CALCIUM AND CALCIUM ALLOYS

1. Introduction

Calcium [7440-70-2], Ca, a member of Group 2 (IIA) of the Periodic Table between magnesium and strontium, is classified, together with barium and strontium, as an alkaline-earth metal and is the lightest of the three. Calcium metal does not occur free in nature; however, in the form of numerous compounds, it is the fifth most abundant element, constituting 3.63% of the earth's crust.

The word calcium is derived from calx, the Latin word for lime. The Romans used large quantities of calcium oxide or lime as mortar in construction (see LIME AND LIMESTONE). Because calcium compounds are very stable, elemental calcium was not produced until 1808, when a mercury amalgam resulted from electrolysis of calcium chloride in the presence of a mercury cathode. However, attempts to isolate the pure metal by distilling the mercury were only marginally successful.

Calcium metal was produced in 1855 by electrolysis of a mixture of calcium, strontium, and ammonium chlorides, but the product was highly contaminated with chlorides (1). By 1904 fairly large quantities of calcium were obtained by the electrolysis of molten calcium chloride held at a temperature above the melting point of the salt but below the melting point of calcium metal. An iron cathode just touched the surface of the bath and was raised slowly as the relatively chloride-free calcium solidified on the end. This process became the basis for commercial production of calcium metal until World War II.

Prior to 1939, calcium was manufactured exclusively in France and Germany. However, with the outbreak of World War II, an electrolytic calcium plant was constructed in the United States at Sault Ste. Marie, Michigan, by the Electro Metallurgical Corp. Large amounts of calcium were required as the reducing agent for uranium production (see URANIUM AND URANIUM COMPOUNDS). In addition, calcium was used to produce calcium hydride, which could easily be transported to remote areas and used as a source of hydrogen for meteorological balloons.

Calcium is mainly used as a reducing agent for many reactive, less common metals; to remove bismuth from lead (qv); as a desulfurizer and deoxidizer for ferrous metals and alloys; and as an alloying agent for aluminum, silicon, and lead. Small amounts are used as a dehydrating agent for organic solvents and as a purifying agent for removal of nitrogen and other impurities from argon and other rare gases (see HELIUM-GROUP GASES).

2. Physical Properties

Pure calcium is a bright silvery white metal, although under normal atmospheric conditions freshly exposed surfaces of calcium quickly become covered with an oxide layer. The metal is extremely soft and ductile, having a hardness between

Table 1. **Physical Properties of Calcium**[a]

Property	Value		
atomic weight	40.08		
electron configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$		
stable isotopes			
atomic weight 40 42 43	44	46	48
natural abundance, % 96.947 0.646 0.135 0.18	2.083	0.186	
specific gravity at 20°C, kg/m^3	1.55×10^3		
melting point, °C	839 ± 2		
boiling point, °C	1484		
heat of fusion, ΔH_{fus}, kJ/mol[b]	9.2		
heat of vaporization, ΔH_{vap}, kJ/mol[b]	161.5		
heat of combustion, kJ/mol[b]	634.3		
vapor pressure			
pressure, kPa[c] 0.133 1.33 101.3	13.3	53.3	
temperature, °C 800 970	1200	1390	1484
specific heat at 25°C, J/(g · K)[b]	0.653		
coefficient of thermal expansion, 0–400°C, m/(m · K)	22.3×10^{-6}		
electrical resistivity at 0°C, $\mu\Omega \cdot$ cm	3.91		
electron work function, eV	2.24		
tensile strength (annealed), MPa[c]	48		
yield strength (annealed), MPa[c]	13.7		
modulus of elasticity, GPa[c]	22.1–26.2		
hardness (as cast)			
HB[d]	16–18		
HR B[e]	36–40		

that of sodium and aluminum. It can be work-hardened to some degree by mechanical processing. Although its density is low, calcium's usefulness as a structural material is limited by its low tensile strength and high chemical reactivity (2).

Calcium has a face-centered cubic crystal structure ($a = 0.5582$ nm) at room temperature but transforms into a body-centered cubic ($a = 0.4477$ nm) form at 428 ± 2°C (3). Some of the more important physical properties of calcium are given in Table 1. For additional physical properties, see Refs. (7–12). Measurements of the physical properties of calcium are usually somewhat uncertain owing to the effects that small levels of impurities can exert.

3. Chemical Properties

Calcium has a valence electron configuration of $4s^2$ and characteristically forms divalent compounds. It is very reactive and reacts vigorously with water, liberating hydrogen and forming calcium hydroxide, $Ca(OH)_2$. Calcium does not readily oxidize in dry air at room temperature but is quickly oxidized in moist air or in dry oxygen at about 300°C. The oxide layer is nonprotective, and complete oxidation of a massive piece of calcium eventually occurs. Calcium reacts with fluorine at room temperature and with the other halogens at 400°C. When heated to 900°C, calcium reacts with nitrogen to form calcium nitride [12013-82-0], Ca_3N_2 (see CALCIUM COMPOUNDS, SURVEY). The metal becomes incandescent when heated to 400–500°C in an atmosphere of hydrogen with the formation of calcium hydride [7789-78-8], CaH_2, which reacts with water to give hydrogen:

$$CaH_2 + 2\ H_2O \longrightarrow Ca(OH)_2 + 2\ H_2$$

Thus the hydride is a very efficient carrier of hydrogen. Upon heating, calcium reacts with boron, sulfur, carbon, and phosphorus to form the corresponding binary compounds and with carbon dioxide to form calcium carbide [75-20-7], CaC_2, and calcium oxide [1305-78-8], CaO.

Calcium is an excellent reducing agent and is widely used for this purpose. At elevated temperatures, it reacts with the oxides or halides of almost all metallic elements to form the corresponding metal. It also combines with many metals, forming a wide range of alloys and intermetallic compounds. Among the phase systems that have been better characterized are those with Ag, Al, Au, Bi, Cd, Co, Cu, Hg, Li, Na, Ni, Pb, Sb, Si, Sn, Tl, Zn, and the other Group 2 (IIA) metals (13).

Commercially produced calcium metal is analyzed for metallic impurities by emission spectroscopy. Carbon content is determined by combustion, whereas nitrogen is measured by Kjeldahl determination.

4. Manufacture

4.1. Electrolysis. Although in Western countries the aluminothermic process has now completely replaced the electrolytic method, electrolysis is believed to be the method used for calcium production in the People's Republic of China and the Commonwealth of Independent States (CIS). This process likely involves the production of a calcium–copper alloy, which is then redistilled to give calcium metal.

4.2. Aluminothermal Method. Calcium metal is produced by high-temperature vacuum reduction of calcium oxide in the aluminothermal process. This process, in which aluminum [7429-90-5] metal serves as the reducing agent, was commercialized in the 1940s. The reactions, which are thermodynamically unfavorable at temperatures below 2000°C, have been summarized as follows:

$$6\ CaO + 2\ Al \rightleftarrows 3CaO \cdot Al_2O_3 + 3\ Ca(g)$$

$$33\ CaO + 14\ Al \rightleftarrows 12CaO \cdot 7Al_2O_3 + 21\ Ca(g)$$

$$4\ CaO + 2\ Al \rightleftarrows CaO \cdot Al_2O_3 + 3\ Ca(g)$$

In the range of 1000–1200°C a small but finite equilibrium pressure of calcium vapor is established. The calcium vapor is then transferred using a vacuum pump to a cooled region of the reactor where condensation takes place, shifting the equilibrium at the reaction site and allowing more calcium vapor to be formed.

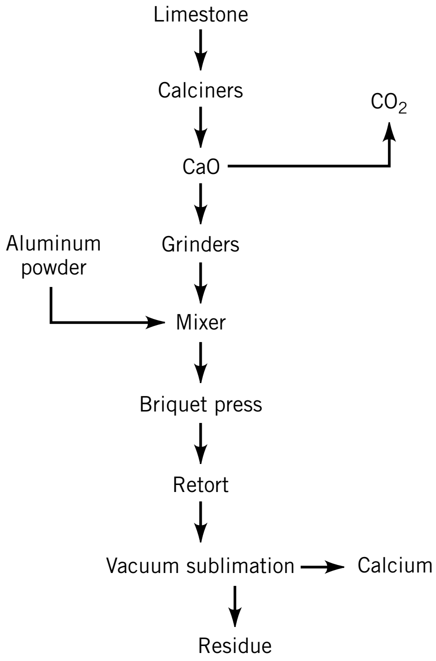

Fig. 1. Flow sheet for aluminum reduction process.

A typical flow sheet for the process is given in Figure 1. High calcium limestone, $CaCO_3$, is quarried and calcined to form calcium oxide. The calcium oxide is ground to a small particle size and dry-blended with the desired amount of finely divided aluminum. This mixture is then compacted into briquettes to ensure good contact of reactants. The briquettes are placed in horizontal metal tubes, ie, retorts made of heat-resistant steel and heated in a furnace to 1100–1200°C. The open ends of the retorts protrude from the furnace and are cooled by water jackets to condense the calcium vapor. The retorts are then sealed and evacuated to a pressure of less than 13 Pa (0.1 mm Hg). After the reaction has been allowed to proceed for about 24 h, the vacuum is broken with argon and the condensed blocks of ca. 99% pure calcium metal, known as crowns, and calcium aluminate [12042-78-3] residue are removed. Large amounts of energy are required by this method, partially because of the high temperatures of the process and partially because of the energy-intensive raw materials employed, ie, the calcined CaO and electrolytically produced aluminum.

The calcium crowns can be sold as such for certain applications. However, further processing may be required, and the crowns can be reduced in size to pieces of about 25 cm or nodules of about 3 mm. They can also be melted under a protective atmosphere of argon and cast into billets or ingots. Calcium wire can be made by extrusion, and calcium turnings are produced as lathe cuttings from cast billets. Technologies have also been developed to manufacture calcium metal particulates and powders by atomization, comminution, and grinding processes.

4.3. Redistillation.

For certain applications, especially those involving reduction of other metal compounds, better than 99% purity is required. This can be achieved by redistillation. In one method, crude calcium is placed in the bottom of a large vertical retort made of heat-resistant steel equipped with a water-cooled condenser at the top. The retort is sealed and evacuated to a pressure of less than 6.6 Pa (0.05 mm Hg) while the bottom is heated to 900–925°C. Under these conditions, calcium quickly distills to the condensing section, leaving behind the bulk of the less volatile impurities. Variations of this method have been used for commercial production. Subsequent processing must take place under exclusion of moisture to avoid oxidation.

Redistillation does not greatly reduce the impurity level of volatile materials such as magnesium. Volatile alkali metals can be separated from calcium by passing the vapors over refractory oxides such as TiO_2, ZrO_2, or Cr_2O_3 to form the nonvolatile Na_2O and K_2O (14). Purification techniques include reactive distillation (15), growth of crystals from the melt (16), and combined crystal growth and distillation techniques (17).

5. Shipment

Because of its extreme chemical reactivity, calcium metal must be carefully packaged for shipment and storage. The metal is packaged in sealed argon-filled containers. Calcium is classed as a flammable solid and is nonmailable. Sealed quantities of calcium should be stored in a dry, well-ventilated area so as to remove any hydrogen formed by reaction with moisture.

6. Economic Aspects

Calcium is produced in the United States by Pfizer Incorporated in Canaan, Conn., in Canada by Timminco Ltd., and in France by Société Electrometallurgique du Planet (S.E.M.P.) (18). The world capacity is 5000 t/yr. The United States accounts for production of over 50% of the calcium used worldwide (19).

Domestic consumption of calcium metal increased in 1991. Table 2 lists the amounts and values of the United States imports of calcium from 1987 to 1991 (recent data were not able to be found as this has no longer been collected). Imports increased by more than 26% compared with imports from the previous year. The main countries calcium is imported from are, in decreasing order, China, France, and Canada.

Table 2. **United States Imports for Consumption of Calcium**

Year	Quantity, kg	Value, $
1987	352,089	1,918,099
1988	664,419	3,243,663
1989	679,603	3,210,216
1990	651,000	3,779,410
1991	821,457	5,237,589

Calcium consumption is primarily for the production of maintenance-free and sealed lead–acid batteries, in the steel industry, and for permanent magnet manufacture. These markets are fairly stable and strong markets. Use as a reducing agent of rare-earth oxides for permanent magnet manufacture is expected to increase due to an expansion of this market.

7. Grades and Specifications

Calcium is usually sold as crowns, broken crown pieces, nodules, or billets. The purity of these forms is at least 98%. If a higher quality of the metal is required, it can be redistilled to remove additional impurities. There are three different grades of calcium metal: commercial, melted, and redistilled. In both commercial- and melted-grade calcium, the minimum calcium content is 98.8%. In the redistilled grade, the minimum calcium content is 99.5%. The difference between the commercial and melted grades is in the percents of impurities in the product. Impurities include magnesium, nitrogen, aluminum, iron, manganese, and copper (only in the commercial grade). The redistilled grade has a much lower level of these impurities with the addition of 150 ppm of carbon being present (19).

8. Health and Safety Factors

Inhalation of calcium metal produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat and difficulty breathing. It may also cause lung edema, which is a medical emergency. If breathing is difficult, give oxygen and get medical attention (20). If ingested, caustic lime will form due to reaction with moisture. Large amounts can have a corrosive effect. Abdominal pain, nausea, vomiting, and diarrhea are symptoms. If swallowed, do not induce vomiting but give large amounts of water. As calcium metal is corrosive, contact with the skin can cause pain, redness, and a severe burn. Contact with the eyes will cause redness and pain with possible burns and damage to the eye tissues. If calcium metal comes in contact with the skin or eyes, flush with water for at least 15 min and get medical attention. Protective clothing should include boots, gloves, lab coat, apron, or coveralls in addition to chemical safety goggles. As calcium metal is a very water-reactive flammable sold, reaction with water, steam, and acids to release flammable/explosive hydrogen gas should be avoided. Water must not be used to extinguish a fire with calcium metal.

Calcium metal should be stored in a tightly closed contained in a cool, dry, ventilated area under nitrogen. It should be kept away from water or locations where water may be needed for a fire. This material should be handled as a hazardous waste for diposal purposes.

In the case of a spill, the material should be collected quickly and transferred to a container of kerosene, light oil, or similar hydrocarbon fluid for recovery. Exposure to air should be minimized. Do not use water on the metal or where it spilled if significant quantities still remain. Waste calcium should be packaged under hydrocarbon fluid and sent to an approved waste disposal facility.

9. Calcium Alloys

Calcium alloys can be produced by various techniques. However, direct alloying of the pure metals is normally used in the production of 80% calcium–magnesium, 70% magnesium–calcium, and 75% calcium–aluminum alloys.

Lead alloys containing small amounts of calcium are formed by plunging a basket containing a 77 or 75% calcium–23–25% Al alloy into a molten lead bath or by stirring the Ca–Al alloy into a vortex created by a mixing impellor (21).

Alloys of calcium with silicon are used in ferrous metallurgy (qv) and are generally produced in an electric furnace from CaO (or CaC_2), SiO_2, and a carbonaceous reducing agent (22). The resulting alloy, calcium disilicide [12013-56-8], is nominally of composition $CaSi_2$ and has a typical wt % analysis of 30–33% Ca, 60–65% Si, 1.5–3% Fe (23). Proprietary Ca–Si alloys containing other elements such as Ba, Al, Ti, or Mn are sometimes produced by a combination of carbothermic ore reduction followed by direct alloying. In general, the chemical reactivity of calcium is greatly reduced when it is present in an alloyed state.

10. Uses

The most significant use of calcium is for improvement of steel (qv). It is used as an aid in removing bismuth in lead refining and as a desulfurizer and deoxidizer in steel refining (24–27). Addition of calcium causes inclusions in the steel to float out by modifying the melting point of these inclusions. Any remaining inclusions will be morphologically altered, making them spherical in shape and very small. This results in an overall improvement of the quality of steel and its properties.

Calcium metal is also used in the manufacture of maintenance-free and sealed lead–acid batteries (28). Use of calcium improves the electrical performance and battery life (see BATTERIES). The calcium improves the conductivity and current capacity of the cell.

Calcium has multiple other uses: reducing oxides of the rare-earth neodymium and boron for alloying with metallic iron for use in neodymium–iron–boron permanent magnets and use as a reducing agent to recover hafnium (29), plutonium (30), thorium (31), tungsten (32), uranium (33,34), vanadium (35), and the rare-earth (36) metals from their oxides and fluorides.Calciumatomic weight 40.08 electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ atomic weight natural abundance 40 96.947% atomic weight natural abundance 42 0.646 % atomic weight natural abundance 43 0.135% atomic weight natural abundance 44 2.083% atomic weight natural abundance 46 0.186% atomic weight natural abundance 48 0.18% specific gravity at 20°C 1.55×10^3 kg/m^3 melting point 839 ± 2 °C boiling point 1484 °C heat of fusion, ΔH_{fus}, 9.2 kJ/mol heat of vaporization, ΔH_{vap} 161.5 kJ/mol heat of combustion 634.3 kJ/mol temperature 0.133 800 °C temperature 1.33 970 °C temperature 13.3 1200 °C temperature 53.3 1390 °C temperature 101.3 1484 °C specific heat at 25°C 0.653 J/(g · K) coefficient of thermal expansion, 0–400°C 22.3×10^{-6} m/(m · K) electrical resistivity at 0°C 3.91 $\mu\Omega \cdot$ cm electron work function 2.24 eV tensile strength (annealed) 48 MPa yield strength (annealed) 13.7 MPa modulus of elasticity 22.1–26.2 GPa hardness (as cast) HB 16–18 hardness (as cast) HR B 36–40

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