

Chapter 4

Group 2: The Alkaline Earth Metals

4.1 The Alkaline Earth Elements¹

The Group 2 metals have a particular name: the alkaline earth metals. The name is derived from the observation that they have such high melting points (Table 4.1) that they remain solids (“earths”) in a fire. Table 4.2 lists the derivation of the names of the alkali metals.

Alkali metal	Melting point (°C)	Alkaline earth metal	Melting point (°C)
Li	180.54	Be	1287
Na	97.72	Mg	650
K	63.38	Ca	842
Rb	39.31	Sr	777
Cs	28.44	Ba	727
Fr	27 (estimated)	Ra	700

Table 4.1: Melting points of the alkaline earth metals in comparison with the alkali metals.

Element	Symbol	Name
Beryllium	Be	From the Greek <i>bērullos</i> meaning <i>to become pale</i> , in reference to the pale semiprecious gemstone beryl
<i>continued on next page</i>		

¹This content is available online at <<http://cnx.org/content/m31948/1.4/>>.

Magnesium	Mg	From the <i>Magnesia</i> district in Greece
Calcium	Ca	From the Latin <i>calcis</i> meaning <i>lime</i>
Strontium	Sr	From the mineral <i>strontianite</i> named after the Scottish village of <i>Strontian</i>
Barium	Ba	From the Greek <i>bary</i> , meaning <i>heavy</i>
Radium	Ra	From the Latin <i>radius</i> meaning <i>ray</i>

Table 4.2: Derivation of the names of the alkaline earth metals.

4.1.1 Discovery

4.1.1.1 Beryllium

Beryllium was discovered by Louis-Nicolas Vauquelin (Figure 4.1) in 1798 as a component in beryls and emeralds; however, Fredrich Wöhler (Figure 4.2) and Antoine Bussy (Figure 4.3) independently isolated the metal in 1828 by reacting potassium with beryllium chloride, (4.1).

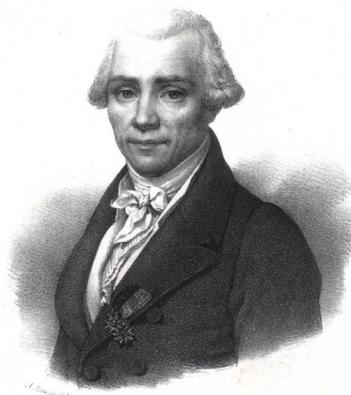


Figure 4.1: French pharmacist and chemist Louis Nicolas Vauquelin (1763 - 1829).

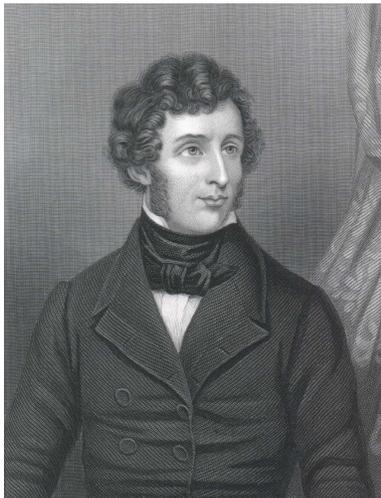


Figure 4.2: German chemist Friedrich Wöhler (1800 - 1882) also known for his synthesis of urea and, thus, the founding of the field of natural products synthesis.

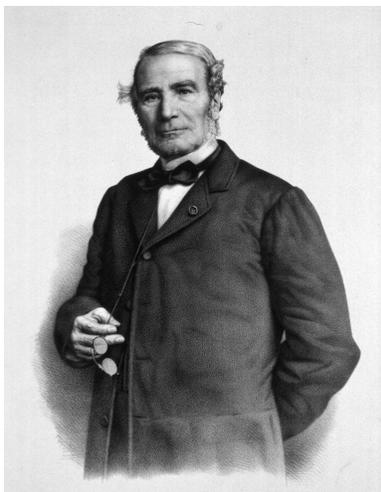


Figure 4.3: French chemist Antoine Alexandre Brutus Bussy (1794 - 1882).

4.1.1.2 Magnesium

Magnesium is found in large deposits of magnesite and dolomite, and in mineral waters where the Mg^{2+} ion is soluble. In 1618 a farmer at Epsom in England attempted to give his cows water from a well. The

farmer noticed that the water seemed to heal scratches and rashes. These *Epsom salts* were recognized to be hydrated magnesium sulfate, MgSO_4 . The metal was first isolated in 1808 by Sir Humphry Davy (Figure 4.4) via the electrolysis of a mixture of magnesia and mercury oxide.



Figure 4.4: British chemist and inventor Sir Humphry Davy FRS (1778 - 1829).

Antoine Bussy (Figure 4.3) subsequently prepared magnesium by heating magnesium chloride and potassium in a glass tube, (4.2). When the potassium chloride was washed out, small globules of magnesium remained.



4.1.1.3 Calcium

Calcium oxide or lime was known in ancient Rome, while even in 975 AD, Plaster of Paris (calcium sulphate) was reported to be useful for setting broken bones. The element itself was not isolated until 1808 when Sir Humphry Davy (Figure 4.4) electrolyzed a mixture of lime and mercuric oxide (HgO). His work was based upon prior work by Jöns Berzelius (Figure 4.5) who had prepared calcium amalgam (an alloy of calcium and mercury) by electrolyzing lime in mercury.



Figure 4.5: Swedish chemist Jöns Jacob Berzelius (1779 – 1848).

4.1.1.4 Strontium

Discovered in lead mines in 1787 the mineral strontianite was named after the Scottish village of Strontian. Although it was realized that this mineral was different from others that contained barium, it wasn't until 1798 that Thomas Hope (Figure 4.6) suggested the presence of a new element. As with calcium, metallic strontium was first isolated by Sir Humphry Davy (Figure 4.4) in 1808 using electrolysis of a mixture containing strontium chloride and mercuric oxide.



Figure 4.6: Scottish chemist Thomas Charles Hope (1766 - 1844).

4.1.1.5 Barium

Barium minerals were known by alchemists in the early Middle Ages. Stones of the mineral barite found in Bologna, Italy (also known as *Bologna stones*), were known to glow after exposure to light. Carl Scheele (Figure 4.7) identified barite in 1774, but did not isolate barium. Barium was first isolated as Ba^{2+} in solution by Sir Humphry Davy (Figure 4.4) in 1808. The oxidized barium was at first called *barote*, by Guyton de Morveau, (Figure 4.8) which was changed by Antoine Lavoisier (Figure 4.9) to *baryta*, from which *barium* was derived to describe the metal.



Figure 4.7: German-Swedish pharmaceutical chemist Carl Wilhelm Scheele (1742 - 1786). Author Isaac Asimov has called him "hard-luck Scheele" because he made a number of chemical discoveries before others who are generally given the credit.



Figure 4.8: French chemist and politician Louis-Bernard Guyton de Morveau (1737 - 1816) changed his name to Guyton-Morveau after the French Revolution.



Figure 4.9: French chemist and biologist Antoine-Laurent de Lavoisier (1743 – 1794).

4.1.1.6 Radium

Radium was discovered by Marie Curie (Figure 4.10) and her husband Pierre (Figure 4.11) in 1898 while studying pitchblende. After removing uranium they found that the remaining material was still radioactive. They then separated out a radioactive mixture consisting mostly of barium and an element that gave crimson spectral lines that had never been documented before. In 1910, radium was isolated as a pure metal by Curie and André-Louis Debierne (Figure 4.12) through the electrolysis of a radium chloride solution by using a mercury cathode and distilling in an atmosphere of hydrogen gas.



Figure 4.10: Marie Curie (1867-1934). Copyright Academy of Achievement.



Figure 4.11: French physicist Pierre Curie (1859 – 1906).



Figure 4.12: French chemist André-Louis Debierne (1874 - 1949).

4.1.2 Abundance

The abundance of the alkaline earth elements is given in Table 4.3. Beryllium is rare, but found in the mineral beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$). While magnesium is widespread within the Earth's crust, commercial sources tend to be from sea water as well as the carbonate minerals magnesite (MgCO_3) and dolomite [$(\text{Ca},\text{Mg})\text{CO}_3$]. Calcium is also commonly found as the carbonate, however, strontium and barium are present as the sulphates celestine (SrSO_4) and barites (BaSO_4), respectively.

Element	Terrestrial abundance (ppm)
Be	2.6 (Earth's crust), 6 (soil), 2×10^{-7} (sea water)
Mg	23,000 (Earth's crust), 10,000 (soil), 1,200 (sea water)
Ca	41,000 (Earth's crust), 20,000 (soil), 400 (sea water)
Sr	370 (Earth's crust), 200 (soil), 8 (sea water)
Ba	500 (Earth's crust), 500 (soil), 0.001 (sea water)
Ra	6×10^{-7} (Earth's crust), 8×10^{-7} (soil), 1×10^{-10} (sea water)

Table 4.3: Abundance of alkaline earth elements.

Calcium is a key element for living. Not only is it present as the skeletal material for shell fish and crabs (CaCO_3) its phosphate derivative, hydroxyapatite [$\text{Ca}_5(\text{OH})(\text{PO}_4)_3$] is the structural material of bones and teeth. Calcium is also present in soft tissue at a level of ca. 22g/kg. Calcium is a vital metal for the following:

- Links large molecules together.
- Used in the activation of muscles
- Used in enzyme activation by stabilization of particular conformations of proteins to be acted upon by enzymes.

4.1.3 Isotopes

The naturally abundant isotopes of the alkaline earth elements are listed in Table 4.4. All of the 25 isotopes of radium are radioactive, and while radium-223, radium-224, and radium-226 are found in nature as decay products of either uranium or thorium, they are only present in trace amounts.

Isotope	Natural abundance (%)
Beryllium-9	100
Magnesium-24	78.99
Magnesium-25	10
Magnesium-26	11.01
Calcium-40	96.941
Calcium-42	0.647
Calcium-43	0.135
Calcium-44	2.086
Calcium-46	0.004
Calcium-48	0.187
Strontium-84	0.56
Strontium-86	9.86
Strontium-87	7.0
Strontium-88	82.58
Barium-130	0.106
Barium-132	0.101
Barium-134	2.417
Barium-135	6.592
Barium-136	7.854
Barium-137	11.23
Barium-138	71.7
Radium-226	100

Table 4.4: Abundance of the major isotopes of the alkaline earth elements.

Although beryllium-7 and beryllium-10 are found as trace isotopes, they are so rare beryllium is considered mononuclidic element (a chemical element which is found essentially as a single nuclide, of only one atomic mass). Calcium has four stable isotopes plus two more isotopes (calcium-46 and calcium-48) that have such long half-lives (2.8×10^{15} and 4×10^{19} years, respectively) that for all practical purposes they can be considered stable.

Measurement of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio allows for geological dating of minerals and rocks. Strontium-90 (half-life = 28.9 years) is a by-product of nuclear fission and found in nuclear fallout. For example, the 1986 Chernobyl nuclear accident contaminated released a large amount of strontium-90. Since strontium substitutes for calcium in bones it prevents excretion from the body and thus presents a significant health risk, however, strontium-89 is a short-lived artificial radioisotope that is used in the treatment of bone cancer.

Naturally occurring barium is a mix of seven stable isotopes (Table 4.4), but there are a total twenty-two isotopes known, most of which are highly radioactive and have half-lives in the several millisecond to several day range. The only notable exception is barium-133 which has a half-life of 10.51 years.

4.1.4 Industrial production

The industrial production of beryllium is usually from the reaction of beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) with $\text{Na}_2(\text{SiF}_6)$ which yields the beryllium fluoride, $\text{Na}_2(\text{BeF}_4)$. Subsequent reactions with base give the hydroxide.



Reaction of the hydroxide with the ammonium salt of HF_2^- , followed by thermolysis gives beryllium fluoride (BeF_2). Finally, reduction of the fluoride with magnesium yields beryllium.



Although magnesium is an abundant metal in dozens of mineral the majority of commercial production comes from sea water, where it is present at about a level of 12% that of sodium. Calcium hydroxide is added to seawater to form magnesium hydroxide precipitate.



Subsequent reaction with hydrochloric acid yields concentrated magnesium chloride solution.



Electrolysis of the magnesium chloride produces magnesium. At the cathode, the Mg^{2+} ion is reduced to magnesium metal, (4.7), while at the anode chlorine gas is formed, (4.8).



Strontium metal is produced in an analogous manner; however, it may also be prepared from strontium oxide by reduction with aluminum in vacuum at a temperature at which strontium distills off.



4.1.5 Reactivity and toxicity

The chemistry of the Group 2 elements is dominated by the +2 oxidation state and the noble gas configuration of the M^{2+} cation.

Calcium, strontium, and barium react with water on contact to produce the hydroxide and hydrogen gas. Although the lighter alkaline earth metals do not react violently with water, they do burn in air.

Magnesium burns with a very bright white flame such that caution should be taken not to look at the flame directly. Magnesium is capable of reducing water, (4.10), and as a result, water cannot be used to extinguish magnesium fires; the hydrogen gas produced will only intensify the fire. In addition, magnesium also reacts with carbon dioxide, (4.11), precluding the use of carbon dioxide fire extinguishers. Class D dry chemical fire extinguisher or sand are used for magnesium fires.





Strontium and barium burn in air to produce both the oxide and the nitride, but since the metals do not react with nitrogen except at high temperatures they only form the oxide spontaneously at room temperature.

Beryllium is a class 1 carcinogen, i.e., it is carcinogenic to both animals and humans. Beryllium is harmful if inhaled; if the concentration in air is high enough (greater than $100 \mu\text{g}/\text{m}^3$) an acute condition can result, called acute beryllium disease, which resembles pneumonia. Acute beryllium disease was reported as being associated with the manufacture of fluorescent lighting tubes (a practice that ceased in 1949).

The human body absorbs strontium as if it were calcium, and while stable isotopes have pose no significant health threat, the uptake of radioactive strontium-90 can lead to various bone disorders and diseases, including bone cancer. All water or acid soluble barium compounds are extremely poisonous. At low doses, barium acts as a muscle stimulant, while higher doses affect the nervous system. Radium is highly radioactive and its decay product, radon gas, is also radioactive.

4.2 Calcium the Archetypal Alkaline Earth Metal

4.2.1 Solid State and Solution Chemistry²

Calcium represents the typical Group 2 metal. The chemical properties of its compounds can be applied to all the heavier homologs.

4.2.1.1 Solid state

In the solid state the compounds of the alkaline metals generally form ionic lattices. In fact (except for beryllium and to a lesser extent magnesium) the lattice parameters calculated from the ionic radii of Group 2 metals are within 1% of the experimentally determined values, indicating the highly ionic character.

Due to the increased ionic charge the cations of the alkaline earths are less than that of their alkali metal neighbors. Thus, the ionic radius of Ca^{2+} (0.99 Å) is less than that of K^+ (1.33 Å), but more similar to Na^+ (0.97 Å). This diagonal relationship is seen for the other metals in Group 2.

4.2.1.1.1 Oxides

Combustion of the Group 2 metals gives the monoxide, MO. In the case of SrO and BaO further reaction occurs by the absorption of oxygen under pressure to give the peroxides, MO_2 . The peroxide and superoxides are not stable for the lighter homologs because the smaller M^{2+} ions are more polarizing and cause the peroxide and superoxides to decompose to the monoxide. Calcium peroxide can be prepared by the reaction of the hydroxide with hydrogen peroxide.



As typical for the Group 2 oxides, calcium monoxide is basic and reacts with water to give the hydroxide, (4.13). In fact, thin films of the Group 2 oxides of calcium, barium and strontium will readily absorb water and form the hydroxides.



²This content is available online at <<http://cnx.org/content/m31937/1.3/>>.

4.2.1.1.2 Carbonate

Calcium carbonate (CaCO_3) 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 usually the principal cause of hard water. Most calcium carbonate used is extracted by quarrying or mining. However, pure calcium carbonate (e.g., for pharmaceutical use) can be produced from a pure quarried source (usually marble) or manufactured by the sequential reaction involving the thermal decomposition of the carbonate to the monoxide, (4.14), followed by the reaction with water to give the hydroxide, (4.13), and finally, the reaction with carbon dioxide to reform the carbonate, (4.15).



Calcium carbonate crystallizes as a variety of mineral forms.

- Aragonite
- Calcite (Figure 4.13)
- Vaterite
- Chalk
- Travertine
- Limestone
- Marble

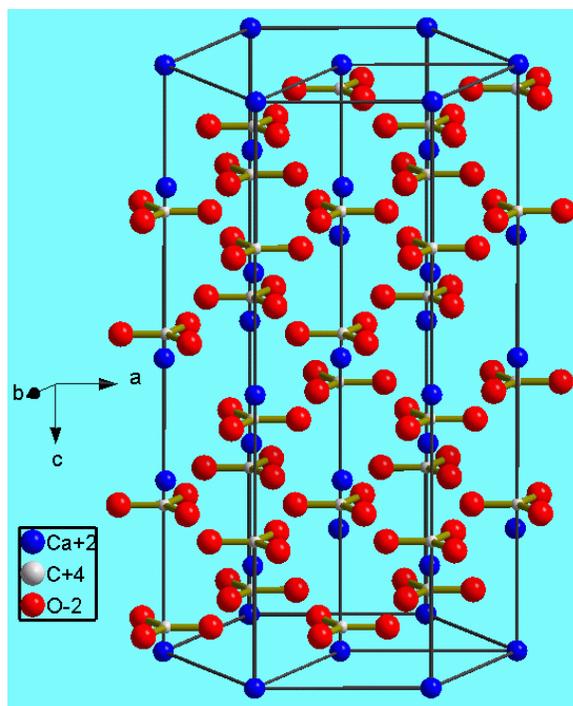


Figure 4.13: Unit cell of calcite a common form of calcium carbonate (CaCO_3).

Calcium carbonate is one of the most widely used mineral materials, the following represents a list of some of the main applications.

- Construction industry as a building material (marble) or as an ingredient of cement.
- Purification of iron from iron ore in a blast furnace.
- A drilling fluids in the oil industry.
- Filler material for latex gloves.
- Filler (extender) in paints.
- Filler in plastics.
- Babies' diapers.
- DIY adhesives, sealants, and decorating fillers.
- Whiting in ceramics/glazing application.
- The filler in glossy paper.
- The production of blackboard chalk (CaSO_4).
- An abrasive in household cleaning products.
- Dietary calcium supplement.
- Inert filler for tablets and pharmaceuticals.
- Toothpaste.

4.2.1.1.3 Halides

Calcium chloride, bromide, and iodide are all ionic, water-soluble salts. In contrast, due to its high lattice energy for the small fluoride ion, CaF_2 is only slightly soluble (Table 4.5). The *fluorite* structure typified for CaF_2 (Figure 4.14) is found for most of the MX_2 ionic solids.

Compound	Solubility @ 20 °C (g/100 mL)	Solubility @ 100 °C (g/100 mL)
CaF_2	0.0016	0.0017
CaCl_2	74.5	159
CaBr_2	142	312
CaI_2	209	426

Table 4.5: Solubility of calcium halides in water.

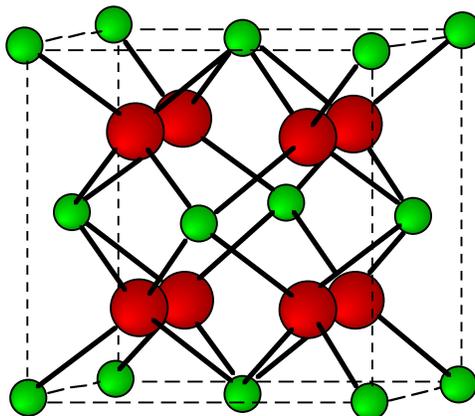


Figure 4.14: Unit cell for the fluorite (CaF_2) structure. Calcium atoms are shown in green (small), fluorine atoms are shown in red (large), and the dashed lines show the unit cell.

4.2.1.2 Complexes

The coordination complexes of the alkaline earth metal cations (M^{2+}) involve electrostatic, or ion-dipole, interactions that have no preferred direction of interaction. Calcium will tolerate a wide range of coordination numbers, however, 6 and 8 are the most common. Complexes generally form with oxygen donors in a wide range of ligands, including: ROH , R_2O , $\text{R}_2\text{C}=\text{O}$, RCO_2^- , and PO_4^{2-} . While complexes with nitrogen donor ligands are known they are usually present with oxygen donors as well. As with the Group 1 metals, the aquo complex readily exchanges the water for other ligands, however, since the bond energy is larger for Ca^{2+} than for Na^+ , the equilibrium constants are larger for analogous complexes.

4.2.1.3 Bibliography

- J. M. Buriak, L. K. Cheatham, R. G. Gordon, J. J. Graham, and A. R. Barron, *Euro J. Solid State Inorg. Chem.*, 1992, **29**, 43.
- R. E. Anderson and A. R. Barron, *Main Group Chem.*, 2005, **4**, 279.
- C. Lupu, R. S. Arvidson, A. Lüttge and A. R. Barron, *Chem. Commun.*, 2005, 2354.

4.2.2 Calcium Carbide: From Gaslight to Fertilizer³

Calcium carbide has an interesting role in the societal and commercial changes that took place in the late 19th and early 20th centuries. However, in order to understand the effects of calcium carbide it is important to realize the state of the art of lighting in the late 18th century.

It was in 1792 that William Murdoch (Figure 4.15) first began experimenting with the use of gas, derived from the heating of coal and other materials, for lighting. Murdoch produced this “coal gas,” or “manufactured gas” and conveyed it through metal pipes, lighting his cottage and offices in Redruth, Cornwall (Figure 4.16).

³This content is available online at <<http://cnx.org/content/m31935/1.4/>>.



Figure 4.15: Scottish engineer, inventor, and pioneer of gas lighting William Murdoch (1754 - 1839).



Figure 4.16: Murdoch's house at Redruth was the first domestic residence to be lit by gas.

In 1802 as part of the public celebrations of the Peace of Amiens (between England and France) Murdoch made a public exhibition of his lighting by illuminating the exterior of the Soho Foundry in Birmingham, England. Then in 1807 an entrepreneur, Fredrick Winsor (originally Friedrich Albrecht Winzer) displayed gaslights along the top of the wall between Carlton House and the Mall in London. This demonstration for city use was a revelation. By 1823 Britain had 300 miles of gas pipe and by 1850 it was 2000 miles. Gaslight had a profound impact on society. Walking the streets at night was safer, and it allowed for longer working hours. It also made evening activities easier. As a consequence reading and evening schools became popular pastimes. Unfortunately, gaslight was rather dull orange in color (Figure 4.17), but it was due to another area of chemical research that a brighter alternative was discovered.



Figure 4.17: A gas light still in use on the streets of London.

In 1895 the Frenchman Henry Moissan (Figure 4.18) was trying to make diamonds by the reaction of carbon (graphite) with almost anything he could lay his hands on. Although highly unsuccessful, one of his experiments did prove useful. By reacting carbon with lime, the common name for calcium oxide (CaO) at $2000\text{ }^\circ\text{C}$ (in an electric arc furnace that he had helped develop) he produced calcium carbide (CaC_2).



Figure 4.18: French chemist Ferdinand Frederick Henri Moissan (1852 - 1907).

Pure calcium carbide is colorless, but most samples have a color ranging from black to grayish-white, depending on the grade. As an ionic salt it has a high melting point (2160 °C). While the structure of calcium carbide (Figure 4.19) has a tetragonal lattice, it is related to that of a cubic rock salt structure, but where the anion is the linear C_2^{2-} moiety.

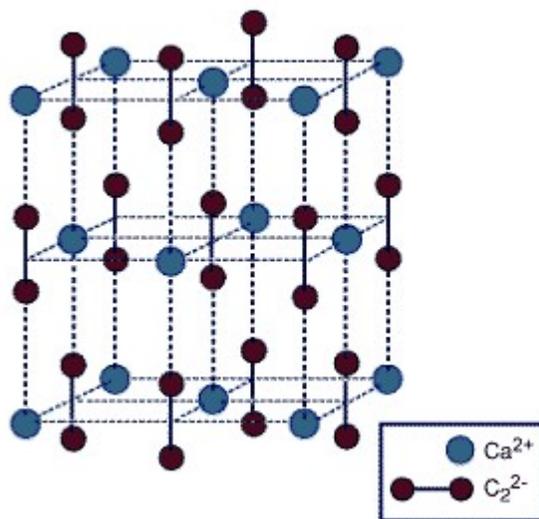


Figure 4.19: The unit cell of calcium carbide (CaC_2). Adapted from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann (1984).

Although now used extensively, at the time of its discovery calcium carbide itself did not prove very interesting, its reaction with water had a profound effect on illumination. The reaction of calcium carbide with water yields acetylene, (4.16).



Unlike coal gas, acetylene burns with a very bright white flame. Although electricity was starting to become more commonly used it was very expensive and acetylene offered a cheaper alternative for domestic lighting. Thus, by 1899 there were over 250,000 acetylene gas jets in Germany alone. The reaction of calcium carbide to form acetylene was used in a variety of portable lamps. These so-called carbide lamps were used in slate, copper and tin mines, and were also used extensively as headlights in early automobiles and bikes (Figure 4.20).



Figure 4.20: The carbide lamp on a 1911 Renault.

Unfortunately for acetylene there was one discovery and one economic change that brought the use of acetylene as a light source to an end. In 1893 Auer von Welsbach (Figure 4.21) invented the gas mantel (Figure 4.22). By the impregnation of silk or cotton with a mixture of thorium dioxide and cerium(IV) oxide (99:1), and using this in combination with gas he was able to produce a very white flame.



Figure 4.21: Austrian scientist and inventor Carl Auer Freiherr von Welsbach (1858 - 1929).



Figure 4.22: Gas mantles. Copyright Science Museum, London.

The other impact on acetylene, was that by 1905 the cost of electricity was significantly lower, and as a consequence the price of CaC_2 dropped to 30%. There were stockpiles of calcium carbide all over Europe and America. This may have been the end of calcium carbide's usefulness, however, in 1895 Heinrich Caro (Figure 4.23) and Adolf Frank (Figure 4.24), at the German chemical giant Badische Anilin- und Soda-Fabrik (BASF), were trying to make hydrogen cyanide (HCN) to use in its color dye business. In 1898, one of their colleagues demonstrated that what was actually produced during the reaction at temperatures exceeding $1000\text{ }^\circ\text{C}$ was not cyanide, as they had hoped. It turned out that what Caro and Frank had found was that when calcium carbide is reacted with nitrogen at $1000\text{ }^\circ\text{C}$ it forms calcium cyanamide (CaCN_2), (4.17). The cyanamide anion has the structure $[\text{N}=\text{C}=\text{N}]^{2-}$.



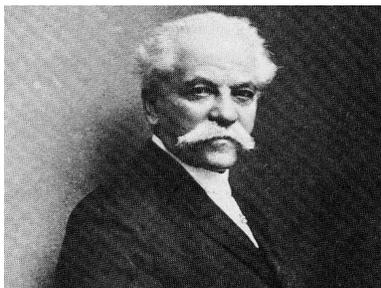


Figure 4.23: German chemist Heinrich Caro (1834 - 1910).



Figure 4.24: German chemist, engineer, and businessman Adolph Frank (1834 – 1916).

In contact with water calcium cyanamide decomposes and liberates ammonia:



As such, CaCN_2 is an excellent solid fertilizer that is readily plowed into the soil. By 1908 calcium cyanamide was also found to be a plant protection agent, which, at a time when all weed control was performed mechanically, represented a great step forward. Consequently, the output of calcium cyanamide grew enormously. In 1910, 30,000 tons were produced, but in 1928, global production had reached 1.2 million tons. After a temporary decline, demand has again risen in recent years owing to the ban on several pesticides due to the environmental damage they cause. Even after 100 years of use, no harmful long-term effects to the earth or environment have been observed, nor have weeds or pests developed a resistance to calcium cyanamide.

4.2.2.1 Bibliography

- N.-G. Vannerberg, *Acta Chem. Scand.*, 1962, **16**, 1212.
- M. A. Bredig, *J. Am. Chem. Soc.*, 1942, **64**, 1730.
- Y. Yamamoto, K. Kinoshita, K. Tamaru, and T. Yamanaka, *Bull. Chem. Soc. Japan*, 1958, **31**, 501.

4.2.3 Portland Cement

4.2.3.1 Chemical Composition of Portland Cement⁴

4.2.3.1.1

There are four chief minerals present in a Portland cement grain: tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_5$) and calcium aluminoferrite ($\text{Ca}_4\text{Al}_n\text{Fe}_{2-n}\text{O}_7$). The formula of each of these minerals can be broken down into the basic calcium, silicon, aluminum and iron oxides (Table 4.6). Cement chemists use abbreviated nomenclature based on oxides of various elements to indicate chemical formulae of relevant species, i.e., C = CaO, S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 . Hence, traditional cement nomenclature abbreviates each oxide as shown in Table 4.6.

Mineral	Chemical formula	Oxide composition	Abbreviation
Tricalcium silicate (alite)	Ca_3SiO_5	3CaO.SiO ₂	C3S
Dicalcium silicate (belite)	Ca_2SiO_4	2CaO.SiO ₂	C2S
Tricalcium aluminate	$\text{Ca}_3\text{Al}_2\text{O}_4$	3CaO.Al ₂ O ₃	C3A
Tetracalcium aluminoferrite	$\text{Ca}_4\text{Al}_n\text{Fe}_{2-n}\text{O}_7$	4CaO.Al _n Fe _{2-n} O ₃	C4AF

Table 4.6: Chemical formulae and cement nomenclature for major constituents of Portland cement. Abbreviation notation: C = CaO, S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 .

The composition of cement is varied depending on the application. A typical example of cement contains 50–70% C3S, 15–30% C2S, 5–10% C3A, 5–15% C4AF, and 3–8% other additives or minerals (such as oxides of calcium and magnesium). It is the hydration of the calcium silicate, aluminate, and aluminoferrite minerals that causes the hardening, or setting, of cement. The ratio of C3S to C2S helps to determine how fast the cement will set, with faster setting occurring with higher C3S contents. Lower C3A content promotes resistance to sulfates. Higher amounts of ferrite lead to slower hydration. The ferrite phase causes the brownish gray color in cements, so that “white cements” (i.e., those that are low in C4AF) are often used for aesthetic purposes.

The calcium aluminoferrite (C4AF) forms a continuous phase around the other mineral crystallites, as the iron containing species act as a fluxing agent in the rotary kiln during cement production and are the last to solidify around the others. Figure 4.25 shows a typical cement grain.

⁴This content is available online at <<http://cnx.org/content/m16445/1.9/>>.

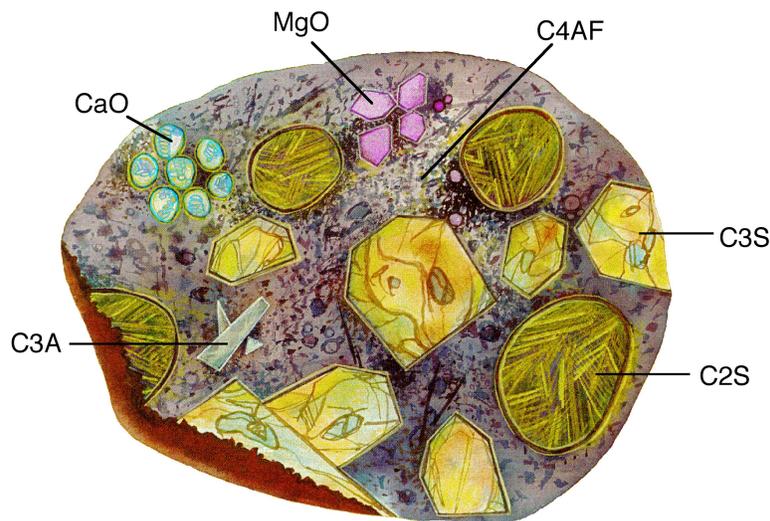


Figure 4.25: A pictorial representation of a cross-section of a cement grain. Adapted from Cement Microscopy, Halliburton Services, Duncan, OK.

It is worth noting that a given cement grain will not have the same size or even necessarily contain all the same minerals as the next grain. The heterogeneity exists not only within a given particle, but extends from grain to grain, batch-to-batch, plant to plant.

4.2.3.1.2 Bibliography

- H. F. W. Taylor, *Cement Chemistry*, 2nd Ed., Academic Press, London (1997).

4.2.3.2 Manufacture of Portland Cement⁵

4.2.3.2.1

Portland Cement is manufactured by heating calcium carbonate and clay or shale in a kiln. During this process the calcium carbonate is converted to calcium oxide (also known as lime) and the clay minerals decompose to yield dicalcium silicate (Ca_2SiO_4 , C2S) and other inorganic oxides such as aluminate and ferrite. Further heating melts the aluminate and ferrite phases. The lime reacts with dicalcium silicate to form tricalcium silicate (Ca_3SiO_5 , C3S). As the mixture is cooled, tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$, C3A) and tetracalcium aluminoferrite ($\text{Ca}_4\text{Al}_n\text{Fe}_{2-n}\text{O}_7$, C4AF) crystallize from the melt and tricalcium silicate and the remaining dicalcium silicate undergo phase transitions. These four minerals (C3S, C2S, C3A, and C4AF) comprise the bulk of most cement mixtures. Initially Portland cement production was carried out in a furnace, however, technological developments such as the rotary kiln have enhanced production capabilities and allowed cement to become one of the most widely used construction materials.

Cement plants generally produce various grades of cement by two processes, referred to as either the wet or dry process. The dry process uses a pneumatic kiln system which uses superheated air to convert raw materials to cement, whereas the wet process slurries the raw materials in water in preparation for conversion

⁵This content is available online at <<http://cnx.org/content/m16448/1.5/>>.

to cement. Cement manufacturers due to its higher energy efficiency generally favor the dry process, but the wet process tends to produce cement with properties more palatable to the energy services industry. The American Petroleum Institute (API) Class H cement used in energy service applications is produced by the wet process, and thus will be the focus of the following discussion.

The cement manufacturing process begins at the quarry (Figure 4.26), where limestone formations are ripped and crushed in two crushers to a mean particle size of 4". The quarry formation is not entirely limestone, and no attempt is made to isolate the limestone from the other minerals. On the contrary, the rippers act to blend in the "impurity" minerals as evenly as is feasible while still maintaining an acceptable limestone content so as not to "waste" the formation. This is accomplished by ripping the formation face at a 45° (Figure 4.27). The rock is quality controlled via mobile X-ray fluorescence (XRF) spectroscopy (Figure 4.28) at the starting point of a mobile covered conveyor belt system (Figure 4.29), which transports the material to a dome storage unit (Figure 4.30).



Figure 4.26: Limestone quarry face in Midlothian, TX (Copyright Halliburton Energy Services).



Figure 4.27: Limestone quarry formation, showing the 45° ripping technique (Copyright Halliburton Energy Services).



Figure 4.28: Mobile crusher and XRF unit (Copyright Halliburton Energy Services).
