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CALCIUM\*

by

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## CALCIUM

Calcium is a member of the alkaline earth family (group IIa) of the periodic table and ranks fifth in abundance of all the elements in the earth's crust. The word, calcium, is derived from the Latin word, calx, meaning lime, which is the common oxide form of the element. Though calx was prepared by the Romans in the first century, it was not until 1808 that elemental calcium was discovered by Sir Humphrey Davy and independently at about the same time by Berzelius and Pontin. Davy prepared the metal by the electrolysis of calcium chloride whereas the latter two investigators prepared a calcium amalgam electrolytically and removed the mercury by distillation.

During and subsequent to World War II calcium metal has been produced in tonnage quantities for use as a reducing agent in the preparation of several of the less common metals, an alloying agent for aluminum, silicon and lead, a debismuthizer for lead, a decarburizer, desulfurizer and deoxidizer for ferrous metals and alloys, a dehydrating agent for alcohol and other organic solvents, and for the purification of argon and other rare gases.

Prior to 1939 calcium metal was produced exclusively in France and Germany. The United States imported between ten and twenty-five tons of the metal annually from France during the two decades preceding this date. In 1939 at the outbreak of World War II the Electro Metallurgical Corporation (3) of the United States began the construction of a plant at Sault Ste. Marie, Michigan, based on the French electrolytic process. In 1940 when France was occupied by the German armies the production

capacity of the Electromet plant was further expanded by the installation of new electrical generators and other equipment.

Because of the demands of the United States government for increased quantities of metallic calcium during World War II, alternative processes were investigated. High purity calcium was required in increased amounts as the reducing agent in the production of uranium for the atomic energy program and by the United States Army Signal Corps for the preparation of calcium hydride by the direct union of calcium and hydrogen. The hydride was used as a source of hydrogen for meteorological balloons since it was easily transported to the more remote areas. These and other military requirements provided impetus to the development of the aluminothermic reduction of lime as a commercial process. This method is now the basic process of the New England Lime Company and also of the Dominion Magnesium Ltd. of Canada for the production of calcium.

#### OCCURRENCE

Because of its chemical reactivity calcium does not occur in nature in native form. The most abundant natural compounds of calcium are the carbonates, halides and sulfates. Calcium carbonate,  $\text{CaCO}_3$ , occurs as limestone, chalk, aragonite, calcite and marl. The common sulfate is the dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , which occurs either as gypsum or alabaster. Calcium fluoride occurs as the mineral fluorite or fluorspar,  $\text{CaF}_2$ , and calcium chloride as tachhydrite,  $\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ . Calcium chloride is present in sea water to the extent of about 0.15%.

An important source of pure  $\text{CaCl}_2$  is the Solvay soda process of which the chloride is a by-product. Probably the most important mineral in the production of calcium metal is limestone. A source of high grade limestone is essential to the aluminum reduction process since the purity of the metal obtained is dependent upon the quality of the starting ingredients. The New England Lime Company of Canaan, Connecticut, which is the largest producer of calcium metal in the United States, uses a limestone from deposits near Adams, Massachusetts. The limestone is calcined to the oxide in a lime kiln at  $1200^\circ\text{C}$  to give a product with the following typical analysis: 0.5% loss on ignition, 97.5%  $\text{CaO}$ , 0.65%  $\text{MgO}$ , 0.7%  $\text{SiO}_2$ , 0.6%  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , 0.6%  $\text{Na}_2\text{O}$  and 0.009%  $\text{K}_2\text{O}$ .

#### PHYSICAL PROPERTIES

Calcium metal corrodes rapidly in air under normal atmospheric conditions, is extremely soft and ductile and has a low tensile strength. These properties tend to limit its usefulness as a structural material or as a base metal in commercial applications. Some of the more important physical properties of calcium are listed in Table I.

As many as four allotropic modifications of calcium have been reported, a face-centered cubic form at room temperature, hexagonal and complex forms between  $300$  and  $500^\circ\text{C}$  and a body-centered cubic form at higher temperatures. Later work by Smith (22, 23) on high-purity calcium indicates that it is dimorphic with a face-centered cubic form at room temperature transforming to body-centered cubic at  $464^\circ\text{C}$ . The hexagonal and complex forms were found to be associated with the presence of carbon, nitrogen and hydrogen impurities in the metal.

Table I

## Physical Properties of Calcium Metal (6, 18, 23)

Atomic number	20
Atomic weight	40.08
Melting point	838°C
Boiling point	1440°C
Crystal forms	fcc and bcc
Transformation temperature	464°C
Lattice constants	5.582A (fcc) 4.477A (bcc)
Density	1.55 g/cc at 20°C
Coefficient of thermal expansion	
26° to 370°C	22.3 x 10 <sup>-6</sup> per °C
465° to 600°C	33.6 x 10 <sup>-6</sup> per °C
Heat of fusion	52 cal/g
Heat of vaporization	1000 cal/g
Heat of combustion	3783 cal/g
Tensile strength	6900 psi
Yield strength	1990 psi
Modulus of elasticity	3.2-3.8 x 10 <sup>6</sup> psi
Hardness	
Brinell	16-18
Rockwell B	36-40

Very little information is available on the mechanical working of calcium. It has been extruded into wire or rods at 420°C and cast into ingots under a protective flux or an inert gas. Calcium can be melted in an iron crucible under an inert atmosphere at 900°C and cast into ingot

form. This generally results in a high concentration of voids or cavities with the density of the casting lying between 1.42 and 1.45 g/cc which is only 90% of the theoretical density. Compression of the ingot under a hydrostatic pressure of 40 tons/in<sup>2</sup> gives a density of 1.54 g/cc very close to the theoretical value.

Calcium is soft and ductile with a hardness between that of sodium and pure aluminum both of which are generally considered to be soft metals.

#### CHEMICAL PROPERTIES

Calcium is a strongly electropositive element with an electronegativity value of 1.0 on Pauling's scale. Calcium is more reactive than magnesium and only slightly less active than strontium and barium. A freshly cut surface of calcium is silvery white in appearance but tarnishes rapidly upon exposure to moist air due to the formation of a layer of Ca(OH)<sub>2</sub>. Calcium is relatively inert to dry oxygen and nitrogen at ordinary temperatures, but reacts rapidly with oxygen at 300°C and above and with nitrogen at 900°C to form the nitride, Ca<sub>3</sub>N<sub>2</sub>.

Calcium reacts readily with fluorine at room temperatures and violently with all of the halogens at 400°C. It reacts readily with ammonia to form Ca(NH<sub>3</sub>)<sub>6</sub> and Ca(NH<sub>2</sub>)<sub>2</sub>, with carbon dioxide to form CaC<sub>2</sub> and CaO and becomes incandescent in hydrogen at 400 to 500°C to form CaH<sub>2</sub>. The hydride dissociates thermally into calcium and hydrogen between 750 and 900°C and reacts exothermically with water as follows



The above reaction is the basis for the use of the hydride as a carrier for hydrogen gas.

The most common impurities in commercial calcium are carbon, oxygen, chlorine, nitrogen, iron, nickel, manganese, aluminum and magnesium. The carbon content is determined by the combustion method and nitrogen by the Kjeldahl method. Small amounts of iron, nickel and aluminum are determined in calcium spectrophotometrically (11, 26) or spectrographically. Magnesium in the range of 1 to 1000 ppm is determined by spectrographic analysis. Oxygen can be determined by the conversion of calcium oxide in the metal to water and titrating this by the Karl Fischer reagent (10).

#### MANUFACTURE

Two basic methods are employed in the production of calcium metal, the electrolysis of calcium chloride and the aluminothermic reduction of calcium oxide. Both processes yield a relatively crude product that can be purified by vacuum distillation. Other methods that have been investigated on the experimental scale only, are the thermal decomposition of calcium carbide or calcium hydride, the reduction of calcium chloride with sodium and the reduction of a calcium salt with silicon, titanium, aluminum or beryllium. Most of these methods result either in low yields or in reactions which would be difficult to carry out on a large scale.

Perhaps the method that shows the most promise as an alternative commercial process is the thermal decomposition of  $\text{CaC}_2$ . In 1958 the Air Reduction Company, Inc., of New York, was granted a patent on the preparation of calcium by this method (13). Calcium carbide

containing some lime is heated to its dissociation temperature and the calcium vapor collected after CO and other extraneous gases have been removed. The USSR Central Scientific Research Institute for Ferrous Metals (19) also reports the preparation of calcium metal by the thermal decomposition of  $\text{CaC}_2$ . At a decomposition temperature of 1720 to 1770°C and a pressure of 0.5 to 1.0 mm, metal of 95 to 98% purity was obtained in yields of 80%.

Electrolytic Method - - For more than thirty-five years prior to 1940, calcium metal was produced almost entirely by an electrolytic process (15). A deposit of metallic calcium containing 15 to 25% entrapped salts is produced by the electrolysis of calcium chloride. This deposit, referred to as a "carrot", contains considerable quantities of chloride, oxide, nitride, carbon, alkali and alkaline earth impurities. The carrot is subsequently remelted to remove many of these impurities but greater than 0.5% chlorine and appreciable amounts of nitrogen are retained in the final metal.

A cell of the type shown in Fig. 1 is operated at 780 to 800°C which is just above the melting point of  $\text{CaCl}_2$ . The cell consists of a graphite liner inside a steel casing in which fused calcium chloride is contained. An unmelted layer of  $\text{CaCl}_2$  adheres to the liner wall and bottom thus minimizing the interaction of the salt with the graphite liner. Calcium is collected on a water-cooled cathode of either graphite or iron which is gradually raised from the melt as the deposit accumulates. The cell is brought to operating temperature by passage of an alternating current



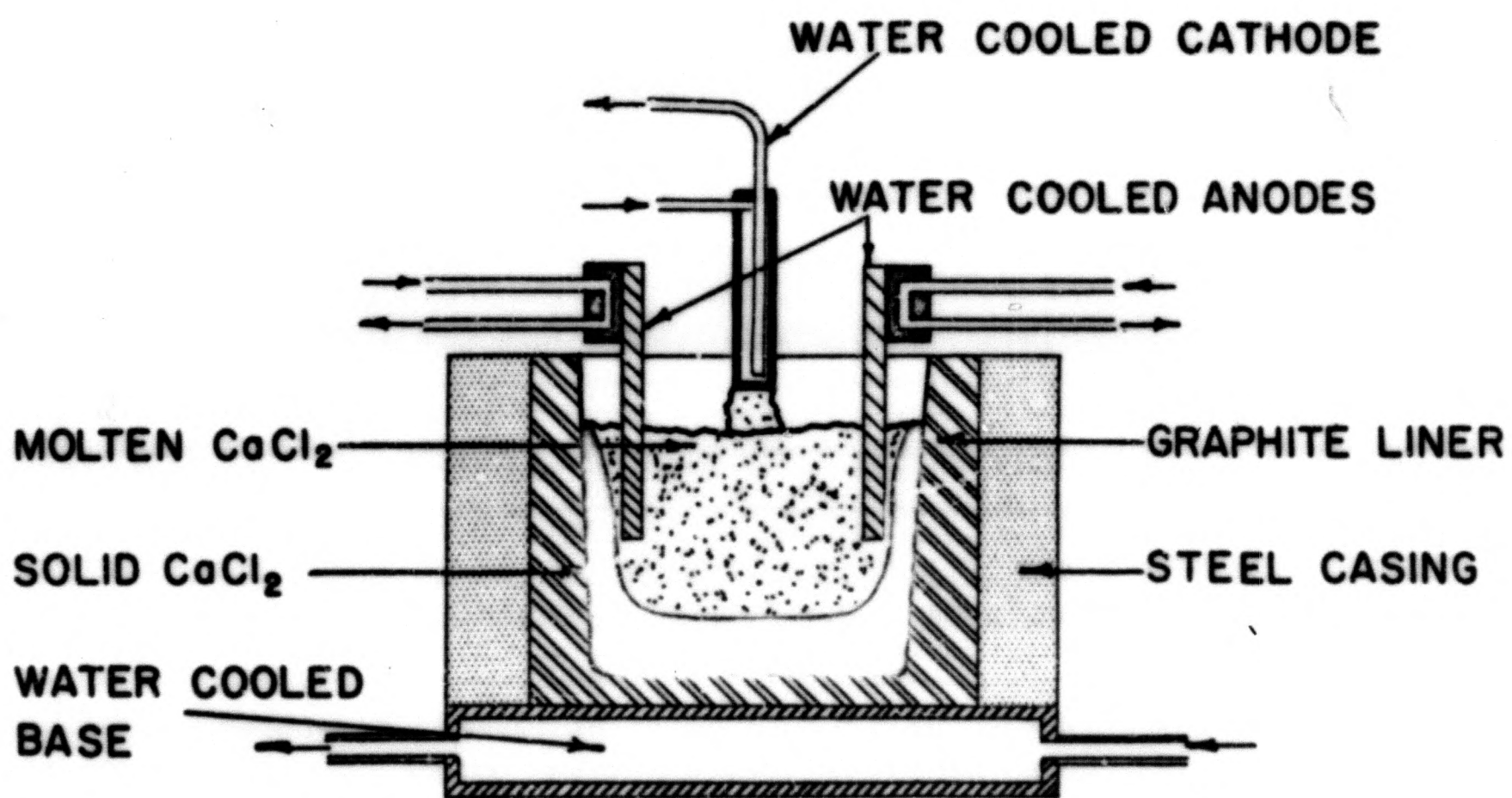


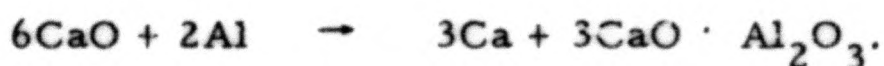
Figure 1

CELL FOR MANUFACTURING CALCIUM METAL BY THE  
ELECTROLYSIS OF FUSED CALCIUM CHLORIDE

through the salt after which the temperature is maintained by the direct electrolyzing current.

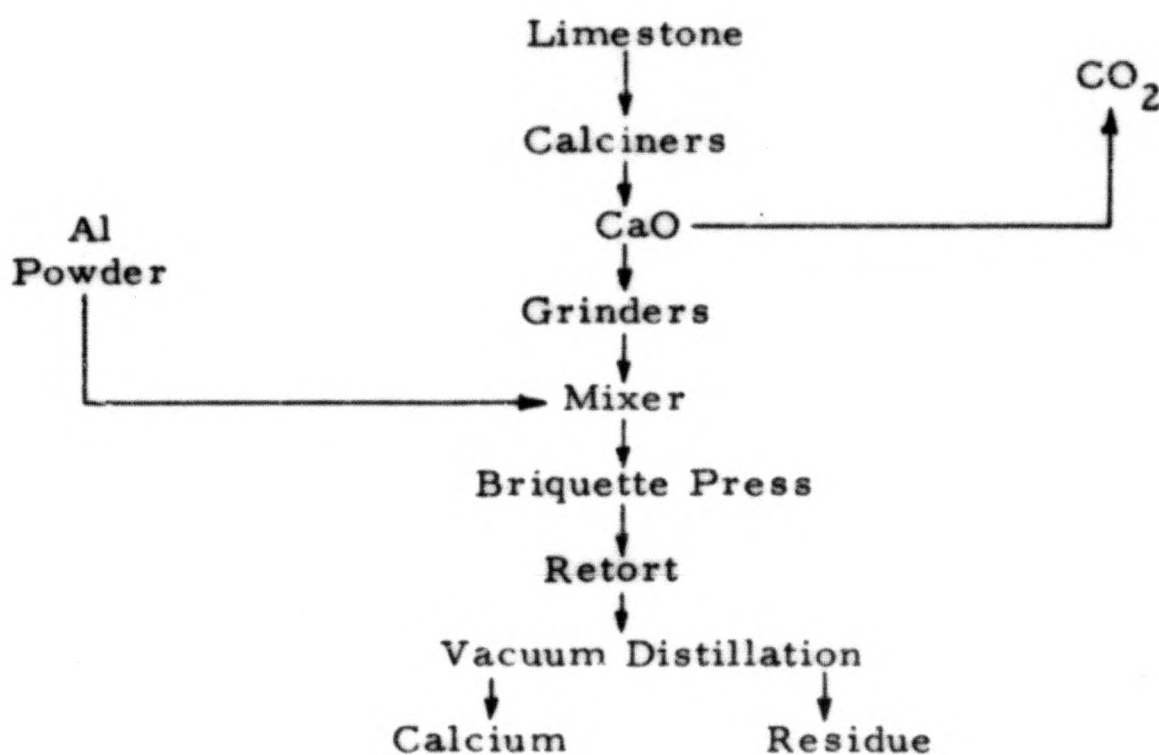
The power consumption of a cell of this type is 15 to 25 kw-hr per pound of metal produced and the efficiency is approximately 60% based on the amount of metal obtained per pound of  $\text{CaCl}_2$  consumed.

Aluminothermic Method--The reduction of lime with aluminum was first attempted by Biltz in the early 1920's. He operated on a small laboratory scale and obtained only low recoveries. The method was developed into a commercial process by the New England Lime Company (14) during the early part of World War II. The reduction proceeds by the following reaction



It is carried out under a dynamic vacuum at  $1200^\circ\text{C}$  with the calcium being distilled from the reaction zone.

Flow Sheet of Aluminum Reduction Process



An excess of pulverized lime is mixed with aluminum powder and pressed into briquettes. These are charged into a stainless steel retort in a hot furnace and a vacuum is then drawn on the system. The charge is heated to the reaction temperature and the calcium product collected on a water-cooled condenser as a cylindrical mass referred to as a "crown". Typical analysis of the material thus produced is as follows: 0.3-1.0% Mg, 0.1-0.2% Al, 0.02-0.05% Mn, 0.02-0.1% N, 0.01% Fe and 0.02% Si.

Pidgeon and Atkinson (21) have concluded from thermodynamic data and other calculations that the reduction proceeds by the reaction of solid lime with aluminum vapor. The continuous removal of calcium by distillation and the formation of calcium aluminate by reaction of the  $Al_2O_3$  product with excess lime cause the reaction to proceed to completion.

Redistillation--The use of calcium as the reductant in the preparation of other metals requires a higher purity material than that normally obtained by either of the above methods. The apparatus shown in Fig. 2 has been employed at the Ames Laboratory (4) to produce several tons of purified calcium. Approximately 200 lbs of metal can be distilled per batch in this equipment. The distilled calcium collects on the skirt and condenser as a bright, fibrous deposit. The temperature of the condenser is maintained at  $300 \pm 50^\circ C$  during the distillation by a flow of air onto the external surface. A dynamic vacuum of less than 5 microns pressure is maintained on the system using a high capacity oil diffusion pump backed by a 115 cfm mechanical pump. The retort is heated to 900 to  $925^\circ C$  in a gas-fired

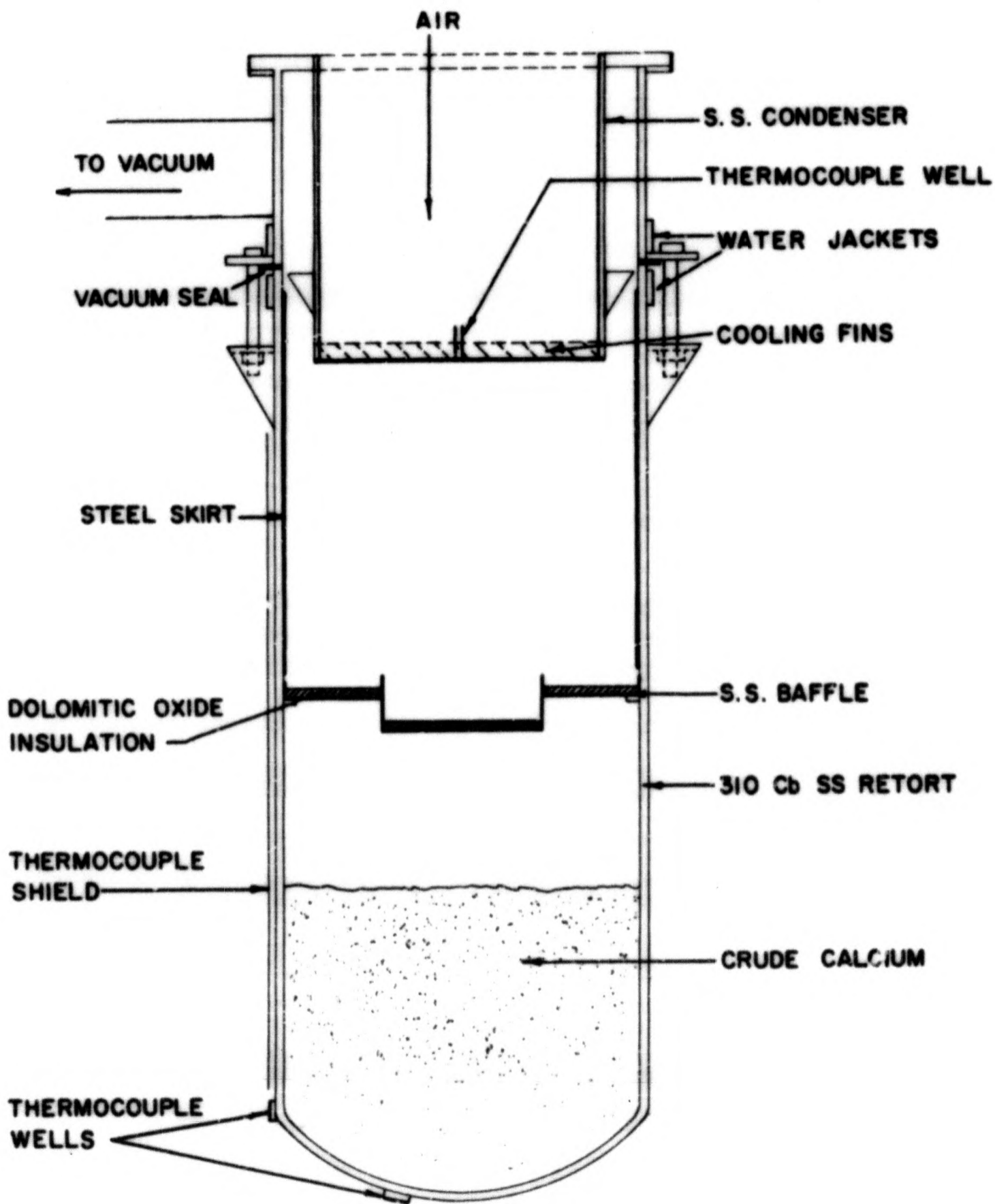


Figure 2  
RETORT ASSEMBLY FOR REDISTILLATION OF  
CALCIUM METAL

furnace to give a distillation rate of about 25 lbs of calcium per hour. The condensate is removed quickly and all subsequent grinding and screening of the calcium carried out in a dry room.

Typical analysis of the aluminum-reduced calcium before and after distillation is presented in Table II. Purification of electrolytic calcium by this procedure likewise results in the removal of most impurities but does not eliminate chlorine entirely since significant amounts of  $\text{CaCl}_2$  are carried over during distillation.

Table II  
Effect of Distillation on Purity of Calcium Metal

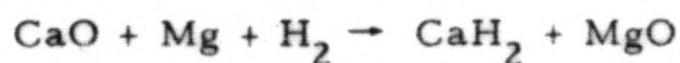
<u>Impurity</u>	<u>Before Distillation, wt %</u>	<u>After Distillation, wt %</u>
Aluminum	0.1	0.002
Magnesium	0.5	0.5
Manganese	0.05	0.002
Nitrogen	0.06	0.005
Oxygen	0.3	0.03
Iron	0.01	0.005
Silicon	0.02	0.001

Equipment similar to that described above is used by the New England Lime Co. for redistilling commercial quantities of calcium metal. Redistilled calcium is also produced by Dominion Magnesium Ltd. using a similar procedure.

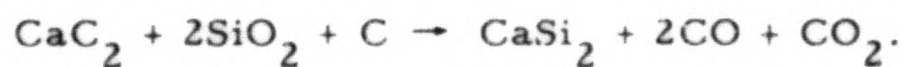
The removal of magnesium from calcium by fractional distillation has been carried out by several investigators (5, 12, 16, 23). Metal of 99.9+% purity containing less than 0.01 wt % magnesium has been prepared

at Iowa State University for use in research on the properties of calcium metal. Likewise, scientists at the Los Alamos Scientific Laboratory have prepared 100-g quantities of calcium of 99.95% purity containing less than 1 ppm magnesium. This material is used in the preparation of high purity uranium and for other uses. Alexander (2) developed a method for removing sodium and potassium from calcium during distillation by passing the vapors over  $\text{TiO}_2$ ,  $\text{ZrO}_2$  or  $\text{Cr}_2\text{O}_3$  powders. The alkali metals react with the refractory oxides to form non-volatile  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ .

Production of Calcium Alloys -- Calcium hydride has been produced commercially by the direct union of calcium metal with hydrogen gas at temperatures as low as  $250^\circ\text{C}$  at an initial pressure of 50 cm of Hg. The use of high purity calcium as the starting material results in higher yields of the hydride with yields of 99.2% being obtained by reaction with hydrogen over a 2-hr period. Alexander (1) developed a cheaper and more direct method for producing the hydride from lime by the following procedure:



A Ca - Si alloy, containing 60-65% Si (approximately  $\text{CaSi}_2$ ) is produced by an electric arc process utilizing the following reaction:



#### ECONOMIC ASPECTS (20)

Complete production figures on calcium metal are not available from several suppliers in the world market, particularly in the United States and the USSR. Dominion Magnesium Limited of Canada reported the production of 71,610 lbs of metal in 1959 and 25,227 in 1958, reflecting the variability of the market. United States import figures for the period

of 1951 through 1960 (see Table III) show these same variations in the demand for the commercial grade calcium and for the Ca-Si alloy.

Table III

## United States Imports of Calcium and Calcium Alloys

<u>Year</u>	<u>Calcium</u>	<u>Ca-Si Alloy</u>
1951-55 (ave.)	740,217	173,450
1956	8,387	194,869
1957	24,204	498,735
1958	15,694	130,866
1959	7,425	918,556
1960	12,618	352,762

Nearly all of the calcium metal imported by the United States during this period was obtained from Canada. The Ca-Si alloy is produced in large quantities in France, Norway, Canada, Germany, Japan and the United Kingdom. While the Ca-Si alloy was also produced in the United States, total production and consumption figures from that country are not available.

The 1960 prices quoted by the New England Lime Company varied from \$0.95 to \$3 per pound for commercial-grade calcium, depending upon the quantity and form desired. For redistilled calcium they varied from \$1.50 to \$3.75 per pound. Canadian prices were \$0.90 per pound for commercial calcium and \$3.50 for the higher purity material. Union Carbide and Carbon sold electrolytic calcium at \$2.05 to \$3.30 per pound, with redistilled metal quoted at \$3.75 to \$4.55. The Ca-Si alloy was priced at \$0.28 per pound in tonnage quantities.

## USES

Undoubtedly one of the most important uses for calcium metal in recent years has been as a reducing agent for preparing many of the less common metals. Because of its strongly electropositive nature and the high energy of formation of its oxide and halide compounds, calcium is an effective reducing agent for many metals and alloys. Zirconium (7, 9), hafnium (7), vanadium (17), tungsten, thorium (27), uranium (28), yttrium (8), scandium (25) and most of the rare-earth metals (24) have been prepared by the reduction of their oxides or fluorides with calcium.

High purity calcium metal is of importance in the preparation of calcium hydride which is of interest both as a reducing agent for several oxides such as  $\text{UO}_2$ ,  $\text{V}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$  and as a portable source of hydrogen gas.

Calcium is also used extensively in various industrial applications as an alloying additive. Calcium-silicon alloys are finding wide use in the steel industry to control grain size and inhibit carbide formation and in powder form for making spun pipes and for thermit welding. A Ca - Mg - Si alloy, called Saudamet, is used as a ladle addition to the open hearth process and also as a furnace and ladle additive in electric steel making. Castings treated with this alloy show exceptional uniformity of structure, high ductility and freedom from internal flaws. A Mg-5% Ca-50% Si alloy developed by the Union Carbide and Carbon Corporation increases the efficiency of the production of ductile cast iron when added in small amounts. It is also used to scavenge steel in induction furnace melting thus reducing the rejection rate of nickel-chrome steel castings from 30% to less than 5%.



Small amounts of calcium are also added to aluminum, beryllium, copper, lead and magnesium. Calcium is used to debismuthize lead in the refining process and a lead-0.04 wt % calcium alloy, possessing increased tensile and fatigue strength, is used as cable sheathing and in the manufacture of lead storage batteries. A lead alloy containing 0.1% Ca exhibits properties equal to those of the lead-9% Sb alloy.

Other applications for calcium which capitalize on its chemical reactivity are the decarburization, deoxidation and desulfurization for the ferrous metals and their alloys, dehydration of alcohol and other organic solvents, a desulfurization petroleum and the gettering of nitrogen in the purification of argon gas.

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