CALCIUM CHLORIDE

1. Introduction

Calcium chloride [10043-52-4], $CaCl_2$, is a white, crystalline salt that is very soluble in water. In its anhydrous form it is 36.11% calcium and 63.89% chlorine. It forms mono-, di-, tetra-, and hexahydrates. Calcium chloride is found in small quantities, along with other salts, in seawater and in many mineral springs. It also occurs as a constituent of some natural mineral deposits. Natural brines account for 70–75% of the United States $CaCl_2$ production.

Calcium chloride was discovered in the 15th century but received little attention or study until the latter part of the 18th century. All of the early work was done with laboratory prepared samples, since it was not produced on a commercial scale until after the ammonia–soda process for manufacture of soda ash was in operation. It was actually considered a waste product until its uses were discovered.

2. Properties

The properties of calcium chloride and its hydrates are summarized in Table 1. Accurate data are now available for the heats of fusion of the hexahydrate, the incongruent fusion of the tetrahydrate, and the molar heat capacities of the hexahydrate, tetrahydrate, and dihydrate (1). These data are important when considering the calcium chloride hydrates as thermal storage media. A reevaluation and extension of the phase relationships of the calcium chloride hydrates has led

Table 1. **Properties of Calcium Chloride Hydrates**

Property	$CaCl_2 \cdot 6H_2O$	$CaCl_2 \cdot 4H_2O$	$CaCl_2 \cdot 2H_2O$	$CaCl_2 \cdot H_2O$	$CaCl_2$
CAS Registry Number	[7774-34-7]	[25094-02-4]	[10035-04-8]	[22691-02-7]	[10043-52-4]
mol wt	219.09	183.05	147.02	129.00	110.99
composition, wt % $CaCl_2$	50.66	60.63	75.49	86.03	100.00
mp, °C	30.08	45.13	176	187	772
sp gravity, d_4^{25}	1.71	1.83	1.85	2.24	2.16
heat of fusion or transition, kJ/mol[a]	43.4[b]	30.6b	12.9	17.3	28.5
heat of solution in water[c], kJ/mol[a]	15.8	−10.8	−44.05[d]	−52.16d	−81.85[d]
heat of formation, at 25°C, kJ/mola	−2608	−2010	−1403	−1109	−795.4
heat capacity, at 25°C, J/(g·°C)a	1.66[b]	1.35b	1.17b	0.84	0.67

[a] To convert J to cal, divide by 4.184.

[b] Ref. 1.

[c] To infinite dilution.

[d] Ref. 2.

to new values for the heats of infinite dilution for the dihydrate, monohydrate, 0.33-hydrate, and pure calcium chloride (1).

A study on the solubility of calcium chloride hydrates (3) has generated polymonials relating the weight percent of anhydrous salt in a saturated solution to temperature (°C). For $9.33 < {}^{\circ}\mathrm{C} < 28.16$

$$\mathrm{wt\,\%\,CaCl_2} = 1.783 + 28.93\,t^{0.5} - 7.70\,t + 0.73\ {}^{1.5}$$

for $33.54 < t{}^{\circ}\mathrm{C} < 44.81$

$$\mathrm{wt\,\%\,CaCl_2} = -238.3 + 146.6\,t^{0.5} - 25.47\,t + 1.51\,t^{1.5}$$

for $49.37 < t{}^{\circ}\mathrm{C} < 97.65$

$$\mathrm{wt\,\%\,CaCl_2} = 39.17 + 5.28\,t^{0.5} - 0.624\,t + 0.03\,t^{1.5}$$

These three equations represent saturation with respect to the hexahydrate, tetrahydrate, and dihydrate in the temperature ranges indicated. The phase relationships among calcium chloride, its hydrates, and a saturated solution are illustrated in the diagram in Figure 1.

2.1. Calcium Chloride Solutions. Because of its high solubility in water, calcium chloride is used to obtain solutions having relatively high densities. For example, densities as high as 1430 kg/m^3 are achieved at 20°C and as high as 1570 kg/m^3 at 80°C. The oil- and gas-drilling industries frequently

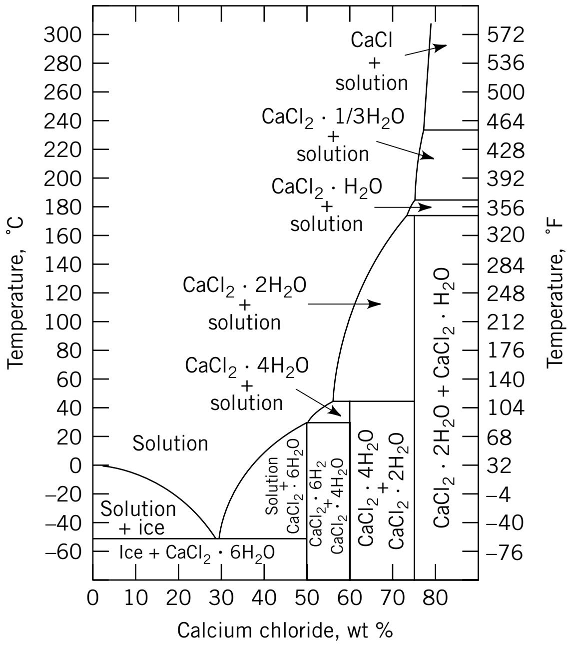

Fig. 1. The phase relationships among calcium chloride, its hydrates, and a saturated solution.

exploit these high densities when completing or reworking wells. Density, or specific gravity, can also be used to determine the molal concentration, c, of calcium chloride in water (4).

$$c = 30.8 - 129.6\,d + 180.8\,d^2 - 106.8\,d^3 + 24.89\,\mathrm{d}^4$$

where c is in units of moles of calcium chloride per kg of water and d is the specific gravity of solution relative to water at 25°C. The densities of calcium chloride solution at various wt% $CaCl_2$ values and different temperatures have been listed (5). Densities and apparent molar volumes of aqueous calcium chloride solutions at temperatures from 323 K (50°C) to 600 K (327°C) and at pressures up to 40 MPa (395 atm) have also been reported (6).

Viscosity is an important property of calcium chloride solutions in terms of engineering design and in application of such solutions to flow through porous media. Data and equations for estimating viscosities of calcium chloride solutions over the temperature range of 20–50°C are available (4). For example, at 25°C and in the concentration range from 0.27 to 5.1 molal (2.87–36.1 wt%) $CaCl_2$, the viscosity increases from 0.96 to 5.10 mPa·s (= cP).

Numerous studies on the thermodynamics of calcium chloride solutions were published in the 1980s. Many of these were oriented toward verifying and expanding the Pitzer equations for determination of activity coefficients and other parameters in electrolyte solutions of high ionic strength. A review article covering much of this work is available (7). Application of Pitzer equations to the modeling of brine density as a function of composition, temperature, and pressure has been successfully carried out (8).

3. Manufacture and Production

Calcium chloride is produced in commercial amounts using many different procedures: (*1*) refining of natural brines, (*2*) reaction of calcium hydroxide with ammonium chloride in Solvay soda and production, and (*3*) reaction of hydrochloric acid with calcium carbonate. The first two processes account for over 90% of the total calcium chloride production (9).

In the United States, the primary route for making calcium chloride is by the evaporation of underground brines. An integrated process is used to extract various brine components. Calcium chloride is derived from the brine left over after processing magnesium chloride into magnesium hydroxide. This brine is ca. 25% $CaCl_2$. A 32–45% solution is produced after being processed through a double- or triple-effect evaporator (9). Unwanted alkali chlorides are precipitated and removed. The brine is then further evaporated, attaining a 78–94% calcium chloride concentration.

Production involves removal of other chlorides (primarily magnesium) by precipitation and filtration followed by concentration of the calcium chloride solution, either for ultimate sale or for evaporation to dry product. Commercial dry products vary by the amount of water removed and by the nature of the drying equipment used. Production and capacity figures for the United States are indicated in Table 2.

Table 2. **Calcium Chloride Statistics**[a]

	Year				
	1987	1988	1989	1990	1991
no. of operations	10	10	10	9	9
production[b], t	597,000	663,000	727,000	626,000	584,000
value[c]	87,400	86,700	133,000	102,000	101,000
exports[d], t	31,496	16,974	20,316	23,300	30,568
imports for consumption, t	208,620	201,328	119,296	145,534	124,094
consumption[e]	774,124	847,354	825,950	748,980	677,526

[a] Ref. 9.

[b] Estimated based on the response of a survey of all but two operations where production from previous years, published plant capacity, and contacts within industry were used to estimate production.

[c] A large percentage of the total was estimated due to producers that did not provide this information.

[d] Bureau of Census.

[e] Consumption = Production + Imprts − Exports.

Mixed chloride brines not yet passing specifications containing calcium chloride, magnesium chloride, sodium chloride, and minor quantities of other salts are also produced in the United States in considerable quantities from natural brines and are marketed mainly in the form of brines of various concentrations.

The Solvay Process Company introduced the ammonia–soda process, which originated in Belgium in 1861, to the United States by 1881. Through a series of purchases and sales, this company now operates under the name of General Chemical with United States headquarters in Parsippany, NJ, and Canadian headquarters in Mississauga, Ontario. About 95% of synthetic calcium chloride produced is recovered from this process. The sole producer of calcium chloride in the United States by that route closed operation in the 1890s and consolidated production with Canada.

In 1896, brine was concentrated further to produce a solid containing 73–75% actual calcium chloride. In 1900, a granular product was produced, which greatly facilitated handling and dissolving. Later the granular product was replaced by flaked material containing 77–80% actual calcium chloride that, through high-temperature drying, acquires a superficial anhydrous coating, thus preventing caking.

The ammonia–soda process involves the reaction of sodium chloride (ordinary salt) with calcium carbonate (limestone) using ammonia as a catalyst to form sodium carbonate (soda ash) and calcium chloride. The process was originally designed to produce soda ash, producing calcium chloride as a waste product. However, the importance of calcium chloride has grown such that calcium chloride is now considered a co-product rather than a by-product.

Additional commercial material is available by action of hydrochloric acid on limestone. Typically the hydrochloric acid is a by-product of some other commercial process and the conversion to calcium chloride is motivated by waste avoidance.

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O$$

Significant quantities of calcium chloride are produced in the United States, Canada, Mexico, Germany, Belgium, Sweden, Finland, Norway, and Japan. In 1989 there were 10 producers of calcium chloride in the United States. In 1990 this decreased to nine, Table 2 (9). The Dow Chemical Company and Wilkinson Corporation recover calcium chloride from brines in Mason and Lapeer Counties, MI. Calcium chloride pellets, flake, and liquid were produced by Dow's Ludington plant. Wilkinson markets calcium chloride solutions. National Chloride Company of America, Cargill's Leslie Salt Company, and Hills Brothers Chemical Company also produces calcium chloride from dry-lake brine wells in San Bernadino County, CA. Hills Brothers also produced calcium chloride from an operation near Cadiz Lake, CA, and marketed calcium chloride that resulted as a by-product of magnesium production in Rowly, UT, produced by Magnesium Corporation of America.

Calcium chloride was synthesized by Tetra Chemicals at a plant near Lake Charles, LA., and from its liquid plant at Norco, LA. Calcium chloride was recovered as a by-product of the reaction of hydrochloric acid and limestone and marketed by Allied Signal (now Honeywell) Incorporated. Occidental Chemical Corporation also manufactured calcium chloride from this process in Tacoma, WI. Solution production is centered around Michigan (brines), California and Utah (brines), and Louisiana (by-product acid). Michigan is the leading state in natural calcium chloride production with California second.

Calcium chloride is odorless, colorless, and not flammable. Therefore, under current regulations by the DOT, it is not subject to specific handling regulations. Bulk rail cars, bulk trucks, box rail cars, and van and flatbed trucks transport it.

4. Economic Aspects

Calcium chloride consumption is very dependent on the weather. The deicing, dust control, and road stabilization markets are, thus, effected by these conditions. In 1990 and 1991 the winter was mild, thus hurting the deicing market. However, in 1996, production delays, a harsh winter in 1995, and early signs of another one for 1996 created some snugness in the dry calcium chloride market. As for liquid calcium chloride, which is used largely in dust control and oil-well completion, a rainy summer in 1996 reduced demand for calcium chloride as a dust-control product. Aside from yearly changes in precipitation, these markets remain fairly stable. However, oil-drilling activity has declined, slowing the expected increase in the growth of this market. Use as a concrete set accelerator should see an increase as the construction industry continues to soar. About 12% of calcium chloride goes into cement manufacture and concrete accelerating. Industry sources believe that the use of calcium chloride as a growth-enhancing macronutrient may be a future market in the agricultural sector.

There is currently an excess of capacity in the calcium chloride industry, which is only expected to become more actue as additional synthetic or by-product capacity increases. Calcium chloride production is used as a solution to the oversupply of hydrochloric acid. As processes convert from using caustic soda to using hydrated lime for propylene oxide production, an additional 225,000 tons of calcium chloride by-product has the potential for being generated

Table 3. **United States Exports of Calcium Chloride**

Country	1990 Quantity, t	1990 Value,[a] $	1991 Quantity, t	1991 Value,[a] $
Canada	16,463	3,214,953	25,006	4,467,701
Egypt	1,014	259,847	336	325,203
Mexico	250	81,370	338	217,005
Taiwan	1	3,684	1,053	263,234
Trinidad	7	8,145	546	187,094
United Arab Emirates	2,428	659,282	238	104,404
United Kingdom	561	189,082	716	211,830
other	2,576	2,197,298	2,335	2,253,710
Total	*23,300*	*6,614,664*	*30,568*	*8,030,181*

[a] U.S. Customs declared value.

(9). With capacity outweighing demand, new niche markets are being developed for using the product: mining, water treatment, fertilizer, pulp and paper, agriculture, and food-grade applications.

Table 2 gives a summary of the calcium chloride statistics for production, value, exports, imports for consumption, and consumption (9). Exports for 1990 and 1991 totaled 23,300 and 30,568 metric tons, respectively. Of this, 16,463 (70%) and 25,006 (81%) metric tons were exported to Canada. Statistics for the United States exports by country are given in Table 3. Calcium chloride canvassing discontinued beginning 1993. However, export statistics were gathered for 1999: 66,197 metric tons were exported with a value of $18,319,470 (10). Of this total, 52.5% ($9,920,969) was to Canada, 2% ($511,167) was to Mexico, 4% ($714,340) was to Trinidad, 4.78% ($631,990) was to Venezuela, 6% ($731,333) was to Italy, 4.5% ($466,411) was to the Netherlands, and 14.9% ($2,420,665) was to United Arab Emirates. The rest was in small amounts experted to other countries (10).

Estimated imports of calcium chloride increased more than ten-fold between 1984 and 1988, from 10,000 to 139,700 metric tons on a 100 wt% basis (9). The United States imports most of its calcium chloride from Canada (1990, 109,880 metric tons; 1991, 92,838 metric tons). The location of production facilities close to the United States/Canada border make this a particularly inviting country to export from because of calcium chloride's use as a deicing material. The other countries the United States imports calcium chloride from are Mexico (1989, 17,800 metric tons), the former Federal Republic of Germany (1989, 6,900 metric tons), and Sweden (1989, 4,800 metric tons). Table 4 lists the United States imports for consumption of calcium by country for 1990 and 1991. As stated previously, calcium chloride canvassing discontinued beginning 1993. However, import statistics were gathered for 1999: 219,249 metric tons were imported with a valve of $26,810,352 (10). Of this total, 78% ($14,347, 984) was from Canada, 16% ($7,160,676) was from Mexico, and 4.7% ($2,342, 994) was from Finland, with the rest being in small amounts from other countries (10).

Table 4. **United States Imports for Consuption of Crude Calcium Chloride**

	1990		1991	
Country	Quantity, t	Value,[a] $	Quantity, t	Value,[a] $
Canada	109,880	13,276,894	92,838	11,276,937
Former Federal Republic of Germany	9,471	2,264,418	13,639	2,901,992
Mexico	18,251	4,143,726	13,000	3,157,007
Sweden	2,517	291,482	3,950	612,256
other	5,415	1,364,858	667	661,960
Total	*145,534*	*21,341,378*	*124,094*	*18,610,152*

[a] U.S. Customs, insurance, freight.

5. Grades and Specifications

Most solution calcium chloride is sold as 38 or 45 wt% concentration; however, different uses require concentrations ranging from 28 to 45 wt%. The principal uses (deicing and dust control) do not require high-purity calcium chloride. However, it must be free of chemicals harmful to the environment. Producers ship the most concentrated form, and the distributors make final adjustments in concentration.

The majority of dry calcium chloride comes in one of two forms: flake or pellet. Lesser amounts are sold as minipellets, powders, or briquettes. Six agencies grade calcium chloride, Table 5. For a product containing 90.5% calcium chloride, the American Society of Testing Materials (ASTM) and the American Association of State Highway and Transportation Officials (AASHTO) has set up standards for calcium chloride content (assay), total alkali chlorides ($<8.0\%$ as NaCl), total magnesium ($<0.5\%$ as magnesium chloride), and other impurities ($<1.0\%$ after accounting for sodium, calcium, potassium, and magnesium chlorides, water, and calcium hydroxide) (9). There are three grades of commercial calcium chloride: Grade 1, 77 wt% $CaCl_2$ minimum; Grade 2, 90 wt% $CaCl_2$; and Grade 3, 94 wt% $CaCl_2$. Adjusted standards exist for all grades (17,18). Calcium chloride manufactured in the United States routinely meets these standards. Table 6 summarized sieve analysis for key commercial grades.

Calcium chloride meeting the Food Chemical Codex (FCC) specifications is used as a food additive. The specifications for this grade of anhydrous calcium chloride are as follows: assay, not less than 93.0%; arsenic (as As), <3 ppm; fluoride, $<0.004\%$; heavy metals (as Pb), $<0.002\%$; lead, <10 ppm; magnesium and alkali salts, $<5\%$; acid-insoluble material, $<0.02\%$; and no particles of sample greater than 2 mm in any dimension.

6. Environmental Concerns

Calcium chloride is not considered to be harmful to the environment. Calcium is essential for all organisms. At concentrations above 1000 ppm, calcium

Table 5. **Calcium Chloride Specifications**

Specification	Uses	Products specified	Reference
ASTM D98–87, AASHTO[a] M144–86	road conditioning/ maintenance; curing concrete	solution: unspecified concentrations; dry: three grades based on 77%, 90%, and 94% minimum assay	11, 12
AWWA[b]	treatment of municipal and industrial water supplies	dry: as flake, pellet, or granular powder or briquette	13
FCC third ed.	sequesterant in food, cross-linker, firming agent in canning, multipurpose food additive	solution: unspecified concentrations; dry: dihydrate 99–107% of formula weights; anhydrous: 93.0% $CaCl_2$ minimum	14
ACS reagent chemicals	reagent-grade desiccant-grade	dihydrate: 74–78% $CaCl_2$ not less than 96% $CaCl_2$	15
USP XXII reagent specifications	dihydrate and anhydrous for drying	use ACS specifications for dihydrate and anhydrous	16
USP XXII	general	dihydrate: 99–107% $CaCl_2 \cdot 2H_2O$; calcium chloride for injections, sterile solution in water, 95–105% of labeled $CaCl_2 \cdot 2H_2O$	

[a] AASHTO = American Association of State Highway and Transportation Officials.

[b] FOOTNOTE ID="CALCREID.A01-T005FNB">AWWA = American Water Works Association.

Table 6. **Sieve Analysis for $CaCl_2$ Commercial Grades, Mass %, Passing**[a]

	Sieve size, mm[b]					
Class, solid form	31.5	9.5	4.75 (No. 4)	2.36 (No. 8)	0.830 (No. 20)	0.600 (No. 30)
Grade 1, 77 wt% $CaCl_2$ min						
A, flake		100	80–100			0–5
B, granular		100	0–80			0–5
Grade 2, 90 wt% $CaCl_2$ min						
A, flake		100	80–100			0–5
B, pellets		100	80–100		0–10	0–5
C, granular	100		0–5			
D, powder			100	80–100		0–65
Grade 3, 94 wt% $CaCl_2$ min						
A, flake		100	80–100			0–5
B, pellets		100	80–100		0–10	0–5
C, granular	100		0–5			
D, powder			100	80–100		0–65

[a] ASTM specifications.

[b] Mesh number appears in parentheses.

chloride has been found to retard plant growth and can damage plant foliage. These effects are most likely caused by excess chloride ion as calcium is a nutrient for plants. In testing United States water supplies, high chloride concentrations are rarely found, even in areas of high salt usage for ice and dust control (19).

Calcium chloride is found in the marine environment. Many organisms and aquatic species are tolerant of the concentrations of calcium and chloride ions in seawater (400 ppm calcium, 18,900 ppm chloride ions). Toxicity arises when possible toxic doses of calcium chloride from spills, surface runoff, or underground percolation get into typically freshwater streams or aquifers. Various agencies have guidelines for calcium and chloride in potable water (20). The European Economic Community (EEC) is the only agency to have a minimum specification for calcium in softened water.

The ability of plants to take up calcium chloride (ion selectivity) and the toxicity of calcium in plants and soils varies widely. Studies of herbaceous crop species, where water defect is not a constraint, point to low levels of chloride ion as being responsible for inhibiting growth (21). However, deicing salts can be toxic to roadside vegetation. The use of both calcium chloride and sodium chloride as deicing salts and the effects on various grasses, shrubs, and trees has been studied. As calcium chloride use with sodium chloride is more effective at deicing roads, thus less is used, the overall chloride ion content is lower than with rock salt alone. From studies in Europe, calcium chloride in blends of deicing salts can have beneficial effects on the regulation of sodium, and of potassium over sodium, in spruce trees (22). Recommendations for calcium chloride tolerant species are available (23,24). Concentrations of 10,000–20,000 ppm in water have been shown to be hazardous to animals and fish. The effects vary widely, ranging from reduced growth rate and impaired reproduction to death. Both calcium chloride (35% solution) and oil-field brine received the lowest toxicity ratings in a study, indicating the environmental advantages of using these products.

7. Health and Safety Factors

In general, calcium chloride is not considered to be toxic. Because calcium chloride is hygroscopic, common safety precautions should be used: wearing gloves, long-sleeved clothing, shoes, and safety glasses. Contact with skin may cause mild irritation on dry skin. Strong solutions or solid in contact with moist skin may cause severe irritation and possibly burns (25). Calcium chloride can irritate and burn eyes from the heat of hydrolysis and chloride irritation. Inhalation may irritate the lungs, nose, and throat with symptoms of coughing and shortness of breath. Ingestion may cause irritation to the mucous membrane due to the heat of hydrolysis. Large amounts can cause gastrointestinal upset, vomiting, and abdominal pain.

Dry bulk calcium chloride can be stored in construction-grade bins. Care should be taken to minimize moisture. It should be kept in a tightly closed container, stored in a cool, dry, ventilated area.

Table 7. **$CaCl_2$ Use in the United States**

Use	Percent
deicing	30
dust control, road stabilization	25
industrial (refrigerant, coal thawing, etc)	15
oil and gas drilling fluids	10
concrete	5
tire ballast	4
miscellaneous	11

8. Uses

Calcium chloride, manufactured for over 100 years, has been used for a variety of purposes. The primary $CaCl_2$ markets have not changed since the 1950s. A breakdown of the United States consumption by percent is given in Table 7 (26). All markets and uses are summarized in Table 8. Significant markets in the United States are for deicing during winter, roadbed stabilization, and as a dust palliative during the summer. Use as an accelerator in the ready-mix concrete industry is sizable, but there is still concern about chlorine usage because of possible corrosion of steel in highways and buildings. Calcium chloride is also used in oil- and gas-well drilling.

8.1. Deicing. The largest market for calcium chloride is for deicing roads, sidewalks, and parking lots (30%). It is more effective than rock salt at lower temperatures. Calcium chloride melts ice at temperatures as low as −51°C (−60 °F). Because it liberates heat upon exposure to moisture, ice melts quickly after application. Anhydrous calcium chloride, 94–97 wt% calcium chloride pellets, and 77–80 wt% calcium chloride flakes are used for highway deicing and in institutional and consumer markets. Under normal conditions, when temperatures drop below −9°C, untreated road salt loses its ability to generate quickly the heat necessary for melting snow and ice. Calcium chloride solutions (28–32 wt%) are used with rock salt or abrasives such as sand or cinders before spreading on highways to enhance their effectiveness. The result is more efficient utilization of road salt and safer roads. Instead of watching the road salt bounce off the roads during colder days, it will be actively melting the ice and snow. Solutions of 42–45 wt% concentration are also used to pretreat stockpiles of these materials. Calcium chloride is the deicer of choice for use at temperatures <-6.7°C (27–29).

8.2. Roadbed Stabilization/Dust Control. One of the earliest uses of calcium chloride was for dust control and roadbed stabilization of unpaved gravel roads. Dust control accounts for ca. 25% of calcium chloride production. Because calcium chloride is hygroscopic and deliquescent, it absorbs moisture from the atmosphere and forms a solution, binding the dust particles and keeping the surface damp. Calcium chloride in dry and solution forms are used both typically and mixed with the aggregate. If aggregate is mixed with dry calcium chloride

Table 8. **Markets and Uses for Calcium Chloride**

Market	Use	Reason for use
building maintenance	freeze-proofing water in fire pails	lowers freezing point
chemical manufacture	production of calcium salts	source of calcium
construction	cold-weather concrete additive	accelerates set
	soil solidification	solidifies loose, sandy soils when injected together with sodium silicate
	tractor tire weighting	lowers freezing temperature of water put in tires to improve traction by incresing weight
drying air and gases	direct drying compound	removes moisture by hygroscopicity
highway construction	shoulder and base stabilization	retains moisture which improves compaction of soil
highway maintenance	dust laying	moisture absorbed from the air prevents dust formation
	snow and ice control	melts ice
mining	dust-profing and freeze-resisting ore and coal	freezing point of residual water
paper manufacture	increases web strength of corrugating media	provides artificial water hardness that allows web to drain better
	improves dye retention	provides artificial water hardness that helps set paper dyes
petroleum	additive to oil well completion fluids	increases density
	cementing finished oil wells	accelerates set of cement
	drilling mud additive	reduces shale swelling
	drying petroleum fractions	absorbs water
portland cement manufacture	additive to klin feed or fuel	reduce alkali content of cement to eliminate expansive reactions in f inished concrete
railroad right-of-way maintenance	weed-killer additive	prevents weed killer from drying out and becoming flammable
refrigeration	brine ingredient	calcium chloride brines have low freezing points
rubber manufacture	coagulating latex emulsions	coagulant
steel and pig iron manufacture	treatment of pelletized ore and blast furnace additive	elimination of alkalies that attack furnace refractory
waterwaste treatment	removal of fluorides	precipitant
	treatment of oily wastes	breaks oil emulsions
	removal of silicates	densifies floc

or a calcium chloride solution and then compacted, the presence of calcium chloride draws in moisture to bind the fine particles in the aggregate matrix. This process leads to well compacted, maximum density gravel road. Due to its low vapor pressure, calcium chloride is slow to evaporate; thus, this dust-free condition is retained over a long period of time.

8.3. Oilfield Uses. Calcium chloride has two uses in the oil field: as a primary ingredient in completion fluids and as the brine phase in an invert emulsion oil mud. An excellent review of oil-well drilling fluids is available (30).

8.4. Accelerator in Ready-Mix Concrete. Calcium chloride has been used in concrete since 1885 and finds application mainly in cold weather, when it allows the strength gain to approach that of concrete cured under normal curing temperatures. In normal conditions, calcium chloride is used to speed up the setting and hardening process for earlier finishing or mold turnaround.

Effects of calcium chloride on concrete properties are also widely studied and quantified. Aside from affecting setting time, calcium chloride has a minor effect on fresh concrete properties. It has been observed that addition of $CaCl_2$ slightly increases the workability, reduces the amount of water required to produce a given slump, and reduces bleeding. Using calcium chloride significantly reduces initial and final setting times of concrete. The total effect of adding calcium chloride depends on dosage, type of cement used, and temperature of the mix.

Addition of as little as 1–2% calcium chloride accelerates the set time of concrete, giving it a high early strength development. It is not an antifreeze, but by using it during cold weather, it can offset problems associated with lower temperatures (31). Reviews of the concerns and possible remedies of calcium chloride corrosion problems in concrete are available (32,33). There is no consensus on what the safe levels of calcium chloride in concrete are.

8.5. Food. Calcium chloride is used in the food industry to increase firmness of fruits and vegetables, such as tomatoes, cucumbers, and jalapenos, and prevent spoilage during processing. Food-grade calcium chloride is used in cheese making to aid in rennet coagulation and to replace calcium lost in pasteurization. It also is used in the brewing industry both to control the mineral salt characteristics of the water and as a basic component of certain beers.

BIBLIOGRAPHY

"Calcium Compounds (Halides)," in *ECT* 1st ed., Vol. 2, pp. 759–761, by G. H. Kimber; "Calcium Compounds (Calcium Chloride)," in *ECT* 2nd ed., Vol. 4, pp. 11–14, by R. F. Armstrong, Diamond Alkali Co.; in *ECT* 3rd ed., Vol. 4, pp. 432–436, by W. L. Shearer, Dow Chemical, U.S.A.; "Calcium Compounds, Calcium Chloride" in *ECT* 4th ed., Vol. 4, pp. 801–812, by Kenneth I. G. Reid, Roger Kust, Tetra Chemicals; "Calcium Chloride" in *ECT* (online), posting date: November 27, 2000, by Kenneth I. G. Reid, Roger Kust, Tetra Chemicals.

CITED PUBLICATIONS

1. K. K. Meissingset and F. Gronvold, *J. Chem. Thermodynam.* (18), 159–173 (1986).
2. G. C. Sinke, E. H. Mossner, and J. L. Curnutt, *J. Chem. Thermodynam.* (17), 893–899 (1985).
3. R. W. Potter and M. A. Clynne, *J. Res. U.S. Geol. Surv.* **6**(6), 701–705 (1978).
4. F. A. Goncalves and J. Kestin, *Ber. Bunsenges. Phys. Chem.* **82**(1), 24–27 (1979).

5. O. Sohnel and P. Novotny, *Densities of Aqueous Solutions of Inorganic Substances*, Elsevier, Amsterdam, The Netherlands, 1985, p. 78.
6. J. A. Gates and R. H. Wood, *J. Chem. Eng. Data*, (34), 53–56 (1989).
7. J. Ananthaswamy and G. Atkinson, *J. Chem. Eng. Data*, (30), 120–128 (1985).
8. N. P. Kemp, D. C. Thomas, G. Atkinson, and B. L. Atkinson, *SPE Prod. Eng.*, 394–400 (Nov. 1989).
9. M. Miller, "Calcium and Calcium Compounds,"*Minerals Yearbook*, Vol. **1**, U.S. Bureau of Mines, U.S. Department of the Interior, Washington, D.C., 1991, pp. 317–324.
10. Statistics for 1999 collected by M. Michael Miller, U.S. Geological Survey, 2000.
11. *ASTM Standard D98-87 Standard Specifications for Calcium Chloride*, Issue 90-06, American Society of Testing Materials, Information Handling Services, Englewood, Colo., Dec. 1990–Jan. 1991.
12. *Standard Specifications for Calcium Chloride*, American Association of State Highway and Transportation Officials, 14th ed., Part I, M144-86, Washington, D.C., 1986, 209–211.
13. *Calcium Chloride*, 2nd ed., Standard B550-90, American Water Works Association, Denver, Colo., 1990.
14. *Food Chemicals Codex*, 3rd ed., National Research Council, National Academy Press, Washington, D.C., 1981, 47–49.
15. Committee on Analytic Reagents, *American Chemical Society, Specifications*, 6th ed., American Chemical Society, Washington, D.C., 1981.
16. *United States Pharmacopeia XXII*, United States Pharmacopeial Convention, Inc., Rockville, Md., 1989.
17. *ASTM Standard D98-87: Standard Specification for Calcium Chloride*, Issue 90-06, American Society of Testing Materials, Information Handling Services, Englewood, Colio., Dec. 1990–Jan. 1991.
18. *Standard Specifications for Calcium Chloride*, American Association of State Highway and Transporation Officials, 14th ed., Part 1, M144-86, Washington, D.C., 1978.
19. F. E. Hutchinson, *The Influence of Salts Applied to Highways on the Levels of Sodium Chloride Ion Present in Water and Soil Samples*, U.S. Department of the Interior, Project No. A-007-ME,U.S. Government Printing Office, Washington, D.C., June 1969.
20. F. W. Pontius, ed.,*Water Quality and Treatment; A Handbook of Community Water Supplies*, American Water Works Association, 4th ed., McGraw-Hill, Inc., New York, 1990, pp. 8–59.
21. H. Greenway and R. Munns, *Annu. Rev. Plant Physiol.* **31**, 149–190 (1980).
22. J. Boegemans, L. Neimnckx, and J. M. Stassart, *Plant Soil* **113**, 3–11 (1989).
23. R. E. Hanes and co-workers, in *National Copperative Highway Research Program Report 170*, Transportation Research Board, National Research Council, Washington, D.C., 1976, p. 88.
24. R. Paul, M. Rocher, and R. Impens, *Sci. Total Environ.* **59**, 277–282 (1987).
25. *Calcium Chloride MSDS*, Mallinckrodt Baker, Inc., Phillipsburg, NH, 2000.
26. In W. Gerhartz, ed., *Ullmann's Encyclopedia of Industrial Chemistry*, 4th ed., Vol. **A4**, Weinheim, Germany; Deerfield Beach, FL, 1995, pp. 547–553.
27. G. C. Sinke and E. H. Mossner, *Transportation Research Record, 598*, Transportation Research Board, National Research Council, Washington, D.C., 1976, pp. 54–57.
28. A. D. McElroy and co-workers, *Transportation Research Record, 1157*, Transportation Research Board, National Research Council, Washington, D.C., 1988, pp. 1–11.
29. *Public Works* **119**, 80–81 (July 1988).
30. G. R. Gray and H. C. H. Darley, *Composition and Properties of Oil Well Drilling Fluids*, 4th ed., Gulf Publishing, Houston, Texas, 1980.

31. National Ready Mixed Concrete Association; *Cold Weather Ready Mixed Concrete*, Silver Spring, Md., 1968, pp. 11–12.
32. ACI Committee 222, *Corrosion of Metal in Concrete*, ACI 222R-85 (89), American Concrete Institute, Detroit, Mich., 1989, p. 30.
33. F. W. Gibon, ed., *Corrosion, Concrete and Chlorides*, ACI SP-102, American Concrete Institute, Detroit, Mich., 1987.

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