]	3.20		24.84[a]	0
	20.58[a]	0		25.70[b]	0
	21.30[b]	0			

[a] Oakes *et al.* (1990).
[b] Seidell (1958).
[c] Mun and Darar (1956).

Table 2.25

Calcium Chloride and Sodium Chloride Solutions in Equilibrium with Ice (Oakes *et al.*, 1990)

1.000		0.593		0.195		0.000	
θ	wt.%	θ	wt.%	θ	wt.%	θ	wt.%
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.84	3.08	1.70	3.13	1.55	3.18	1.42	3.13
2.03	3.40	2.06	3.77	2.03	4.09	2.08	4.42
5.42	8.45	3.01	5.32	3.37	6.34	3.68	7.09
6.98	10.48	4.05	6.92	4.40	7.87	4.06	7.64
9.22	13.11	5.19	8.50	5.05	8.75	5.21	9.16
10.27	14.25	5.21	8.54	6.00	9.95	6.02	10.15
12.49	16.46	6.02	9.58	7.02	11.13	6.03	10.20
12.86	16.78	7.08	10.88	8.09	12.27	7.06	11.35
14.91	18.57	8.10	12.05	9.02	13.18	8.08	12.39
16.91	20.18	9.10	13.10	10.04	14.12	8.42	12:64[a]
19.17	21.80	10.03	14.03	11.13	15.06	9.08	13.34
20.64	22.80	11.02	14.96	11.97	15.75	10.98	14.83[a]
21.48	23.34	12.19	16.00	13.96	17.22	11.62	15.46
		13.24	16.89	16.09	18.65	12.03	15.72
		14.08	17.55	18.07	19.82	13.50	16.77
		15.14	18.36	20.36	21.08	14.21	17.31
		17.04	19.69	22.01	21.94	15.30	18.04[a]
		19.06	21.02			16.02	18.42

(*continues*)

Table 2.25
(*continued*)

0.796		0.393		0.169		0.000	
θ	wt.%	θ	wt.%	θ	wt.%	θ	wt.%
		21.02	22.19			17.80	19.46
		23.23	23.41			19.32	20.19
		23.28	23.43			19.64	20.40
						20.78	20.97
						21.12	21.16
						21.97	21.56
0.00	0.00	0.00	0.00	19.99	20.86	23.08	22.04
1.71	3.03	1.59	3.12	22.11	21.94	24.02	22.41
2.01	3.54	2.04	3.88	24.05	22.85	25.23	23.01
3.05	5.20	2.10	4.02	25.98	23.70	25.25	22.95
4.01	6.68	3.18	5.84	28.02	24.54	26.08	23.37
4.55	7.43	4.22	7.40	30.08	25.34	27.06	23.73
4.94	7.97	5.46	9.08	30.21	25.39	27.08	23.73
4.98	8.09	6.94	10.88	32.11	26.09	27.21	23.78
6.12	9.57	8.06	12.10	34.03	26.75	27.22	23.82
6.13	9.56	9.16	13.24			28.08	24.16
7.03	10.69	10.06	14.09			28.98	24.44
8.84	12.78	11.11	15.04			30.16	24.89
10.12	14.12	12.06	15.84			32.09	25.52
11.00	14.98	13.00	16.60			32.13	25.56
11.91	15.81	14.02	17.37			34.07	26.17
13.32	17.05	15.32	18.30			35.72	26.69
14.19	17.79	16.95	19.39			36.03	26.78
15.19	18.58	17.03	19.41			37.07	27.08
16.05	19.25	19.36	20.85			38.08	27.39
17.03	19.96	21.22	21.87			39.03	27.66
18.01	20.65	23.21	22.96			39.83	27.88
18.99	21.30	25.07	23.85			40.80	28.14
18.99	21.30	25.07	23.85			42.16	28.50
19.00	21.31	26.93	24.71			42.89	28.68
20.05	21.99					43.15	28.71
20.96	22.56					44.00	28.97
22.13	23.25					44.77	29.16
22.48	23.63[a]					45.64	29.37
						46.55	29.58
						46.66	29.61
						48.28	29.94
						49.37	30.23
						50.14	30.39
						50.51	30.46
						51.20	30.59[a]

Freezing point depressions (θ, °C) and total salinities (wt.%) for NaCl/(NaCl + $CaCl_2$) wt ratios shown in parentheses at the head of each pair of data columns.

[a] Uncertain values.

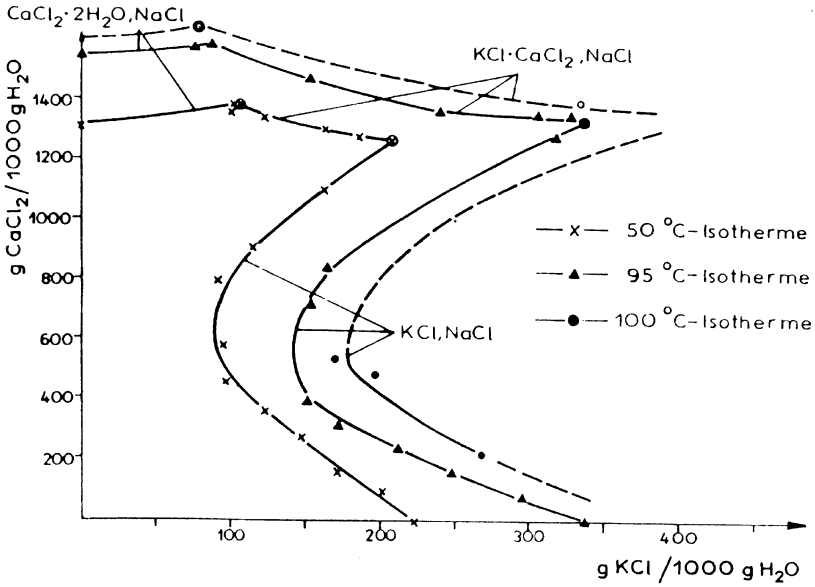


Figure 2.68 Plot of the $CaCl_2$–NaCl–KCl–H_2O phase diagram, with all points saturated with NaCl (Holdorf *et al.*, 1993; reprinted from the Seventh Symposium on Salt (ISBN 0444891439), vol. 1, p. 573, Fig, 3, ©1993, with permission form Elsevier).

can also provide a rough estimate of the $CaCl_2$–$MgCl_2$–NaCl system, where there is much less data. Some of these phase data for calcium chloride with magnesium chloride and sodium chloride in water are listed in Table 2.27, and other data are given by Luzhnaya and Vereshchetina (1946). This system would be encountered in the processing of natural brines when the magnesium is not precipitated. However, the amount of data available on this system is very limited, but eutectic temperatures down to −57°C are indicated when the NaCl is < 2% (for example: −53°C with 1.6% NaCl, 20.85% $CaCl_2$, 6.95% $MgCl_2$; Reps and Schuhmann, 1965). Charykova *et al.* (1992) used the Pitzer equation on the $CaCl_2$–$MgCl_2$–NaCl–H_2O system to predict that tachyhydrite would only begin to be stable above 22.8°C. Majima *et al.* (1980) found that when crystallized at 110°C, $2CaCl_2{\cdot}MgCl_2{\cdot}6H_2O$ was formed.

Some of the similar data with potassium chloride instead of sodium chloride are shown in Table 2.28 (these data are also very limited). Potassium chloride is slightly more soluble than sodium chloride, but other than that, the data should be reasonably similar. Perova (1957) presented 25 and 55°C isotherms for this system with KCl instead of NaCl, and Holdorf *et al.* (1993) plotted

Table 2.26

The System Calcium Chloride–Magnesium Chloride–Water (wt.%) (Seidell, 1958)

Results at 15°C

$CaCl_2$	$MgCl_2$	Solid phase	$CaCl_2$	$MgCl_2$	Solid phase
0.0	35.50	$MgCl_2{\cdot}6H_2O$	31.00	10.60	$CaCl_2{\cdot}6H_2O$
20.30	20.30	$MgCl_2{\cdot}6H_2O$	38.60	2.80	$CaCl_2{\cdot}6H_2O$
22.60	18.40	$MgCl_2{\cdot}6H_2O + CaCl_2{\cdot}6H_2O$	41.20	0.0	$CaCl_2{\cdot}6H_2O$

Results at 25°C

Density	$CaCl_2$	$MgCl_2$	Solid phase	Density	$CaCl_2$	$MgCl_2$	Solid phase
1.470	45.06	0.0	$CaCl_2{\cdot}6H_2O$	1.455	31.17	14.54	$1.2.12 + MgCl_2{\cdot}6H_2O$
1.465	41.87	4.06	$CaCl_2{\cdot}6H_2O$	1.441	28.12	16.31	$MgCl_2{\cdot}6H_2O$
1.472	38.95	7.93	$CaCl_2{\cdot}6H_2O$	1.428	25.09	18.13	$MgCl_2{\cdot}6H_2O$
1.486	38.70	9.43	$CaCl_2{\cdot}6H_2O + 1.2.12$	1.391	16.05	23.33	$MgCl_2{\cdot}6H_2O$
1.473	36.37	10.78	1.2.12	1.371	10.33	27.61	$MgCl_2{\cdot}6H_2O$
1.460	32.82	13.55	1.2.12	1.341	0.0	35.54	$MgCl_2{\cdot}6H_2O$

Results at 25°C (second author)

$CaCl_2$	$MgCl_2$	Solid Phase	$CaCl_2$	$MgCl_2$	Solid Phase
45.0	0.0[a]	$C + Mg(OH)_2$	7.46	29.84[a]	3.1.11
44.88	0.168[a]	$C + Mg(OH)_2$	48.80	0.0	C4α
44.55	0.612[a]	C + 3.1.11	46.49	2.739	C4α
42.14	3.098	C	44.71	4.742	C4α
41.48	4.115	C	43.42	5.97	C4α
39.58	6.47	C	43.38	6.01	C4α
38.82	8.14[a]	C + 3.1.11	43.19	6.24	C4α
38.80	9.42[a]	C + 1.2.12	41.99	7.30	C4α
33.36	13.58[a]	3.1.11 + 1.2.12	40.03	8.52	C4α
31.32	14.60[a]	3.1.11 + 1.2.12 + M	38.88	9.43	C4α
22.29	19.32[a]	3.1.11 + M	38.94	9.38	C4α
7.87	29.25[a]	3.1.11			

Results at 35°

g per 100 g sat. sol.		
$CaCl_2$	$MgCl_2$	Solid Phase
51.33	0.0	$CaCl_2{\cdot}4H_2O\alpha$
49.09	2.10	$CaCl_2{\cdot}4H_2O\alpha$
47.75	3.50	$CaCl_2{\cdot}4H_2O\alpha$
45.03	6.20	$CaCl_2{\cdot}4H_2O\alpha + CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$
45.03	6.20	$CaCl_2{\cdot}4H_2O\alpha + CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$
45.07	6.22	$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$
39.25	9.49	$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$
35.64	11.88	$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$
35.15	12.19	$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$
30.06	15.67	$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$
26.98	17.95	$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$
26.78	18.04	$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$
26.70	18.13	$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O + MgCl_2{\cdot}6H_2O$
26.66	18.24	$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O + MgCl_2{\cdot}6H_2O$

(*continues*)

Table 2.26

(*continued*)

Results at 35°

g per 100 g sat. sol.		
$CaCl_2$	$MgCl_2$	Solid Phase
23.15	20.28	$MgCl_2\cdot 6H_2O$
18.89	23.17	$MgCl_2\cdot 6H_2O$
9.81	29.07	$MgCl_2\cdot 6H_2O$
3.63	33.56	$MgCl_2\cdot 6H_2O$
0.0	36.28	$MgCl_2\cdot 6H_2O$

Results at 75°

58.58	0.0	$CaCl_2\cdot 2H_2O$
55.76	2.53	$CaCl_2\cdot 2H_2O$
52.59	5.27	$CaCl_2\cdot 2H_2O + CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
52.57	5.28	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
45.01	8.74	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
34.97	14.70	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
29.15	18.63	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
19.28	25.55	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
13.83	29.65	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
12.52	30.59	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
10.15	32.39	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
9.97	32.59	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O$
8.31	33.90	$CaCl_2\cdot 2MgCl_2\cdot 12H_2O + MgCl_2\cdot 6H_2O$
8.31	33.91	$MgCl_2\cdot 6H_2O$
8.04	34.07	$MgCl_2\cdot 6H_2O$
3.84	36.62	$MgCl_2\cdot 6H_2O$
0.0	39.12	$MgCl_2\cdot 6H_2O$

Results at 110°C

g per 100 g sat. sol.			g per 100 g sat. sol.		
$CaCl_2$	$MgCl_2$	Solid phase	$CaCl_2$	$MgCl_2$	Solid phase
0.0	42.8	$MgCl_2\cdot 6H_2O$	49.0	9.5	1:1:2 + 1:2:6
2.0	41.4	$MgCl_2\cdot 6H_2O$ + 1:1:12	51.0	8.0	1:2:6
13.6	30.8	1:1:12	53.5	6.2	1:2:6
18.2	28.0	1:1:12	55.7	4.7	1:2:6 + $CaCl_2\cdot 2H_2O$
26.9	21.2	1:1:12	56.8	4.0	$CaCl_2\cdot 2H_2O$
40.0	14.0	1:1:12	62.3	0.0	$CaCl_2\cdot 2H_2O$
47.8	10.0	1:1:12			

Results at 0°C

g per 100 g sat. sol.			g per 100 g sat. sol.		
$CaCl_2$	$MgCl_2$	Solid phase	$CaCl_2$	$MgCl_2$	Solid phase
	(Y.)			(P. & T.) (I. & T.)	
0.0	34.80	$MgCl_2\cdot 6H_2O$	37.44	0.0	$CaCl_2\cdot 6H_2O$
14.00	23.50	$MgCl_2\cdot 6H_2O + CaCl_2\cdot 6H_2O$	30.22	6.82	$CaCl_2\cdot 6H_2O$

(*continues*)

Table 2.26

(*continued*)

Results at 0°C

g per 100 g sat. sol.			g per 100 g sat. sol.		
$CaCl_2$	$MgCl_2$	Solid phase	$CaCl_2$	$MgCl_2$	Solid phase
	(Y.)			(P. & T.) (I. & T.)	
18.50	18.50	$CaCl_2 \cdot 6H_2O$	27.17	9.81	$CaCl_2 \cdot 6H_2O$
27.80	9.40	$CaCl_2 \cdot 6H_2O$	25.10	11.95	$CaCl_2 \cdot 6H_2O$
35.20	2.60	$CaCl_2 \cdot 6H_2O$	22.12	14.94	$CaCl_2 \cdot 6H_2O$
37.26	0.0	$CaCl_2 \cdot 6H_2O$	14.89	22.83	$CaCl_2 \cdot 6H_2O$
			13.88	23.83	$CaCl_2 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$
			13.87	23.91	$MgCl_2 \cdot 6H_2O$
			5.84	29.91	$MgCl_2 \cdot 6H_2O$
			5.70	30.04	$MgCl_2 \cdot 6H_2O$
			4.51	30.89	$MgCl_2 \cdot 6H_2O$
			0.0	34.62	$MgCl_2 \cdot 6H_2O$

Results at − 5° (Y.)			Results at − 10° (Y.)		
g per 100 g sat. sol.			g per 100 g sat. sol.		
$CaCl_2$	$MgCl_2$	Solid phase	$CaCl_2$	$MgCl_2$	Solid phase
8.40	0.0	Ice	14.80	0.0	Ice
8.20	0.70	Ice	14.20	1.00	Ice
6.40	2.20	Ice	10.80	3.60	Ice
4.60	4.60	Ice	7.00	7.00	Ice
0.0	7.40	Ice	0.0	11.60	Ice
0.0	34.40	$MgCl_2 \cdot 6H_2O$	0.0	33.60	$MgCl_2 \cdot 8H_2O$
10.60	26.00	$MgCl_2 \cdot 6H_2O + CaCl_2 \cdot 6H_2O$	10.40	25.40	Ice + $CaCl_2 \cdot 6H_2O$
17.80	17.80	$CaCl_2 \cdot 6H_2O$	17.60	17.60	$CaCl_2 \cdot 6H_2O$
27.20	9.10	$CaCl_2 \cdot 6H_2O$	26.60	8.80	$CaCl_2 \cdot 6H_2O$
34.40	2.20	$CaCl_2 \cdot 6H_2O$	33.60	2.20	$CaCl_2 \cdot 6H_2O$
36.20	0.0	$CaCl_2 \cdot 6H_2O$	35.50	0.0	$CaCl_2 \cdot 6H_2O$

Results at − 15°

g per 100 g sat. sol.			g per 100 g sat. sol.		
$CaCl_2$	$MgCl_2$	Solid phase	$CaCl_2$	$MgCl_2$	Solid phase
	(Y.)			(P. & T.)	
18.50	0.0	Ice	0.0	34.78	$CaCl_2 \cdot 6H_2O$
17.20	1.20	Ice	2.83	31.92	$CaCl_2 \cdot 6H_2O$
13.20	4.40	Ice	3.90	30.50	$CaCl_2 \cdot 6H_2O$
8.50	8.50	Ice	11.97	22.42	$CaCl_2 \cdot 6H_2O$
0.0	14.60	Ice	24.14	10.73	$CaCl_2 \cdot 6H_2O$ $MgCl_2 \cdot 8H_2O\alpha$
0.0	32.60	$MgCl_2 \cdot 8H_2O$	25.71	9.43^b	$CaCl_2 \cdot 6H_2O$
10.78	24.21	$MgCl_2 \cdot 8H_2O + CaCl_2 \cdot 6H_2O$	28.07	7.52^b	$CaCl_2 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$
17.40	17.40	$CaCl_2 \cdot 6H_2O$	29.98	5.11^b	$MgCl_2 \cdot 6H_2O$
26.00	8.60	$CaCl_2 \cdot 6H_2O$	33.86	0.0^b	$MgCl_2 \cdot 6H_2O$

(*continues*)

Table 2.26

(*continued*)

Results at − 15°					
g per 100 g sat. sol.			g per 100 g sat. sol.		
$CaCl_2$	$MgCl_2$	Solid phase	$CaCl_2$	$MgCl_2$	Solid phase
(Y.)			(P. & T.)		
32.80	2.10	$CaCl_2\cdot 6H_2O$	25.68	8.67	$MgCl_2\cdot 8H_2O\alpha$
34.50	0.0	$CaCl_2\cdot 6H_2O$	26.15	7.70	$MgCl_2\cdot 8H_2O\alpha$
			27.17	6.46	$MgCl_2\cdot 8H_2O\alpha$
			28.70	4.42	$MgCl_2\cdot 8H_2O\alpha$
			31.85	0.0	$MgCl_2\cdot 8H_2O\alpha$
			0.0	12.23	Ice
			14.69	0.0	Ice
			10.85	5.0	Ice
			4.01	13.35	Ice

Results at − 20° (Y.)			Results at − 25° (Y.)		
$CaCl_2$	$MgCl_2$	Solid phase	$CaCl_2$	$MgCl_2$	Solid phase
21.00	0.0	Ice	23.50	0.0	Ice
20.00	1.30	Ice	21.80	1.40	Ice
15.00	5.00	Ice	16.60	5.60	Ice
9.60	9.60	Ice	10.60	10.60	Ice
0.0	16.80	Ice	0.0	18.80	Ice
0.0	26.60	$MgCl_2\cdot 12H_2O$	0.0	24.30	$MgCl_2\cdot 12H_2O$
17.20	17.20	$CaCl_2\cdot 6H_2O$	16.30	17.40	$MgCl_2\cdot 12H_2O$ + $CaCl_2\cdot 6H_2O$
25.40	8.40	$CaCl_2\cdot 6H_2O$	16.90	16.90	$CaCl_2\cdot 6H_2O$
32.20	2.00	$CaCl_2\cdot 6H_2O$	25.00	8.40	$CaCl_2\cdot 6H_2O$
34.00	0.0	$CaCl_2\cdot 6H_2O$	31.60	2.10	$CaCl_2\cdot 6H_2O$
			33.60	0.0	$CaCl_2\cdot 6H_2O$

Results at − 30°					
$CaCl_2$	$MgCl_2$	Solid phase	$CaCl_2$	$MgCl_2$	Solid phase
(Y.)			(P. & T.)		
25.00	0.0	Ice	32.92	0.0	$CaCl_2\cdot 6H_2O$
23.60	1.60	Ice	30.07	2.50	$CaCl_2\cdot 6H_2O$
18.00	6.00	Ice	27.04	5.49	$CaCl_2\cdot 6H_2O$
11.40	11.40	Ice	23.55	8.61	$CaCl_2\cdot 6H_2O$ + $MgCl_2\cdot 12H_2O$
0.0	24.40	Ice	19.78[b]	12.26	$CaCl_2\cdot 6H_2O$
0.0	22.50	$MgCl_2\cdot 12H_2O$	15.23[b]	16.76	$CaCl_2\cdot 6H_2O$
15.80	15.80	$MgCl_2\cdot 12H_2O$ + $CaCl_2\cdot 6H_2O$	7.40[b]	25.55	$CaCl_2\cdot 6H_2O$
18.20	15.20	$CaCl_2\cdot 6H_2O$	6.14[b]	27.20	$CaCl_2\cdot 6H_2O$
24.60	8.20	$CaCl_2\cdot 6H_2O$	19.13	9.94	$MgCl_2\cdot 12H_2O$

(*continues*)

Table 2.26

(*continued*)

Results at −30°

(Y.)

$CaCl_2$	$MgCl_2$	Solid phase
31.20	2.00	$CaCl_2{\cdot}6H_2O$
33.40	0.0	$CaCl_2{\cdot}6H_2O$

Results at −35° (Y.)

$CaCl_2$	$MgCl_2$	Solid phase
26.60	0.0	Ice
25.00	1.60	Ice
19.20	6.40	Ice
12.20	12.20	Ice
8.00	16.40	Ice + $MgCl_2{\cdot}12H_2O$
14.30	14.30	$MgCl_2{\cdot}12H_2O$
21.00	11.60	$MgCl_2{\cdot}12H_2O$ + $CaCl_2{\cdot}6H_2O$
24.30	8.10	$CaCl_2{\cdot}6H_2O$
30.60	2.00	$CaCl_2{\cdot}6H_2O$
32.40	0.0	$CaCl_2{\cdot}6H_2O$

Results at −45° (Y.)

$CaCl_2$	$MgCl_2$	Solid phase
29.50	0.0	Ice
27.60	1.60	Ice
21.10	6.00	Ice
17.10	10.40	Ice + $MgCl_2{\cdot}12H_2O$
22.60	7.50	$MgCl_2{\cdot}12H_2O$
25.00	6.50	$MgCl_2{\cdot}12H_2O$ + $CaCl_2{\cdot}6H_2O$
29.40	1.90	$CaCl_2{\cdot}6H_2O$
31.80	0.0	$CaCl_2{\cdot}6H_2O$

(P. & T.)

$CaCl_2$	$MgCl_2$	Solid phase
19.44	10.20	$MgCl_2{\cdot}12H_2O$
11.39	14.70	$MgCl_2{\cdot}12H_2O$
11.27	14.65	$MgCl_2{\cdot}12H_2O$
7.63	16.99	$MgCl_2{\cdot}12H_2O$
0.0	22.19	$MgCl_2{\cdot}12H_2O$
0.0	20.47	Ice
4.83	16.45	Ice
6.18	17.16	Ice
25.03	0.0	Ice

Results at −40° (Y.)

$CaCl_2$	$MgCl_2$	Solid phase
28.20	0.0	Ice
26.40	1.70	Ice
20.30	6.70	Ice
12.70	12.70	Ice
11.00	14.40	Ice + $MgCl_2{\cdot}12H_2O$
13.40	13.40	$MgCl_2{\cdot}12H_2O$
23.40	8.80	$MgCl_2{\cdot}12H_2O$ + $CaCl_2{\cdot}6H_2O$
24.00	8.10	$CaCl_2{\cdot}6H_2O$
30.00	1.95	$CaCl_2{\cdot}6H_2O$
32.00	0.0	$CaCl_2{\cdot}6H_2O$

Other temperatures

	g per 100 g sat. sol.			
t(°C)	$CaCl_2$	$MgCl_2$	Solid phase	
(−49.8°)	30.40	0.0	Ice + $CaCl_2{\cdot}6H_2O$	(Y.)
(−51.7°)	28.86	2.08	Ice + $CaCl_2{\cdot}6H_2O$	(Y.)
(−55.0°)	26.00	5.00	Ice + $CaCl_2{\cdot}6H_2O$ + $MgCl_2{\cdot}12H_2O$	(Y.)
(−52.2°)	27.40	2.93	Ice + $CaCl_2{\cdot}6H_2O$ + $MgCl_2{\cdot}12H_2O$	(P.&T.)
(−20.7°)	10.56	23.23	$CaCl_2{\cdot}6H_2O$ + $MgCl_2{\cdot}12H_2O$ + $MgCl_2{\cdot}8H_2O\alpha$	(P.&T.)
(−6.7°)	9.90	26.40	$CaCl_2{\cdot}6H_2O$ + $MgCl_2{\cdot}8H_2O$ + $MgCl_2{\cdot}6H_2O$	(P.&T.)
(−50.2°)	21.50	7.30	Ice + $MgCl_2{\cdot}12H_2O$	(Y.)
(−43.0°)	13.0	13.00	Ice + $MgCl_2{\cdot}12H_2O$	(Y.)
(−33.6°)	0.0	21.38	Ice + $MgCl_2{\cdot}12H_2O$	(Y.)

1.2.12 = Tachhydrite = $CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$. C = $CaCl_2{\cdot}6H_2O$; 3.1.11 = $3MgO{\cdot}MgCl_2{\cdot}11H_2O$; M = $MgCl_2{\cdot}6H_2O$; C4α = $CaCl_2{\cdot}4H_2O\alpha$; 1:1:12 = $MgCl_2{\cdot}CaCl_2{\cdot}12H_2O$; 1:2:6 = $MgCl_2{\cdot}2CaCl_2{\cdot}6H_2O$; Y and P&T are two different sources; Y = Second author; P&T = Third author.

[a] These solutions also contained 0.002 g MgO.

[b] Metastable.

Table 2.27

The System Calcium Chloride–Magnesium Chloride–Sodium Chloride–Water (wt.%) (Seidell, 1965)

Temperature (°C)	g $CaCl_2$ per 100 g sat. sol.	g $MgCl_2$ per 100 g sat. sol.	g NaCl per 100 g sat. sol.	Solid phase
System at 25°C				
	38.83	9.56	0.30	$CaCl_2\cdot 6H_2O + 2MgCl_2\cdot CaCl_2\cdot 12H_2O + NaCl$
	30.50	14.95	0.38	$MgCl_2\cdot 6H_2O + 2MgCl_2\cdot CaCl_2\cdot 12H_2O + NaCl$
	23.40	19.15	0.32	$MgCl_2\cdot 6H_2O + NaCl$
	10.44	27.70	0.32	$MgCl_2\cdot 6H_2O + NaCl$
−21.5	3.50	3.50	16.0	Ice + $NaCl\cdot 2H_2O$
−22.5	4.80	1.60	17.00	Ice + $NaCl\cdot 2H_2O$
−24.3	3.05	6.15	13.90	Ice + $NaCl\cdot 2H_2O$
−26.5	3.43	10.29	8.6	Ice + $NaCl\cdot 2H_2O$
−26.5	7.20	7.20	9.0	Ice + $NaCl\cdot 2H_2O$
−27.0	11.49	3.81	9.20	Ice + $NaCl\cdot 2H_2O$
−39.0	5.84	17.54	1.72	Ice + $NaCl\cdot 2H_2O$
−44.0	12.30	12.30	2.00	Ice + $NaCl\cdot 2H_2O$
−52.0	20.96	6.98	1.66	Ice + $NaCl\cdot 2H_2O$
−0.5	3.95	3.95	18.5	$NaCl\cdot 2H_2O + NaCl$
−1.2	2.45	7.35	16.0	$NaCl\cdot 2H_2O + NaCl$
−1.3	3.52	1.84	19.10	$NaCl\cdot 2H_2O + NaCl$
−6.5	12.70	4.23	10.40	$NaCl\cdot 2H_2O + NaCl$
−6.5	3.97	11.93	9.3	$NaCl\cdot 2H_2O + NaCl$
−8.0	7.90	7.90	10.2	$NaCl\cdot 2H_2O + NaCl$
−19.5	13.85	13.85	2.40	$NaCl\cdot 2H_2O + NaCl$
−23.8	6.75	20.25	2.05	$NaCl\cdot 2H_2O + NaCl$
−25.0	14.65	14.65	1.60	$NaCl\cdot 2H_2O + NaCl$
−27.5	22.28	7.42	1.70	$NaCl\cdot 2H_2O + NaCl$
−38.3	5.69	17.09	0.32	Ice + $MgCl_2\cdot 12H_2O$
−42.5	12.18	12.18	1.38	Ice + $MgCl_2\cdot 12H_2O$
−17.5	8.28	24.86	0.56	$MgCl_2.\cdot 12H_2O + NaCl\cdot {}_2H_2O$
−27.0	14.82	14.82	0.65	$MgCl_2.\cdot 12H_2O + NaCl\cdot {}_2H_2O$
−30.0	13.15	13.15	1.42	$MgCl_2.\cdot 12H_2O + NaCl\cdot {}_2H_2O$
−35	0.0	22.71	1.56	Ice + $MgCl_2\cdot 12H_2O + NaCl\cdot 2H_2O$
−26	0.0	23.35	1.81	$MgCl_2\cdot 12H_2O + NaCl\cdot 2H_2O + NaCl$

The Quaternary Eutectic is about −58° with a ratio of about 17:83 $MgCl_2$:$CaCl_2$ in solution.

Table 2.28

The System Calcium Chloride–Magnesium Chloride–Potassium Chloride–Water (wt.%) (Seidell, 1958)

Results at 35°							
g per 100 g sat. sol.				g per 100 g sat. sol.			
$MgCl_2$	$CaCl_2$	KCl	Solid phase	$MgCl_2$	$CaCl_2$	KCl	Solid phase
27.33	0.0	3.81	C + K	5.83	31.66	3.38	C + K
20.61	9.12	3.69	C + K	4.07	35.51	3.44	C + K
10.59	23.57	3.47	C + K	4.01	35.60	3.43	C + K

	Results at 35°				Results at 75°			
	g per 100 g sat. sol.				g per 100 g sat. sol.			
	$MgCl_2$	$CaCl_2$	KCl	Solid phase	$MgCl_2$	$CaCl_2$	KCl	Solid phase
	2.31	41.00	3.80	C + K	29.26	0.0	5.57	C + K
	1.30	45.85	4.71	C + K	23.14	8.56	5.56	C + K
	1.15	48.34	5.69	C + K	16.71	18.07	5.61	C + K
	1.17	48.89	6.04	C + K	10.89	27.57	5.85	C + K
Av.	1.02	49.76	6.46	C + K + Ca4	6.39	36.76	6.73	C + K
	36.17	0.0	0.14	C + Mg6	4.48	41.95	7.81	C + K
	26.66	12.97	0.16	C + Mg6	3.85	44.63	8.80	C + K
Av.	18.07	26.74	0.23	C + Mg6 + T	3.47	46.31	9.70	C + K + D
	14.23	32.01	0.32	C + T	38.86	0.0	0.32	C + Mg6
	13.83	32.60	0.33	C + T	36.20	4.26	0.38	C + Mg6
	7.28	42.75	0.71	C + T	33.68	8.40	0.39	C + Mg6 + T
	6.98	43.27	0.76	C + T	26.95	16.96	0.67	C + T
	6.15	44.44	0.97	C + T	16.12	32.00	1.58	C + T
Av.	5.91	45.30	0.99	C + Ca4 + T	7.92	44.90	3.68	C + T
	4.42	46.56	1.33	C + Ca4	6.76	46.43	5.11	C + T + D
	2.69	48.40	2.28	C + Ca4	5.58	46.69	6.25	C + D
	1.72	49.25	3.92	C + Ca4	0.0	57.66	3.59	Ca2 + D
	1.36	49.54	5.10	C + Ca4	1.85	55.23	3.35	Ca2 + D
	0.0	50.45	6.48	K + Ca4	5.28	52.58	0.0	Ca2 + T
	0.71	50.06	6.46	K + Ca4	4.66	52.47	2.65	Ca2 + T
	0.93	49.83	6.45	K + Ca4	4.55	52.51	3.07	Ca2 + T + D
	6.20	45.03	0.0	T + Ca4	4.51	52.29	3.19	T + D
	6.13	45.18	0.33	T + Ca4	4.97	51.21	3.44	T + D
	5.82	45.43	0.70	T + Ca4	5.44	50.06	3.81	T + D
	18.18	26.68	0.0	T + Mg6	6.68	46.63	5.02	T + D
	4.34[a]	48.18	1.41	C + T	0.0	51.20	10.33	K + D
	4.22[a]	48.63	1.53	C + T	2.71	47.32	9.84	K + D
	3.97[a]	49.24	1.64	C + T	33.91	8.31	0.0	T + Mg6
Av.	3.39[a]	50.49	2.10	C + T + Ca4				
	3.06[a]	50.81	2.10	C + Ca4				
	2.05[a]	51.78	3.91	C + Ca4				
	1.51[a]	52.05	4.53	C + Ca4				
Av.	0.89[a]	50.70	7.01	C + K + Ca4				

C = $KCl{\cdot}MgCl_2{\cdot}6H_2O$; T = $CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$; Ca4 = $CaCl_2{\cdot}4H_2O$; Av. = Average; K = KCl; D = $2KCl{\cdot}CaCl_2{\cdot}2H_2O$; Ca2 = $CaCl_2{\cdot}2H_2O$; Mg6 = $MgCl_2{\cdot}6H_2O$.

[a] Metastable.

Table 2.29

The Density of Calcium Chloride Solutions, ρ_4^T (Perry and Chilton, 1978)

(A)

(%)	−5°C	0°C	20°C	30°C	40°C	60°C	80°C	100°C	120°C	140°C
2		1.0171	1.0148	1.0120	1.0084	0.9994	0.9881	0.9748	0.9596	0.9428
4		1.0346	1.0316	1.0286	1.0249	1.0158	1.0046	0.9915	0.9765	0.9601
8	1.0708	1.0703	1.0659	1.0626	1.0586	1.0492	1.0382	1.0257	1.0111	0.9954
12	1.1083	1.1072	1.1015	1.0978	1.0937	1.0840	1.0730	1.0610	1.0466	1.0317
16	1.1471	1.1454	1.1386	1.1345	1.1301	1.1202	1.1092	1.0973	1.0835	1.0691
20	1.1874	1.1853	1.1775	1.1730	1.1684	1.1581	1.1471	1.1352	1.1219	1.1080
25		1.2376	1.2284	1.2236	1.2186	1.2079	1.1965	1.1846		
30		1.2922	1.2816	1.2764	1.2709	1.2597	1.2478	1.2359		
35			1.3373	1.3316	1.3255	1.3137	1.3013	1.2893		
40			1.3957	1.3895	1.3826	1.3700	1.3571	1.3450		

(B) Potter and Clynne, 1976, ρ_4^T

Temperature (°C)										
wt.%	1	3	5.26	7	9.99	14.27	18.16	21.72	24.98	27.98
Molality			0.5		1	1.5	2	2.5	3.0	3.5
125	0.948	0.967	0.986	1.001	1.026	1.064	1.101	1.137	1.173	1.208
150	0.927	0.947	0.967	0.982	1.008	1.046	1.083	1.118	1.154	1.188
175	0.902	0.923	0.945	0.960	0.987	1.025	1.062	1.097	1.132	1.166
200	0.876	0.899	0.920	0.936	0.963	1.002	1.038	1.073	1.107	1.141
225	0.841	0.868	0.892	0.909	0.938	0.978	1.015	1.051	1.085	1.118
250	0.803	0.833	0.860	0.878	0.909	0.951	0.990	1.027	1.062	1.096
275	0.762	0.794	0.823	0.843	0.876	0.921	0.962	1.001	1.038	1.074
300	0.717	0.751	0.872	0.803	0.830	0.886	0.931	0.973	1.013	1.052

(*continues*)

Table 2.29

(*continued*)

(B) Potter and Clynne, 1976, ρ_4^T

wt.%	30.74	33.31	35.69	37.90	39.97	41.91	43.72	45.42
Molality	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5
0	1.301							
25	1.287	1.315	1.342	1.367	1.391	1.414	1.435	
50	1.264	1.292	1.319	1.346	1.372	1.398	1.424	1.449
75	1.252	1.280	1.308	1.335	1.362	1.389	1.416	1.442
100	1.238	1.267	1.294	1.322	1.349	1.376	1.403	1.430

(C) Oakes, 1990; ρ_T^T (for ρ_4^T divide by the ρ of water; 25°C = 0.997077, 35°C = 0.994061, 15.56°C (60°F) = 0.9990412)

wt.%	25°C	35°C	wt.%	25°C	35°C
41.58	1.4086	1.4021	17.78	1.1541	—
39.96	1.3905	1.3841	16.40	1.1410	1.1368
38.00	1.3681	—	14.46	1.1228	—
36.10	1.3468	—	14.39	—	1.1180
35.99	1.3456	1.3396	12.40	1.1038	—
33.99	1.3232	1.3174	10.16	1.0837	—
31.05	1.2906	—	9.98	1.0820	1.0783
29.23	1.2708	—	6.91	1.0551	—
28.93	—	1.2624	6.19	—	1.0455
28.01	—	1.2525	5.08	1.0395	—
26.38	1.2405	—	3.84	1.0290	—
22.39	1.1994	—	3.61	1.0270	1.0237
21.99	—	1.1908	1.94	1.0131	—
21.72	1.1928	—	1.57	1.0100	—
21.11	1.1867	—	1.03	—	1.0025

three isotherms of the $CaCl_2$–NaCl–KCl system when saturated with NaCl (Fig. 2.68).

A great deal of other solubility data exist for calcium chloride with many other salts and other solvents. The latter data have been used for systems attempting to extract or salt-out calcium chloride from solution, such as the solubility data on dimethylformamide by Spiridonov *et al.* (1976).

Physical Properties

The density of calcium chloride solutions is listed in Tables 2.29 and 2.30, and plotted in Fig. 2.69. The method of reporting the density should be noted, since the common scientific notation assumes that the density at a given temperature is compared with water at 4°C (where it is 1.00000 g/cc), or ρ_4^{25} for 25°C. When the data are reported as being compared with water at the same temperature (i.e., ρ_{25}^{25}) it must be divided by the density of water to give the true density. Additional density data for the $CaCl_2$–H_2O and $CaCl_2$–NaCl–H_2O systems are given by many other authors, such as Hu (2000), Zhang *et al.* (1997), Oakes (1992), Oakes *et al.* (1990), Kumar and Atkinson (1983), Kumar *et al.* (1982), Ivanov (1964), Klochko *et al.* (1959; the last two also listed viscosity and electric conductivity), Yuan *et al.* (2000a) and Yuan and Liu (2000; the last two made estimates based upon the Pitzer equation). Some of the density data for the ternary system $CaCl_2$–NaCl–H_2O are listed in Table 2.31, and shown in Figs. 2.70 and 2.71. As seen by the figures, it would appear that the density of $CaCl_2$ and NaCl mixtures are closely approximated by a linear combination of the two pure solutions' density at that temperature.

Viscosity data for calcium chloride solutions are shown in Tables 2.32 and 2.33 and Fig. 2.72. Other authors presenting viscosity data include Isono (1984; also density and electrical conductivity data), Nowlan *et al.* (1980) and Goncalves and Kestin (1979). The specific heat of $CaCl_2$ solutions is shown in Table 2.34 and Fig. 2.73 (note that the values for cal/g/°C are the same as for Btu/lb/°F), and other values are given by Perron *et al.* (1981). Vapor pressure data for calcium chloride solutions are shown in Figs. 2.74–2.76. Additional values are given by Lannung (1940), Mun and Darar (1956), Baker and Waite (1921; from 150 to 350°), Zarembo *et al.* (1980; with activity coefficients), and Tkachenko and Shmulovich (1994; from 400 to 600°C). Boiling point data are listed in Table 2.35 and Figs. 2.77 and 2.78 (the temperature when the vapor pressure is 760 mm of Hg. Above 69% $CaCl_2$, there is no boiling point because the dihydrate decomposes). The vapor pressure over calcium chloride solutions is listed in Table 2.36, and the surface tension of $CaCl_2$ solutions listed in Table 2.37 and plotted in Fig. 2.79. The heat evolved when solid calcium chloride is added to water is listed in Table 2.38, while the temperature increase in dissolving flake calcium chloride is listed in Table 2.39. Fig. 2.80 shows these two values graphically. The enthalpy of various calcium chloride solutions is given in Table

Table 2.30

The Density, Viscosity, Index of Refraction, Freezing Point Depression, Osmolality and Specific Conductance of Calcium Chloride Solutions at 20°C (Weast, 1977)

A% by wt.	$\rho\ D_4^{20}$	*C* (g/liter)	*M* (g mol/liter)	*n*	*Δ* (°C)	*O* (Os/kg)	η/η_0	γ (mmho/cm)
0.50	1.0024	5.0	0.045	1.3342	0.222	0.119	1.013	8.1
1.00	1.0065	10.1	0.091	1.3354	0.440	0.237	1.026	15.7
1.50	1.0106	15.2	0.137	1.3366	0.661	0.355	1.037	22.7
2.00	1.0148	20.3	0.183	1.3378	0.880	0.473	1.048	29.4
2.50	1.0190	25.5	0.230	1.3390	1.102	0.593	1.061	36.1
3.00	1.0232	30.7	0.277	1.3402	1.330	0.715	1.076	42.6
3.50	1.0274	36.0	0.324	1.3414	1.567	0.843	1.091	48.9
4.00	1.0316	41.3	0.372	1.3426	1.815	0.976	1.108	55.1
4.50	1.0358	46.6	0.420	1.3438	2.074	1.115	1.125	61.1
5.00	1.0401	52.0	0.469	1.3451	2.345	1.261	1.141	67.0
5.50	1.0443	57.4	0.518	1.3463	2.630	1.414	1.157	72.8
6.00	1.0486	62.9	0.567	1.3475	2.930	1.575	1.173	78.3
6.50	1.0529	68.4	0.617	1.3487	3.244	1.744	1.189	83.6
7.00	1.0572	74.0	0.667	1.3500	3.573	1.921	1.206	88.7
7.50	1.0615	79.6	0.717	1.3512	3.917	2.106	1.222	93.6
8.00	1.0659	85.3	0.768	1.3525	4.275	2.299	1.240	98.4
8.50	1.0703	91.0	0.820	1.3537	4.649	2.499	1.257	103.0
9.00	1.0747	96.7	0.871	1.3549	5.04	2.71	1.276	108.0
9.50	1.0791	102.5	0.924	1.3562	5.44	2.92	1.295	112.0
10.00	1.0835	108.3	0.976	1.3575	5.86	3.15	1.316	117.0
11.00	1.0923	120.2	1.083	1.3600	6.74	3.63	1.359	125.0
12.00	1.1014	132.2	1.191	1.3625	7.70	4.14	1.405	133.0
13.00	1.1105	144.4	1.301	1.3651	8.72	4.69	1.454	141.0
14.00	1.1198	156.8	1.412	1.3677	9.83	5.28	1.505	148.0
15.00	1.1292	169.4	1.526	1.3704	11.01	5.92	1.561	154.0
16.00	1.1386	182.2	1.641	1.3730	12.28	6.60	1.622	160.0
17.00	1.1482	195.2	1.759	1.3757	13.65	7.34	1.688	165.0
18.00	1.1579	208.4	1.878	1.3784	15.11	8.12	1.760	169.0
19.00	1.1677	221.9	1.999	1.3812	16.7	8.98	1.839	173.0
20.00	1.1775	235.5	2.122	1.3839	18.3	9.84	1.926	177.0
22.00	1.1976	263.5	2.374	1.3895	21.7	11.67	2.123	182.0
24.00	1.2180	292.3	2.634	1.3951	25.3	13.60	2.351	183.0
26.00	1.2388	322.1	2.902	1.4008	29.7	15.97	2.640	182.0
28.00	1.2600	352.8	3.179	1.4066	34.7	18.66	2.994	179.0
30.00	1.2816	384.5	3.464	1.4124	41.0	22.04	3.460	172.0
32.00	1.3036	417.1	3.758	1.4183	49.7	26.72	4.027	162.0
34.00	1.3260	450.8	4.062	1.4242			4.810	150.0
36.00	1.3488	485.6	4.375	1.4301			5.795	137.0
38.00	1.3720	521.4	4.697	1.4361			7.306	123.0
40.00	1.3957	558.3	5.030	1.4420			8.979	106.0

A% = anhydrous solute weight per cent, g solute/100 g solution; ρ or D_4^{20} = relative density at 20°C, kg/liter; C_s = anhydrous solute concentration, g/liter; *M* = molar concentration, g mol/liter; *n* = index of refraction at 20°C relative to air for sodium yellow light; *Δ* = freezing point depression, °C; *O* = osmolality, Os/kg water; η/η_0 = relative viscosity, ratio of the absolute viscosity of a solution at 20°C to the absolute viscosity of water at 20°C. (Water's viscosity at 20°C is 1.002); γ = specific conductance (electrical) at 20°C, mmho/cm.

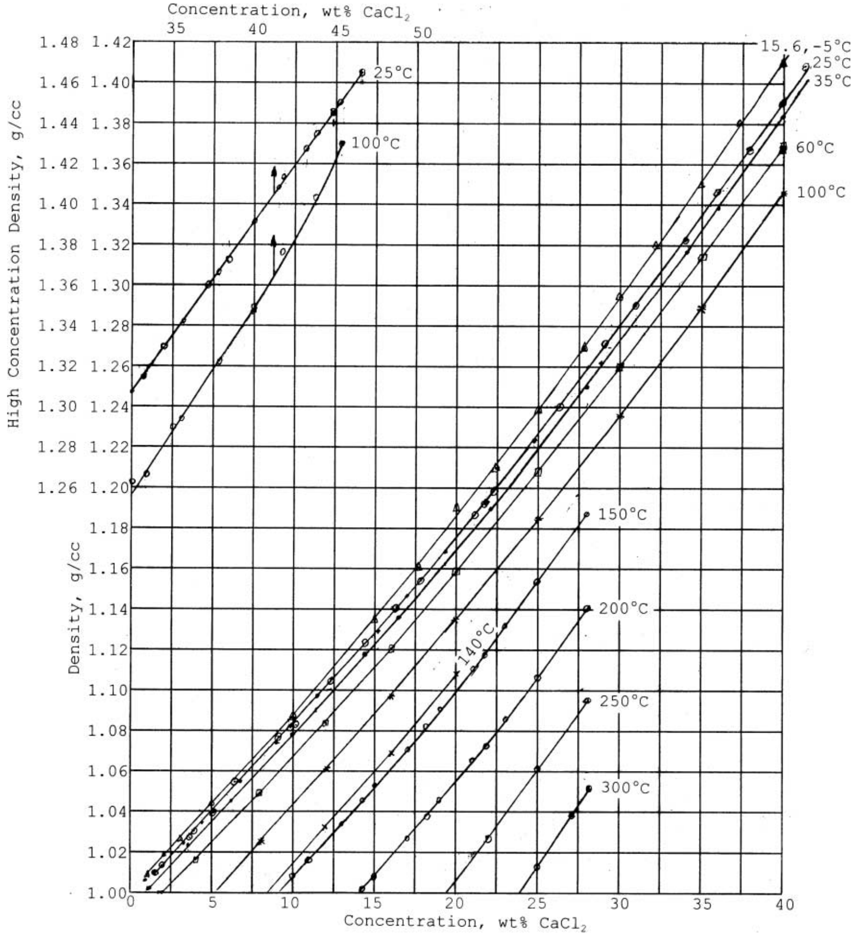


Figure 2.69 The density of calcium chloride solutions at various temperatures.

2.40. The freezing point depression, refractive index, osmolality and specific conductance are all listed in Table 2.30. An *et al.* (1978) list activity and osmotic coefficients. The water absorbed by solid calcium chloride is listed in Table 2.41 and Fig. 2.81.

Electrical conductance and ionization constants have been presented by Frantz and Marshall (1982). Other volumetric properties of calcium chloride solutions have been given by Potter and Clynne (1973) and Tsay *et al.* (1988; at high temperatures and pressure). Various bulk properties are presented by Alekhin *et al.* (1980). The activity coefficients of calcium chloride are given by Long *et al.*

Table 2.31

Density of Mixed $CaCl_2$–NaCl–H_2O Solutions (Concentrations as wt.%)

$CaCl_2$				
wt.%	Fraction	wt.% NaCl	Total wt.%	Density
25°C Hu (2000)				
1.90	62.7	1.13	3.03	1.0208
0.60	17.5	2.82	3.42	1.0221
1.32	23.0	4.41	5.73	1.0396
4.04	64.8	2.19	6.23	1.0464
1.53	19.1	6.45	7.98	1.0567
2.80	34.3	5.37	8.17	1.0591
5.33	62.4	3.21	8.54	1.0649
3.07	28.2	7.81	10.88	1.0798
5.98	53.5	5.19	11.17	1.0852
8.30	72.7	3.11	11.41	1.0905
4.57	31.4	9.99	14.56	1.1097
7.21	49.1	7.48	14.69	1.1137
9.84	66.4	4.98	14.82	1.1186
12.99	86.7	1.99	14.98	1.1252
5.09	30.4	11.67	16.76	1.1276
8.08	48.0	8.75	16.83	1.1318
11.07	65.5	5.83	16.90	1.1367
13.06	77.1	3.88	16.94	1.1406
17.46	90.2	1.89	19.35	1.1670
15.59	80.5	3.77	19.36	1.1642
13.72	70.8	5.65	19.37	1.1609
11.85	61.1	7.54	19.39	1.1578
8.11	41.8	11.30	19.41	1.1522
6.24	32.1	13.19	19.43	1.1502
20.09	91.7	1.83	21.92	1.1925
16.57	75.2	5.47	22.04	1.1878
13.06	58.9	9.10	22.16	1.1825
8.69	39.0	13.62	22.31	1.1772
22.25	89.4	2.63	24.88	1.2210
17.33	68.8	7.87	25.20	1.2157
14.89	58.7	10.47	25.36	1.2128
10.83	42.3	14.78	25.61	1.2082
8.41	32.6	17.35	25.76	1.2059
25°C Oakes et al. (1990)				
5.11	20.41	19.91	25.02	1.1950
4.62	20.41	18.00	22.62	1.1741
4.26	20.41	16.63	20.89	1.1594
4.01	20.41	15.64	19.65	1.1490
3.57	20.41	13.91	17.48	1.1311
3.10	20.41	12.09	15.19	1.1125
2.66	20.41	10.36	13.02	1.0952
2.26	20.41	8.80	11.06	1.0799
2.05	20.41	8.25	10.03	1.0719
1.64	20.41	6.38	8.02	1.0565

(*continues*)

Table 2.31

(*continued*)

$CaCl_2$				
wt.%	Fraction	wt.% NaCl	Total wt.%	Density
1.37	20.41	5.36	6.73	1.0468
1.02	20.41	3.98	5.00	1.0338
0.61	20.41	2.38	2.99	1.0190
0.41	20.41	1.60	2.01	1.0118
0.20	20.41	0.79	0.99	1.0043
0.13	20.41	0.51	0.64	1.0018
10.23	40.67	14.92	25.15	1.2042
9.77	40.67	14.25	24.02	1.1938
9.52	40.67	13.90	23.42	1.1884
8.67	40.67	12.65	21.32	1.1695
7.92	40.67	11.56	19.48	1.1534
6.30	40.67	9.20	15.50	1.1194
4.73	40.67	6.90	11.63	1.0874
3.17	40.67	4.62	7.79	1.0568
2.28	40.67	3.34	5.62	1.0398
1.57	40.67	2.29	3.86	1.0263
0.79	40.67	1.16	1.95	1.0118
0.40	40.67	0.58	0.98	1.0044
15.96	60.68	10.35	26.31	1.2238
14.70	60.68	9.53	24.23	1.2038
13.78	60.68	8.92	22.70	1.1892
12.38	60.68	8.02	20.40	1.1678
11.14	60.68	7.21	18.35	1.1493
9.90	60.68	6.42	16.32	1.1312
8.42	60.68	5.45	13.87	1.1099
7.42	60.68	4.81	12.23	1.0959
6.21	60.68	4.03	10.24	1.0791
4.95	60.68	3.20	8.15	1.0619
3.77	60.68	2.44	6.21	1.0461
3.01	60.68	1.95	4.96	1.0361
2.50	60.68	1.62	4.12	1.0294
1.86	60.68	1.20	3.06	1.0210
1.21	60.68	0.78	1.99	1.0126
0.62	60.68	0.40	1.02	1.0050
0.34	60.68	0.22	0.56	1.0014
21.11	80.48	5.11	26.22	1.2311
20.55	80.48	4.99	25.54	1.2242
18.59	80.48	4.50	23.09	1.1999
17.13	80.48	4.15	21.28	1.1823
15.56	80.48	3.77	19.33	1.1637
13.64	80.48	3.31	16.95	1.1415
11.97	80.48	2.90	14.87	1.1226
10.28	80.48	2.49	12.77	1.1038
8.46	80.48	2.05	10.51	1.0841

(*continues*)

Table 2.31

(*continued*)

CaCl$_2$				
wt.%	Fraction	wt.% NaCl	Total wt.%	Density
7.24	80.48	1.75	8.99	1.0710
5.94	80.48	1.44	7.38	1.0574
5.11	80.48	1.24	6.35	1.0487
4.28	80.48	1.03	5.31	1.0402
3.40	80.48	0.82	4.22	1.0312
2.58	80.48	0.62	3.20	1.0228
1.69	80.48	0.41	2.10	1.0140
0.87	80.48	0.21	1.08	1.0057
0.40	80.48	0.10	0.50	1.0011
23.06	83.11	4.69	27.75	1.2478
21.85	83.11	4.44	26.29	1.2329
20.12	83.11	4.09	24.21	1.2119
18.92	83.11	3.85	22.77	1.1976
17.01	83.11	3.45	20.46	1.1752
16.27	83.11	3.30	19.57	1.1667
15.42	83.11	3.14	18.56	1.1571
0	0	26.09	—	1.19529
0[a]	0	26.00	—	1.19443
0[a]	0	24.00	—	1.17726
0	0	23.50	—	1.17388
0	0	21.30	—	1.15588
0[a]	0	20.00	—	1.145330
0	0	18.74	—	1.13545
0	0	17.12	—	1.12276
0	0	16.09	—	1.11479
0[a]	0	16.00	—	1.11401
0	0	15.09	—	1.10713
0	0	12.62	—	1.08840
0[a]	0	12.00	—	1.08365
0	0	10.73	—	1.07423
0	0	9.29	—	1.06364
0[a]	0	8.00	—	1.05412
0	0	6.89	—	1.04605
0	0	4.45	—	1.02858
0[a]	0	4.00	—	1.02530
0	0	2.86	—	1.01730
0[a]	0	2.00	—	1.01712
0[a]	0	1.00	—	1.00409
35°C Oakes (1900)				
5.11	20.41	19.91	25.02	1.1899
4.26	20.41	16.63	20.89	1.1544
3.10	20.41	12.09	15.19	1.1080
2.05	20.41	7.98	10.03	1.0679
1.02	20.41	3.98	5.00	1.0302

(*continues*)

Table 2.31

(*continued*)

$CaCl_2$				
wt.%	Fraction	wt.% NaCl	Total wt.%	Density
0.41	20.41	1.60	2.01	1.0085
0.13	20.41	0.51	0.64	0.9986
10.23	40.67	14.92	25.15	1.1990
7.92	40.67	11.56	19.48	1.1487
7.22	40.67	10.53	17.75	1.1339
4.73	40.67	6.90	11.63	1.0833
2.28	40.67	3.34	5.62	1.0362
1.57	40.67	2.29	3.86	1.0229
0.79	40.67	1.16	1.95	1.0085
0.20	40.67	0.29	0.49	0.9977
15.96	60.67	10.35	26.31	1.2186
12.37	60.67	7.67	20.04	1.1631
8.42	60.67	5.45	13.87	1.1057
3.77	60.67	2.44	6.21	1.0425
1.21	60.67	0.78	1.99	1.0094
0.62	60.67	0.40	1.02	1.0019
21.10	80.48	5.12	26.22	1.2258
17.13	80.48	4.15	21.28	1.1776
11.97	80.48	2.90	14.87	1.1184
7.24	80.48	1.75	8.99	1.0673
3.40	80.48	0.82	4.22	1.0278
0.87	80.48	0.21	1.08	1.0026
0	0	23.08	—	1.16508
0	0	19.99	—	1.14038
0	0	17.00	—	1.11705
0	0	13.06	—	1.08720
0	0	10.03	—	1.06490
0	0	7.03	—	1.04323
0	0	3.76	—	1.02019
0	0	1.51	—	1.00448
0	0	0.51	—	0.99759
0	0	0.49	—	0.99745
41.58	100	0	0	1.40211
39.96	—	0	0	1.38415
35.99	—	0	0	1.33961
33.99	—	0	0	1.31743
28.93	—	0	0	1.26240
28.01	—	0	0	1.25254
21.99	—	0	0	1.19080
16.40	—	0	0	1.13681
14.39	—	0	0	1.11799
9.98	—	0	0	1.07833
6.19	—	0	0	1.04545
3.61	—	0	0	1.02372
1.03	–	0	0	1.00248

[a] Perry and Chilton (1978).

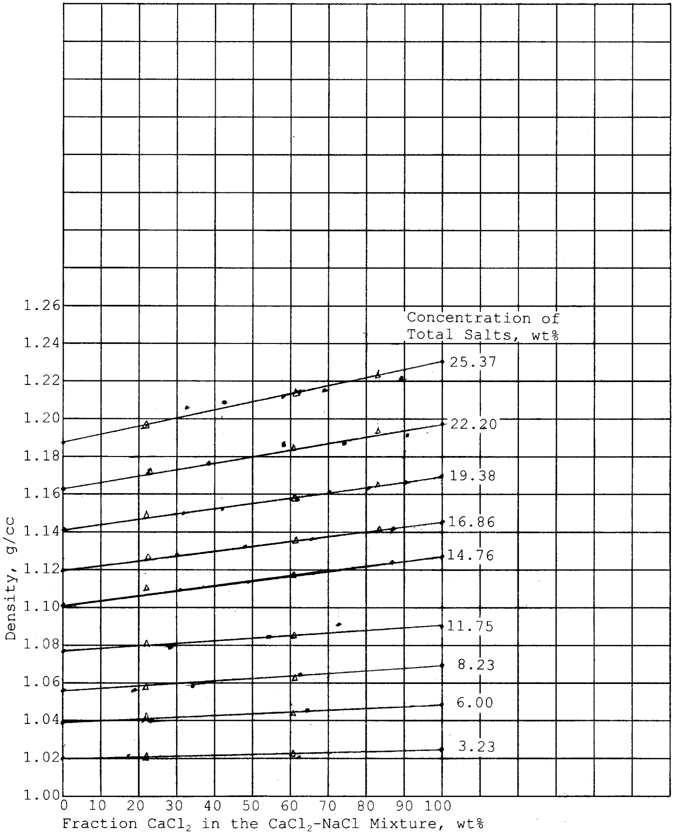


Figure 2.70 The density of calcium chloride–sodium chloride solutions at 25°C (• = Hu, 2000; Δ = Oakes *et al.*, 1990).

(1999) and Galleguillos *et al.* (1999). The activity coefficient in seawater are noted by Tishchenko and Popova (1992), while other ionic forms of calcium chloride in seawater have been suggested by Kesov and Sychkova (1983). The vapor pressure of HCl over solid phase $CaCl_2$ as it decomposes at temperatures from 380 to 500°C are given by Bischoff *et al.* (1996).

For $CaCl_2$–NaCl solutions, various physical properties have also been determined. The solutions' density (Table 2.31), and the activity coefficients of the ions at temperatures to 250°C and 400 bars (395 psi) pressure have been determined by Oakes (1992), and the heat of dilution and mixing from 100 to 300°C and 21.5 MPa (145 psi) pressure by Oakes *et al.* (1998). Low temperature Raman spectroscopic investigations have been made by Samson and Walker

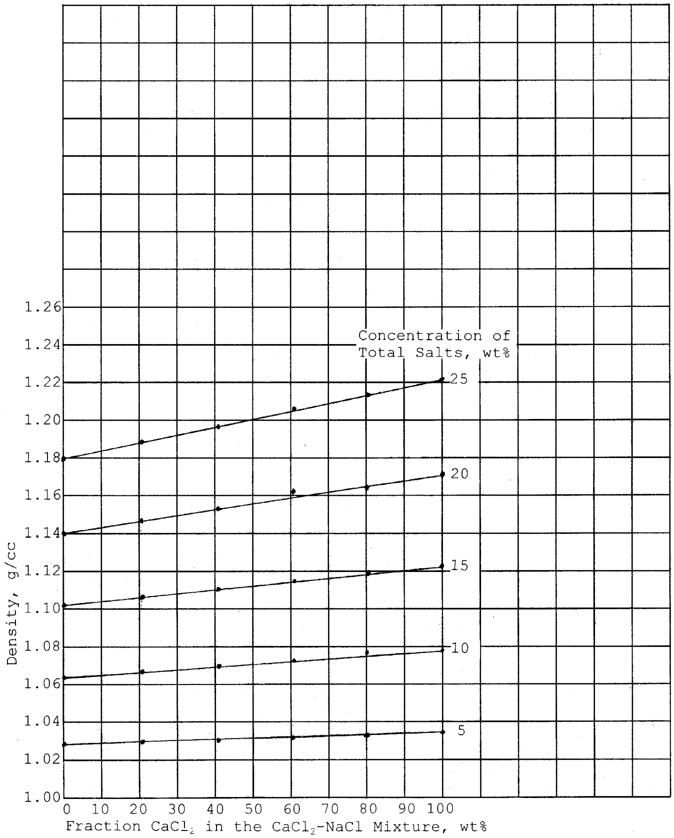


Figure 2.71 The density of calcium chloride–sodium chloride solutions at 35°C (• = Oakes *et al.*, 1990).

Table 2.32

The Density and Viscosity of Calcium Chloride Solutions at 25°C, g/cm^3 and Centipoise (= mPa s) (Zhang *et al.*, 1997)

wt.%	Molality	Density	Viscosity	wt.%	Molality	Density	Viscosity
0	0	0.99708	0.8904	8.646	0.8528	1.0703	1.1386
0.244	0.0220	0.9991	0.8977	8.780	0.8673	1.0714	1.1431
0.265	0.0239	0.9993	0.8982	11.387	1.1578	1.0947	1.2430
0.518	0.0469	1.0014	0.9046	15.951	1.7100	1.1368	1.4636
0.651	0.0590	1.0025	0.9082	17.254	1.8788	1.1491	1.5409
0.755	0.0685	1.0033	0.9106	18.008	1.9790	1.1563	1.5897

(*continues*)

Table 2.32
(*continued*)

wt.%	Molality	Density	Viscosity	wt.%	Molality	Density	Viscosity
1.071	0.0975	1.0059	0.9186	18.849	2.0929	1.1645	6.6476
1.572	0.1439	1.0101	0.9311	18.947	2.1063	1.1654	1.6543
2.016	0.1854	1.0138	0.9425	21.769	2.5073	1.1932	1.8825
2.220	0.2046	1.0155	0.9476	22.647	2.6380	1.2021	1.9666
2.839	0.2633	1.0206	0.9637	24.406	2.9091	1.2201	2.1566
3.145	0.2926	1.0232	0.9719	27.655	3.4443	1.2540	2.6110
4.185	0.3936	1.0320	1.0001	30.259	3.9093	1.2820	3.1142
4.258	0.4007	1.0325	1.0020	34.579	4.7625	1.3297	4.4138
4.417	0.4164	1.0339	1.0063	37.299	5.3599	1.3604	5.7327
5.550	0.5295	1.0435	1.0392	38.409	5.6189	1.3729	6.4365
6.090	0.5843	1.0481	1.0554	43.198	6.8525	1.4268	11.2940
6.187	0.5942	1.0490	1.0583	44.868	7.3330	1.4454	14.0283
6.285	0.6043	1.0497	1.0610	45.290	7.4589	1.4502	14.8392
6.378	0.6139	1.0506	1.0641	46.648	7.8783	1.4650	17.8223
8.052	0.7890	1.0651	1.1182				

$\mu = \mu_{\text{water}}(1 + \text{Am}^{0.5} + \text{Bm} + \text{Cm}^2 + \text{Dm}^{3.5} + \text{Em}^7)$.

Table 2.33

Viscosities of Calcium Chloride Solutions, Centipoise

	Temperature (°C)										
wt.% $CaCl_2$	−25	−20	−15	−10	0	10	18	20	25	30	40
0[a]	—	—	—	—	1.77	1.29	—	1.02	—	0.79	0.67
0	—	—	—	—	1.79	1.31	1.06	—	0.89	—	—
1.1	—	—	—	—	—	—	1.09	—	0.92	—	—
1.6	—	—	—	—	1.80	1.32	—	—	—	—	—
2.7	—	—	—	—	—	—	1.14	—	0.96	—	—
3.4	—	—	—	—	1.85	1.36	—	—	—	—	—
5.0[a]	—	—	—	—	1.84	1.35		1.07	—	0.82	0.73
5.0	—	—	—	—	1.92	1.41	—	—	—	—	—
5.3	—	—	—	—	—	—	1.21	—	1.03	—	—
6.8	—	—	—	—	2.00	1.46	—	—	—	—	—
8.7	—	—	—	—	2.10	1.53	—	—	—	—	—
10.0[a]	—	—	—	—	2.13	1.52	1.37	1.16	1.19	0.93	0.86
10.5	—	—	—	—	2.21	1.61	—	—	—	—	—
12.2	—	—	—	—	2.33	1.70	—	—	—	—	—
14.1	—	—	—	—	2.49	1.81	—	—	—	—	—
15.0[a]	—	—	—	4.09	2.50	1.84	—	1.40	—	1.20	1.03
16.0	—	—	—	4.22	2.68	1.95	—	—	—	—	—
17.8	—	—	—	4.52	2.89	2.11	—	—	—	—	—
18.2	—	—	—	—	—	2.25	1.84	—	1.59	—	1.19
19.8	—	—	6.30	4.89	3.12	2.31	—	—	—	—	—

(*continues*)

Table 2.33

(*continued*)

	Temperature (°C)										
wt.% $CaCl_2$	−25	−20	−15	−10	0	10	18	20	25	30	40
20.0[a]	—	—	—	4.97	3.12	2.33	—	1.81	—	1.54	1.22
21.8	—	8.52	6.82	5.34	3.41	2.56	—	—	—	—	—
23.7	11.45	9.33	7.48	5.85	3.76	2.84	—	—	—	—	—
25.0[a]	—	9.94	—	6.32	4.04	3.07	—	2.38	—	1.97	1.54
25.7	12.90	10.51	8.40	6.59	4.22	3.20	—	—	—	—	—
27.6	14.96	12.01	9.60	7.57	4.85	3.68	—	—	—	—	—
29.7	—	14.27	11.17	8.86	5.69	4.34	—	—	—	—	—
30.0[a]	—	14.27	—	9.04	5.77	4.30	—	3.33	—	2.62	2.07
30.8	—	—	—	—	—	4.55	3.74	—	3.22	—	2.44
31.8	—	17.26	13.44	10.61	6.74	5.10	—	—	—	—	—
34.0	—	—	—	—	8.16	6.12	—	—	—	—	—
35.0[a]	—	—	—	—	8.83	6.62	—	4.99	—	3.87	3.07
36.1	—	—	—	—	9.90	7.23	—	—	—	—	—
37.2	—	—	—	—	10.86	7.87	—	—	—	—	—
40.0[a]	—	—	—	—	—	11.75	—	8.48	—	6.39	4.90
40.0	—	—	—	—	—	12.29	9.50	—	7.60	—	5.38
45.0[a]	—	—	—	—	—	—	—	—	—	11.50	8.90

	50°C	60	70	80	90	100
0[a]	0.53	0.46	0.40	0.34	0.30	0.26
5[a]	0.57	0.51	0.45	0.39	0.35	0.28
10[a]	0.64	0.57	0.51	0.47	0.42	0.35
15[a]	0.76	0.68	0.62	0.55	0.49	0.42
20[a]	0.99	0.85	0.74	0.68	0.59	0.49
25[a]	1.27	1.07	0.90	0.82	0.70	0.59
30[a]	1.73	1.43	1.24	1.01	0.89	0.73
35[a]	2.54	2.17	1.82	1.46	1.22	1.03
40[a]	4.00	3.26	2.72	2.15	1.74	1.52
45[a]	6.57	5.24	4.25	3.39	2.77	2.33
50[a]	11.80	9.24	7.45	5.97	4.95	4.28

Data from Allied Chemical (1980).

[a] Data from Dow Chemical (1980).

(2000) and Walker (1994). Thermodynamic properties have been estimated by Galleguillos *et al.* (1999).

A comparison of the boiling points for pure calcium chloride with that of commercial solutions of 77% $CaCl_2$ (Fig. 2.78) indicates that the commercial

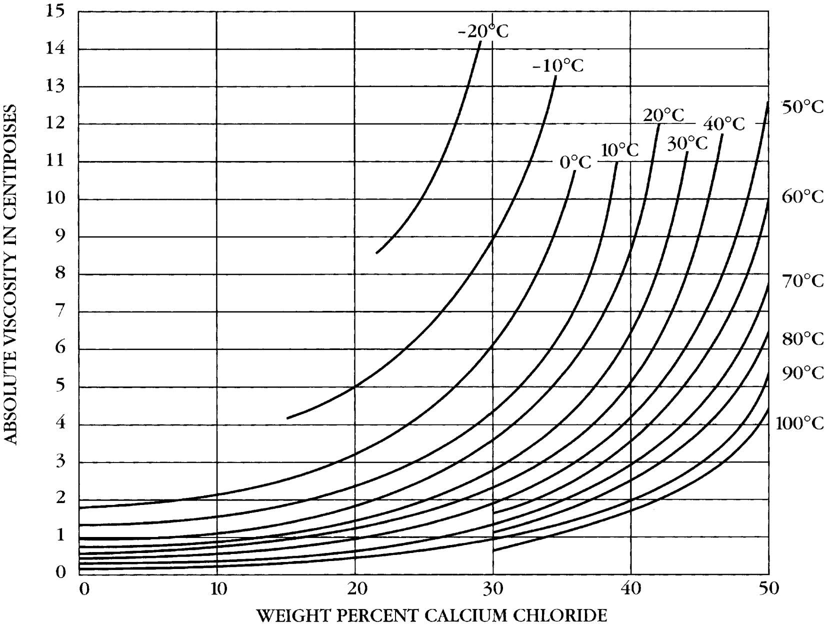


Figure 2.72 The viscosity of calcium chloride solutions, centipoises (Dow, 2001, courtesy of the Dow Chemical Company).

solutions have 1–3°C higher boiling points than pure solutions. Table 2.42 lists the density of a commercial $CaCl_2$ solution and its crystallization temperatures. The densities were measured at 60°F (15.56°C), and compared to water at 60°F (i.e., considering it to be 1.000), while the crystallization data were taken with a very short residence time, making it quite supersaturated (i.e., indicating temperatures up to 10% lower than equilibrium solubility data). The pH of solutions of commercial calcium chloride (after caustic soda [NaOH] has been added to make it basic) are listed in Table 2.43. Calcium chloride solutions are inherently acidic, since they are the salt of a strong acid (HCl) and a week base ($Ca[OH]_2$). However, to reduce their (acidity) corrosiveness, the solutions are usually neutralized and made slightly basic during processing. Finally, Table 2.44 lists various physical properties of $CaCl_2$ and the calcium chloride hydrates, using the convention for thermochemical values used by the National Bureau of Standards. A negative sign indicates that the process is exothermic (gives off heat). Additional detail on thermodynamic properties is given by Sinke *et al.* (1985). Various other properties, such as sublimation pressures are given by Sommer (1958).

Table 2.34

Specific Heats of Pure Calcium Chloride Solutions

% $CaCl_2$	Specific heat in Btu per pound[a] −40°C; −40°F	−30°C; −22°F	−20°C; −4°F	−10°C; +14°F	0°C; 32°F	+10°C; 50°F	20°C; 68°F	30°C; 86°F
8					0.882	0.887	0.892	0.897
9					0.867	0.872	0.877	0.882
10					0.853	0.858	0.863	0.868
11					0.839	0.844	0.849	0.855
12					0.825	0.831	0.836	0.842
13					0.812	0.818	0.823	0.829
14					0.799	0.805	0.811	0.817
15					0.787	0.793	0.799	0.805
16				0.768	0.775	0.781	0.787	0.792
17				0.756	0.763	0.770	0.775	0.780
18				0.745	0.752	0.759	0.764	0.769
19				0.734	0.741	0.748	0.754	0.759
20				0.723	0.731	0.738	0.744	0.749
21				0.713	0.721	0.728	0.733	0.739
22			0.695	0.704	0.711	0.718	0.724	0.729
23			0.686	0.694	0.702	0.709	0.715	0.721
24			0.678	0.686	0.693	0.700	0.706	0.712
25			0.670	0.678	0.685	0.692	0.698	0.704
26		0.656	0.663	0.670	0.677	0.683	0.690	0.696
27		0.649	0.656	0.663	0.669	0.676	0.682	0.689
28	0.636	0.642	0.649	0.656	0.662	0.669	0.675	0.682
29	0.634	0.639	0.644	0.649	0.655	0.662	0.668	0.675
30	0.631	0.635	0.638	0.643	0.649	0.655	0.661	0.668

[a] International Critical Tables, vol. 2, p. 328, 1929.

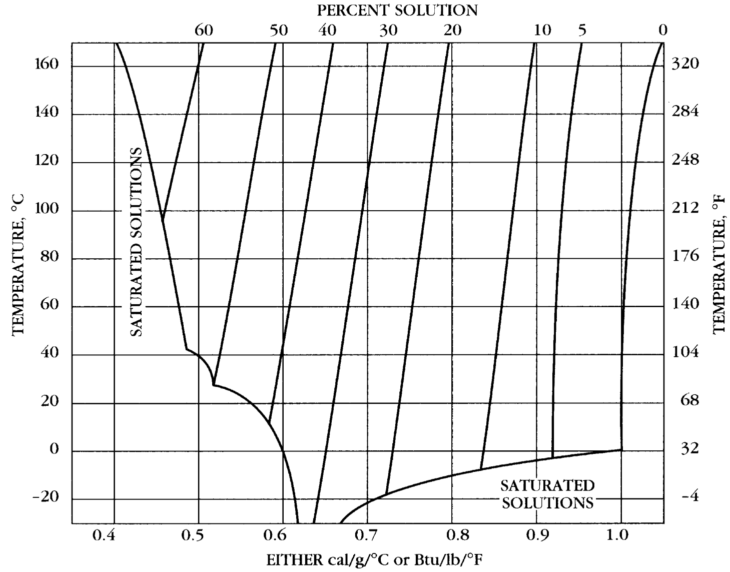


Figure 2.73 The specific heat of calcium chloride solutions, cal/g °C (Dow, 2001, courtesy of the Dow Chemical Company).

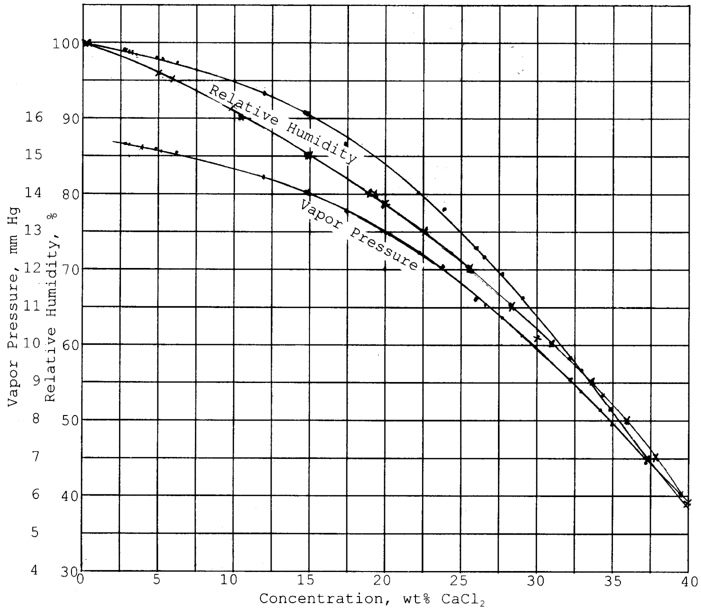


Figure 2.74 The vapor pressure and relative humidity of calcium chloride solutions at 18°C (Lannung, 1936; × = Dow, 2001).

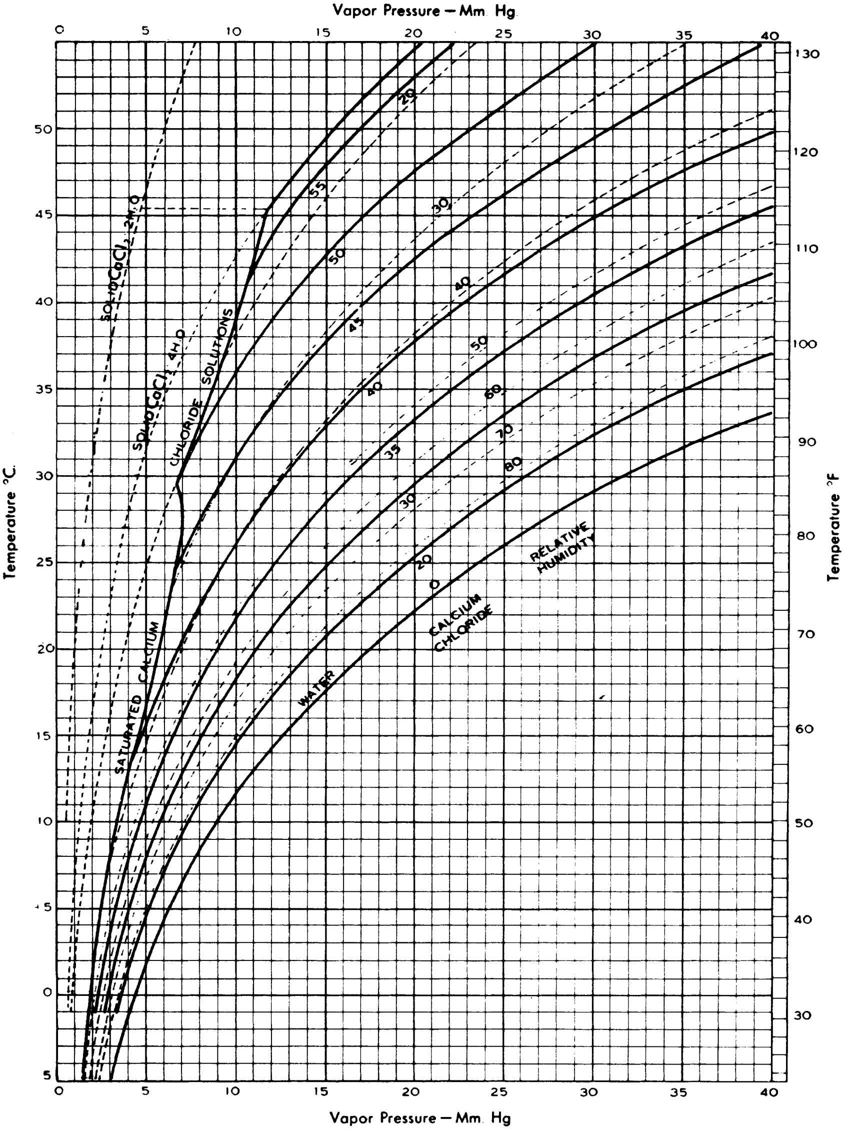


Figure 2.75 The vapor pressure of calcium chloride solutions, lower temperature range, mm Hg (Allied, 1980).

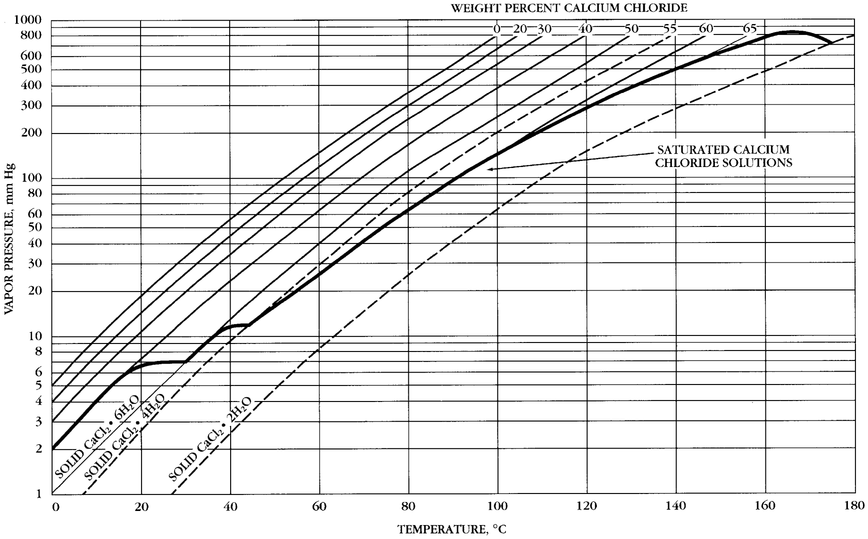


Figure 2.76 The vapor pressure of calcium chloride solutions, higher temperature range, mm Hg (Dow, 2001, courtesy of the Dow Chemical Company).

Table 2.35

Boiling Points of Calcium Chloride Solutions (Allied Chemical, 1980)

wt.% $CaCl_2$	Boiling Points (°C)
5	100.7
10	101.6
15	102.9
20	104.6
25	107.0
30	110.2
35	114.8
40	119.8
45	124.8
50	130.6
55	137.3
60	144.6
70	165

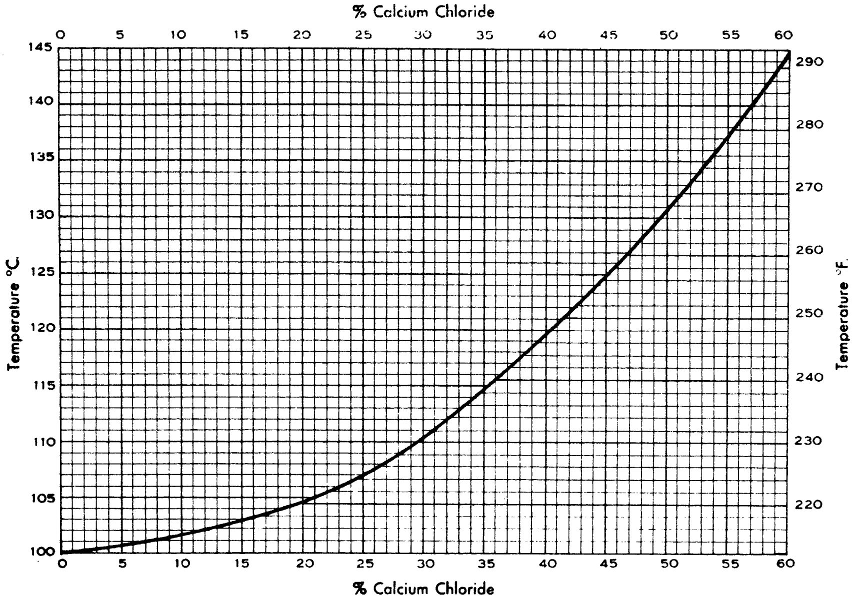


Figure 2.77 The boiling temperature of calcium chloride solutions, lower temperature range (Allied, 1980).

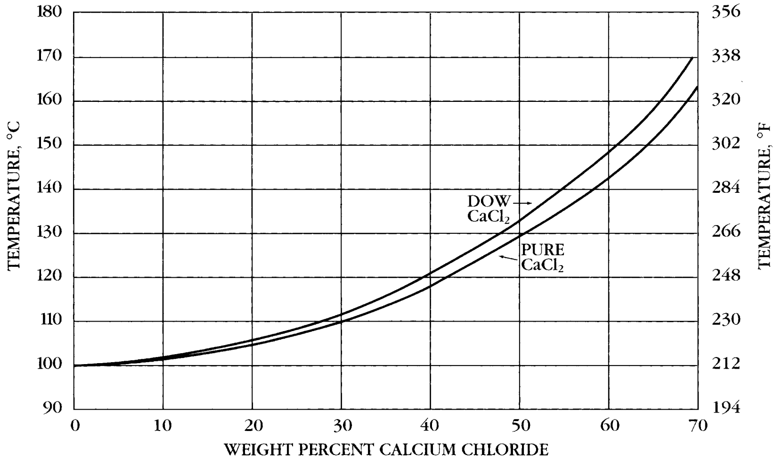


Figure 2.78 The boiling temperature of calcium chloride solutions to higher temperatures, and commercial solutions (Dow, 2001, courtesy of the Dow Chemical Company).

Table 2.36

Examples of the Vapor Pressure of Calcium Chloride Solids and Solution (Lannung, 1936)

Temperature (°C)	Pressure (mm Hg)	Relative humidity	Temperature (°C)	Pressure (mm Hg)	Relative humidity	Temperature (°C)	Pressure (mm Hg)	Relative humidity
(A) The solids $CaCl_2 \leftrightarrow CaCl_2{\cdot}H_2O\alpha$								
0	0.0075	0.00164	30	0.095	0.00298	60	0.82	0.00549
92.3	6.04	0.0105						
(B) The solids $CaCl_2{\cdot}H_2O\alpha \leftrightarrow CaCl_2{\cdot}2H_2O$								
0	0.135	0.0295	17.45	0.544	0.0364	18.5	0.594	0.0372
28.7	1.25	0.0423	31.6	1.51	0.0433	47.4	4.00	0.0492
54.1	5.97	0.0528						
(C) The solids $CaCl_2{\cdot}2H_2O \leftrightarrow CaCl_2{\cdot}4H_2O\alpha$								
0	0.244	0.0533	17.2	1.25	0.0850	18.0	1.33	0.0859
30.0	3.65	0.1147	31.7	4.28	0.1221	43.4	10.24	0.1548
(D) The solids $CaCl_2{\cdot}4H_2O\alpha \leftrightarrow CaCl_2{\cdot}6H_2O$								
0	0.60	0.1310	9.7	1.36	0.1507	17.2	2.55	0.1733
17.5	2.61	0.1740	18.0	2.73	0.1764	22.0	3.78	0.1906
28.0	6.14	0.2166						

(E) Two-phase equilibrium points with calcium chloride in water

Temperature (°C)	Solid phases	Vapor pressure (mm Hg)	Relative humidity
−49.8	Ice, $CaCl_2{\cdot}6H_2O$	0.0157	—
29.5	$CaCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}4H_2O\alpha$	6.74	0.223
45.3	$CaCl_2{\cdot}4H_2O\alpha$, $CaCl_2{\cdot}2H_2O$	11.99	0.164
175.5	$CaCl_2{\cdot}2H_2O$, $CaCl_2{\cdot}H_2O\alpha$	842	0.124
260	$CaCl_2{\cdot}H_2O$, $CaCl_2$	3-4 atm	0.08

(F) The vapor pressure of $CaCl_2$ solutions at 18°C

Concentration (wt.%)	Pressure (mm Hg)	Relative humidity	Concentration (wt.%)	Pressure (mm Hg)	Relative humidity	Concentration (wt.%)	Pressure (mm Hg)	Relative humidity
43.21	4.81	0.311	27.64	10.76	0.695	12.01	14.46	0.934
42.05	5.22	0.337	26.61	10.09	0.717	6.28	15.07	0.974
37.43	6.97	0.450	25.95	11.29	0.729	5.05	15.15	0.979
34.94	7.97	0.515	23.83	12.10	0.782	4.47	15.19	0.981
34.26	8.32	0.538	22.21	12.43	0.803	3.68	15.24	0.985
32.86	8.80	0.569	17.35	13.56	0.876	3.14	15.29	0.988
32.20	9.07	0.586	14.82	14.00	0.905	2.90	15.31	0.989
28.98	10.28	0.664	14.65	14.04	0.907	2.69	15.32	0.990

Table 2.37

Surface Tensions of Pure Calcium Chloride Solutions

	Surface tension in dynes per centimeter[a]	
% $CaCl_2$	at 10°C (50°F)	at 25°C (77°F)
0	74.22	71.97
1.10	—	72.32
2.70	—	72.75
5.26	75.74	73.49
9.99	77.42	75.17
18.17	81.12	78.87
24.98	85.22	82.97
30.75	89.17	86.92
35.69	—	90.37
43.75	—	97.07
55.42	—	106.97

[a] International Critical Tables vol. 4, p. 465, 1929.

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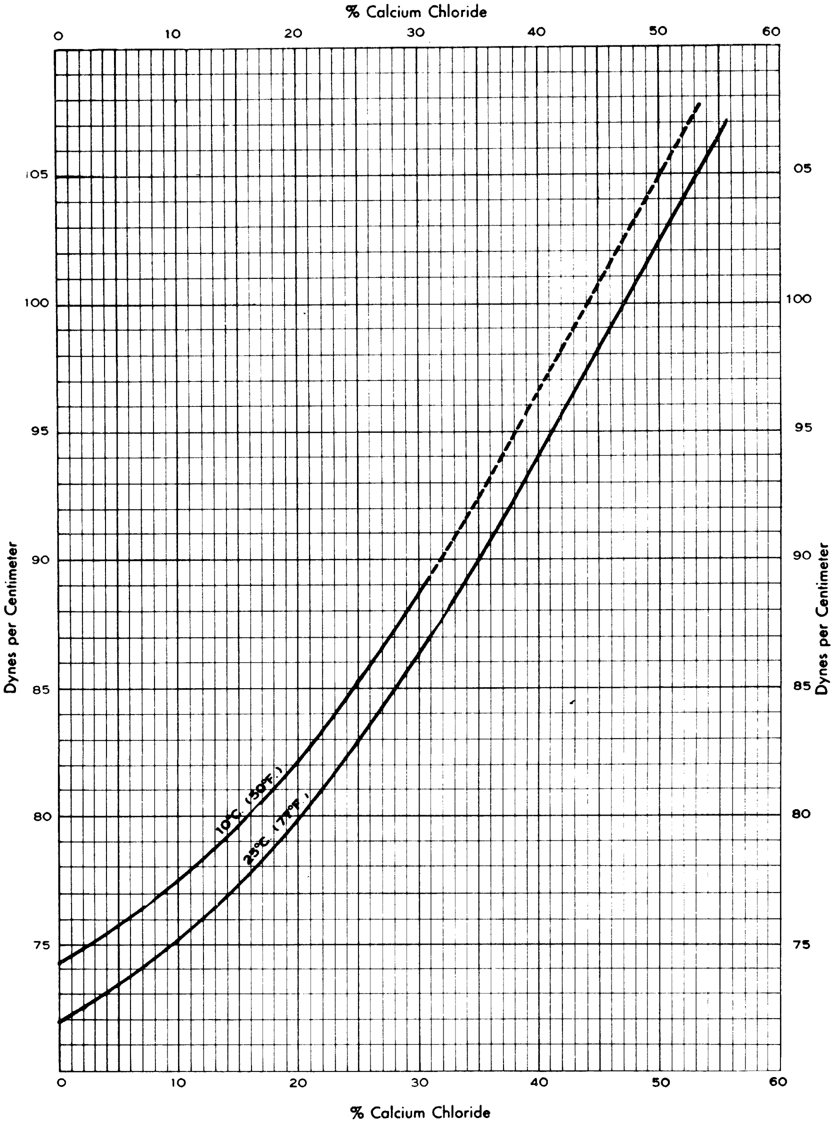

Figure 2.79 Surface tensions of pure calcium chloride solutions. International Critical Tables (1929), vol. 4. p. 465.

Table 2.38

Heat Evolved in Dissolving Anhydrous Calcium Chloride in Water

			Heat evolved					
Water per mol (111 g) $CaCl_2$			Gram calories		Btu		Approximate temperature rise calculated from previous column[a]	
Moles	Grams	% $CaCl_2$ in solution by weight	Per mol $CaCl_2$	Per gram $CaCl_2$	Per lb $CaCl_2$	Per lb solution	°F	°C
400	7200	1.5	17,921	161.5	290.6	4.4	4.5	0.25
200	3600	3.0	17,921	161.5	290.6	8.7	9	0.5
100	1800	5.8	17,754	159.9	287.9	16.7	18	1
50	900	11.0	17,635	158.9	286.0	31.4	37	20.5
20	360	23.6	17,037	153.5	276.3	65.1	92	51
10	180	38.1	15,412	138.8	249.9	95.3	160	89
6	108	50.7	13,381	120.6	217.0	110.0	200	111

[a] Assuming no heat loss. (Allied, 1980).

Table 2.39

Temperature Increase in Dissolving Regular Flake (77–80%) Calcium Chloride in Water at 60°F (Tested in Insulated Flask, Allied, 1980)

Final solution					
	Pounds regular flake $CaCl_2$			Temperature rise (approximate)	
Specific gravity at 60/60°F	Per gallon of water	Per gallon of solution	%$CaCl_2$	°F	°C
1.073	1	0.96	8.4	18	10
1.135	2	1.83	15.1	33	18
1.190	3	2.63	20.6	48	26
1.242	4	3.36	25.3	59	33
1.286	5	4.02	29.2	68	38
1.324	6	4.62	32.7	74	41
1.334	7	5.16	35.6	77	43

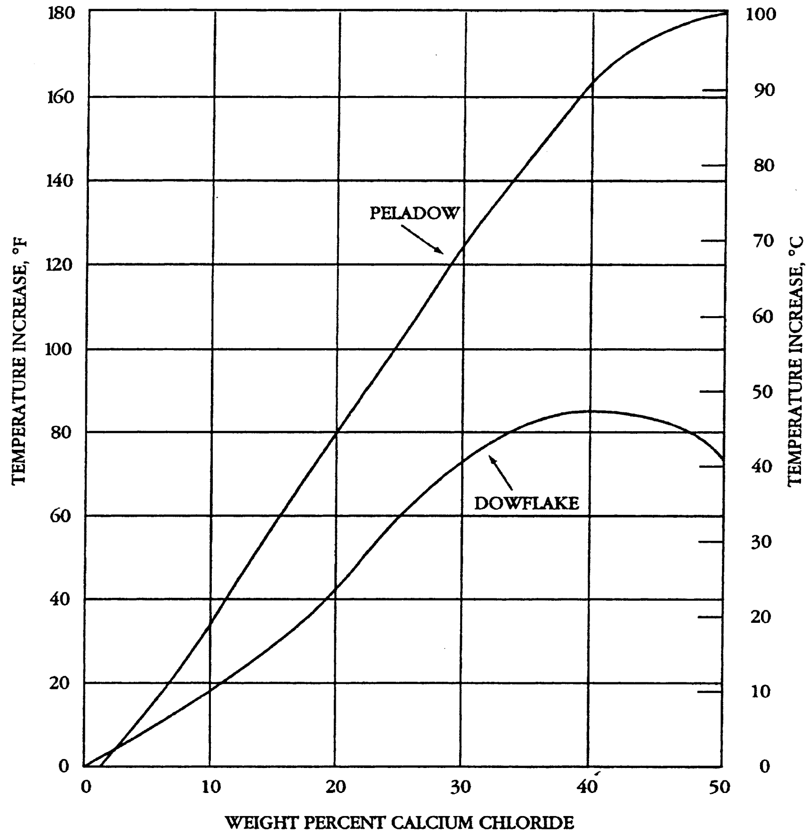

Figure 2.80 Theoretical temperature increase in dissolving Dow's 77% $CaCl_2$ Dowflake or 94% $CaCl_2$ Peladow (Dow Chemical, 2000, courtesy of the Dow Chemical Company).

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Table 2.40

Enthalpy of Pure Calcium Chloride Solutions—Btu per Pound (Allied, 1980). (Reference state = 0°C and 1 atm where heat content of liquid water equals zero; enthalpy of $CaCl_2$ solution equals its heat of solution)

Temperature		% $CaCl_2$											
°C	°F	0	5	10	12.5	15	17.5	20	22.5	25	27.5	29.8	32
30	86	54.1	64.7	75.3	80.5	85.7	90.8	96.0	101.4	106.6	111.2	115.3	118.8
25	77	45.1	56.3	67.5	73.0	78.5	83.7	89.2	94.9	100.2	105.0	109.2	112.9
20	68	36.1	47.9	59.7	65.4	71.2	76.9	82.6	88.4	93.9	98.9	103.2	107.1
15	59	27.1	39.6	51.9	58.0	64.1	69.9	75.9	81.9	87.5	92.7	97.2	101.4
10	50	18.1	31.3	44.2	50.5	56.9	63.0	69.2	75.4	81.2	86.6	91.3	95.6
5	41	9.1	23.0	36.5	43.1	49.8	56.2	62.6	68.9	75.0	80.6	85.5	89.9
0	32	0	14.7	28.8	35.7	42.7	49.3	56.0	62.5	68.7	74.5	79.6	84.2
−5	23	−146.0	−59.0	21.1	28.3	35.6	42.5	49.4	56.1	62.5	68.5	73.8	78.6
−10	14	−148.5	−91.4	−30.3	0.1	28.6	35.7	42.9	49.7	56.3	62.5	68.0	72.9
−15	5	−150.9	−105.4	−54.0	−28.3	−2.6	23.1	36.4	43.4	50.1	56.5	62.2	67.3
−20	−4	−153.2	−114.9	−68.8	−45.7	−22.6	0.4	23.5	37.1	44.0	50.6	56.4	61.7
−25	−13	−155.6	−122.6	−80.1	−58.8	−37.5	−16.2	5.1	27.1	37.9	44.6	50.5	56.1
−30	−23	−157.8	−129.3	−89.4	−69.4	−49.4	−29.4	−9.4	10.6	30.5	38.7	44.9	50.5
−35	−31	−160.1	−135.0	−96.9	−77.8	−57.8	−39.6	−20.6	−1.2	18.9	32.8	39.2	45.0
−40	−40	−162.2	−140.2	−103.3	−87.0	−66.3	−47.8	−29.4	−10.9	7.6	25.5	33.5	34.2
−45	−49	−164.4	−145.1	−109.1	−91.1	−73.1	−55.2	−37.1	−19.1	−1.2	16.9	27.8	25.0
−50	−58	−166.5	−149.7	−114.5	−97.0	−79.4	−61.8	−44.3	−26.7	−9.1	8.5	22.2	15.8
−55	−67	−168.6	−154.1	−119.7	−102.5	−85.3	−68.1	−50.9	−33.7	−21.5	0.7	16.5	6.5

Below −55°C, solid mixture of ice and $CaCl_2 \cdot 6H_2O$.

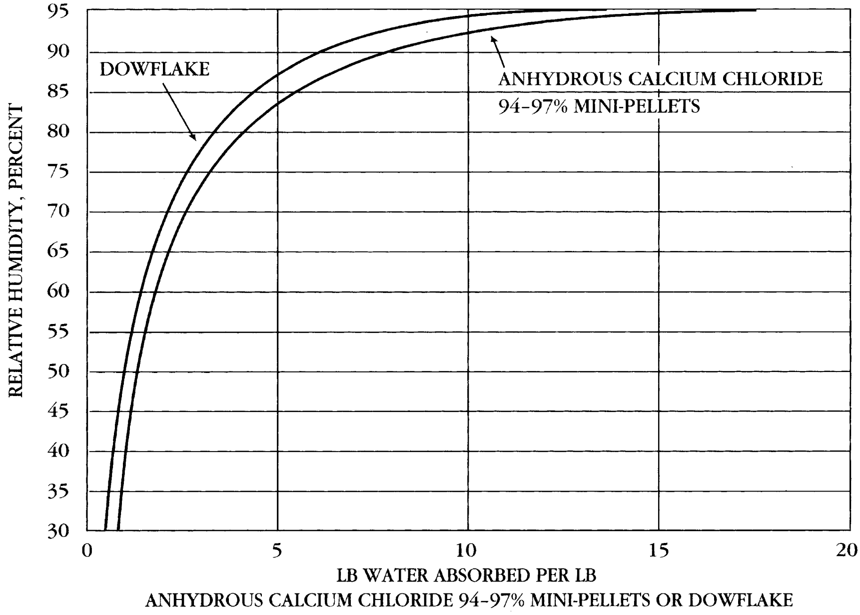

Figure 2.81 The amount of water adsorbed by commercial calcium chloride at 25°C, lbs/lb of product (Dow, 2001, courtesy of the Dow Chemical Company).

Table 2.41

Water Absorbed by Solid Calcium Chloride at Various Relative Humidities (25°C)[a]

	Final Solution		kg water absorbed/kg $CaCl_2$				
Relative humidity (%)	Concentration	% $CaCl_2$	Flake[b]			Anhydrous[c]	
	1	2	1	3	2	1	2
100	0	0	0		0	0	0
95	5.2	8.5	14.0	8.4	8.2	17.3	10.2
90	10.4	14.2	6.5	5.0	4.5	8.2	5.7
85	14.8	18.3	4.3	3.5	3.3	5.4	4.2
80	19.1	22.0	3.1	2.8	2.5	4.0	3.3
75	22.6	25.0	2.5		2.1	3.2	2.8
70	25.6	27.5	2.1	2.0	1.8	2.7	2.5
65	28.3	29.8	1.8		1.6	2.4	2.2
60	31.1	32.0	1.5	1.6	1.4	2.1	2.0
55	33.8	34.0	1.3		1.3	1.8	1.8
50	36.0	36.0	1.2		1.2	1.6	1.6
45	37.8	37.9	1.1		1.1	1.5	1.5

(*continues*)

Table 2.41

(*continued*)

	Final Solution		kg water absorbed/kg $CaCl_2$				
Relative humidity (%)	Concentration	% $CaCl_2$	Flake[b]			Anhydrous[c]	
40	39.5	39.9	1.0		1.0	1.4	1.4
36	—	—	—	1.0	—	—	—
35	41.7	42.1	0.9		0.9	1.3	1.3
30	43.9	44.5	0.8		0.8	1.2	1.1

B. Deliquescence (lowest relative humidity and temperature at which the exposed piece of anhydrous $CaCl_2$ will take up enough water to dissolve)

Relative humidity, %	20	30	40	43
Temperature, °C	37.8	23.3	6.7	5.6
°F	100	74	44	42

1 and 2 are estimates from two producers of calcium chloride, Dow and Allied Chemical (1980), respectively. 3 is from Tetra (2002).

[a] See Figs. 2.61 and 2.81 for similar data.

[b] 77–80% $CaCl_2$, average ~79.3%.

Table 2.42

Typical Densities and Freezing Points of Commercial Calcium Chloride Solutions (Dow 2001) (Courtesy of the Dow Chemical Company)

% $CaCl_2$	Approximate specific gravity at 25°C ρ_{25}^{25}	Weight (kg/liter) at 25°C ρ_{4}^{25}	Liters per metric ton of sol. at 25°C	DOWFLAKE Equiv. kg per liter of sol. at 25°C	DOWFLAKE Equiv. lbs per gal of sol. at 77°F	Freezing points (°C)	Freezing points (°F)
0	1.000	0.997	—	—	—	+0	+32
5	1.047	1.045	957	0.068	0.57	−3	+27
6	1.056	1.055	948	0.083	0.69	−4	+25
7	1.065	1.063	941	0.098	0.82	−4	+24
8	1.074	1.073	932	0.114	0.95	−5	+23
9	1.083	1.081	925	0.131	1.09	−6	+21
10	1.090	1.087	920	0.139	1.16	−7	+20
11	1.100	1.097	912	0.155	1.29	−8	+18
12	1.110	1.107	903	0.170	1.42	−9	+16
13	1.120	1.117	895	0.186	1.55	−10	+14
14	1.129	1.126	888	0.202	1.68	−11	+12
15	1.139	1.136	880	0.218	1.82	−12	+10
16	1.149	1.146	873	0.235	1.96	−13	+8
17	1.159	1.156	865	0.252	2.10	−15	+5
18	1.169	1.165	858	0.269	2.24	−17	+2

(*continues*)

Table 2.42

(*continued*)

% $CaCl_2$	Approximate specific gravity at 25°C ρ^{25}_{25}	Weight (kg/liter) at 25°C ρ^{25}_{4}	Liters per metric ton of sol. at 25°C	DOWFLAKE Equiv. kg per liter of sol. at 25°C	DOWFLAKE Equiv. lbs per gal of sol. at 77°F	Freezing points (°C)	Freezing points (°F)
19	1.179	1.175	851	0.286	2.39	−18	−1
20	1.189	1.185	844	0.304	2.53	−20	−4
21	1.199	1.195	837	0.322	2.68	−22	−8
22	1.209	1.205	830	0.340	2.83	−24	−12
23	1.219	1.215	823	0.358	2.99	−27	−16
24	1.228	1.224	817	0.377	3.14	−29	−20
25	1.240	1.236	809	0.396	3.30	−32	−25
26	1.251	1.247	802	0.416	3.47	−35	−31
27	1.263	1.259	794	0.436	3.63	−39	−38
28	1.275	1.271	787	0.456	3.81	−43	−46
29	1.287	1.283	779	0.477	3.97	−47	−53
29.6	1.294	1.290	775	0.490	4.08	−51	−60
30	1.298	1.294	773	0.498	4.15	−47	−52
31	1.310	1.306	766	0.519	4.33	−37	−34
32	1.322	1.318	759	0.541	4.51	−27	−17
33	1.334	1.330	752	0.563	4.69	−20	−4
34	1.345	1.341	746	0.585	4.87	−12	+10
35	1.357	1.353	739	0.607	5.06	−7	+20
36	1.369	1.365	733	0.630	5.25	−1	+30
37	1.381	1.377	726	0.653	5.45	+4	+39
38	1.392	1.388	720	0.676	5.64	+9	+48
39	1.404	1.400	714	0.700	5.84	+13	+55
40	1.416	1.412	708	0.724	6.04	+16	+61
41	1.428	1.424	702	0.748	6.24	+18	+65
42	1.439	1.435	697	0.773	6.44	+21	+69
45	1.474	1.470	680	0.848	7.07	+26	+78

Table 2.43

An Example of the pH of Calcium Chloride Solutions after the Addition of Sodium Hydroxide (Allied, 1980)

$CaCl_2$ (%)	0.25	0.5	1.0	1.5	3.0	4.0	5.9	10.3	15.6	20.5	25.1	30.5	40.0
pH	7.1	8.5	9.4	10.0	10.3	10.3	10.3	10.3	10.1	9.9	9.7	9.3	8.6

Table 2.44

Miscellaneous Properties of Calcium Chloride and Its Hydrates (Dow Chemical 1980, 2001)[a]

Property	$CaCl_2 \cdot 6H_2O$	$CaCl_2 \cdot 4H_2O$	$CaCl_2 \cdot 2H_2O$	$CaCl_2 \cdot H_2O$	$CaCl_2$
Percent $CaCl_2$	50.660	60.632	75.492	86.035	100.00
Molecular wt.[b]	219.075	183.0445	147.014	128.999	110.983
Melting point (°C)	29.92[c]–29.9	45.13[c]–45.3	175.5[c]–176	187,260[c]	772,782[c]
Boiling point (°C)	—	—	174–175[c]	181[c]–183	1935
Density (25°C)	1.71	1.83	1.85	2.24	2.16
	(1.7182 at 4°, 1.68 at 17°C)[c]	—	—	—	(2.152 at 15°C, 2.155 at 20°C)[c]
Heat of fusion (cal/g)	47.3[c]–50	39–40[c]	21	32	61.4[c]–61.5
	40.7[c]	—	—	—	55.0[c], 54.2[c]
Heat of solution, ∞ dil. (cal/g)	17.2	− 14.2 (0.1[c])	− 71.6[c,d]–72.8	− 96.8 (0.6[c])	− 176.2 (0.3[c])
Heat of formation (kcal/mol)	− 623.3	− 480.3 (0.17, 0.4)[c]	265.49 (0.06[c])	− 190.1 (0.6[c])	335.58 (0.23, 0.25, 0.31)[c]
Free energy, 25°C (kcal/mol)	—	—	—	—	179.8, 195.36[c]
Heat capacity, 25°C (cal/g/°C)	0.34–0.40[c]	0.32	0.28	0.20	0.16
	0.32 at 0°C[c]	—	—	—	(0.164 at 61°C[c,e])
Coefficient of expansion	—	—	—	—	0.00062[c]
Refractive findex, 20°C	—	—	—	—	1.52[c]

[a] Negative sign means that heat is evolved. The molecule $CaCl_2 \cdot 0.33H_2O$ has also been claimed with a heat of solution to infinite dilution of − 17.06 kcal/mol.

[b] 1995 revised atomic weights.

[c] Other sources (Allied Chemical, 1980, Tetra Chemicals, 1992, Sinke *et al.*, 1985, etc.)

[d] 18°C; heat of solution in 400 mol water.

[e] Heat capacity, cal/g mol/°C = 16.9 + 0.00386°K (claimed for 0–700°C). Multiply by 4.184 to convert calories to joules.

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