

# Calcium

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## 1 . Introduction :

**Calcium** is the chemical element with the symbol **Ca** and atomic number 20. It has an atomic mass of 40 amu. Calcium is a soft grey alkaline earth metal, and is the fifth most abundant element by mass in the Earth's crust. Calcium is also the fifth most abundant dissolved ion in seawater by both molarity and mass, after sodium, chloride, magnesium, and sulfate .

Calcium is essential for living organisms, particularly in cell physiology, where movement of the calcium ion  $\text{Ca}^{2+}$  into and out of the cytoplasm functions as a signal for many cellular processes. As a major material used in mineralization of bones and shells, calcium is the most abundant metal by mass in many animals .

Appearance	Dull grey , Silver
Name , Symbol , Number	Calcium, Ca , 20
Element category	Alkaline earth metal

Group, period, block	2 , 4 , s
Standard atomic weight	40 g · mol <sup>-1</sup>
Electron configuration	[ Ar ] 4s <sup>2</sup>
Electrons per shell	2 , 8 , 8 , 2
Phase	Solid
Density	1.55 g · cm <sup>-3</sup>
Liquid density at m.p.	1.378 g · cm <sup>-3</sup>
Melting Point	842 ° C
Boiling point	1484 °C
Heat of fusion	8.54 kJ · mol <sup>-1</sup>
Heat of vaporization	154.7 kJ · mol <sup>-1</sup>
Specific heat capacity	(25 °C) 25.929 J·mol <sup>-1</sup> ·K <sup>-1</sup>
Oxidation states	2 ( strongly basic oxide )
Electronegativity	1.00 ( Pauling scale )
Ionization energies (more)	1 <sup>st</sup> : 589.8 kJ · mol <sup>-1</sup> 2 <sup>nd</sup> : 1145.4 kJ · mol <sup>-1</sup> 3 <sup>rd</sup> : 4912.4 kJ · mol <sup>-1</sup>
Atomic radius	197 pm
Covalent radius	176 ± 10 pm
Crystal structure	Face - centered cubic
Magnetic ordering	Diamagnetic
Electrical resistivity	( 20 °C ) 33.6 nΩ · m
Thermal conductivity	( 300 K ) 201 W·m <sup>-1</sup> ·K <sup>-1</sup>
Thermal expansion	(25 °C) 22.3 μm·m <sup>-1</sup> ·K <sup>-1</sup>
Speed of sound (thin rod)	( 20 °C ) 3810 m / s
Young's modulus	20 GPa
Shear modulus	7.4 GPa
Bulk modulus	17 GPa
Poisson ratio	0.31
Mohs hardness	1.75
Brinell hardness	167 MPa

## 2 . Notable characteristics

Calcium carbonate wetted with hydrochloric acid ( thus forming  $\text{CaCl}_2$  ) held at a flame and showing red - orange flame color of Ca .

Chemically calcium is reactive and soft for a metal ( though harder than lead, it can be cut with a knife with difficulty ) . It is a silvery metallic element that must be extracted by electrolysis from a fused salt like calcium chloride . Once produced, it rapidly forms a grey - white oxide and nitride coating when exposed to air. It is somewhat difficult to ignite, unlike magnesium, but when lit, the metal burns in air with a brilliant high-intensity red light. Calcium metal reacts with water, evolving hydrogen gas at a rate rapid enough to be noticeable, but not fast enough at room temperature to generate much heat. In powdered form, however, the reaction with water is extremely rapid, as the increased surface area of the powder accelerates the reaction with the water. Part of the slowness of the calcium-water reaction results from the metal being partly protected by insoluble white calcium hydroxide. In water solutions of acids where the salt is water soluble, calcium reacts vigorously.

Calcium, with a specific mass of  $1.55 \text{ g / cm}^3$ , is the lightest of the alkali earth metals; magnesium is heavier ( 1.74 ) and beryllium even more heavy ( 1.84 ) despite these two elements being lighter in atomic mass. From strontium on the alkali earth metals get heavier along with the atomic mass.

Calcium has a higher resistivity than copper or aluminium. Yet, weight for weight, allowing for its much lower density, it is a rather better conductor than either. However, its use in terrestrial applications is usually limited by its high reactivity with air.

Calcium salts are colorless from any contribution of the calcium, and ionic solutions of calcium (  $\text{Ca}^{2+}$  ) are colorless as well. Many calcium salts are not soluble in water. When in solution, the calcium ion to the human taste varies remarkably, being reported as mildly salty, sour, "mineral like" or even "soothing." It is apparent that many animals can taste, or develop a taste, for calcium, and use this sense to detect the mineral in salt licks or other sources.<sup>[3]</sup> In human nutrition,

soluble calcium salts may be added to tart juices without much effect to the average palate.

Calcium is the fifth most abundant element by mass in the human body, where it is a common cellular ionic messenger with many functions, and serves also as a structural element in bone. It is the relatively high atomic-numbered calcium in the skeleton which causes bone to be radio - opaque. Of the human body's solid components after drying ( as for example, after cremation ), about a third of the total mass is the approximately one kilogram of calcium which composes the average skeleton (the remainder being mostly phosphorus and oxygen ) .

### **3 . Occurrence**

Calcium is not naturally found in its elemental state. Calcium occurs most commonly in sedimentary rocks in the minerals calcite, dolomite and gypsum. It also occurs in igneous and metamorphic rocks chiefly in the silicate minerals: plagioclase, amphiboles, pyroxenes and garnets.

### **4 . Applications**

*Some uses are :*

- as a reducing agent in the extraction of other metals, such as uranium, zirconium, and thorium.
- as a deoxidizer, desulfurizer, or decarbonizer for various ferrous and nonferrous alloys.
- as an alloying agent used in the production of aluminium, beryllium, copper, lead, and magnesium alloys.
- in the making of cements and mortars to be used in construction.
- in the making of cheese, where calcium ions influence the activity of rennin in bringing about the coagulation of milk.

## 4.1. Calcium compounds

- Calcium carbonate (  $\text{CaCO}_3$  ) used in manufacturing cement and mortar, lime, limestone ( usually used in the steel industry ) ; aids in production in the glass industry, also has chemical and optical uses as mineral specimens in tooth pastes, for example.
- Calcium hydroxide solution (  $\text{Ca}(\text{OH})_2$  ) ( also known as lime water ) is used to detect the presence of carbon dioxide by being bubbled through a solution. It turns cloudy where  $\text{CO}_2$  is present.
- Calcium arsenate (  $\text{Ca}_3(\text{AsO}_4)_2$  ) is used in insecticides.
- Calcium carbide (  $\text{CaC}_2$  ) is used: to make acetylene gas ( for use in acetylene torches for welding ) and in the manufacturing of plastics.
- Calcium chloride (  $\text{CaCl}_2$  ) is used : in ice removal and dust control on dirt roads, in conditioner for concrete, as an additive in canned tomatoes, and to provide body for automobile tires.
- Calcium cyclamate (  $\text{Ca}(\text{C}_6\text{H}_{11}\text{NHSO}_3)_2$  ) was used as a sweetening agent but is no longer permitted for use because of suspected cancer-causing properties.
- Calcium gluconate (  $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_7)_2$  ) is used as a food additive and in vitamin pills.
- Calcium hypochlorite (  $\text{Ca}(\text{OCl})_2$  ) is used: as a swimming pool disinfectant, as a bleaching agent, as an ingredient in deodorant, and in algacide and fungicide.
- Calcium permanganate (  $\text{Ca}(\text{MnO}_4)_2$  ) is used in liquid rocket propellant, textile production, as a water sterilizing agent and in dental procedures.
- Calcium phosphate (  $\text{Ca}_3(\text{PO}_4)_2$  ) is used as a supplement for animal feed, fertilizer, in commercial production for dough and yeast products, in the manufacture of glass, and in dental products.
- Calcium phosphide (  $\text{Ca}_3\text{P}_2$  ) is used in fireworks, rodenticide, torpedoes and flares.
- Calcium stearate (  $\text{Ca}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$  ) is used in the manufacture of wax crayons, cements, certain kinds of plastics

and cosmetics, as a food additive, in the production of water resistant materials and in the production of paints.

- Calcium sulfate (  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  ) is used as common black board chalk , as well as, in its hemihydrate form being more well known as Plaster of Paris.
- Calcium tungstate (  $\text{CaWO}_4$  ) is used in luminous paints, fluorescent lights and in X - ray studies.
- Hydroxyl apatite (  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  ) , but is usually written  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  ) makes up seventy percent of bone. Also carbonated - calcium deficient hydroxylapatite is the main mineral of which dental enamel and dentin are comprised.

#### 4 . 2 . H and K lines

In the visible portion of the spectrum of many stars, including the Sun, strong absorption lines of singly - ionized calcium are shown. Prominent among these are the H - line at  $3968.5 \text{ \AA}$  and the K line at  $3933.7 \text{ \AA}$  of singly - ionized calcium, or Ca II. For the Sun and stars with low temperatures, the prominence of the H and K lines can be an indication of strong magnetic activity in the chromosphere. Measurement of periodic variations of these active regions can also be used to deduce the rotation periods of these stars .

#### 5 . History

Calcium ( Latin word *calcis* meaning "lime" ) was known as early as the first century when the Ancient Romans prepared lime as calcium oxide. Literature dating back to 975 AD notes that plaster of paris (calcium sulphate), is useful for setting broken bones. It was not isolated until 1808 in England when Sir Humphry Davy electrolyzed a mixture of lime and mercuric oxide. Davy was trying to isolate calcium; when he heard that Swedish chemist Jöns Jakob Berzelius and Pontin prepared calcium amalgam by electrolyzing lime in mercury, he tried it himself. He worked with electrolysis throughout his life and also discovered/isolated sodium, potassium, magnesium, boron and barium. Calcium metal was not available in large scale until the beginning of the 20 th century.

## 6 . Compounds

Calcium combined with phosphate to form hydroxyl apatite , is the mineral portion of human and animal bones and teeth. The mineral portion of some corals can also be transformed into hydroxylapatite.

Calcium hydroxide ( slaked lime ) is used in many chemical refinery processes and is made by heating limestone at high temperature ( above  $825^{\circ}\text{C}$  ) and then carefully adding water to it. When lime is mixed with sand, it hardens into a mortar and is turned into plaster by carbon dioxide uptake. Mixed with other compounds, lime forms an important part of Portland cement.

Calcium carbonate ( $\text{CaCO}_3$  ) is one of the common compounds of calcium. It is heated to form quick lime (  $\text{Ca O}$  ) , which is then added to water (  $\text{H}_2\text{O}$  ) . This forms another material known as slaked lime (  $\text{Ca ( OH )}_2$  ) , which is an inexpensive base material used throughout the chemical industry. Chalk, marble, and limestone are all forms of calcium carbonate.

When water percolates through limestone or other soluble carbonate rocks, it partially dissolves the rock and causes cave formation and characteristic stalactites and stalagmites and also forms hard water. Other important calcium compounds are calcium nitrate, calcium sulfide, calcium chloride, calcium carbide, calcium cyanamide and calcium hypochlorite.

## 7 . Isotopes of calcium

Calcium has four stable isotopes (  $^{40}\text{Ca}$  and  $^{42}\text{Ca}$  through  $^{44}\text{Ca}$  ) plus two more isotopes (  $^{46}\text{Ca}$  and  $^{48}\text{Ca}$  ) that have such long half-lives that for all practical purposes they can be considered stable. It also has a cosmogenic isotope, radioactive  $^{41}\text{Ca}$ , which has a half - life of 103,000 years. Unlike cosmogenic isotopes that are produced in the atmosphere,  $^{41}\text{Ca}$  is produced by neutron activation of  $^{40}\text{Ca}$ . Most of its production is in the upper metre or so of the soil column, where the cosmogenic neutron flux is still sufficiently strong.  $^{41}\text{Ca}$  has received

much attention in stellar studies because it decays to  $^{41}\text{K}$ , a critical indicator of solar - system anomalies.

97 % of naturally occurring calcium is in the form of  $^{40}\text{Ca}$ .  $^{40}\text{Ca}$  is one of the daughter products of  $^{40}\text{K}$  decay, along with  $^{40}\text{Ar}$ . While K- Ar dating has been used extensively in the geological sciences, the prevalence of  $^{40}\text{Ca}$  in nature has impeded its use in dating. Techniques using mass spectrometry and a double spike isotope dilution have been used for K - Ca age dating.

The most abundant isotope,  $^{40}\text{Ca}$ , has a nucleus of 20 protons and 20 neutrons. This is the heaviest stable isotope of any element which has equal numbers of protons and neutrons. In supernova explosions, calcium is formed from the reaction of carbon with various numbers of alpha particles ( helium nuclei ) until the most common calcium isotope ( containing 10 helium nuclei ) has been synthesized .

## 8 . Nutrition : ( calcium in biology and calcium metabolism )

### Recommended Adequate Intake by the IOM for Calcium

Age	Calcium ( mg / day )
0 – 6 months	210
7 – 12 months	270
1 – 3 years	500
4 – 8 years	800
9 – 18 years	1300
19 – 50 years	1000
51+ years	1200

Calcium is an important component of a healthy diet and a mineral necessary for life. The National Osteoporosis Foundation says, " Calcium plays an important role in building stronger, denser bones early in life and keeping bones strong and healthy later in life ." Approximately ninety - nine percent of the body's calcium is stored in the bones and teeth. The rest of the calcium in the body has other



important uses, such as some exocytosis, especially neurotransmitter release, and muscle contraction. In the electrical conduction system of the heart, calcium replaces sodium as the mineral that depolarizes the cell, proliferating the action potential. In cardiac muscle, sodium influx commences an action potential, but during potassium efflux, the cardiac myocyte experiences calcium influx, prolonging the action potential and creating a plateau phase of dynamic equilibrium. Long - term calcium deficiency can lead to rickets and poor blood clotting and in case of a menopausal woman, it can lead to osteoporosis, in which the bone deteriorates and there is an increased risk of fractures. While a lifelong deficit can affect bone and tooth formation, over-retention can cause hypercalcemia ( elevated levels of calcium in the blood ) , impaired kidney function and decreased absorption of other minerals . High calcium intakes or high calcium absorption were previously thought to contribute to the development of kidney stones. However, a high calcium intake has been associated with a lower risk for kidney stones in more recent research . Vitamin D is needed to absorb calcium.

Dairy products, such as milk and cheese, are a well-known source of calcium. How ever, some individuals are allergic to dairy products and even more people, particularly those of non Indo - European descent, are lactose - intolerant, leaving them unable to consume non - fermented dairy products in quantities larger than about half a liter per serving. Others, such as vegans, avoid dairy products for ethical and health reasons. Fortunately, many good sources of calcium exist. These include seaweeds such as kelp, wakame and hijiki; nuts and seeds ( like almonds and sesame ) ; blackstrap molasses; beans; oranges; figs; quinoa; amaranth; collard greens; okra; rutabaga; broccoli; dandelion leaves; kale; and fortified products such as orange juice and soy milk. ( However, calcium fortified orange juice often contains vitamin D3 derived from lanolin, and is thus unacceptable for vegans ) . An overlooked source of calcium is egg shell, which can be ground into a powder and mixed into food or a glass of water . Cultivated vegetables generally have less calcium than wild plants .

The calcium content of most foods can be found in the USDA National Nutrient Database.

### **8 . 1 . Dietary calcium supplements**

Calcium supplements are used to prevent and to treat calcium deficiencies. Most experts recommend that supplements be taken with food and that no more than 600 mg should be taken at a time because the percent of calcium absorbed decreases as the amount of calcium in the supplement increases . It is recommended to spread doses throughout the day . Recommended daily calcium intake for adults ranges from 1000 to 1500 mg. It is recommended to take supplements with food to aid in absorption.

Vitamin D is added to some calcium supplements. Proper vitamin D status is important because vitamin D is converted to a hormone in the body which then induces the synthesis of intestinal proteins responsible for calcium absorption.<sup>[17]</sup>

- The absorption of calcium from most food and commonly-used dietary supplements is very similar . This is contrary to what many calcium supplement manufacturers claim in their promotional materials.
- Milk is an excellent source of dietary calcium because it has a high concentration of calcium and the calcium in milk is excellently absorbed .
- Calcium carbonate is the most common and least expensive calcium supplement. It should be taken with food. It depends on low pH levels for proper absorption in the intestine . Some studies suggests that the absorption of calcium from calcium carbonate is similar to the absorption of calcium from milk . While most people digest calcium carbonate very well, some might develop gastrointestinal discomfort or gas. Taking magnesium with it can help to avoid constipation. Calcium carbonate is 40 % elemental calcium. 1000 mg will provide 400 mg of calcium. However, supplement labels will usually indicate how much calcium is present in each serving, not how much calcium carbonate is present.

- Antacids, such as Tums, frequently contain calcium carbonate, and are a very commonly - used, inexpensive calcium supplement.
- Coral Calcium is a salt of calcium derived from fossilized coral reefs. Coral calcium is composed of calcium carbonate and trace minerals.
- Calcium citrate can be taken without food and is the supplement of choice for individuals with achlorhydria or who are taking histamine - 2 blockers or proton-pump inhibitors . It is more easily digested and absorbed than calcium carbonate if taken on empty stomach and less likely to cause constipation and gas than calcium carbonate. It also has a lower risk of contributing to the formation of kidney stones. Calcium citrate is about 21% elemental calcium. 1000 mg will provide 210 mg of calcium. It is more expensive than calcium carbonate and more of it must be taken to get the same amount of calcium.
- Calcium phosphate costs more than calcium carbonate, but less than calcium citrate. It is easily absorbed and is less likely to cause constipation and gas than either.
- Calcium lactate has similar absorption as calcium carbonate , but is more expensive. Calcium lactate and calcium gluconate are less concentrated forms of calcium and are not practical oral supplements .
- Calcium chelates are synthetic calcium compounds, with calcium bound to an organic molecule, such as malate, aspartate, or fumarate. These forms of calcium may be better absorbed on an empty stomach. However, in general they are absorbed similarly to calcium carbonate and other common calcium supplements when taken with food.<sup>[24]</sup> The 'chelate' mimics the action that natural food performs by keeping the calcium soluble in the intestine. Thus, on an empty stomach, in some individuals, chelates might theoretically be absorbed better.
- Microcrystalline hydroxy apatite ( MH ) is marketed as a calcium supplement, and has in some randomized trials been found to be more effective than calcium carbonate.
- Orange juice with calcium added is a good dietary source for persons who have lactose intolerance.

In July 2006, a report citing research from Fred Hutchinson Cancer Research Center in Seattle, Washington claimed that women in their 50s gained 5 pounds less in a period of 10 years by taking more than 500 mg of calcium supplements than those who did not. However, the doctor in charge of the study, Dr. Alejandro J. Gonzalez also noted it would be "going out on a limb" to suggest calcium supplements as a weight-limiting aid.

### **8.2. Prevention of fractures due to osteoporosis**

Such studies often do not test calcium alone, but rather combinations of calcium and vitamin D. Randomized controlled trials found both positive and negative effects. The different results may be explained by doses of calcium and underlying rates of calcium supplementation in the control groups.<sup>[32]</sup> However, it is clear that increasing the intake of calcium promotes deposition of calcium in the bones, where it is of more benefit in preventing the compression fractures resulting from the osteoporotic thinning of the dendritic web of the bodies of the vertebrae, than it is at preventing the more serious cortical bone fractures which happen at hip and wrist.

### **8.3. Possible cancer prevention**

A meta-analysis by the international Cochrane Collaboration of two randomized controlled trials found that calcium "might contribute to a moderate degree to the prevention of adenomatous colonic polyps".

More recent studies were conflicting, and one which was positive for effect (Lappe, et al) did control for a possible anti-carcinogenic effect of vitamin D, which was found to be an independent positive influence from calcium - alone on cancer risk.

- A randomized controlled trial found that 1000 mg of elemental calcium and 400 IU of vitamin D<sub>3</sub> had no effect on colorectal cancer.
- A randomized controlled trial found that 1400–1500 mg supplemental calcium and 1100 IU vitamin D<sub>3</sub> reduced aggregated cancers with a relative risk of 0.402.

- An observational cohort study found that high calcium and vitamin D intake was associated with " lower risk of developing premenopausal breast cancer" .

#### **8 . 4 . Over dose**

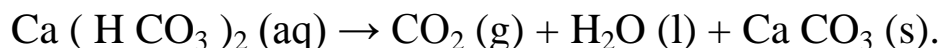
Exceeding the recommended daily calcium intake for an extended period of time can result in hypercalcemia and calcium metabolism disorder.

## Calcium bicarbonate

**Calcium bicarbonate** (  $\text{Ca}(\text{HCO}_3)_2$  ), also called **calcium hydrogen carbonate** , does not refer to a known solid compound; it exists only in aqueous solution containing the ions calcium (  $\text{Ca}^{2+}$  ) , dissolved carbon dioxide (  $\text{CO}_2$  ) , bicarbonate (  $\text{HCO}_3^-$  ) , and carbonate (  $\text{CO}_3^{2-}$  ) . The relative concentrations of these carbon-containing species depend on the pH ; bicarbonate predominates within the range 6.36 - 10.25 in fresh water.

All waters in contact with the atmosphere absorb carbon dioxide, and as these waters come into contact with rocks and sediments they acquire metal ions, most commonly calcium and magnesium, so most natural waters that come from streams, lakes, and especially wells, can be regarded as dilute solutions of these bicarbonates. These hard waters tend to form carbonate scale in pipes and boilers and they react with soaps to form an undesirable scum.

Attempts to prepare compounds such as calcium bicarbonate by evaporating its solution to dryness invariably yield the solid carbonate instead :



Very few solid bicarbonates other than those of the alkali metals and ammonium ion are known to exist .

The above reaction is very important to the formation of stalactites, stalagmites , columns, and other speleothems within caves and , for that matter, in the formation of the caves themselves. As water containing carbon dioxide ( including extra  $\text{CO}_2$  acquired from soil organisms ) passes through lime stone or other calcium carbonate containing minerals, it dissolves part of the calcium carbonate and hence becomes richer in bicarbonate. As the ground water enters the cave, the excess carbon dioxide is released from the solution of the bicarbonate, causing the much less soluble calcium carbonate to be deposited.

Other Names	Calcium hydrogen carbonate
Molecular Formula	$\text{Ca} (\text{HCO}_3)_2$
Molar Mass	162 g / mol
Solubility in Water	16.1 g /100 mL ( 0 ° C ) 16.6 g / 100 mL ( 20° C ) 18.4 g / 100 mL ( 100 ° C )
Flash Point	Non - Flammable

# Calcium Carbonate

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## 1 . Introduction :

**Calcium carbonate** is a chemical compound with the chemical formula Ca CO<sub>3</sub> . It is a common substance found in rock in all parts of the world, and is the main component of shells of marine organisms , snails , pearls , and eggshells . Calcium carbonate is the active ingredient in agricultural lime, and is usually the principal cause of hard water. It is commonly used medicinally as a calcium supplement or as an antacid, but high consumption can be hazardous.

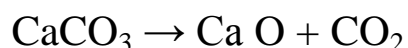
## 2 . Chemical properties

Calcium carbonate shares the typical properties of other carbonates . Notably :

1. it reacts with strong acids, releasing carbon dioxide :  

$$\text{Ca CO}_3 \text{ (s)} + 2\text{H Cl} \text{ (aq)} \rightarrow \text{Ca Cl}_2 \text{ (aq)} + \text{CO}_2 \text{ (g)} + \text{H}_2\text{O} \text{ (l)}$$
2. it releases carbon dioxide on heating ( to above 840 °C in the case of Ca CO<sub>3</sub> ) , to form calcium oxide , commonly called quick lime , with reaction enthalpy 178 kJ / mole :





Calcium carbonate will react with water that is saturated with carbon dioxide to form the soluble calcium bicarbonate.

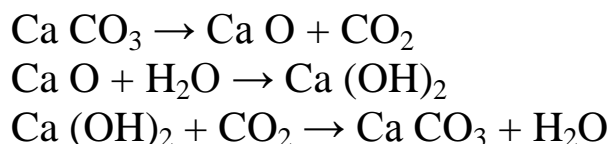


This reaction is important in the erosion of carbonate rocks, forming caverns, and leads to hard water in many regions.

### 3 . Preparation

The vast majority of calcium carbonate used in industry is extracted by mining or quarrying. Pure calcium carbonate ( e.g. for food or pharmaceutical use ) , can be produced from a pure quarried source ( usually marble ) .

Alternatively, calcium oxide is prepared by calcining crude calcium carbonate. Water is added to give calcium hydroxide, and carbon dioxide is passed through this solution to precipitate the desired calcium carbonate, referred to in the industry as precipitated calcium carbonate ( PCC ) :



### 4 . Occurrence

Calcium carbonate is found naturally as the following minerals and rocks :

- Aragonite , Calcite , Vaterite or (  $\mu - \text{Ca CO}_3$  ) , Lime stone , Marble , Travertine

The trigonal crystal structure of calcite is most common. To test whether a mineral or rock contains carbonate, strong acids such as hydrochloric acid or sulfuric acid can be added to it; if the sample does contain carbonate, it will fizz and produce carbon dioxide and water. ( Although sulfuric acid reacts, the reaction soon ceases

because the calcium sulfate produced is rather insoluble in water and limits the reaction ). Weak acids such as acetic acid will react, albeit less vigorously. All of the rocks / minerals mentioned above will react with acid.

To test for calcium, prepare a platinum or nichrome wire and dip it into some hydrochloric acid. Then dip the wire into some crushed sample to be tested. Place the wire in a bunsen burner flame; if calcium is present in the sample a brick-red flame will be produced.

If a sample gives positive results for both of the two tests above, the presence of calcium carbonate is indicated.

## **5 . Uses**

### **5 . 1 . Industrial applications**

The main use of calcium carbonate is in the construction industry, either as a building material in its own right ( e.g. marble ) or limestone aggregate for road building or as an ingredient of cement or as the starting material for the preparation of builder's lime by burning in a kiln.

Calcium carbonate is also used in the purification of iron from iron ore in a blast furnace. Calcium carbonate is calcined *in situ* to give calcium oxide, which forms a slag with various impurities present, and separates from the purified iron .

Calcium carbonate is also used in the oil industry in drilling fluids as a formation bridging and filter cake sealing agent and may also be used as a weighting material to increase the density of drilling fluids to control down hole pressures.

Calcium carbonate is also one of the main sources used in growing Sea Crete , or Bio Rock .

Precipitated Calcium carbonate , pre - dispersed in slurry form, is also now widely used as filler material for latex gloves with the aim of achieving maximum saving in material and production costs .

Calcium carbonate is widely used as an extender in paints,<sup>[5]</sup> in particular matte emulsion paint where typically 30 % by weight of the paint is either chalk or marble .

Calcium carbonate is also widely used as a filler in plastics. Some typical examples include around 15 to 20% loading of chalk in uPVC drain pipe, 5 to 15 % loading of stearate coated chalk or marble in uPVC window profile. PVC cables can use calcium carbonate at loadings of up to 70 phr (parts per hundred parts of resin) to improve mechanical properties ( tensile strength and elongation ) and electrical properties ( volume resistivity ) . Polypropylene compounds are often filled with calcium carbonate to increase rigidity, a requirement that becomes important at high use temperatures.<sup>[6]</sup> It also routinely used as a filler in thermosetting resins (Sheet and Bulk moulding compounds)<sup>[6]</sup> and has also been mixed with ABS, and other ingredients, to form some types of compression molded "clay" Poker chips.

Fine ground calcium carbonate is an essential ingredient in the micro porous film used in babies' diapers and some building films as the pores are nucleated around the calcium carbonate particles during the manufacture of the film by biaxial stretching.

Calcium carbonate is also used in a wide range of trade and DIY adhesives, sealants, and decorating fillers . Ceramic tile adhesives typically contain 70 to 80 % lime stone. Decorating crack fillers contain similar levels of marble or dolomite. It is also mixed with putty in setting stained glass windows, and as a resist to prevent glass from sticking to kiln shelves when firing glazes and paints at high temperature.

Calcium carbonate is known as *whiting* in ceramics / glazing applications, where it is used as a common ingredient for many glazes in its white powdered form. When a glaze containing this material is fired in a kiln, the whiting acts as a flux material in the glaze.

In North America, calcium carbonate has begun to replace kaolin in the production of glossy paper. Europe has been practicing

this as alkaline papermaking or acid-free papermaking for some decades. Carbonates are available in forms: ground calcium carbonate ( GCC ) or precipitated calcium carbonate ( PCC ) . The latter has a very fine and controlled particle size, on the order of 2 micro meters in diameter, useful in coatings for paper.

It is used in swimming pools as a pH corrector for maintaining alkalinity " buffer " to offset the acidic properties of the disinfectant agent.

It is commonly called chalk as it has traditionally been a major component of black board chalk. Modern manufactured chalk is now mostly gypsum , hydrated calcium sulfate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

Ground calcium carbonate is further used as an abrasive (both as scouring powder and as an ingredient of household scouring creams), in particular in its calcite form, which has the relatively low hardness level of 3 on the Mohs scale of mineral hardness, and will therefore not scratch glass and most other ceramics, enamel, bronze, iron, and steel, and have a moderate effect on softer metals like aluminium and copper.

## **5 . 2 . Health and dietary applications**

Calcium carbonate is widely used medicinally as an inexpensive dietary calcium supplement or antacid . It may be used as a phosphate binder for the treatment of hyperphosphatemia ( primarily in patients with chronic renal failure ) . It is also used in the pharmaceutical industry as an inert filler for tablets and other pharmaceuticals .

Calcium carbonate is used in the production of toothpaste and is also used in homeopathy as one of the constitutional remedies.

Excess calcium from supplements, fortified food and high - calcium diets, can cause the "milk alkali syndrome ," which has serious toxicity and can be fatal. In 1915, Bertram Sippy introduced the " Sippy regimen " of hourly ingestion of milk and cream, and the gradual addition of eggs and cooked cereal, for 10 days, combined with alkaline powders, which provided symptomatic relief for peptic

ulcer disease. Over the next several decades, the Sippy regimen resulted in renal failure, alkalosis, and hypercalcemia, mostly in men with peptic ulcer disease. These adverse effects were reversed when the regimen stopped, but it was fatal in some patients with protracted vomiting. Milk alkali syndrome declined in men after effective treatments for peptic ulcer disease. But during the past 15 years, it has been reported in women taking calcium supplements above the recommended range of 1200 to 1500 mg daily, for prevention and treatment of osteoporosis, and is exacerbated by dehydration. Calcium has been added to over-the-counter products, which contributes to inadvertent excessive intake. Excessive calcium intake can lead to hypercalcemia, complications of which include vomiting, abdominal pain and altered mental status.<sup>[9]</sup>

A form of food additive is designated as E170 . It is used in some soy milk products as a source of dietary calcium; one study suggests that calcium carbonate might be as bioavailable as the calcium in cow's milk.

### 5.3. Environmental applications

In 1989, a researcher, Ken Simmons, introduced  $\text{Ca CO}_3$  into the Whet stone Brook in Massachusetts . His hope was that the calcium carbonate would counter the acid in the stream from acid rain and save the trout that had ceased to spawn. Although his experiment was a success, it did increase the amounts of aluminium ions in the area of the brook that was not treated with the limestone. This shows that  $\text{Ca CO}_3$  can be added to neutralize the effects of acid rain in river ecosystems. Currently calcium carbonate is used to neutralize acidic conditions in both soil and water . Since the 1970s, such *liming* has been practiced on a large scale in Sweden to mitigate acidification and several thousand lakes and streams are limed repeatedly .

## 6. Calcinations equilibrium

Equilibrium Pressure of $\text{CO}_2$ over $\text{CaCO}_3$	
550 ° C	0.055 kPa
587 ° C	0.13 kPa

605 ° C	0.31 kPa
680 ° C	1.80 kPa
727 ° C	5.9 kPa
748 ° C	9.3 kPa
777 ° C	14 kPa
800 ° C	24 kPa
830 ° C	34 kPa
852 ° C	51 kPa
871 ° C	72 kPa
881 ° C	80 kPa
891 ° C	91 kPa
898 ° C	101 kPa
937 ° C	179 kPa
1082 ° C	901 kPa
1241 ° C	3961 kPa

Calcinations of lime stone using charcoal fires to produce quick lime has been practiced since antiquity by cultures all over the world. The temperature at which lime stone yields calcium oxide is usually given as 825 ° C, but stating an absolute threshold is misleading. Calcium carbonate exists in equilibrium with calcium oxide and carbon dioxide at any temperature. At each temperature there is a partial pressure of carbon dioxide that is in equilibrium with calcium carbonate. At room temperature the equilibrium overwhelmingly favors calcium carbonate, because the equilibrium CO<sub>2</sub> pressure is only a tiny fraction of the partial CO<sub>2</sub> pressure in air, which is about 0.035 kPa . At temperatures above 550 ° C the equilibrium CO<sub>2</sub> pressure begins to exceed the CO<sub>2</sub> pressure in air. So above 550 °C, calcium carbonate begins to outgas CO<sub>2</sub> into air. But in a charcoal fired kiln, the concentration of CO<sub>2</sub> will be much higher than it is in air. Indeed if all the oxygen in the kiln is consumed in the fire, then the partial pressure of CO<sub>2</sub> in the kiln can be as high as 20 kPa.

The table shows that this equilibrium pressure is not achieved until the temperature is nearly 800 ° C. For the out gassing of CO<sub>2</sub>

from calcium carbonate to happen at an economically useful rate, the equilibrium pressure must significantly exceed the ambient pressure of CO<sub>2</sub>. And for it to happen rapidly, the equilibrium pressure must exceed total atmospheric pressure of 101 kPa, which happens at 898 °C.

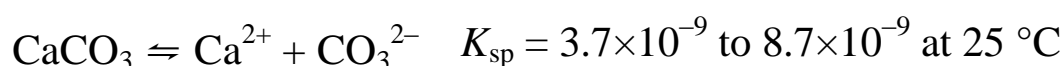
## 7. Solubility

### 7.1. With varying CO<sub>2</sub> pressure

<b>Calcium ion solubility as a function of CO<sub>2</sub> partial pressure at 25 °C ( <math>K_{sp} = 4.47 \times 10^{-9}</math> )</b>		
( atm )	pH	[ Ca <sup>2+</sup> ] ( mol / L )
10 <sup>-12</sup>	12.0	5.19 × 10 <sup>-3</sup>
10 <sup>-10</sup>	11.3	1.12 × 10 <sup>-3</sup>
10 <sup>-8</sup>	10.7	2.55 × 10 <sup>-4</sup>
10 <sup>-6</sup>	9.83	1.20 × 10 <sup>-4</sup>
10 <sup>-4</sup>	8.62	3.16 × 10 <sup>-4</sup>
<b>3.5 × 10<sup>-4</sup></b>	<b>8.27</b>	<b>4.70 × 10<sup>-4</sup></b>
10 <sup>-3</sup>	7.96	6.62 × 10 <sup>-4</sup>
10 <sup>-2</sup>	7.30	1.42 × 10 <sup>-3</sup>
10 <sup>-1</sup>	6.63	3.05 × 10 <sup>-3</sup>
1	5.96	6.58 × 10 <sup>-3</sup>
10	5.30	1.42 × 10 <sup>-2</sup>

Calcium carbonate is poorly soluble in pure water ( 47 mg / L at normal atmospheric CO<sub>2</sub> partial pressure as shown below ) .

The equilibrium of its solution is given by the equation (with dissolved calcium carbonate on the right ) :



where the solubility product for [ Ca<sup>2+</sup> ] [ CO<sub>3</sub><sup>2-</sup> ] is given as anywhere from  $K_{sp} = 3.7 \times 10^{-9}$  to  $K_{sp} = 8.7 \times 10^{-9}$  at 25 °C, depending upon the data source . What the equation means is that the product of

molar concentration of calcium ions ( moles of dissolved  $\text{Ca}^{2+}$  per liter of solution ) with the molar concentration of dissolved  $\text{CO}_3^{2-}$  cannot exceed the value of  $K_{\text{sp}}$ . This seemingly simple solubility equation, however, must be taken along with the more complicated equilibrium of carbon dioxide with water. Some of the  $\text{CO}_3^{2-}$  combines with  $\text{H}^+$  in the solution according to:

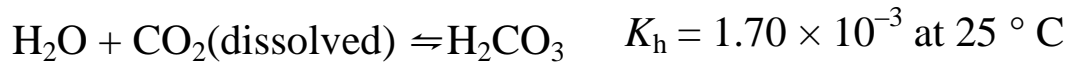


$\text{HCO}_3^-$  is known as the bicarbonate ion . Calcium bicarbonate is many times more soluble in water than calcium carbonate—indeed it exists *only* in solution.

Some of the  $\text{HCO}_3^-$  combines with  $\text{H}^+$  in solution according to:



Some of the  $\text{H}_2\text{CO}_3$  breaks up into water and dissolved carbon dioxide according to:



And dissolved carbon dioxide is in equilibrium with atmospheric carbon dioxide according to :

$$\frac{P_{\text{CO}_2}}{[\text{CO}_2]} = k_H \quad \text{where } k_H = 29.76 \text{ atm}/(\text{mol} / \text{L})$$

at  $25^\circ \text{C}$  ( Henry constant ) ,  
being the  $\text{CO}_2$  partial pressure.

For ambient air, is around  $3.5 \times 10^{-4}$  atmospheres (or equivalently 35 Pa ) . The last equation above fixes the concentration of dissolved  $\text{CO}_2$  as a function of , independent of the concentration of dissolved  $\text{Ca CO}_3$ . At atmospheric partial pressure of  $\text{CO}_2$ , dissolved  $\text{CO}_2$  concentration is  $1.2 \times 10^{-5}$  moles/liter. The equation before that fixes the concentration of  $\text{H}_2\text{CO}_3$  as a function of  $[\text{CO}_2]$ . For  $[\text{CO}_2] = 1.2 \times 10^{-5}$ , it results in  $[\text{H}_2\text{CO}_3] = 2.0 \times 10^{-8}$  moles per liter. When  $[\text{H}_2\text{CO}_3]$  is known, the remaining three equations together with





(which is true for all aqueous solutions), and the fact that the solution must be electrically neutral,

$$2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

make it possible to solve simultaneously for the remaining five unknown concentrations (note that the above form of the neutrality equation is valid only if calcium carbonate has been put in contact with **pure water** or with a neutral pH solution; in the case where the origin water solvent pH is not neutral, the equation is modified).

The table on the right shows the result for  $[\text{Ca}^{2+}]$  and  $[\text{H}^+]$  (in the form of pH) as a function of ambient partial pressure of  $\text{CO}_2$  ( $K_{\text{sp}} = 4.47 \times 10^{-9}$  has been taken for the calculation).

1) At atmospheric levels of ambient  $\text{CO}_2$  the table indicates the solution will be slightly alkaline with a maximum  $\text{CaCO}_3$  solubility of 47 mg / L.

2) As ambient  $\text{CO}_2$  partial pressure is reduced below atmospheric levels, the solution becomes more and more alkaline. At extremely low, dissolved  $\text{CO}_2$ , bicarbonate ion, and carbonate ion largely evaporate from the solution, leaving a highly alkaline solution of calcium hydroxide, which is more soluble than  $\text{CaCO}_3$ . Note that for  $= 10^{-12}$  atm, the  $[\text{Ca}^{2+}][\text{OH}^-]^2$  product is still below the solubility product of  $\text{Ca}(\text{OH})_2$  ( $8 \times 10^{-6}$ ). For still lower  $\text{CO}_2$  pressure,  $\text{Ca}(\text{OH})_2$  precipitation will occur before  $\text{CaCO}_3$  precipitation.

3) As ambient  $\text{CO}_2$  partial pressure increases to levels above atmospheric, pH drops, and much of the carbonate ion is converted to bicarbonate ion, which results in higher solubility of  $\text{Ca}^{2+}$ .

The effect of the latter is especially evident in day to day life of people who have hard water. Water in aquifers underground can be exposed to levels of  $\text{CO}_2$  much higher than atmospheric. As such water percolates through calcium carbonate rock, the  $\text{CaCO}_3$  dissolves according to the second trend. When that same water then emerges

from the tap, in time it comes into equilibrium with  $\text{CO}_2$  levels in the air by out gassing its excess  $\text{CO}_2$ . The calcium carbonate becomes less soluble as a result and the excess precipitates as lime scale. This same process is responsible for the formation of stalactites and stalagmites in limestone caves.

Two hydrated phases of calcium carbonate, monohydrocalcite,  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$  and ikaite,  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ , may precipitate from water at ambient conditions and persist as meta stable phases.

## 7.2. With varying pH

We now consider the problem of the maximum solubility of calcium carbonate in normal atmospheric conditions (  $p = 3.5 \times 10^{-4}$  atm ) when the pH of the solution is adjusted. This is for example the case in a swimming pool where the pH is maintained between 7 and 8 ( by addition of sodium bisulfate  $\text{Na HSO}_4$  to decrease the pH or of sodium bicarbonate  $\text{Na HCO}_3$  to increase it ) . From the above equations for the solubility product, the hydration reaction and the two acid reactions, the following expression for the maximum  $[\text{Ca}^{2+}]$  can be easily deduced:

showing a quadratic dependence in  $[\text{H}^+]$  . The numerical application with the above values of the constants gives

pH	7.0	7.2	7.4	7.6	7.8	8.0	8.2	8.27	8.4
$[\text{Ca}^{2+}]_{\text{max}} ( 10^{-4} \text{ mol / L or } ^\circ\text{f} )$	1590	635	253	101	40.0	15.9	6.35	4.70	2.53
$[\text{Ca}^{2+}]_{\text{max}} ( \text{ mg / L } )$	6390	2540	1010	403	160	63.9	25.4	18.9	10.1

- decreasing the pH from 8 to 7 increases the maximum  $\text{Ca}^{2+}$  concentration by a factor 100. Water with a pH maintained to 7 can dissolve up to 15.9 g / L of  $\text{Ca CO}_3$  . This explains the high  $\text{Ca}^{2+}$  concentration in some mineral waters with pH close to 7.
- note that the  $\text{Ca}^{2+}$  concentration of the previous table is recovered for pH = 8.27

- keeping the pH to 7.4 in a swimming pool (which gives optimum HClO / ClO<sup>-</sup> ratio in the case of "chlorine" maintenance) results in a maximum Ca<sup>2+</sup> concentration of 1010 mg / L. This means that successive cycles of water evaporation and partial renewing may result in a very hard water before CaCO<sub>3</sub> precipitates [ water with a Ca<sup>2+</sup> concentration above 120 mg / L or 30 °f ( French degrees ) is considered very hard ] . Addition of a calcium sequestering agent or complete renewing of the water will solve the problem .

### 7.3. Solubility in a strong or weak acid solution

Solutions of strong ( HCl ) or weak ( acetic , sorbic , lactic , phosphoric ) acids are commercially available. They are commonly used as descaling agents to remove lime scale deposits. The maximum amount of Ca CO<sub>3</sub> that can be "dissolved" by one liter of an acid solution can be calculated using the above equilibrium equations.

- In the case of a strong monoacid with decreasing acid concentration [ A ] = [ A<sup>-</sup> ], we obtain ( with CaCO<sub>3</sub> molar mass = 100 g ) :

[ A ] ( mol / L )	1	10 <sup>-1</sup>	10 <sup>-2</sup>	10 <sup>-3</sup>	10 <sup>-4</sup>	10 <sup>-5</sup>	10 <sup>-6</sup>	10 <sup>-7</sup>	10 <sup>-10</sup>
Initial pH	0.00	1.00	2.00	3.00	4.00	5.00	6.00	6.79	7.00
Final pH	6.75	7.25	7.75	8.14	8.25	8.26	8.26	8.26	8.27
Dissolved CaCO <sub>3</sub> ( g per liter of acid )	50.0	5.00	0.514	0.0849	0.0504	0.0474	0.0471	0.0470	0.0470

where the initial state is the acid solution with no Ca<sup>2+</sup> ( not taking into account possible CO<sub>2</sub> dissolution ) and the final state is the solution with saturated Ca<sup>2+</sup>. For strong acid concentrations, all species have a negligible concentration in the final state with respect to Ca<sup>2+</sup> and A<sup>-</sup> so that the neutrality equation reduces approximately to 2 [ Ca<sup>2+</sup> ] = [ A<sup>-</sup> ] yielding . When the concentration decreases, [ HCO<sub>3</sub><sup>-</sup> ] becomes non negligible so that the preceding expression is no longer valid. For vanishing acid concentrations, we recover the final pH and the solubility of CaCO<sub>3</sub> in pure water.

- In the case of a weak monoacid (here we take acetic acid with  $pK_A = 4.76$ ) with decreasing total acid concentration  $[A] = [A^-] + [AH]$ , we obtain :

<b>[ A ] ( mol / L )</b>	<b>1</b>	<b><math>10^{-1}</math></b>	<b><math>10^{-2}</math></b>	<b><math>10^{-3}</math></b>	<b><math>10^{-4}</math></b>	<b><math>10^{-5}</math></b>	<b><math>10^{-6}</math></b>	<b><math>10^{-7}</math></b>	<b><math>10^{-10}</math></b>
<b>Initial pH</b>	<b>2.38</b>	<b>2.88</b>	<b>3.39</b>	<b>3.91</b>	<b>4.47</b>	<b>5.15</b>	<b>6.02</b>	<b>6.79</b>	<b>7.00</b>
<b>Final pH</b>	<b>6.75</b>	<b>7.25</b>	<b>7.75</b>	<b>8.14</b>	<b>8.25</b>	<b>8.26</b>	<b>8.26</b>	<b>8.26</b>	<b>8.27</b>
<b>Dissolved <math>\text{CaCO}_3</math> ( g per liter of acid )</b>	<b>49.5</b>	<b>4.99</b>	<b>0.513</b>	<b>0.0848</b>	<b>0.0504</b>	<b>0.0474</b>	<b>0.0471</b>	<b>0.0470</b>	<b>0.0470</b>

We see that for the same total acid concentration, the initial pH of the weak acid is less acid than the one of the strong acid; however, the maximum amount of  $\text{CaCO}_3$  which can be dissolved is approximately the same. This is because in the final state, the pH is larger than the  $pK_A$ , so that the weak acid is almost completely dissociated, yielding in the end as many  $\text{H}^+$  ions as the strong acid to "dissolve" the calcium carbonate.

- The calculation in the case of phosphoric acid (which is the most widely used for domestic applications) is more complicated since the concentrations of the four dissociation states corresponding to this acid must be calculated together with  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ ,  $[\text{Ca}^{2+}]$ ,  $[\text{H}^+]$  and  $[\text{OH}^-]$ . The system may be reduced to a seventh degree equation for  $[\text{H}^+]$  the numerical solution of which gives :

<b>[A] ( mol / L )</b>	<b>1</b>	<b><math>10^{-1}</math></b>	<b><math>10^{-2}</math></b>	<b><math>10^{-3}</math></b>	<b><math>10^{-4}</math></b>	<b><math>10^{-5}</math></b>	<b><math>10^{-6}</math></b>	<b><math>10^{-7}</math></b>	<b><math>10^{-10}</math></b>
<b>Initial pH</b>	<b>1.08</b>	<b>1.62</b>	<b>2.25</b>	<b>3.05</b>	<b>4.01</b>	<b>5.00</b>	<b>5.97</b>	<b>6.74</b>	<b>7.00</b>
<b>Final pH</b>	<b>6.71</b>	<b>7.17</b>	<b>7.63</b>	<b>8.06</b>	<b>8.24</b>	<b>8.26</b>	<b>8.26</b>	<b>8.26</b>	<b>8.27</b>
<b>Dissolved <math>\text{CaCO}_3</math> ( g per liter of acid )</b>	<b>62.0</b>	<b>7.39</b>	<b>0.874</b>	<b>0.123</b>	<b>0.0536</b>	<b>0.0477</b>	<b>0.0471</b>	<b>0.0471</b>	<b>0.0470</b>

where  $[A] = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$  is the total acid concentration. We see that phosphoric acid is more efficient than a monoacid since at the final almost neutral pH, the second dissociated state concentration  $[\text{HPO}_4^{2-}]$  is not negligible.

# Calcium Carbonate ( Marble )

## Contents

- 1 Introduction
- 2 Etymology
- 3 Origins
- 4 Types
- 5 Construction marble
- 6 Industrial use
- 7 Production
- 8 Artificial marble
- 9 Cultural associations

### 1 . Introduction :

**Marble** is a non foliated metamorphic rock resulting from the metamorphism of lime stone, composed mostly of calcite (a crystalline form of calcium carbonate,  $\text{CaCO}_3$ ). It is extensively used for sculpture, as a building material, and in many other applications. The word "marble" is colloquially used to refer to many other stones that are capable of taking a high polish.

### 2 . Etymology

The word " marble " derives from the Ancient Greek μάρμαρον (*mármaron*) or μάρμαρος (*mármaros*), "crystalline rock " , "shining stone " , from the verb μαρμαίρω ( *marmairō* ) , " to flash, sparkle, gleam ". This stem is also the basis for the English word *marmorea l*, meaning " marble – like " .

### 3 . Origins

Marble is a metamorphic rock resulting from regional or rarely contact metamorphism of sedimentary carbonate rocks, either limestone or dolomite rock, or metamorphism of older marble. This metamorphic process causes a complete recrystallization of the original rock into an interlocking mosaic of calcite, aragonite and/or dolomite crystals. The temperatures and pressures necessary to form

marble usually destroy any fossils and sedimentary textures present in the original rock .

Pure white marble is the result of metamorphism of very pure lime stones . The characteristic swirls and veins of many colored marble varieties are usually due to various mineral impurities such as clay , silt , sand , iron oxides , or chert which were originally present as grains or layers in the limestone. Green coloration is often due to serpentine resulting from originally high magnesium lime stone or dolo stone with silica impurities. These various impurities have been mobilized and recrystallized by the intense pressure and heat of the metamorphism.

#### 4 . Types

Historically notable marble varieties and locations :

Marble name	Color	Location	Country
Carrara marble	white or blue - gray	Carrara	Italy
Parian marble	Fine - grained semitranslucent pure - white	Island of Paros	Greece
Rouge de Rance	Red	Rance	Belgium
Macedonian Bianco Sivec	White	Prilep	Republic of Macedonia
Tennessee marble	Pale pink to cedar - red	Knox, Blount and Hawkins Counties, Tennessee	United States
Yule	Uniform pure white	Marble, Colorado	United States

White marbles have been prized for sculpture since classical times. This preference has to do with the softness and relative isotropy and homogeneity, and a relative resistance to shattering. Also, the low index of refraction of calcite allows light to penetrate several millimeters into the stone before being scattered out, resulting

in the characteristic " waxy " look which gives " life " to marble sculptures of the human body.

## **5 . Construction marble**

In the construction, specifically the dimension stone trade, the term " marble " is used for any crystalline calcitic rock ( and some non - calcitic rocks ) useful as building stone. For example " Tennessee marble " is really a dense granular fossiliferous gray to pink to maroon Ordovician limestone that geologists call the Holston Formation.

## **6 . Industrial use**

Colorless or light - colored marbles are a very pure source of calcium carbonate, which is used in a wide variety of industries. Finely ground marble or calcium carbonate powder is a component in paper, and in consumer products such as toothpaste, plastics, and paints. Ground calcium carbonate can be made from limestone, chalk, and marble; about three - quarters of the ground calcium carbonate worldwide is made from marble. Ground calcium carbonate is used as a coating pigment for paper because of its high brightness and as a paper filler because it strengthens the sheet and imparts high brightness. Ground calcium carbonate is used in consumer products such as a food additive, in toothpaste, and as an inert filler in pills. It is used in plastics because it imparts stiffness, impact strength, dimensional stability, and thermal conductivity. It is used in paints because it is a good filler and extender, has high brightness, and is weather resistant. However, the growth in demand for ground calcium carbonate in the last decade has mostly been for a coating pigment in paper.

Calcium carbonate can also be reduced under high heat to calcium oxide ( also known as " lime" ), which has many applications including being a primary component of many forms of cement .

## **7 . Production**

According to the United States Geological Survey, U.S. dimension marble production in 2006 was 46,400 tons valued at \$18.1 million , compared to 72,300 tons valued at \$ 18.9 million in 2005. Crushed marble production ( for aggregate and industrial uses ) in 2006 was 11.8 million tons valued at \$ 116 million, of which 6.5 million tons was finely ground calcium carbonate and the rest was construction aggregate. For comparison, 2005 crushed marble production was 7.76 million tons valued at \$ 58.7 million, of which 4.8 million tons was finely ground calcium carbonate and the rest was construction aggregate. U.S. dimension marble demand is about 1.3 million tons. The DSAN World Demand for ( finished ) Marble Index has shown a growth of 12 % annually for the 2000 - 2006 period, compared to 10.5 % annually for the 2000 – 2005 period. The largest dimension marble application is tile.

## **8 . Artificial marble**

Faux marble or faux marbling is a wall painting technique that imitates the color patterns of real marble ( not to be confused with paper marbling ) . Marble dust can be combined with cement or synthetic resins to make *reconstituted* or *cultured marble*.

## **9 . Cultural associations**

As the favorite medium for Greek and Roman sculptors and architects , marble has become a cultural symbol of tradition and refined taste. Its extremely varied and colorful patterns make it a favorite decorative material, and it is often imitated in background patterns for computer displays, etc.



# Calcium Chloride

## Contents :

- 1 Introduction
- 2 Chemical properties
- 3 Uses
  - . 3 . 1 Uses in industry
  - . 3 . 2 Uses in food
  - . 3 . 3 Uses in drugs
- 4 Precautions
- 5 Natural occurrence

## 1 . Introduction :

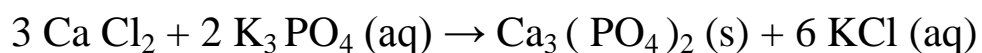
**Calcium chloride** ,  $\text{CaCl}_2$  , is a common salt. It behaves as a typical ionic halide, and is solid at room temperature. It has several common applications such as brine for refrigeration plants, ice and dust control on roads, and in concrete. The anhydrous salt is also widely used as a desiccant, where it will absorb so much water that it will eventually dissolve in its own crystal lattice water. It can be produced directly from limestone, but large amounts are also produced as a by-product of the Solvay process. Because of its hygroscopic nature, the anhydrous form must be kept in tightly - sealed containers. It is used to turn kelp into a solid .

Other Names	Calcium ( II ) chloride, Calcium dichloride , E 509
Molecular Formula	$\text{CaCl}_2$
Molar Mass	111 g / mol ( anhydrous ) 129 g / mol ( mono hydrate ) 147 g / mol ( di hydrate ) 183 g / mol ( tetra hydrate ) 219 g / mol ( hexa hydrate )
Appearance	White solid
Density	$2.15 \text{ g / cm}^3$ ( anhydrous )

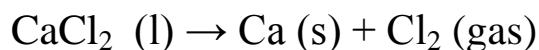
	1.83 g / cm <sup>3</sup> ( di hydrate ) 1.83 g / cm <sup>3</sup> ( tetra hydrate ) 1.71 g / cm <sup>3</sup> ( hexa hydrate )
Melting Point	772 °C ( anhydrous ) 260 °C ( monohydrate ) 176 °C ( di hydrate ) 45.5 °C ( tetra hydrate ) 30 °C ( hexa hydrate )
Boiling Point	1935 °C (anhydrous)
Solubility in Water	74.5 g / 100 mL ( 20 °C ) 59.5 g / 100 mL ( 0 °C )
Solubility in Alcohol	soluble
Acidity (pK <sub>a</sub> )	8 - 9 ( anhydrous ) 6.5 - 8.0 ( hexa hydrate )
EU Classification	Irritant ( <b>Xi</b> )
LD <sub>50</sub>	1000 mg / kg ( oral , rat )

## 2 . Chemical properties

Calcium chloride can serve as a source of calcium ions in solution , for instance for precipitation because many calcium compounds are insoluble : this is made out of calcium and chlorine elements.



Molten CaCl<sub>2</sub> can be electrolysed to give calcium metal and chlorine gas :

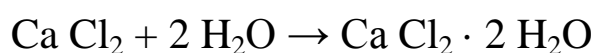


## 3 . Uses :

### 3 . 1 . Uses in industry

Because the anhydrous salt is strongly hygroscopic, air or other gases may be channeled through a column of calcium chloride to

remove moisture. In particular, calcium chloride is usually used to pack drying tubes to exclude atmospheric moisture from a reaction set - up while allowing gases to escape. It cannot, however, be used to dry alkaline gases such as ammonia because it will form addition products. It is used to dry kelp, which is then used to produce soda ash. It can also be added to liquids to remove suspended or dissolved water. The dissolving process is highly exothermic and rapidly produces temperatures of around 60 °C ( 140 °F ) . In this capacity, it is known as a drying agent or desiccant. It is converted to a brine as it absorbs the water or water vapor from the substance to be dried:



Aided by the intense heat evolved during its dissolution, calcium chloride is also used as an ice - melting compound . Unlike the more - common sodium chloride ( rock salt or halite ) , it is relatively harmless to plants and soil; however, recent observations in Washington state suggest it may be particularly harsh on roadside evergreen trees. It is also more effective at lower temperatures than sodium chloride. When distributed for this use, it usually takes the form of small white balls a few millimeters in diameter, called prills .

Used for its hygroscopic property, it can be applied to keep a liquid layer on the surface of the roadway, which holds dust down . It is used in concrete mixes to help speed up the initial setting, but chloride ion leads to corrosion of steel rebar, so it should not be used in reinforced concrete . The anhydrous form of calcium chloride may also be used for this purpose and can provide a measure of the moisture in concrete .

Aqueous calcium chloride (in solution with water) lowers the freezing point as low as - 52 °C , making it ideal for filling agricultural implement tires as a liquid ballast, aiding traction in cold climates .

Calcium Chloride is also commonly used as an additive in swimming pool water as it increases the " Calcium Hardness" value for the water. Low Calcium Hardness values in pool water cause pool water to be corrosive on equipment, pumps and metal fittings.

Other industrial applications include use as an additive in plastics, as a drainage aid for wastewater treatment, as an additive in fire extinguishers, as an additive in control scaffolding in blast furnaces , and as a thinner in fabric softener .

### **3 . 2 . Uses in food**

As an ingredient, it is listed as a permitted food additive in the European Union for use as a sequestrant and firming agent with the E number E509 , and considered as generally recognized as safe ( GRAS ) by the U.S. Food and Drug Administration . The average intake of calcium chloride as food additives has been estimated to be 160 - 345 mg / day for individuals . Ingestion of concentrated or pure calcium chloride products may cause gastrointestinal irritation or ulceration.<sup>[11]</sup> The anhydrous form has been approved by the FDA as a packaging aid to ensure dryness .

Calcium chloride is commonly used as an electrolyte and has an extremely salty taste , as found in sports drinks and other beverages such as Smartwater and Nestle bottled water. It can also be used as a preservative to maintain firmness in canned vegetables or in higher concentrations in pickles to give a salty taste while not increasing the food's sodium content . It is even found in snack foods , including Cadbury Caramilk chocolate bars ( purpose un known ) .

It can be used to make a caviar substitute from vegetable or fruit juices or added to processed milk to restore the natural balance between calcium and protein for the purposes of making cheese such as brie and stilton. Calcium chloride's exothermic properties are exploited in many 'self heating' food products where it is activated ( mixed ) with water to start the heating process, providing a non - explosive, dry fuel that is easily activated .

In brewing beer, calcium chloride is sometimes used to correct mineral deficiencies in the brewing water. It affects flavor and chemical reactions during the brewing process, and it can also affect yeast function during fermentation .

### **3 . 3 . Uses in drugs**

Calcium chloride can be injected as intravenous therapy for the treatment of hypo calcaemia ( low serum calcium ) . It can be used for insect bites or stings ( such as Black Widow Spider bites ) ; sensitivity reactions, particularly when characterized by urticaria ( hives ) ; magnesium intoxication ; as an aid in management of the acute symptoms in lead colic; in cardiac resuscitation, particularly after open heart surgery. Parenteral calcium can be used when epinephrine has failed to improve weak or ineffective myocardial contractions. Calcium chloride injection may antagonize cardiac toxicity as measured by electro cardiogram .

It can help to protect the myocardium from dangerously-high levels of serum potassium in hyperkalemia. Calcium chloride can be used to quickly treat Calcium Channel Blocker toxicity, from the side effects of drugs such as Diltiazem ( Cardizem ) —helping avoid potential heart attacks .

The aqueous form of calcium chloride is used in genetic transformation of cells by increasing the cell membrane permeability, inducing competence for DNA uptake ( allowing DNA fragments to enter the cell more readily ) .

It can also be used in the reef aquarium hobby for adding bio-available calcium in solution for calcium - using animals such as algae, snails, hard tube worms, and corals although the use of calcium hydroxide ( kalkwasser mix ) or a calcium reactor is the preferred method of adding calcium. However, calcium chloride is the quickest method to increase calcium levels as it dissolves readily in water.

### **4 . Precautions**

Dry calcium chloride reacts exo thermically when exposed to water. Burns can result in the mouth and esophagus if humans or other animals ingest dry calcium chloride pellets. Small children are more susceptible than adults ( who generally have had experience trying to eat hot food , and can react accordingly ) so calcium chloride pellets should be kept out of their reach .

## **5 . Natural occurrence**

Natural occurrence of a dihydrate ( mineral sinjarite ) and hexahydrate ( antarcticite ) is very rare and connected mainly with dry lakes and brines. Chloro calcite  $K Ca Cl_3$  is a related mineral ( also very rare ) .

# Calcium hydroxide

## Contents

- 1 Introduction
- 2 Uses
- 3 Health risks

## 1 . Introduction :

**Calcium hydroxide**, traditionally called **slaked lime**, **hydrated lime**, **slack lime** or **pickling lime**, is a chemical compound with the chemical formula  $\text{Ca}(\text{OH})_2$ . It is a colourless crystal or white powder, and is obtained when calcium oxide (called *lime* or *quicklime*) is mixed, or "slaked" with water. It can also be precipitated by mixing an aqueous solution of calcium chloride and an aqueous solution of sodium hydroxide. The name of the natural, mineral form is portlandite. It is relatively rare mineral, known from some volcanic, plutonic and metamorphic rocks. It has also been known to arise in burning coal dumps.

When heated to  $512\text{ }^{\circ}\text{C}$ , the partial pressure of water in equilibrium with calcium hydroxide reaches 101 kPa and decomposes into calcium oxide and water .

A suspension of fine calcium hydroxide particles in water is called milk of lime. The solution is called lime water and is a medium strength base that reacts violently with acids and attacks many metals in presence of water. It turns milky if carbon dioxide is passed through, due to precipitation of calcium carbonate .

Other names	Slaked lime Milk of lime Calcium(II) hydroxide Pickling lime
Molecular Formula	$\text{Ca}(\text{OH})_2$
Molar Mass	74 g / mol

Appearance	Soft white powder , Colourless liquid
Odor	Odorless
Density	2.211 g / cm <sup>3</sup> , solid
Melting point	512 °C ( decomp )
Solubility in Water	0.189 g / 100 mL ( 0 °C ) 0.173 g / 100 mL ( 20 °C )
Solubility product, $K_{sp}$	$7.9 \times 10^{-6}$
Basicity ( $pK_b$ )	2.37
EU Index	Corrosive ( C )
Flash point	Non - flammable
LD <sub>50</sub>	7340 mg / kg ( oral , rat )

## 2 . Uses

Because of its strong basic properties , calcium hydroxide has many and varied uses :

- A flocculent , in water and sewage treatment and improvement of acid soils
- An ingredient in white wash , mortar , and plaster
- An alkali used as a lye substitute in no - lye hair relaxers
- A chemical depilatory agent found in Nair
- A calcium supplement in mineral fortified baby formulas
- A chemical reagent
  - In Bordeaux mixture to neutralise the solution and form a long lasting fungicide .
  - In the reef aquarium hobby for adding bio-available calcium in solution for calcium - using animals such as algae , snails , hard tube worms , and corals ( often referred to as *Kalkwasser* mix ) , and also to increase the alkalinity of the water.
  - In the tanning industry for neutralization of acid , the liming of hides and skins and the flocculation of waste water .



- In the petroleum refining industry for the manufacture of additives to oils ( salicatic , sulphatic, fenatic ) .
- In the chemical industry for manufacture of calcium stearate .
- In the food industry for processing water ( for alcoholic and soft drinks ) .
- Used in the separation of sugar from sugar cane in the sugar industry .
- Used in the processing of Norwegian lutefisk . Dried cod fish is soaked in a mixture of slaked lime and soda to produce a soft - fleshed fish fillet that is steamed or baked and served with potato lefse .
- For clearing a brine of carbonates of calcium and magnesium in the manufacture of salt for food and pharmacopoeia
- In Native American and Latin American cooking , calcium hydroxide is called " cal " . Corn cooked with cal becomes nixtamal which significantly increases its nutrition value , and is also considered tastier and easier to digest .
- In chewing betel nut or coca leaves , calcium hydroxide is usually chewed alongside to keep the alkaloid stimulants chemically available for absorption by the body
- Similarly , Native Americans traditionally chewed tobacco leaves with calcium hydroxide derived from burnt shells to enhance the effects .
- A filler
  - In the petro chemical industry for manufacturing solid oil of various marks
  - In the manufacture of brake pads
  - In the manufacture of ebonite
  - For preparation of dry mixes for painting and decorating
  - In manufacturing mixes for pesticides

- In manufacturing the trademarked compound " Polikar " , an antifungal and antimicrobial preservative for vegetables in storage
- In dentistry , it is used as dressing in paste form used for anti-microbial effect during a dental root canal procedure. Calcium hydroxide is known to have a strong anti-microbial effect and is a bone-regeneration stimulant.<sup>[2]</sup>
- It has been proposed to add it to sea water in great quantities to reduce atmospheric CO<sub>2</sub> and fight the greenhouse effect .
  - Used as an acid suppressor in the production of metals . Lime is injected into the waste gas stream to neutralise acids such as fluorides and chlorides prior to being released to atmosphere
- In the beauty industry, used in relaxers for permanently straightening very curly hair.

### **3 . Health risks**

As with many chemicals , exposure may pose health risks :

- Inhalation : Respiratory tract irritation . Coughing , shortness of breath , chemical bronchitis.
- Ingestion : Internal bleeding, possible perforation of esophagus, severe pain , vomiting , diarrhea , and collapse.
- Eyes : severe irritation, pain , ulceration , blindness.
- Skin : burns , blistering .
- Chronic Exposure: dermatitis or severe irritation to skin.

# Calcium Hypochlorite

## Contents :

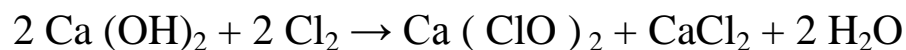
- 1 Introduction
- 2 Preparation
- 3 Properties
- 4 Uses

## 1 . Introduction :

**Calcium hypochlorite** is a chemical compound with formula  $\text{Ca}(\text{ClO})_2$ . It is widely used for water treatment and as a bleaching agent ( bleaching powder ). This chemical is considered to be relatively stable and has greater available chlorine than sodium hypochlorite ( liquid bleach ).

Other names	Calcium salt of hypochlorous acid Bleaching powder
Molecular Formula	$\text{Ca}(\text{ClO})_2$
Molar Mass	143 g / mol
Appearance	White / gray powder
Density	2.35 g / cm <sup>3</sup> ( 20 ° C )
Melting Point	100 ° C
Boiling Point	175 ° C , decomposes
Solubility in Water	21 g / 100 ml , reacts
Solubility	reacts in alcohol
EU Classification	Oxidant ( <b>O</b> ) Corrosive ( <b>C</b> ) Harmful ( <b>Xn</b> ) Dangerous for the environment ( <b>N</b> )
Flash Point	Non – flammable
LD <sub>50</sub>	850 mg / kg ( oral , rat )

## 2 . Preparation

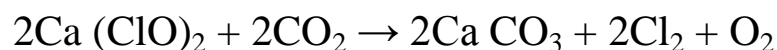


Bleaching powder is actually a mixture of calcium hypochlorite  $\text{Ca (ClO)}_2$  and the basic chloride  $\text{CaCl}_2$ ,  $\text{Ca (OH)}_2$ ,  $\text{H}_2\text{O}$  with some slaked lime,  $\text{Ca (OH)}_2$ .

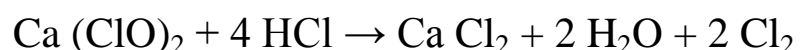
## 3 . Properties

It is a yellow white solid which has a strong smell of chlorine. Calcium hypochlorite is not highly soluble in water. For that reason it should preferably be used in soft to medium - hard water. There are two types of calcium hypochlorite - a dry form and a hydrated form. The hydrated form is safer to handle.

Calcium hypochlorite reacts with carbon dioxide to form calcium carbonate and release chlorine:



Calcium hypochlorite reacts with hydrochloric acid to form calcium chloride :



Extreme care should be used in handling this product. Always keep in a cool dry place away from any organic material. When mixing it with water, it is safest to add the calcium hypochlorite to water. This material has been known to undergo self heating and rapid decomposition accompanied by the release of toxic chlorine gas.

## 4 . Uses

Calcium hypochlorite is used for the disinfection of drinking water or swimming pool water. For use in outdoor swimming pools, calcium hypochlorite can be used as a sanitizer in combination with a cyanuric acid stabilizer. The stabilizer will reduce the loss of chlorine because of UV radiation. Calcium does make the water ' hard ' and tends to clog up some filters. However, some types of calcium

hypochlorite do contain anti-scaling agents in order to prevent clogging up of pipes/filters. This grade of calcium hypochlorite can also be used in hard waters. The main advantage of calcium hypochlorite is that it is unstabilized unlike chlorinated iso cyanurates such as sodium di chloro iso cyanurate or tri chloro iso cyanuric acid. Latter products do contain cyanuric acid. If the level of cyanuric acid becomes too high, it will influence the performance of the chlorine. Pools running on chlorinated iso cyanurates should maintain a free chlorine level between 2 and 5 ppm ( mg / L ) , whereas pools running on calcium hypochlorite should have a chlorine level of 1 - 2 ppm ( mg / L) .

Calcium hypochlorite is also used for bleaching cotton and linen and is used in the manufacture of chloroform.

***Other uses are :***

1. As bath room cleaner
2. Clean second hand items .
3. Glow to glass dish ware .
4. House hold disinfectant spray.
5. Remove moss and alga .
6. Sanitize garden tools .
7. Kill weeds in walkways .
8. Preserve the cut flowers fresh .
9. Clean lawn furniture

# Calcium Nitrate

## 1 Introduction :

**Calcium nitrate**, also called Norwegian salt peter , is the inorganic compound with the formula  $\text{Ca} (\text{NO}_3)_2$  . This colourless salt absorbs moisture from the air and is commonly found as a tetra hydrate . It is mainly used as a component in fertilizers. Nitro calcite is the name for a mineral which is a hydrated calcium nitrate that forms as an efflorescence where manure contacts concrete or limestone in a dry environment as in stables or caverns .

Other Names	Kalk saltpeter , nitro calcite, Norwegian saltpeter, lime nitrate ,
Molecular Formula	$\text{Ca} (\text{NO}_3)_2$
Molar Mass	164 g / mol ( anhydrous ) 236 g / mol ( tetra hydrate )
Appearance	Colourless
Density	2.504 g / cm <sup>3</sup> ( anhydrous ) 1.896 g / cm <sup>3</sup> ( tetra hydrate )
Melting Point	561 °C ( anhydrous ) 42.7 °C ( tetra hydrate )
Boiling Point	decomposes ( anhydrous ) 132 °C ( tetra hydrate )
Solubility in Water	<b><i>anhydrous:</i></b> 121.2 g /100 mL ( 20 °C ) 271.0 g /100 mL ( 40° C ) <b><i>tetra hydrate :</i></b> 102 g / 100 mL ( 0 °C ) 129 g / 100 mL ( 20 °C ) 363 g / 100 mL ( 100 °C )
Solubility	dissolves in alcohol and acetone
Crystal Structure	cubic ( anhydrous )

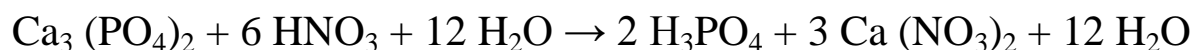
	mono clinic ( tetra hydrate )
Flash Point	Non – flammable

## 2 . Production and reactivity

Norwegian saltpeter was the first nitrogen fertilizer compound to be manufactured. Production began at Notodden, Norway in 1905. Most of the world 's calcium nitrate is now made in Porsgrunn. It is produced by treating limestone with nitric acid, followed by neutralization with ammonia :



It is also a by product of the Odda Process for the extraction of calcium phosphate:



Like related alkaline earth metal nitrates ( as well as  $\text{Li NO}_3$  ), calcium nitrate decomposes upon heating to release nitrogen dioxide :

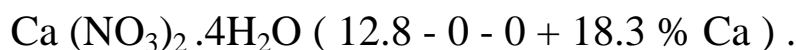


## 3 . Use in fertilizer

The fertilizer grade ( 15.5 - 0 - 0 + 19 % Ca ) is popular in the green house and hydro ponics trades ; it contains ammonium nitrate and water , as the " double salt "



Formulations lacking ammonia are also known :



A liquid formulation ( 9 – 0 - 0 + 11 % Ca ) is also offered .

An anhydrous, air - stable derivative is the urea complex  $\text{Ca} (\text{NO}_3)_2 \cdot 4 [\text{OC} (\text{NH}_2)_2]$  , which has been sold as Cal - Urea.

# Calcium oxide

## 1 . Introduction :

**Calcium oxide (CaO)** , commonly known as **burnt lime** , **lime** or **quicklime** , is a widely used chemical compound. It is a white, caustic and alkaline crystalline solid at room temperature. As a commercial product , lime often also contains magnesium oxide, silicon oxide and smaller amounts of aluminium oxide and iron oxide. The name lime ( native lime ) refers to a very rare mineral of the CaO composition .

Calcium oxide is usually made by the thermal decomposition of materials such as limestone, that contain calcium carbonate (CaCO<sub>3</sub>; mineral name: calcite) in a lime kiln. This is accomplished by heating the material to above 825°C , a process called calcination or *lime - burning*, to liberate a molecule of carbon dioxide (CO<sub>2</sub>) ; leaving CaO . This process is reversible, since once the quicklime product has cooled, it immediately begins to absorb carbon dioxide from the air, until, after enough time, it is completely converted back to calcium carbonate.

Other Names	Quicklime
Molecular Formula	Ca O
Molar mass	56 g / mol
Appearance	White to pale yellow powder
Density	3.35 g / cm <sup>3</sup>
Melting Point	2572 °C ( 2845 K )
Boiling Point	2850 °C ( 3123 K )
Solubility in Water	Reacts
Solubility in :( acids , glycerol , sugar solution )	Soluble
Solubility in ( methanol , diethyl ether , n - octanol )	Insoluble
Acidity ( pK <sub>a</sub> )	12.5

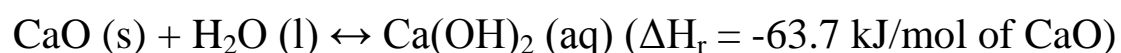


## 2 . Usage

As hydrated or slaked lime ,  $\text{Ca}(\text{OH})_2$  (mineral name : portlandite ) , it is used in mortar and plaster . Hydrated lime is very simple to make as lime is a basic anhydride and reacts vigorously with water . Lime is also used in glass production and its ability to react with silicates is also used in modern metal production industries ( steel in particular ) to remove impurities as slag .

It is also used in water and sewage treatment to reduce acidity, to harden, as a flocculent , and to remove phosphates and other impurities; in paper making to dissolve lignin , as a coagulant, and in bleaching; in agriculture to improve acidic soils; and in pollution control, in gas scrubbers to desulfurize waste gases and to treat many liquid effluents . It has traditionally been used in the burial of bodies in open graves, to hide the smell of decomposition, as well as in forensic science, to reveal fingerprints. It is a refractory and a dehydrating agent and is used to purify citric acid, glucose, dyes and as a  $\text{CO}_2$  absorber. It is also used in pottery, paints and the food industry. Furthermore, quicklime is used in epidemics, plagues, and disasters to disintegrate bodies in order to help fight the spread of disease .  $\text{CaO}$  is a key ingredient in the *nixtamalization* process used to create corn hominy and masa or tortilla dough. In ancient India, before the discovery of soap, it was mixed with sand and used to clean one's body, while it was also used to build houses .

A relatively inexpensive substance,  $\text{CaO}$  produces heat energy by the formation of the hydrate, as in the following equation :



The hydrate can be reconverted to calcium oxide by removing the water in the reversible equation. If the hydrated lime is heated to redness, the  $\text{CaO}$  will be regenerated to reverse the reaction. As it hydrates, an exothermic reaction results. One litre of water combines with approximately 3.1 kg of calcium oxide to give calcium hydroxide plus 3.54 MJ of energy. This process can be used to provide a convenient portable source of heat, as for on-the-spot food warming in a self - heating can.

When quicklime is heated to 4,300°F ( 2,370°C ), it emits an intense glow. This form of illumination is known as a limelight and was used broadly in theatrical productions prior to the invention of electric lighting .

Annual worldwide production of calcium oxide is around 283 million metric tons. The United States and China are the largest producers, producing around 20 and 170 million metric tons, respectively .

### **3 . Use as a weapon**

Historian and philosopher David Hume , in his history of England, recounts how during early in the reign of Henry III the English Navy destroyed an invading French fleet , by blinding the enemy fleet with " quick lime " , the old name for calcium oxide :

D' Albiney employed a stratagem against them, which is said to have contributed to the victory : Having gained the wind of the French, he came down upon them with violence; and throwing in their faces a great quantity of quicklime, which he purposely carried on board, he so blinded them, that they were disabled from defending themselves.

Also, quick lime is thought to be a component in Greek fire to make it ignite on contact with water .

# Calcium phosphate

## 1 . Introduction :

**Calcium phosphate** is the name given to a family of minerals containing calcium ions (  $\text{Ca}^{2+}$  ) together with ortho phosphates (  $\text{PO}_4^{3-}$  ) , meta phosphates or pyro phosphates (  $\text{P}_2\text{O}_7^{4-}$  ) and occasionally hydrogen or hydroxide ions. Seventy percent of bone is made up of hydroxyl apatite , a calcium phosphate mineral. Tooth enamel is also largely calcium phosphate.

## 2 . Uses

For the production of phosphoric acid and fertilizers, for example in the Odda process. Overuse of certain forms of calcium phosphate can lead to nutrient - containing surface runoff and subsequent adverse effects upon receiving waters such as algal blooms and eutrophication .

Calcium phosphate is also a raising agent , with E number E341. It is also used in cheese products. It is also used as a nutritional supplement . There is some debate about the different bioavailabilities of the different calcium salts.

It is used in a variety of dental products for re mineralization and as a diluent in some medications where it will give the tablet a grey colour in the absence of additional colouring agents.

Another practical application of the compound is its use in gene transfection of cells . It is not too well understood, but the calcium phosphate precipitate and DNA form a complex that is thought to help the DNA enter the cell.

## 3 . Calcium phosphate compounds

- Calcium di hydrogen phosphate , E341 (i) :  $\text{Ca} ( \text{H}_2\text{PO}_4 )_2$
- Calcium hydrogen phosphate , E341(ii) :  $\text{Ca HPO}_4$
- Tri calcium phosphate , E341(iii) :  $\text{Ca}_3 ( \text{PO}_4 )_2$

# Calcium Di Hydrogen Phosphate

## Contents

- 1 Introduction
- 2 Uses
  - 2.1 Fertilizer
    - 2.1.1 Superphosphate
    - 2.1.2 Triple superphosphate
  - 2.2 Leavening agent

## 1 . Introduction:

**Mono calcium phosphate** is a chemical compound with the formula  $\text{Ca} (\text{H}_2\text{PO}_4)_2$  . It is commonly found as the mono hydrate,  $\text{Ca} (\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ .

Other Names	Acid calcium phosphate Calcium acid phosphate Calcium bi phosphate Mono basic calcium phosphate Mono calcium ortho phosphate Calcium di ortho phosphate Phosphoric acid calcium salt
Molecular Formula	$\text{Ca H}_4\text{P}_2\text{O}_8$
Molar Mass	234 g / mol
Melting Point	109 °C
Boiling Point	203 °C ( decomposes )
Flash Point	Non - flammable

## 2 . Uses

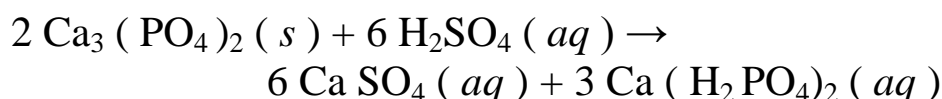
### 2 . 1 . Fertilizer

Phosphorus is an essential nutrient and there fore is a common component of agricultural fertilizers . Tricalcium phosphate  $\text{Ca}_3 (\text{PO}_4)_2$  , a major component of phosphate rock such as phosphorite ,

apatite, and other phosphate minerals, is too insoluble to be an efficient fertilizer. Therefore it can be converted into the more soluble mono calcium phosphate, generally by the use of sulfuric acid  $\text{H}_2\text{SO}_4$ . The result is hydrated to turn the calcium sulfate into the di hydrate gypsum and sold as *super phosphate of lime*. Alternately phosphate rock may be treated with phosphoric acid to produce a purer form of monocalcium phosphate and is sold as *triple phosphate*.

### 2 . 1 . 1 . Super phosphate

**Super phosphate** is a fertilizer produced by the action of concentrated sulfuric acid on powdered phosphate rock .



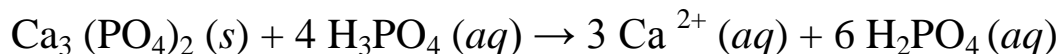
" In 1840 , Justus Von Liebig wrote , 'The crops on the field diminish or increase in exact proportion to the diminution or increase of the mineral substances conveyed to it in manure.' Von Liebig was the first to discover that phosphate of lime in bone meal could be rendered more readily available to plants by treatment with sulfuric acid. Sir John Bennett Lawes about the same time discovered that phosphate rock underwent the same reaction and could be used as a source ingredient. In the 1840s, scientists found that coprolites could be dissolved in sulfuric acid to produce what became known as superphosphate. Bennett Lawes was the first to manufacture superphosphate at his factory in Deptford, England in 1842 " .

A large market for super phosphate was created in the second half of the 20th century by the development of aerial topdressing in New Zealand which allowed superphosphate to be spread economically over large areas .

Superphosphate can be created naturally in large quantities by the action of guano, or bird feces, resulting in deposits around sea bird colonies which can be mined. The most famous mining site is the island of Nauru in the South Pacific much of the "soil" from which was mined, creating temporary wealth for the inhabitants, but destroying their environment .

### 2 . 1 . 2 .Triple super phosphate :

**Triple Super phosphate** is a fertilizer produced by the action of concentrated phosphoric acid on ground phosphate rock .



The active ingredient of the product, monocalcium phosphate, is identical to that of superphosphate, but without the presence of calcium sulfate that is formed if sulfuric acid is used instead of phosphoric acid. The phosphorus content of triple super phosphate ( 17 – 23 % P ; 44 to 52 % P<sub>2</sub>O<sub>5</sub> ) is therefore greater than that of superphosphate ( 7 - 9.5 % P ; 16 to 22 % P<sub>2</sub>O<sub>5</sub> ) . Triple super phosphate was the most common phosphate ( P ) fertilizer in the USA until the 1960s, when ammonium phosphates became more popular. It is produced in granular and non granular form and is used both in fertilizer blends ( with potassium and nitrogen fertilizers ) and by itself.

### 2 . 2 . Leavening agent

Calcium di hydrogen phosphate is also used in the food industry as a leavening agent to cause baked goods to rise. Because it is acidic, when combined with an alkali ingredient – commonly sodium bicarbonate (baking soda) or potassium bicarbonate – it reacts to produce carbon dioxide and a salt. The carbon dioxide gas is what leavens the baked good. When combined in a ready-made baking powder, the acid and alkali ingredients are included in the right proportions such that they will exactly neutralize each other and not significantly affect the overall pH of the product.

Apart from acting as leavening agent, it also inhibits microbial activity because of the phosphate ions present in the molecule .

# Calcium Mono Hydrogen Phosphate

## ( Dicalcium phosphate )

### Contents :

- 1 Introduction
- 2 Production
  - 2 . 1 Treatment of Super phosphate with hydrated lime
  - 2 . 2 Treatment of phosphate rock with nitric acid
  - 2 . 3 Treatment of phosphate rock with sulfuric acid
  - 2 . 4 Treatment of Phosphate Rock with Hydrochloric Acid
    - 2 . 4 . 1 Process Chemistry of Hydrochloric Acid

### 1 . Introduction :

**Calcium Mono Hydrogen Phosphate** , also known as Dicalcium phosphate , is a dibasic calcium phosphate. It is usually found as the di hydrate , with the chemical formula of  $\text{Ca HPO}_4 \cdot 2\text{H}_2\text{O}$ , but it can be thermally converted to the anhydrous form. It is practically insoluble in water, with a solubility of 0.02 g per 100 mL at 25 °C. It contains about 23 percent calcium in its anhydrous form, and is mainly used as a dietary supplement in prepared breakfast cereals, dog treats, enriched flour, and noodle products. It is also used as a tableting agent in some pharmaceutical preparations. It is used in poultry feed.

Other Names	Di calcium phosphate . Phosphoric acid calcium salt ( 1 : 1 )
Molecular Formula	$\text{Ca HPO}_4$
Molar Mass	136 g / mol
Solubility in Water	0.02 g / 100 mL

### 2 – Production :

#### 2 – 1 - Treatment of Super phosphate with hydrated lime :

This invention relates to the preparation of feed grade di calcium phosphate from a source containing mono calcium phosphate such as super phosphate, concentrated super phosphate and the like. The first step consists of leaching water soluble mono calcium phosphate there from with water or recycle wash water from one of the subsequent steps. The supernatant liquid treated with a first quantity of hydrated lime to precipitate impurities such as Fe, Al and F. The filtrate obtained after removing the precipitate is further treated with hydrated lime to raise the pH till mono calcium phosphate present therein gets converted into di calcium phosphate which crystallizes out wash water from the second and the third stages are recycled to the system. By- product obtained is gypsum , which is used in cement industry or as a fertilizer filter.

### **2 – 2 - Treatment of phosphate rock with nitric acid :**

The process is based on the nitric acidulation of phosphate rock concentrate, followed by neutralization of the extract liquor with calcium carbonate. The precipitated di calcium phosphate is then separated from calcium nitrate solution by filtration. The di calcium phosphate thus obtained contains 44 – 47 % total  $P_2O_5$  and can be used as fertilizer or, with an additional low pH filtration step, as animal feed supplement.

### **2 – 3 - treatment of phosphate rock with sulfuric acid**

A new process for the production of de fluorinated di calcium phosphate using phosphate rock was developed. This new process has the main characteristic of being clean, with out the production of any liquid waste. The process has essentially three main steps: phosphate rock digestion, de fluorination and neutralization . In the first step a phosphate rock slurry is batch digested with concentrated sulfuric acid in the presence of some additives that retain the fluorine in the solution, as well as enable the adequate growth of the calcium sulfate crystals and maximize the phosphate dissolution. At the end of the digestion the slurry is filtrated and the mother licquor is sent to the next step. The second step of the process is a fluorine salt precipitate sedimentation carried out by the addition of a potassium or sodium



salt . The clear solution containing mainly a weak phosphoric acid is then neutralized in the third step, in order to produce the final di calcium phosphate product. After filtration the di calcium phosphate is dried and the mother liquor is recycled to the first step of the process, the phosphate rock digestion. All the liquids of the process are recycled and no wastes are produced. This new process is economically interesting because it uses a very cheap raw material, the phosphate rock , instead of the conventional de fluorinated phosphoric acid .

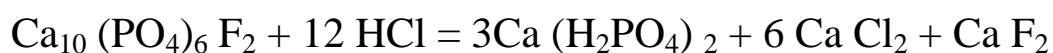
## **2 – 4 - Treatment of Phosphate Rock with Hydrochloric Acid :**

This method , was used by dissolution of rock phosphate in hydrochloric acid to deliver a very pure and crystalline di calcium phosphate. The process starts with the dissolution of finely ground rock phosphate in diluted hydrochloric acid , resulting in the formation of a mono calcium phosphate solution . and calcium chloride as soluble .

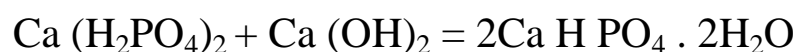
The insoluble fraction, consisting mainly of calcium fluoride, is removed and the liquor is purified . Because mono calcium phosphate is readily soluble in water it cannot be precipitated .

### **2 – 4 – 1 - Process Chemistry of Hydrochloric Acid :**

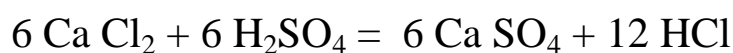
*Dissolution in hydrochloric acid :*



*Saturation of mono calcium phosphate solution to produce di hydrated crystalline di calcium phosphate :*



*Calcium chloride react with Sulfuric acid to produce agian hydrochloric acid :*



# Tri Calcium Phosphate

- 1 . Introduction
- 2 . General case
- 3 . Natural occurrence
- 4 . Uses

## 1 . Introduction :

**Tri calcium phosphate** is a compound with formula  $\text{Ca}_3(\text{PO}_4)_2$ . It is also known as *calcium ortho phosphate* , *tertiary calcium phosphate* , *tri basic calcium phosphate* , or " *bone ash*" (calcium phosphate being one of the main combustion products of bone ).

It has an alpha an alpha' and a beta crystal form, the alpha state being formed at high temperatures. As rock, it is found in Whit lockite.

Other Names	Whit lockite
Molecular Formula	$\text{Ca}_3 \text{O}_8 \text{P}_2$
Molar Mass	310 g / mol
Appearance	White amorphous powder
Density	$3.14 \text{ g / cm}^3$
Melting Point	Liquefies under high pressure at ( 1391 ° C )

## 2 . General case

In minerals, " calcium phosphate " refers to minerals containing calcium ions (  $\text{Ca}^{2+}$  ) together with orthophosphates (  $\text{PO}_4^{3-}$  ) , meta phosphates or pyrophosphates (  $\text{P}_2\text{O}_7^{4-}$  ) and occasionally hydrogen or hydroxide ions.

Especially, the mineral apatite has formula  $\text{Ca}_5 ( \text{PO}_4 )_3 \text{X}$  , where X is F , Cl , OH , or a mixture ; it is hydroxy apatite if the extra ion is mainly hydroxide . Much of the " tri calcium phosphate " on the market is actually powdered hydroxy apatite.

### 3 . Natural occurrence

It is found in nature as a rock in Morocco , Jordon , Philippines , Egypt , Syria , and Kola ( Russia ) and in smaller quantities in some other countries. The natural form is not completely pure , and there are some other components like sand and lime which can change the composition. In terms of  $P_2O_5$  , most calcium phosphate rocks have a content of 30 % to 40 %  $P_2O_5$  in weight.

The skeletons and teeth of vertebrate animals are composed of calcium phosphate, mainly hydroxyl apatite .

### 4 . Uses

Tri calcium phosphate is used in powdered spices as an anti - caking agent .

Calcium phosphate is an important raw material for the production of phosphoric acid and fertilizers, for example in the Odda process.

Calcium phosphate is also a raising agent ( food additives ) E341 . Is a mineral salt found in rocks and bones , it is used in cheese products .

It is also used as a nutritional supplement. There is some debate about the different bio availabilities of the different calcium salts.

It is commonly used in porcelain and dental powders, and medically as an antacid or calcium supplement, although calcium carbonate is more common in this regard.

Another practical application of the compound is its use in gene transfection. The calcium ions can make a cell competent ( a euphemism for " rip holes in its membrane " ) to allow exogenous genes to enter the cell by diffusion. A heat shock afterwards then invokes the cell to repair itself. This is a quick and easy method for transfection, albeit a rather inefficient one.

# Calcium Sulfate

## Contents

- 1 Introduction
- 2 Commercial production and recovery
- 3 Dehydration reactions
- 4 Fouling deposits

## 1 . Introduction :

**Calcium sulfate** is a common laboratory and industrial chemical. In the form of  $\gamma$  - anhydrite ( the nearly anhydrous form ) , it is used as a desiccant. It is also used as a coagulant in products like tofu . In the natural state, unrefined calcium sulfate is a translucent, crystalline white rock. When sold as a color-indicating variant under the name Drierite, it appears blue or pink due to impregnation with cobalt chloride, which functions as a moisture indicator . The hemi hydrate (  $\text{CaSO}_4 \cdot \sim 0.5 \text{H}_2\text{O}$  ) is better known as plaster of Paris , while the di hydrate (  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  ) occurs naturally as gypsum. The anhydrous form occurs naturally as  $\beta$ -anhydrite. Depending on the method of calcination of calcium sulfate dihydrate, specific hemihydrates are sometimes distinguished : alpha – hemi hydrate and beta – hemi hydrate . They appear to differ only in crystal size. Alpha -hemi hydrate crystals are more prismatic than beta – hemi hydrate crystals and , when mixed with water, form a much stronger and harder superstructure .

Other Names	Plaster of Paris Drierite Gypsum
Molecular Formula	$\text{Ca SO}_4$
Molar Mass	136 g / mol ( an hydrous ) 145 g / mol ( hemi hydrate ) 172 g / mol ( di hydrate )
Appearance	White solid
Odor	Odorless

Density	2.96 g / cm <sup>3</sup> (anhydrous) 2.32 g / cm <sup>3</sup> (dihydrate)
Melting point	1460 °C (anhydrous)
Solubility in Water	0.0021 g / 100 mL ( 20 °C , anhydrous ) 0.24 g / 100mL ( 20 °C , dihydrate )
Solubility product, $K_{sp}$	$2.4 \times 10^{-5}$ ( dihydrate )
Solubility in glycerol	Very soluble ( dihydrate )
Crystal structure	Orthorhombic

## 2 . Commercial production and recovery

The main sources of calcium sulfate are naturally occurring gypsum and anhydrite which occur at many locations worldwide as evaporites. These may be extracted by open - cast quarrying or by deep mining. World production of natural gypsum is around 127 million tonnes per annum .

In addition to natural sources, calcium sulfate is produced as a by - product in a number of processes :

- In flue gas desulfurization, exhaust gases from fossil-fuel-burning power stations and other processes ( e.g. cement manufacture ) are scrubbed to reduce their sulfur oxide content, by injecting finely ground limestone or lime. This produces an impure calcium sulfite, which oxidizes on storage to calcium sulfate .
- In the production of phosphoric acid from phosphate rock, calcium phosphate is treated with sulfuric acid and calcium sulfate precipitates.
- In the production of hydrogen fluoride, calcium fluoride is treated with sulfuric acid , precipitating calcium sulfate .
- In the refining of zinc , solutions of zinc sulfate are treated with lime to co - precipitate heavy metals such as barium.
- Calcium sulfate can also be recovered and re-used from scrap drywall at construction sites.

These precipitation processes tend to concentrate radioactive elements in the calcium sulfate product. This is particularly the case with the phosphate by - product, since phosphate rocks naturally contain actinides. Over 200 million tonnes per annum of calcium sulfate waste is produced by the phosphate industry worldwide .

### 3 . Dehydration reactions

Heating gypsum to between 100 °C and 150 °C partially dehydrates the mineral by driving off approximately 75 % of the water contained in its chemical structure. The temperature and time needed depend on ambient partial pressure of H<sub>2</sub>O. Temperatures as high as 170 °C are used in industrial calcination, but at these temperatures  $\gamma$  - anhydrite begins to form. The reaction for the partial dehydration is :



The partially dehydrated mineral is called calcium sulfate hemihydrates or calcined gypsum ( commonly known as plaster of Paris ) (  $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  ) , where n is in the range 0.5 to 0.8 .

The dehydration ( specifically known as calcinations ) begins at approximately 80 °C , although in dry air, some dehydration will take place already at 50 °C . The heat energy delivered to the gypsum at this time ( the heat of hydration ) tends to go into driving off water ( as water vapor) rather than increasing the temperature of the mineral, which rises slowly until the water is gone, then increases more rapidly.

The endothermic property of this reaction is exploited by drywall to confer fire resistance to residential and other structures. In a fire, the structure behind a sheet of drywall will remain relatively cool as water is lost from the gypsum, thus preventing ( or substantially retarding ) damage to the framing ( through combustion of wood members or loss of strength of steel at high temperatures ) and consequent structural collapse.

In contrast to most minerals , which when rehydrated simply form liquid or semi - liquid pastes, or remain powdery, calcined gypsum has an unusual property: when mixed with water at normal ( ambient ) temperatures, it quickly reverts chemically to the preferred dihydrate form, while physically " setting " to form a rigid and relatively strong gypsum crystal lattice :



This reaction is exothermic and is responsible for the ease with which gypsum can be cast into various shapes including sheets ( for dry wall ), sticks ( for black board chalk ) , and molds ( to immobilize broken bones, or for metal casting ) . Mixed with polymers, it has been used as a bone repair cement. Small amounts of calcined gypsum are added to earth to create strong structures directly from cast earth, an alternative to adobe (which loses its strength when wet) The conditions of dehydration can be changed to adjust the porosity of the hemihydrate , resulting in the so - called alpha and beta hemihydrates ( which are more or less chemically identical ) .

On heating to 180 °C, the nearly water - free form, called  $\gamma$  - anhydrite (  $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  where  $n = 0$  to 0.05 ) is produced .  $\gamma$  - Anhydrite reacts slowly with water to return to the di hydrate state, a property exploited in some commercial desiccants. On heating above 250 °C , the completely anhydrous form called  $\beta$  - anhydrite or " natural " anhydrite is formed. Natural anhydrite does not react with water, even over geological timescales, unless very finely ground .

The variable composition of the hemihydrate and  $\gamma$  - anhydrite, and their easy inter-conversion, is due to their possessing nearly-identical crystal structures, containing "channels" that can accommodate variable amounts of water, or other small molecules such as methanol .

#### **4 . Fouling deposits**

Temperature dependence of the solubility of calcium sulfate ( 3 phases ) in pure water.

Calcium sulfate is a common component of fouling deposits in industrial heat exchangers . It is because its solubility decreases with increasing temperature in hot water .



# Gypsum

## Contents

- 1 Introduction
- 2 Crystal varieties
- 3 Occurrence
- 4 Uses of Gypsum

## 1 . Introduction :

**Gypsum** is a very soft mineral composed of calcium sulfate dihydrate , with the chemical formula  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  .

Category	Sulfate mineral
Chemical Formula	Calcium sulfate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Color	Colorless to white ; with impurities may be yellow , tan , blue , pink , brown , reddish brown or gray
Crystal Habit	Massive , flat . Elongated and generally prismatic crystals
Mohs Scale hardness	1.5 – 2
Luster	Vitreous to silky , pearly , or waxy
Streak	White
Specific Gravity	2.31 - 2.33
Optical properties	$2V = 58^\circ$ Biaxial (+)
Refractive index	$n_\alpha = 1.519 - 1.521$ $n_\beta = 1.522 - 1.523$ $n_\gamma = 1.529 - 1.530$

## 2 . Crystal varieties

Gypsum occurs in nature as flattened and often twinned crystals and transparent cleavable masses called selenite. It may also occur silky and fibrous, in which case it is commonly called *satin spar* . Finally it may also be granular or quite compact. In hand - sized samples, it can be anywhere from transparent to opaque. A very fine - grained white or lightly-tinted variety of gypsum is called alabaster,

which is prized for ornamental work of various sorts. In arid areas, gypsum can occur in a flower-like form typically opaque with embedded sand grains called desert rose. Up to the size of 11m long, gypsum forms some of the largest crystals found in nature, in the form of selenite .

### 3 . Occurrence

Gypsum is a common mineral, with thick and extensive evaporite beds in association with sedimentary rocks. Deposits are known to occur in strata from as early as the Permian age. Gypsum is deposited in lake and sea water, as well as in hot springs, from volcanic vapors, and sulfate solutions in veins. Hydrothermal anhydrite in veins is commonly hydrated to gypsum by groundwater in near surface exposures. It is often associated with the minerals halite and sulfur .

The word gypsum is derived from the Greek word γύψος , " chalk " or " plaster " . Because the gypsum from the quarries of the Montmartre district of Paris has long furnished burnt gypsum used for various purposes, this material has been called plaster of Paris . It is also used in foot creams , shampoos and many other hair products . It is water - soluble.

Because gypsum dissolves over time in water , gypsum is rarely found in the form of sand. However, the unique conditions of the White Sands National Monument in the US state of New Mexico have created a 710 km<sup>2</sup> expanse of white gypsum sand , enough to supply the construction industry with drywall for 1,000 years . Commercial exploitation of the area , strongly opposed by area residents, was permanently prevented in 1933 when president Herbert Hoover declared the gypsum dunes a protected national monument.



Commercial quantities of gypsum are found in all the world

Synthetic gypsum is recovered via flue gas desulfurization at some coal - fired electric power plants . It can be used interchangeably with natural gypsum in some applications .

## 4 . Uses of Gypsum

*Gypsum is used in a wide variety of applications :*

- Gypsum Board primarily used as a finish for walls and ceilings; known in construction slang as Dry wall
- Plaster ingredient.
- Fertilizer and soil conditioner. In the late eighteenth and early nineteenth century was a highly sought fertilizer for wheat fields in the United States.
- A Binder in Fast - Dry tennis court clay.
- Plaster of Paris ( surgical splints ; casting moulds ; modeling ) .
- A wood substitute in the ancient world ; for example, when wood became scarce due to deforestation on Bronze Age Crete, gypsum was employed in building construction at locations where wood was previously used .
- A tofu ( soy bean curd ) coagulant , making it ultimately a major source of dietary calcium , especially in Asian cultures which traditionally use few dairy products .
- Adding hardness to water used for home brewing .
- A component of Portland cement used to prevent flash setting of concrete.
- Soil / water potential monitoring ( soil moisture tension )
- Has a common use as an ingredient in making mead.

	
<p><i>Plaster work in Pompeii (79 AD)</i></p>	<p><i>19th century plaster work from House of Borujerdi in Kashan , Iran.</i></p>

## Mortar ( masonry )



*Mortar holding weathered bricks*

### Contents :

- 1 Introduction
- 2 Ancient mortar
- 3 Portland cement mortar
- 4 Polymer cement mortar
- 5 Lime mortar
- 6 Pozzolana mortar
- 7 Radio carbon dating

### 1 – Introduction :

**Mortar** is a workable paste used to bind construction blocks together and fill the gaps between them. The blocks may be stone, brick, cinder blocks, etc. Mortar becomes hard when it sets, resulting in a rigid aggregate structure. Modern mortars are typically made from a mixture of sand, a binder such as cement or lime, and water. Mortar can also be used to fix, or *point*, masonry when the original mortar has washed away.

### 2 - Ancient mortar :

The first mortars were made of mud and clay. Because of a lack of stone and an abundance of clay, Babylonian constructions were of baked brick, using lime or pitch for mortar. According to Roman Ghirshman, the first evidence of humans using a form of mortar was at the ziggurat of Sialk in Iran, built of sun - dried bricks in 2900 BC . The Chogha Zanbil Temple in Iran was built in about 1250 BC with kiln-fired bricks and a strong mortar of bitumen.

In early Egyptian pyramids constructed about 2600 –2500 BC, the limestone blocks were bound by mortar of mud and clay, or clay and sand . In later Egyptian pyramids, the mortar was made of either gypsum or lime . Gypsum mortar was essentially a mixture of plaster and sand and was quite soft.

In the Indian subcontinent, multiple cement types have been observed in the sites of the Indus Valley Civilization, such as the Mohenjo - daro city- settlement that dates to earlier than 2600 BCE. Gypsum cement that was "*light grey and contained sand, clay, traces of calcium carbonate, and a high percentage of lime*" was used in the construction of wells, drains and on the exteriors of "*important looking buildings.*" Bitumen mortar was also used at a lower-frequency, including in the Great Bath at Mohenjo – daro .

Historically, building with concrete and mortar next appeared in Greece. The excavation of the under ground aqueduct of Megara revealed that a reservoir was coated with a pozzolanic mortar 12 mm thick. This aqueduct dates back to c. 500 BC . Pozzolanic mortar is a lime based mortar, but is made with an additive of volcanic ash that allows it to be hardened under water; thus it is known as hydraulic cement. The Greeks obtained the volcanic ash from the Greek islands Thira and Nisiros, or from the then Greek colony of Dicaearchia (Pozzuoli) near Naples, Italy. The Romans later improved the use and methods of making what became known as pozzolanic mortar and cement . Even later, the Romans used a mortar without pozzolana using crushed terra cotta , introducing aluminum oxide and silicon dioxide into the mix. This mortar was not as strong as pozzolanic mortar, but, because it was denser, it better resisted penetration by water.

Hydraulic mortar was not available in ancient China, possibly due to a lack of volcanic ash. Around CE 500, sticky rice soup was mixed with slaked lime to make an inorganic – organic composite mortar that had more strength and water resistance than lime mortar.

It is not understood why the art of making hydraulic mortar and cement, which was perfected and in such wide spread use by both the

Greeks and Romans, was then lost for almost two millennia. During the Middle Ages when the Gothic cathedrals were being built, the only active ingredient in the mortar was lime. Since cured lime mortar can be degraded by contact with water, many structures suffered from wind blown rain over the centuries.



*Laying bricks with portland cement mortar*

### **3 - Portland cement mortar :**

**Portland cement mortar** (often known simply as cement mortar) is created by mixing Ordinary Portland cement (OPC) with sand and water.

It was invented in 1794 by Joseph Aspdin and patented on 18 December 1824, largely as a result of various scientific efforts to develop stronger mortars than existed at the time. It was popularized during the late nineteenth century, and owing to the First World War, by 1930 it had superseded lime mortar for new construction. The main reasons for this were that Portland cement sets hard and quickly, allowing a faster pace of construction, and requires less skilled workers. However, as a general rule, Portland cement should not be used for the repair of older buildings constructed in lime mortar, which require the flexibility, softness and breathability of lime if they are to function correctly.

### **4 - Polymer cement mortar :**

Polymer cement mortars (PCM) are the materials which are made by partially replacing the cement hydrate binders of conventional cement mortar with polymers. The polymeric admixtures include latexes or emulsions, redispersible polymer

powders, water-soluble polymers, liquid resins and monomers. It has low permeability, and it reduces the incidence of drying shrinkage cracking, mainly designed for repairing concrete structures.

### **5 - Lime mortar :**

The speed of set can be increased by using impure lime stones in the kiln, to form a hydraulic lime that will set on contact with water. Such a lime must be stored as a dry powder. Alternatively, a pozzolanic material such as calcined clay or brick dust may be added to the mortar mix. This will have a similar effect of making the mortar set reasonably quickly by reaction with the water in the mortar.

Using Portland cement mortars in repairs to older buildings originally constructed using lime mortar can be problematic. This is because lime mortar is softer than cement mortar, allowing brick work a certain degree of flexibility to move to adapt to shifting ground or other changing conditions. Cement mortar is harder and allows less flexibility. The contrast can cause brickwork to crack where the two mortars are present in a single wall.

Lime mortar is considered breath able in that it will allow moisture to freely move through it and evaporate from its surface. In old buildings with walls that shift over time, there are often cracks which allow rain water into the structure. The lime mortar allows this moisture to escape through evaporation and keeps the wall dry. Repainting or rendering an old wall with cement mortar stops this evaporation and can cause problems associated with moisture behind the cement.

### **6 - Pozzolana mortar**

Pozzolana is a fine, sandy volcanic ash, originally discovered and dug in Italy at Pozzuoli in the region around Mount Vesuvius, but later at a number of other sites. The ancient Roman architect Vitruvius speaks of four types of pozzolana. It is found in all the volcanic areas of Italy in various colours: black, white, grey and red.

Finely ground and mixed with lime it acts like Portland cement and makes a strong mortar that will also set under water.

### **7 - Radio carbon dating :**

An international team headed by Åbo Akademi University has developed a method of determining the age of mortar using radio carbon dating. As the mortar hardens, the current atmosphere is encased in the mortar and thus provides a sample for analysis. One major challenge is various factors that affect the sample and raise the margin of error for the analysis .