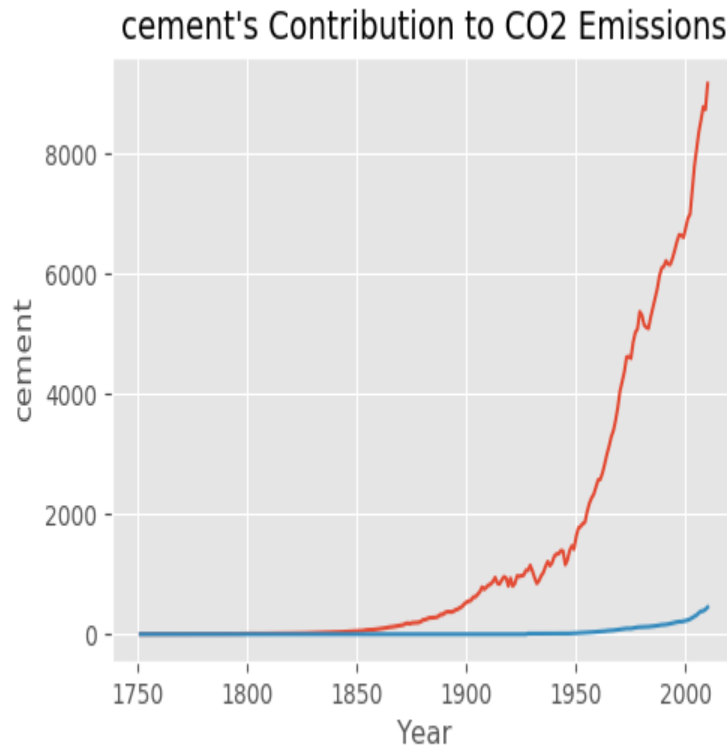


cement



A cement is a binder, a substance used for construction that sets, hardens and adheres to other materials, binding them together. Cement is seldom used on its own, but rather to bind sand and gravel (aggregate) together. Cement is used with fine aggregate to produce mortar for masonry, or with sand and gravel aggregates to produce concrete. Cements used in construction are usually inorganic, often lime or calcium silicate based, and can be characterized as being either hydraulic or non-hydraulic, depending upon the ability of the cement to set in the presence of water (see hydraulic and non-hydraulic lime plaster). Non-hydraulic cement will not set in wet conditions or under water; rather, it sets as it dries and reacts with carbon dioxide in the air. It is resistant to attack by chemicals after setting. Hydraulic cements (e.g., Portland cement) set and become adhesive due to a chemical reaction between the dry ingredients and water. The chemical reaction results in mineral hydrates that are not very water-soluble and so are quite durable in water and safe from chemical attack. This allows setting in wet conditions or under water and further protects the hardened material from chemical attack. The chemical process for hydraulic cement found by ancient Romans used volcanic ash (pozzolana) with added lime (calcium oxide). The word "cement" can be traced back to the Roman term *opus caementicium*, used to describe masonry resembling modern concrete that was made from crushed rock with burnt lime as binder. The volcanic ash and pulverized brick supplements that were added to the burnt lime, to obtain a hydraulic binder, were later referred to as *cementum*, *cimentum*, *cäment*, and *cement*. In modern times, organic polymers are sometimes used as cements in concrete.

== Chemistry == Non-hydraulic cement, such as slaked lime (calcium oxide mixed with water), hardens by carbonation in the presence of carbon dioxide which is naturally present in the air. First calcium oxide (lime) is produced from calcium carbonate (limestone or chalk) by calcination at temperatures above 825 °C (1,517 °F) for about 10 hours at atmospheric pressure: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ The calcium oxide is then spent (slaked) mixing it with water to make slaked lime (calcium hydroxide): $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$ Once the excess water is completely evaporated (this process is technically called setting), the carbonation starts: $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ This reaction takes a significant

amount of time because the partial pressure of carbon dioxide in the air is low. The carbonation reaction requires the dry cement to be exposed to air, and for this reason the slaked lime is a non-hydraulic cement and cannot be used under water. This whole process is called the lime cycle. Conversely, hydraulic cement hardens by hydration when water is added. Hydraulic cements (such as Portland cement) are made of a mixture of silicates and oxides, the four main components being: Belite ($2\text{CaO}\cdot\text{SiO}_2$); Alite ($3\text{CaO}\cdot\text{SiO}_2$); Tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) (historically, and still occasionally, called 'celite'); Brownmillerite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$). The silicates are responsible for the mechanical properties of the cement, the tricalcium aluminate and the brownmillerite are essential to allow the formation of the liquid phase during the kiln sintering (firing). The chemistry of the above listed reactions is not completely clear and is still the object of research.

== History == Perhaps the earliest known occurrence of cement is from twelve million years ago. A deposit of cement was formed after an occurrence of oil shale located adjacent to a bed of limestone burned due to natural causes. These ancient deposits were investigated in the 1960s and 1970s.

=== Alternatives to cement used in antiquity === Cement, chemically speaking, is a product that includes lime as the primary curing ingredient, but is far from the first material used for cementation. The Babylonians and Assyrians used bitumen to bind together burnt brick or alabaster slabs. In Egypt stone blocks were cemented together with a mortar made of sand and roughly burnt gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), which often contained calcium carbonate (CaCO_3).

=== Macedonians and Romans === Lime (calcium oxide) was used on Crete and by the ancient Greeks. There is evidence that the Minoans of Crete used crushed potshards as an artificial pozzolan for hydraulic cement. It is uncertain where it was first discovered that a combination of hydrated non-hydraulic lime and a pozzolan produces a hydraulic mixture (see also: Pozzolan reaction), but concrete made from such mixtures was used by the Ancient Macedonians and three centuries later on a large scale by Roman engineers. There is... a kind of powder which from natural causes produces astonishing results. It is found in the neighborhood of Baiae and in the country belonging to the towns round about Mt. Vesuvius. This substance when mixed with lime and rubble not only lends strength to buildings of other kinds, but even when piers of it are constructed in the sea, they set hard under water. The Greeks used volcanic tuff from the island of Thera as their pozzolan and the Romans used crushed volcanic ash (activated aluminium silicates) with lime. This mixture was able to set under water increasing its resistance. The material was called pozzolana from the town of Pozzuoli, west of Naples where volcanic ash was extracted. In the absence of pozzolan ash, the Romans used powdered brick or pottery as a substitute and they may have used crushed tiles for this purpose before discovering natural sources near Rome. The huge dome of the Pantheon in Rome and the massive Baths of Caracalla are examples of ancient structures made from these concretes, many of which are still standing. The vast system of Roman aqueducts also made extensive use of hydraulic cement.

=== Middle Ages === Although any preservation of this knowledge in literary sources from the Middle Ages is unknown, medieval masons and some military engineers maintained an active tradition of using hydraulic cement in structures such as canals, fortresses, harbors, and shipbuilding facilities.

=== 16th century === Tabby, a building material using oyster-shell lime, sand, and whole oyster shells to form a concrete, was introduced to the Americas by the Spanish in the sixteenth century.

=== 18th century === The technical knowledge for making hydraulic cement was formalized by French and British engineers in the 18th century. John Smeaton made an important contribution to the development of cements while planning the construction of the third Eddystone Lighthouse (1755–59) in the English Channel now known as Smeaton's Tower. He needed a hydraulic mortar that would set and develop some strength in the twelve-hour period between successive high tides. He performed experiments with combinations of different limestones and additives including trass and pozzolanas and did exhaustive market research on the available hydraulic limes, visiting their production sites, and noted that the "hydraulicity" of the lime was directly related to the clay content of the limestone from which it was made. Smeaton was a civil engineer by profession, and took the idea no further. In the South Atlantic seaboard of the United States, tabby relying upon the oyster-shell middens of earlier Native American populations was used in house construction from the 1730s to the 1860s. In Britain particularly, good quality building stone became ever more expensive during a period of rapid growth, and it became a common practice to construct prestige buildings from the new industrial bricks, and to finish them with a stucco to imitate stone. Hydraulic limes were favored for this, but the need for a fast set time encouraged the development of new cements. Most famous was Parker's "Roman cement". This was developed by James Parker in the 1780s, and finally patented in 1796. It was, in fact, nothing like material used by the Romans, but was a "natural cement" made by burning septaria – nodules that are found in certain clay deposits, and that contain both clay minerals and calcium carbonate. The burnt

nodules were ground to a fine powder. This product, made into a mortar with sand, set in 5–15 minutes. The success of "Roman cement" led other manufacturers to develop rival products by burning artificial hydraulic lime cements of clay and chalk. Roman cement quickly became popular but was largely replaced by Portland cement in the 1850s. === 19th century === Apparently unaware of Smeaton's work, the same principle was identified by Frenchman Louis Vicat in the first decade of the nineteenth century. Vicat went on to devise a method of combining chalk and clay into an intimate mixture, and, burning this, produced an "artificial cement" in 1817 considered the "principal forerunner" of Portland cement and "...Edgar Dobbs of Southwark patented a cement of this kind in 1811." In Russia, Egor Cheliev created a new binder by mixing lime and clay. His results were published in 1822 in his book *A Treatise on the Art to Prepare a Good Mortar* published in St. Petersburg. A few years later in 1825, he published another book, which described the various methods of making cement and concrete, as well as the benefits of cement in the construction of buildings and embankments. Portland cement, the most common type of cement in general use around the world as a basic ingredient of concrete, mortar, stucco, and non-speciality grout, was developed in England in the mid 19th century, and usually originates from limestone. James Frost produced what he called "British cement" in a similar manner around the same time, but did not obtain a patent until 1822. In 1824, Joseph Aspdin patented a similar material, which he called Portland cement, because the render made from it was in color similar to the prestigious Portland stone which was quarried on the Isle of Portland, Dorset, England. However, Aspdin's cement was nothing like modern Portland cement but was a first step in its development, called a proto-Portland cement. Joseph Aspdin's son William Aspdin had left his father's company and in his cement manufacturing apparently accidentally produced calcium silicates in the 1840s, a middle step in the development of Portland cement. William Aspdin's innovation was counterintuitive for manufacturers of "artificial cements", because they required more lime in the mix (a problem for his father), a much higher kiln temperature (and therefore more fuel), and the resulting clinker was very hard and rapidly wore down the millstones, which were the only available grinding technology of the time. Manufacturing costs were therefore considerably higher, but the product set reasonably slowly and developed strength quickly, thus opening up a market for use in concrete. The use of concrete in construction grew rapidly from 1850 onward, and was soon the dominant use for cements. Thus Portland cement began its predominant role. Isaac Charles Johnson further refined the production of meso-Portland cement (middle stage of development) and claimed to be the real father of Portland cement. Setting time and "early strength" are important characteristics of cements. Hydraulic limes, "natural" cements, and "artificial" cements all rely upon their belite content for strength development. Belite develops strength slowly. Because they were burned at temperatures below 1,250 °C (2,280 °F), they contained no alite, which is responsible for early strength in modern cements. The first cement to consistently contain alite was made by William Aspdin in the early 1840s: This was what we call today "modern" Portland cement. Because of the air of mystery with which William Aspdin surrounded his product, others (e.g., Vicat and Johnson) have claimed precedence in this invention, but recent analysis of both his concrete and raw cement have shown that William Aspdin's product made at Northfleet, Kent was a true alite-based cement. However, Aspdin's methods were "rule-of-thumb": Vicat is responsible for establishing the chemical basis of these cements, and Johnson established the importance of sintering the mix in the kiln. In the US the first large-scale use of cement was Rosendale cement, a natural cement mined from a massive deposit of a large dolostone rock deposit discovered in the early 19th century near Rosendale, New York. Rosendale cement was extremely popular for the foundation of buildings (e.g., Statue of Liberty, Capitol Building, Brooklyn Bridge) and lining water pipes. Sorel cement was patented in 1867 by Frenchman Stanislas Sorel and was stronger than Portland cement but its poor water resistance and corrosive qualities limited its use in building construction. The next development with the manufacture of Portland cement was the introduction of the rotary kiln which allowed a stronger, more homogeneous mixture and a continuous manufacturing process. === 20th century === Calcium aluminate cements were patented in 1908 in France by Jules Bied for better resistance to sulfates. In the US, the long curing time of at least a month for Rosendale cement made it unpopular after World War One in the construction of highways and bridges and many states and construction firms turned to the use of Portland cement. Because of the switch to Portland cement, by the end of the 1920s of the 15 Rosendale cement companies, only one had survived. But in the early 1930s it was discovered that, while Portland cement had a faster setting time it was not as durable, especially for highways, to the point that some states stopped building highways and roads with cement. Bertrain H. Wait, an engineer whose company had worked on the construction of the New York City's Catskill Aqueduct, was impressed with the durability of Rosendale cement, and came up

with a blend of both Rosendale and synthetic cements which had the good attributes of both: it was highly durable and had a much faster setting time. Wait convinced the New York Commissioner of Highways to construct an experimental section of highway near New Paltz, New York, using one sack of Rosendale to six sacks of synthetic cement. It was proved a success and for decades the Rosendale-synthetic cement blend became common use in highway and bridge construction. == Modern cements == Modern hydraulic cements began to be developed from the start of the Industrial Revolution (around 1800), driven by three main needs: Hydraulic cement render (stucco) for finishing brick buildings in wet climates. Hydraulic mortars for masonry construction of harbor works, etc., in contact with sea water. Development of strong concretes. Modern cements are often Portland cement or Portland cement blends, but other cements are used in industry. === Portland cement === Portland cement is by far the most common type of cement in general use around the world. This cement is made by heating limestone (calcium carbonate) with other materials (such as clay) to 1450 °C in a kiln, in a process known as calcination, whereby a molecule of carbon dioxide is liberated from the calcium carbonate to form calcium oxide, or quicklime, which then chemically combines with the other materials that have been included in the mix to form calcium silicates and other cementitious compounds. The resulting hard substance, called 'clinker', is then ground with a small amount of gypsum into a powder to make 'ordinary Portland cement', the most commonly used type of cement (often referred to as OPC). Portland cement is a basic ingredient of concrete, mortar and most non-specialty grout. The most common use for Portland cement is in the production of concrete. Concrete is a composite material consisting of aggregate (gravel and sand), cement, and water. As a construction material, concrete can be cast in almost any shape desired, and once hardened, can become a structural (load bearing) element. Portland cement may be grey or white. === Portland cement blends === Portland cement blends are often available as inter-ground mixtures from cement producers, but similar formulations are often also mixed from the ground components at the concrete mixing plant. Portland blast-furnace slag cement, or Blast furnace cement (ASTM C595 and EN 197-1 nomenclature respectively), contains up to 95% ground granulated blast furnace slag, with the rest Portland clinker and a little gypsum. All compositions produce high ultimate strength, but as slag content is increased, early strength is reduced, while sulfate resistance increases and heat evolution diminishes. Used as an economic alternative to Portland sulfate-resisting and low-heat cements. Portland-fly ash cement contains up to 40% fly ash under ASTM standards (ASTM C595), or 35% under EN standards (EN 197-1). The fly ash is pozzolanic, so that ultimate strength is maintained. Because fly ash addition allows a lower concrete water content, early strength can also be maintained. Where good quality cheap fly ash is available, this can be an economic alternative to ordinary Portland cement. Portland pozzolan cement includes fly ash cement, since fly ash is a pozzolan, but also includes cements made from other natural or artificial pozzolans. In countries where volcanic ashes are available (e.g. Italy, Chile, Mexico, the Philippines) these cements are often the most common form in use. The maximum replacement ratios are generally defined as for Portland-fly ash cement. Portland silica fume cement. Addition of silica fume can yield exceptionally high strengths, and cements containing 5–20% silica fume are occasionally produced, with 10% being the maximum allowed addition under EN 197-1. However, silica fume is more usually added to Portland cement at the concrete mixer. Masonry cements are used for preparing bricklaying mortars and stuccos, and must not be used in concrete. They are usually complex proprietary formulations containing Portland clinker and a number of other ingredients that may include limestone, hydrated lime, air entrainers, retarders, waterproofers and coloring agents. They are formulated to yield workable mortars that allow rapid and consistent masonry work. Subtle variations of Masonry cement in the US are Plastic Cements and Stucco Cements. These are designed to produce controlled bond with masonry blocks. Expansive cements contain, in addition to Portland clinker, expansive clinkers (usually sulfoaluminate clinkers), and are designed to offset the effects of drying shrinkage that is normally encountered with hydraulic cements. This allows large floor slabs (up to 60 m square) to be prepared without contraction joints. White blended cements may be made using white clinker (containing little or no iron) and white supplementary materials such as high-purity metakaolin. Colored cements are used for decorative purposes. In some standards, the addition of pigments to produce "colored Portland cement" is allowed. In other standards (e.g. ASTM), pigments are not allowed constituents of Portland cement, and colored cements are sold as "blended hydraulic cements". Very finely ground cements are made from mixtures of cement with sand or with slag or other pozzolan type minerals that are extremely finely ground together. Such cements can have the same physical characteristics as normal cement but with 50% less cement particularly due to their increased surface area for the chemical reaction. Even with intensive grinding they can use up to 50%

less energy to fabricate than ordinary Portland cements. === Other cements === Pozzolan-lime cements. Mixtures of ground pozzolan and lime are the cements used by the Romans, and are present in extant Roman structures (e.g. the Pantheon in Rome). They develop strength slowly, but their ultimate strength can be very high. The hydration products that produce strength are essentially the same as those produced by Portland cement. Slag-lime cements. Ground granulated blast-furnace slag is not hydraulic on its own, but is "activated" by addition of alkalis, most economically using lime. They are similar to pozzolan lime cements in their properties. Only granulated slag (i.e. water-quenched, glassy slag) is effective as a cement component. Supersulfated cements contain about 80% ground granulated blast furnace slag, 15% gypsum or anhydrite and a little Portland clinker or lime as an activator. They produce strength by formation of ettringite, with strength growth similar to a slow Portland cement. They exhibit good resistance to aggressive agents, including sulfate. Calcium aluminate cements are hydraulic cements made primarily from limestone and bauxite. The active ingredients are monocalcium aluminate CaAl_2O_4 ($\text{CaO} \cdot \text{Al}_2\text{O}_3$ or CA in Cement chemist notation, CCN) and mayenite $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ($12 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3$, or C12A7 in CCN). Strength forms by hydration to calcium aluminate hydrates. They are well-adapted for use in refractory (high-temperature resistant) concretes, e.g. for furnace linings. Calcium sulfoaluminate cements are made from clinkers that include ye'elimite ($\text{Ca}_4(\text{AlO}_2)_6\text{SO}_4$ or C4A3S in Cement chemist's notation) as a primary phase. They are used in expansive cements, in ultra-high early strength cements, and in "low-energy" cements. Hydration produces ettringite, and specialized physical properties (such as expansion or rapid reaction) are obtained by adjustment of the availability of calcium and sulfate ions. Their use as a low-energy alternative to Portland cement has been pioneered in China, where several million tonnes per year are produced. Energy requirements are lower because of the lower kiln temperatures required for reaction, and the lower amount of limestone (which must be endothermically decarbonated) in the mix. In addition, the lower limestone content and lower fuel consumption leads to a CO_2 emission around half that associated with Portland clinker. However, SO_2 emissions are usually significantly higher. "Natural" cements correspond to certain cements of the pre-Portland era, produced by burning argillaceous limestones at moderate temperatures. The level of clay components in the limestone (around 30–35%) is such that large amounts of belite (the low-early strength, high-late strength mineral in Portland cement) are formed without the formation of excessive amounts of free lime. As with any natural material, such cements have highly variable properties. Geopolymer cements are made from mixtures of water-soluble alkali metal silicates and aluminosilicate mineral powders such as fly ash and metakaolin. Polymer cements are made from organic chemicals that polymerise. Often thermoset materials are employed. While they are often significantly more expensive, they can give a water proof material that has useful tensile strength. == Setting and curing == Cement starts to set when mixed with water which causes a series of hydration chemical reactions. The constituents slowly hydrate and the mineral hydrates solidify; the interlocking of the hydrates gives cement its strength. Contrary to popular perceptions, hydraulic cements do not set by drying out; proper curing requires maintaining the appropriate moisture content during the curing process. If hydraulic cements dry out during curing, the resulting product can be significantly weakened. == Safety issues == Bags of cement routinely have health and safety warnings printed on them because not only is cement highly alkaline, but the setting process is exothermic. As a result, wet cement is strongly caustic (water pH = 13.5) and can easily cause severe skin burns if not promptly washed off with water. Similarly, dry cement powder in contact with mucous membranes can cause severe eye or respiratory irritation. Some trace elements, such as chromium, from impurities naturally present in the raw materials used to produce cement may cause allergic dermatitis. Reducing agents such as ferrous sulfate (FeSO_4) are often added to cement to convert the carcinogenic hexavalent chromate (CrO_4^{2-}) into trivalent chromium (Cr^{3+}), a less toxic chemical species. Cement users need also to wear appropriate gloves and protective clothing. == Cement industry in the world == In 2010, the world production of hydraulic cement was 3,300 million tonnes (3.2×10^9 long tons; 3.6×10^9 short tons). The top three producers were China with 1,800, India with 220, and USA with 63.5 million tonnes for a combined total of over half the world total by the world's three most populated states. For the world capacity to produce cement in 2010, the situation was similar with the top three states (China, India, and USA) accounting for just under half the world total capacity. Over 2011 and 2012, global consumption continued to climb, rising to 3585 Mt in 2011 and 3736 Mt in 2012, while annual growth rates eased to 8.3% and 4.2%, respectively. China, representing an increasing share of world cement consumption, continued to be the main engine of global growth. By 2012, Chinese demand was recorded at 2160 Mt, representing 58% of world consumption. Annual growth rates, which reached 16% in 2010, appear to have softened, slowing to

5–6% over 2011 and 2012, as China's economy targets a more sustainable growth rate. Outside of China, worldwide consumption climbed by 4.4% to 1462 Mt in 2010, 5% to 1535 Mt in 2011, and finally 2.7% to 1576 Mt in 2012. Iran is now the 3rd largest cement producer in the world and has increased its output by over 10% from 2008 to 2011. Due to climbing energy costs in Pakistan and other major cement-producing countries, Iran is in a unique position as a trading partner, utilizing its own surplus petroleum to power clinker plants. Now a top producer in the Middle-East, Iran is further increasing its dominant position in local markets and abroad. The performance in North America and Europe over the 2010–12 period contrasted strikingly with that of China, as the global financial crisis evolved into a sovereign debt crisis for many economies in this region and recession. Cement consumption levels for this region fell by 1.9% in 2010 to 445 Mt, recovered by 4.9% in 2011, then dipped again by 1.1% in 2012. The performance in the rest of the world, which includes many emerging economies in Asia, Africa and Latin America and representing some 1020 Mt cement demand in 2010, was positive and more than offset the declines in North America and Europe. Annual consumption growth was recorded at 7.4% in 2010, moderating to 5.1% and 4.3% in 2011 and 2012, respectively. As at year-end 2012, the global cement industry consisted of 5673 cement production facilities, including both integrated and grinding, of which 3900 were located in China and 1773 in the rest of the world. Total cement capacity worldwide was recorded at 5245 Mt in 2012, with 2950 Mt located in China and 2295 Mt in the rest of the world. === China === "For the past 18 years, China consistently has produced more cement than any other country in the world. [...] (However,) China's cement export peaked in 1994 with 11 million tonnes shipped out and has been in steady decline ever since. Only 5.18 million tonnes were exported out of China in 2002. Offered at \$34 a ton, Chinese cement is pricing itself out of the market as Thailand is asking as little as \$20 for the same quality." In 2006, it was estimated that China manufactured 1.235 billion tonnes of cement, which was 44% of the world total cement production. "Demand for cement in China is expected to advance 5.4% annually and exceed 1 billion tonnes in 2008, driven by slowing but healthy growth in construction expenditures. Cement consumed in China will amount to 44% of global demand, and China will remain the world's largest national consumer of cement by a large margin." In 2010, 3.3 billion tonnes of cement was consumed globally. Of this, China accounted for 1.8 billion tonnes. == Environmental impacts == Cement manufacture causes environmental impacts at all stages of the process. These include emissions of airborne pollution in the form of dust, gases, noise and vibration when operating machinery and during blasting in quarries, and damage to countryside from quarrying. Equipment to reduce dust emissions during quarrying and manufacture of cement is widely used, and equipment to trap and separate exhaust gases are coming into increased use. Environmental protection also includes the re-integration of quarries into the countryside after they have been closed down by returning them to nature or re-cultivating them. === CO2 emissions === Carbon concentration in cement spans from ~5% in cement structures to ~8% in the case of roads in cement. Cement manufacturing releases CO2 in the atmosphere both directly when calcium carbonate is heated, producing lime and carbon dioxide, and also indirectly through the use of energy if its production involves the emission of CO2. The cement industry produces about 10% of global man-made CO2 emissions, of which 60% is from the chemical process, and 40% from burning fuel. Nearly 900 kg of CO2 are emitted for every 1000 kg of Portland cement produced. In the European Union the specific energy consumption for the production of cement clinker has been reduced by approximately 30% since the 1970s. This reduction in primary energy requirements is equivalent to approximately 11 million tonnes of coal per year with corresponding benefits in reduction of CO2 emissions. This accounts for approximately 5% of anthropogenic CO2. The majority of carbon dioxide emissions in the manufacture of Portland cement (approximately 60%) are produced from the chemical decomposition of limestone to lime, an ingredient in Portland cement clinker. These emissions may be reduced by lowering the clinker content of cement. To reduce the transport of heavier raw materials and to minimize the associated costs, it is more economical for cement plants to be closer to the limestone quarries rather than to the consumer centers. In certain applications, lime mortar reabsorbs some of the CO2 as was released in its manufacture, and has a lower energy requirement in production than mainstream cement (citation needed). Newly developed cement types from Novacem and Eco-cement can absorb carbon dioxide from ambient air during hardening. Use of the Kalina cycle during production can also increase energy efficiency. === Heavy metal emissions in the air === In some circumstances, mainly depending on the origin and the composition of the raw materials used, the high-temperature calcination process of limestone and clay minerals can release in the atmosphere gases and dust rich in volatile heavy metals, a.o. thallium, cadmium and mercury are the most toxic. Heavy metals (Pb, Cd, Hg, ...) and also selenium are often found as trace elements in common metal

sulfides (pyrite (FeS₂), zinc blende (ZnS), galena (PbS), ...) present as secondary minerals in most of the raw materials. Environmental regulations exist in many countries to limit these emissions. As of 2011 in the United States, cement kilns are "legally allowed to pump more toxins into the air than are hazardous-waste incinerators." == Heavy metals present in the clinker == The presence of heavy metals in the clinker arises both from the natural raw materials and from the use of recycled by-products or alternative fuels. The high pH prevailing in the cement porewater (12.5 < pH < 13.5) limits the mobility of many heavy metals by decreasing their solubility and increasing their sorption onto the cement mineral phases. Nickel, zinc and lead are commonly found in cement in non-negligible concentrations. Chromium may also directly arise as natural impurity from the raw materials or as secondary contamination from the abrasion of hard chromium steel alloys used in the ball mills when the clinker is ground. As chromate (CrO₄²⁻) is toxic and may cause severe skin allergies at trace concentration, it is sometimes reduced into trivalent Cr(III) by addition of ferrous sulfate (FeSO₄). == Use of alternative fuels and by-products materials == A cement plant consumes 3 to 6 GJ of fuel per tonne of clinker produced, depending on the raw materials and the process used. Most cement kilns today use coal and petroleum coke as primary fuels, and to a lesser extent natural gas and fuel oil. Selected waste and by-products with recoverable calorific value can be used as fuels in a cement kiln (referred to as co-processing), replacing a portion of conventional fossil fuels, like coal, if they meet strict specifications. Selected waste and by-products containing useful minerals such as calcium, silica, alumina, and iron can be used as raw materials in the kiln, replacing raw materials such as clay, shale, and limestone. Because some materials have both useful mineral content and recoverable calorific value, the distinction between alternative fuels and raw materials is not always clear. For example, sewage sludge has a low but significant calorific value, and burns to give ash containing minerals useful in the clinker matrix. Normal operation of cement kilns provides combustion conditions which are more than adequate for the destruction of even the most difficult to destroy organic substances. This is primarily due to the very high temperatures of the kiln gases (2000 °C in the combustion gas from the main burners and 1100 °C in the gas from the burners in the precalciner). The gas residence time at high temperature in the rotary kiln is of the order of 5–10 seconds and in the precalciner more than 3 seconds. Due to bovine spongiform encephalopathy (BSE) in the European beef industry, the use of animal-derived products to feed cattle is now severely restricted. Large quantities of waste animal meat and bone meal (MBM), also known as animal flour, have to be safely disposed or transformed. The production of cement kilns, together with the incineration, is to date one of the two main ways to treat this solid effluent of the food industry. == Green cement == Green cement is a cementitious material that meets or exceeds the functional performance capabilities of ordinary Portland cement by incorporating and optimizing recycled materials, thereby reducing consumption of natural raw materials, water, and energy, resulting in a more sustainable construction material. New manufacturing processes for producing green cement are being researched with the goal to reduce, or even eliminate, the production and release of damaging pollutants and greenhouse gasses, particularly CO₂. Growing environmental concerns and increasing cost of fuels of fossil origin have resulted in many countries in sharp reduction of the resources needed to produce cement and effluents (dust and exhaust gases). Peter Trimble, a design student at the University of Edinburgh has proposed 'DUPE' based on *Sporosarcina pasteurii*, a bacterium with binding qualities which, when mixed with sand and urine produces a concrete said to be 70% as strong as conventional materials. == See also ==

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