

CALCIUM COMPOUNDS, SURVEY

The chemical element calcium [7440-70-2], Ca, atomic number 20, is an alkaline-earth metal which is fifth in abundance among all elements (ca 4%) and the third most abundant metal found in the earth's crust (1). It is too reactive to be found naturally in the free state, but its compounds are widespread as the minerals listed in Table 1 indicate. Calcite [13397-26-7], CaCO_3 , found as limestone, marble, and chalk, makes up approximately 7% of the earth's crust. Gypsum [13397-24-5], $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, fluor spar or fluorite [7789-75-5], CaF_2 , and dolomite [16389-88-1], $\text{CaCO}_3 \cdot \text{MgCO}_3$, are other minerals that occur in sufficient quantities to serve as sources for elemental calcium. Lime feldspar [1302-54-1] (anorthite), $\text{CaAl}_2\text{Si}_2\text{O}_8$, accounts for more than half of the feldspars, which in turn make up some 60% of igneous rocks, eg, basalt and granite (2).

The oceans contain vast quantities of ionic calcium, Ca^{2+} , to the extent of 400 mg/L of seawater (3). Calcium is present in living organisms as a constituent of bones, teeth, shell, and coral. It is essential to plant as well as animal life.

Limestone and marble have been mined as building materials and the oxide of calcium, lime [1305-78-8], has been used in the manufacture of mortar for centuries (see Building materials, survey; Lime and limestone). Lime-burning was one of the first industries in the American colonies, where calcining of limestone was accomplished in kilns dug out of the sides of hills.

As befits the electron configuration of elemental calcium, the metal is very reactive, readily losing two valence electrons to form the dispositive ion. In aqueous solution and in its compounds, Ca^{2+} is colorless. Most calcium compounds are white, unless the cation is paired with a colored anion. The ion has only a weak tendency toward covalent bond formation.

Calcium reacts readily with water, oxygen, sulfur, and the halogens to form the respective ionic compounds calcium hydroxide [1305-62-0], $\text{Ca}(\text{OH})_2$, calcium oxide [1305-78-8], CaO , calcium sulfide [20548-54-3], CaS , and the calcium halides, CaX_2 , where $\text{X} = \text{F}$ [7789-75-5], Cl [10035-04-8], Br [7774-34-7], or I [10102-68-8]. This reactivity of the metal prevents it from being kept in air for any appreciable length of time. At elevated temperatures, calcium also combines directly with nitrogen, hydrogen, and carbon to form calcium nitride [12013-82-0], Ca_3N_2 , calcium hydride [7789-78-8], CaH_2 , and calcium carbide [75-20-7], CaC_2 , respectively.

1. Inorganic Compounds

1.1. Calcium Carbonate

Limestone is the most widely used of all rocks, as such for dimension stone or aggregate in concrete and road building, or as an industrial chemical and precursor of lime and hydrated lime. Calcium carbonate acts as a base in its application as a soil conditioner (agricultural lime is actually limestone), neutralizer of surface waters, industrial acid neutralizer, and in a limestone slurry as a stack gas scrubber to remove SO_2 (see Sulfur removal and recovery). Fluidized-bed combustion of coal using an admixture of pulverized limestone can be used to trap SO_2 before it reaches the exhaust stacks (see Coal conversion processes). Precipitated calcium

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Table 1. Calcium-Containing Minerals

Mineral	CAS Registry Number	Molecular formula
marble		CaCO ₃
limestone		CaCO ₃
calcite	[13397-26-7]	CaCO ₃
dolomite	[17069-72-6]	CaCO ₃ ·MgCO ₃
gypsum	[13397-24-5]	CaSO ₄ ·2H ₂ O
anhydrite	[14798-04-0]	CaSO ₄
fluorspar	[7789-75-5]	CaF ₂
fluorapatite	[1306-05-4]	Ca ₅ F(PO ₄) ₃
hydroxylapatite	[1306-06-5]	Ca ₅ OH(PO ₄) ₃
selenite	[15698-85-8]	CaSO ₄ ·2H ₂ O
anorthite	[1302-54-1]	CaAl ₂ Si ₂ O ₈

carbonate [471-34-1], formed from carbonating suspensions of calcium hydroxide, is finding application as a mineral filler to give brightness and opacity to acid-free paper (4). Limestone is also used as a metallurgical flux.

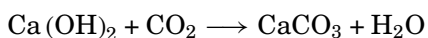
1.2. Lime and Hydrated Lime

Lime, CaO, production in the United States in 1990 amounted to 15,820 metric tons ranking it fifth in tonnage of manufactured chemicals (5). More than 90% of the lime consumed in the United States is used for basic or industrial chemistry. It is produced by thermal decomposition (calcination) of calcium carbonate in various forms including limestone, marble, chalk, oyster shells, and dolomite. Although some purposes require 100% CaO lime, quicklimes used industrially almost always contain impurities such as MgO, SiO₂, Fe₂O₃, Al₂O₃, H₂O, and CO₂ (6). Quicklime containing less than 5% MgO is classified as high calcium lime, that which contains between 5 and 35% MgO, usually between 5 and 10%, is classified as magnesian lime, and lime containing more than 35% MgO, typically between 35 and 40%, is classified as dolomitic lime. Lime is strongly alkaline and has a negative temperature coefficient of solubility.

The hydrolysis process, ie, reaction with water, for lime is called slaking and produces hydrated lime, Ca(OH)₂. Calcium hydroxide is a strong base but has limited aqueous solubility, 0.219 g Ca(OH)₂/100 g H₂O, and is therefore often used as a suspension. As an alkali it finds widespread industrial application because it is cheaper than sodium hydroxide.

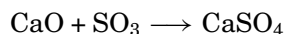
1.2.1. Mortar

Mortar, principally slaked lime and sand, sets because of the evaporation of water, the deposition of calcium hydroxide, and the absorption of water by the bricks or cement blocks, followed by hardening as a result of the absorption and reaction of carbon dioxide.

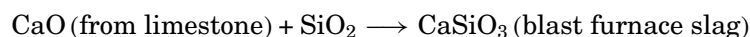


1.2.2. Metallurgy

Calcium oxide reacts readily with acid anhydrides:



Reactions of this type are important in high temperature metallurgical processes in which CaO, which may be produced by decomposition of CaCO_3 , reacts with and removes acidic impurities, eg, in the pig-iron blast furnace(6).



In modern steel (qv) manufacture, pebble quicklime is used as a flux in the basic oxygen, basic open-hearth, basic Bessemer, and basic electric furnaces.

1.2.3. Treatment of Industrial Wastes

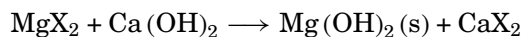
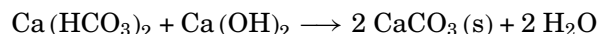
The alkaline nature and inexpensive price of lime make it ideal for treatment of acid waste liquors (6), including waste pickle liquids from steel plants, wastes from metal plating operations, eg, chrome and copper plating, acid wastes from chemical and explosives plants, and acid mine wastewaters.

Great quantities of stack gases containing acidic substances such as H_2S and SO_2 are produced in the smelting and refining of nonferrous metals such as copper, zinc, and lead obtained from sulfide ores. These can be trapped by stack gas scrubbers as a fine spray of lime, or limestone slurry in water is passed down the stack while the hot acidic gases are passing upwards. Control of emission of acid gases, primarily sulfur dioxide, from fossil fuel power plants is also accomplished with $\text{Ca}(\text{OH})_2$ scrubbers (see Air pollution control methods). By-product calcium sulfite [10257-55-3], CaSO_3 , from this process must be dewatered (see Dewatering) and eventually disposed of on land.

Cement (qv) and lime-based technologies are used to immobilize fly ash, cement kiln dust, ground blast furnace slag, and the sludges of sulfides, hydroxides, and phosphates of heavy metals, but not organic wastes that inhibit the setting process. Treatment of the concrete clinker with a sealant may be beneficial when acid leaching is a potential problem (7). Quicklime may be useful in chemically treating polychlorinated biphenyls (PCBs). The success of lime treatment of PCBs has been questioned, however (8).

1.2.4. Treatment of Municipal and Industrial Water Supplies

Hard water (qv) contains dissolved solids, chiefly calcium and magnesium salts. Water hardness results in the formation of insoluble curd from soap, decreased efficiency of detergents, and in the formation of mineral deposits that coat the surfaces of hot water systems, thereby clogging pipes and reducing heating efficiency. Feedwater softening treatment is necessary for boiler water and for water used in dyeing and other textile processing operations. On a large scale, the lime water-softening process is used to remove calcium and magnesium ions from water:



where $\text{X} = \text{Cl}^-$, NO_3^- , HCO_3^- , $1/2 \text{SO}_4^{2-}$, $1/2 \text{CO}_3^{2-}$. The composition of the raw hard water must be monitored so that an excess of slaked lime is not added.

1.2.5. Other Applications

Among other industrial uses of lime are: causticizing agent in kraft (sulfate) paper (qv) plants; recovery of ammonia (qv) from NH_4Cl (Solvay process); recovery of magnesium (qv) from seawater and brines via precipitation of $\text{Mg}(\text{OH})_2$; production of pesticides such as calcium arsenate, lime-sulfur sprays, and Bordeaux mixture, which is copper sulfate and lime in water; and neutralizing acid soils (6, 9, 10). Lime is used in the

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manufacture of several products: in pigments (qv), where satin white is calcium aluminate-hydrated calcium sulfate; in protective and bonding agents for water paints (qv) to serve as rust inhibitor, fire resistance, waterproofing agent, and disinfectant; in glues, such as calcium caseinate; and in gelatin. It is used in refining of beet and cane sugar (qv) and in the treatment of corn prior to conversion to corn meal for tortillas.

1.3. Halogen Compounds

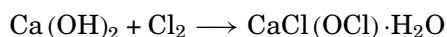
1.3.1. Halides

Calcium halides are made by reaction of elemental calcium and the halogens directly or more conveniently by the reaction of the corresponding hydrohalic acid and CaCO_3 , CaO , or Ca(OH)_2 .

Fluorspar [7789-75-5], CaF_2 , is used as a flux in metallurgical processes such as production of steel in the open-hearth furnace. Pure crystals of this salt have applications in spectroscopy where transparency to visible and ultraviolet radiation is a requirement. CaF_2 is also the precursor for HF (see Fluorine compounds, inorganic) and fluorine (qv). CaCl_2 in its anhydrous form finds application as an industrial and laboratory drying agent because of its deliquescent properties. Water- CaCl_2 solutions are used as refrigeration fluids.

1.3.2. Hypochlorites

A common dry form of chlorine used as a bleach or water purifier is made by reaction of gaseous chlorine and high calcium hydrated lime:

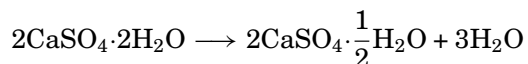


This product, called chloride of lime [67560-00-3] or bleaching powder, has about 35% available chlorine.

Another bleaching agent, calcium hypochlorite [7778-54-3], Ca(OCl)_2 , available chlorine ca 70%, can be made by salting out from a solution of bleaching powder with NaCl. In contrast with bleaching powder, calcium hypochlorite does not decompose on standing (see Bleaching agents).

1.4. Sulfates and Sulfites

Calcium sulfate [7778-18-9] occurs in large deposits as CaSO_4 and as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The dihydrate is a functional additive in Portland cement to control setting time. Gypsum loses some of its water of hydration on heating to near 100°C and forms plaster of Paris, the hemihydrate, approximately as shown:



The reaction reverses when water is added to plaster of Paris and the mixture sets back to the dihydrate accompanied by a slight increase in volume and the evolution of heat.

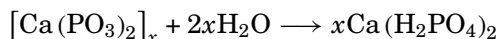
Calcium sulfite [10257-55-3] and acid sulfite may be prepared by reaction of SO_2 and hydrated lime or limestone. Calcium acid sulfite [13780-03-5], $\text{Ca(HSO}_3)_2$, has been used to remove lignin (qv) from wood pulp in paper manufacture (6) (see Paper; Pulp).

1.5. Phosphates

The primary constituent of phosphate rock is fluorapatite, $\text{Ca}_5\text{FP}_3\text{O}_{12}$. Industrial phosphates including phosphate fertilizers (qv), phosphoric acid, and calcium phosphates (11) (see Phosphoric acid and the phosphates) are obtained from the large deposits of fluorapatite found in Florida in the United States, and in Morocco. Because phosphate rock is too insoluble to be useful as a fertilizer, it is converted to superphosphate [12431-88-8],

$\text{Ca}(\text{H}_2\text{PO}_4)_2 + 2 \text{CaSO}_4$, by H_2SO_4 and to triple superphosphate [7758-23-8], $\text{Ca}(\text{H}_2\text{PO}_4)_2$, by H_3PO_4 (12). Phosphoric acid may also be produced from phosphate rock by reaction with H_2SO_4 .

Calcium metaphosphate [13477-39-9] is made by reaction of P_2O_5 in HPO_3 with rock phosphate. The insoluble, polymeric product must be hydrolyzed before it can act as a fertilizer (13):



Monocalcium phosphate [10031-30-8], $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, used in baking powder (see Bakery processes and leavening agents), is crystallized from a hot reaction mixture of concentrated (electric furnace) phosphoric acid and lime, or it is made by spray-drying a slurry of the product of reaction of lime and phosphoric acid (14).

1.6. Calcium Magnesium Acetate

Calcium magnesium acetate [76123-46-1] (CMA), suggested formula $\text{CaMg}_2(\text{C}_2\text{H}_3\text{O}_2)_6$ (15), is an emerging bulk chemical that has found application as a replacement for salt and calcium chloride as a less corrosive and biodegradable road deicer. CMA has been used as a precursor for calcination processes and to capture sulfur during the combustion of lower grade coals.

1.7. Hydride

Calcium hydride [7789-78-8], CaH_2 , is an effective reducing agent at high temperatures and has been used to reduce inorganic oxides to their metals. The hydride, which evolves hydrogen smoothly on reaction with water, has found application as a convenient solid source for hydrogen gas. The compound is a convenient drying agent for gases and organic solvents.

1.8. Silicates

1.8.1. Glass

Ordinary glass (qv), soda-lime glass, is a complex mixture of silicates, chiefly those of sodium and calcium [1344-95-2] (6, 9). Lime, usually dolomitic lime, follows sand, soda ash, and limestone as the fourth most important raw material in the manufacture of glass. The selection of lime versus limestone as starting material is frequently decided by the design of the manufacturing plant.

1.8.2. Portland Cement

Portland cement is obtained by calcining a mixture of substances to produce an appropriate ratio of the oxides CaO , MgO , Al_2O_3 , Fe_2O_3 , and SiO_2 (9) (see Cement).

1.8.3. Whitewares (Earthenware, China, Porcelain)

The chief raw materials of ceramic manufacture are clay, feldspar, and sand (9). All of the three common types of feldspars are used: soda, potash, $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, $\text{M} = \text{Na}$, K , and lime (see Ceramics; Enamels). Clays (qv), hydrated aluminum silicates such as kaolinite [1318-74-7], $\text{Al}_2(\text{Si}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$, are formed by the weathering of igneous rocks such as feldspars (6). Fluxing agents include the calcium compounds apatite, fluor spar, and calcined bones (mainly apatite). Special refractory ingredients may be lime, limestone, or dolomite.

1.8.4. Calcium Silicate Brick

Sand-lime brick is used in masonry in the same way as common clay brick. The bricks, molded from a wet mixture of sand and high calcium hydrated lime, are heated under pressure in a steam atmosphere. Complex hydrosilicates are formed that give the bricks high dimensional stability (6).

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2. Coordination Chemistry of Calcium

Calcium ion shows some tendency to form complexes mainly through coordination with oxygen-containing ligands. An important example is citrate which chelates Ca^{2+} in water solution and can reduce the effective calcium ion concentration in blood below the level that results in triggering the coagulation process (see Blood, coagulants and anticoagulants). Ethylenediaminetetraacetate (EDTA, Versene, Sequestrene)



has an extremely large formation constant for its 1:1 complex with Ca^{2+} (11) (see Chelating agents). EDTA is also used as an anticoagulant for stored blood and as a reagent in volumetric analysis for calcium ion.

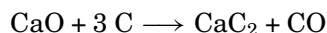
Ca^{2+} can be complexed by crown ethers and cryptate ligands and in this form can be transported across natural and artificial membranes.

A few calcium complexes having nitrogen ligands are known. Calcium halides form addition complexes with NH_3 such as $\text{CaCl}_2 \cdot n\text{NH}_3$ ($n = 2, 4, 8$) and $\text{CaBr}_2 \cdot n\text{NH}_3$ ($n = 2, 4, 6, 8$). Hexaammine calcium [12133-31-2], $\text{Ca}(\text{NH}_3)_6$, is formed by reaction of calcium metal and anhydrous NH_3 (11) (see Coordination compounds).

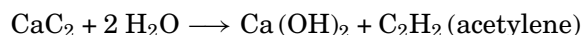
3. Organic Chemistry of Calcium

3.1. Calcium Carbide and its Derivatives

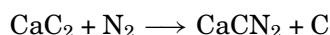
Although hydrocarbon-based acetylene production has become more important, early manufacture of acetylene was based on manufacture of the intermediate, calcium carbide [75-20-7], CaC_2 . This ionic acetylide is produced by reaction of lime and carbon in electric-arc furnaces (16).



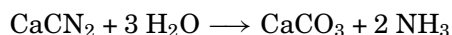
Calcium carbide can be treated with water to produce acetylene from which other organic compounds, eg, ethanol, acetaldehyde, may be obtained (6) (see Acetylene-derived chemicals; Carbides).



Calcium carbide is also used to produce calcium cyanamide [156-62-7], CaCN_2 , (see Cyanamides).



Calcium cyanamide (lime nitrogen) has been used as a fertilizer (6). It hydrolyzes in moist soil to produce ammonia:



Calcium cyanamide can be converted to calcium cyanide [592-01-8], used in cyanidation of metallic ores and production of sodium cyanide and ferrocyanides (11) (see Cyanides). Calcium cyanamide has also been used to make cyanamide which in turn is the starting material for important industrial organic syntheses.

3.2. Salts of Organic Acids

Calcium salts of organic acids may be prepared by reaction of the carbonate hydroxide and the organic acid (9). Calcium lactate [814-80-2] is an intermediate in the purification of lactic acid from fermentation of molasses. Calcium soaps, soaps of fatty acids, are soluble in hydrocarbons, and are useful as waterproofing agents and constituents of greases (9).

In production of sugar, the juice extracted from the sugar cane or sugar beets is treated with a suspension of $\text{Ca}(\text{OH})_2$, which neutralizes the syrup acidity and precipitates calcium sucate, leaving impurities in the solution. This is filtered and the calcium sucate is converted to sugar and CaCO_3 by reaction with CO_2 .

3.3. Reagents in Synthesis

Calcium borohydride [17068-95-0], $\text{Ca}(\text{BH}_4)_2$, produced by reaction of NaBH_4 and CaCl_2 , has been used for reductions (see Hydrides). Hexaamminecalcium [12133-31-2], prepared by passing NH_3 into an ether suspension of calcium, reduces polycyclic aromatic compounds leaving one isolated aromatic ring. Calcium hydride, CaH_2 , and anhydrous calcium sulfate (Drierite), CaSO_4 , are useful as drying agents (17).

3.4. Organometallic Chemistry

Only a few organocalcium compounds have been reported. Alkyl calcium halides have been prepared by reaction of the halides and calcium in tetrahydrofuran (17).

4. Biological Role of Calcium

Biological functions of $\text{Ca}(\text{II})$ ion are numerous but may be classified in one of three categories: the formation of solid skeletal material such as bone, teeth, and shell; the stabilizing of protein conformational structure; and the most varied, the ability of $\text{Ca}(\text{II})$ to trigger certain physiological activities such as muscle contraction and the release of hormones (qv).

The insoluble $\text{Ca}(\text{II})$ salts of weak acids, such as calcium phosphate, carbonate, and oxalate, serve as the hard structural material in bone, dentine, enamel, shells, etc. About 99% of the calcium found in the human body appears in mineral form in the bones and teeth. Calcium accounts for approximately 2% of body weight (18, 19). The mineral in bones and teeth is mostly hydroxyapatite [1306-06-5] having unit cell composition $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. The mineralization process in bone follows prior protein matrix formation. A calcium pumping mechanism raises the concentrations of $\text{Ca}(\text{II})$ and phosphate within bone cells to the level of supersaturation. Granules of amorphous calcium phosphate precipitate and are released to the outside of the bone cell. There the amorphous calcium phosphate, which may make up as much as 30–40% of the mineral in adult bone, is recrystallized to crystallites of hydroxyapatite preferentially at bone collagen sites. These small crystallites do not exceed 10 nm in diameter (20).

The $\text{Ca}(\text{II})$ concentration in blood is closely controlled: normal values lie between 2.1 and 2.6 mmol/L (8.5–10.4 mg/dL) of serum (21). The free calcium ion concentration is near 1.2 mmol/L; the rest is chelated with blood proteins or, to a lesser extent, with citrate. It is the free $\text{Ca}(\text{II})$ in the serum that determines the calcium balance with the tissues. The mineral phase of bone is essentially in chemical equilibrium with calcium and phosphate ions present in blood serum, and bone cells can easily promote either the deposition or dissolution of the mineral phase by localized changes in pH or chelating compounds. Treatment for osteoporosis, the loss of bone mineral that occurs in the aged, especially in postmenopausal women, commonly includes dietary calcium supplements. Excessive calcium ingestion can lead to a problem for those prone to stone formation in the urinary tract.

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Three hormones regulate turnover of calcium in the body (22). 1,25-Dihydroxycholecalciferol is a steroid derivative made by the combined action of the skin, liver, and kidneys, or furnished by dietary factors with vitamin D activity. The apparent action of this compound is to promote the transcription of genes for proteins that facilitate transport of calcium and phosphate ions through the plasma membrane. Parathormone (PTH) is a polypeptide hormone secreted by the parathyroid gland, in response to a fall in extracellular Ca(II). It acts on bones and kidneys in concert with 1,25-dihydroxycholecalciferol to stimulate resorption of bone and reabsorption of calcium from the glomerular filtrate. Calcitonin, the third hormone, is a polypeptide secreted by the thyroid gland in response to a rise in blood Ca(II) concentration. Its production leads to an increase in bone deposition, increased loss of calcium and phosphate in the urine, and inhibition of the synthesis of 1,25-dihydroxycholecalciferol.

Calcium is essential to several steps in the enzyme cascade of the blood clotting process, such as the conversion of prothrombin to thrombin (23). Clotting can be inhibited in stored blood supplies by addition of complexing agents such as EDTA or citrate which reduce the levels of the free ion, Ca(II).

Calcium is the trigger behind the muscle contraction process (24, 25). Neural stimulation activates the release of stored Ca(II) resulting in a dramatic increase in free calcium ion levels. The subsequent binding of Ca(II) resulting in a dramatic increase in free calcium ion levels. The subsequent binding of Ca(II) to the muscle protein troponin C provides the impetus for a conformational change in the troponin complex and sets off successive events resulting in muscle contraction.

The influx of Ca(II) across the presynaptic membrane is essential for nerve signal transmission involving excitation by acetylcholine (26). Calcium is important in transducing regulatory signals across many membranes and is an important secondary messenger hormone. The increase in intracellular Ca(II) levels can result from either active transport of Ca(II) across the membrane via an import channel or by release of Ca(II) from reticulum stores within the cell. More than 30 different proteins have been linked to regulation by the calcium complex with calmodulin (27, 28).

The recommended daily allowances of calcium are: children to 10 years of age, 360–800 mg; teenage children, 1200 mg; adults, 800 mg, increasing to 1200 mg during pregnancy and lactation (29). Cow's milk supplies ca 1.27 g/L of calcium in available form.

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