

THE MANUFACTURE OF PORTLAND CEMENT

Cement is the substance which holds concrete together, which means that it is extremely widely used in our society. It has been manufactured in New Zealand for more than 100 years, and during this century production has increased one hundred-fold.

Portland cement (the only type of cement in common use today) is manufactured in a four step process.

Step 1 - Quarrying

Limestone and a 'cement rock' such as clay or shale are quarried and brought to the cement works. These rocks contain lime (CaCO_3), silica (SiO_2), alumina (Al_2O_3) and ferrous oxide (Fe_2O_3) - the raw materials of cement manufacture.

Step 2 - Raw material preparation

To form a consistent product, it is essential that the same mixture of minerals is used every time. For this reason the exact composition of the limestone and clay is determined at this point, and other ingredients added if necessary. The rock is also ground into fine particles to increase the efficiency of the reaction.

Step 3 - Clinkering

The raw materials are then dried, heated and fed into a rotating kiln. Here the raw materials react at very high temperatures to form $3\text{CaO}\cdot\text{SiO}_2$ (tricalcium silicate), $2\text{CaO}\cdot\text{SiO}_2$ (dicalcium silicate), $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (tricalcium aluminate) and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (tetracalcium alumino-ferrate).

Step 4 - Cement milling

The 'clinker' that has now been produced will behave just like cement, but it is in particles up to 3 cm in diameter. These are ground down to a fine powder to turn the clinker into useful cement.

Cement production has several quite serious environmental hazards associated with it: dust and CO_2 emissions and contaminated run-off water. Both cement works in New Zealand have measures in place to minimise these hazards.

INTRODUCTION

Concrete is an extremely versatile material, being used in the production of anything from nuclear radiation shields to playground structures and from bridges to yachts. It is able to be used in such a wide variety of applications because it can be poured into any shape, reinforced with steel or glass fibres, precast, coloured, has a variety of finishes and can even set under water. Modern concrete is made by mixing aggregate (sand, stones and shingle) with Portland cement and water and allowing it to set. Of these ingredients, the most important is Portland cement.

Cement is a fine grey powder which when reacted with water hardens to form a rigid chemical mineral structure which gives concrete its high strengths. Cement is in effect the glue that holds concrete together. The credit for its discovery is given to the Romans, who mixed lime (CaCO_3) with volcanic ash, producing a cement mortar which was used during

construction of such impressive structures as the Colosseum. When the Roman empire fell, the information on how to make cement was lost and was not rediscovered until the 16th century.

A brief history of Portland cement

Cement has been made since Roman times, but over time the recipes used to make cement have been refined. The earliest cements were made from lime and pozzolana (a volcanic ash containing significant quantities of SiO_2 and Al_2O_3) mixed with ground brick and water. This cement was not improved upon until 1758, when Smeaton noticed that using a limestone that was 20 - 25 % clay and heating the mixture resulted in a cement that could harden under water. He called this new cement 'hydraulic lime'. When the mixture was heated, a small quantity of it was sintered¹. Normally this was discarded as waste, but in the 1800s Aspdin and Johnson discovered that when the entire batch was sintered and then ground, a superior cement was formed. This substance became designated Portland cement (after the region in which they were working) and is the most common cement in use today.

Portland cement was first produced commercially in New Zealand in 1886 by James Wilson and Co., and has been produced here ever since. There are currently two companies producing cement in New Zealand: Golden Bay Cement Ltd. in Whangarei and Milburn New Zealand Ltd. in Westport. Production has increased from around 5 000 t/annum in 1900 to in excess of 500 000 t/annum in 1991 and a New Zealand market demand in 1996 in excess of 800 000 t/annum.

Portland cement is currently defined as a mixture of argillaceous (i.e. clay-like) and calcaneous (i.e. containing CaCO_3 or other insoluble calcium salts) materials mixed with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) sintered and then pulverised into a fine powder. The precise definition of Portland cement varies between different countries, and in New Zealand are controlled by New Zealand's Standard Specification (NZS) 3122. Portland cement differs from its precursors primarily in the fact that it is sintered.

Uses of Portland cement

A summary of the uses of cement in New Zealand is given in **Figure 1**. Cement is produced here in three main grades: ordinary Portland cement (80% of Milburn's and 95% of Golden Bay's domestic sales), rapid hardening cement and moderate-heat cement. Rapid-hardening cement is used in precast concrete, pipes and tiles. It is finer ground so that it hydrates more quickly and has more gypsum than other cements. Moderate-heat cement is used for the construction of hydro-electric dams, as the heat produced by ordinary cement creates uneven expansion and hence cracking when such a large volume of concrete is used. In addition, a few special cements are manufactured in New Zealand for larger projects or export: these include sulphate resisting, flyash blend, blastfurnace slag and Prise Mer cement.

¹Heated such that the material fused together without melting first.

The chemistry of cement function Concrete mix is a mixture of cement and aggregate - sand and gravel. When water is added to this the cement undergoes a series of chemical reactions to form a "gel" (a colloidal² system). The fine cement particles are broken down into even smaller particles (thus increasing the reactive surface) by crystallising out from the supersaturated solution formed. A series of immensely strong Si-O-Si bonds form between the particles, making a network in which the aggregates are trapped. In addition, bonds are formed to the aggregates, but these are much weaker, especially for smooth, inert, hard aggregates: because they have a smaller surface area than rough aggregates, a smaller area can be involved in bonding.

These reactions continue to take place for some time (depending on the exact composition of the cement), and after the initial brief expansion of the cement the material shrinks as unreacted water is lost. It is rare for all the cement to react: usually after five months the grains are only hydrated to a depth of 6-9µm, while cement grains range up to 100µm in diameter.

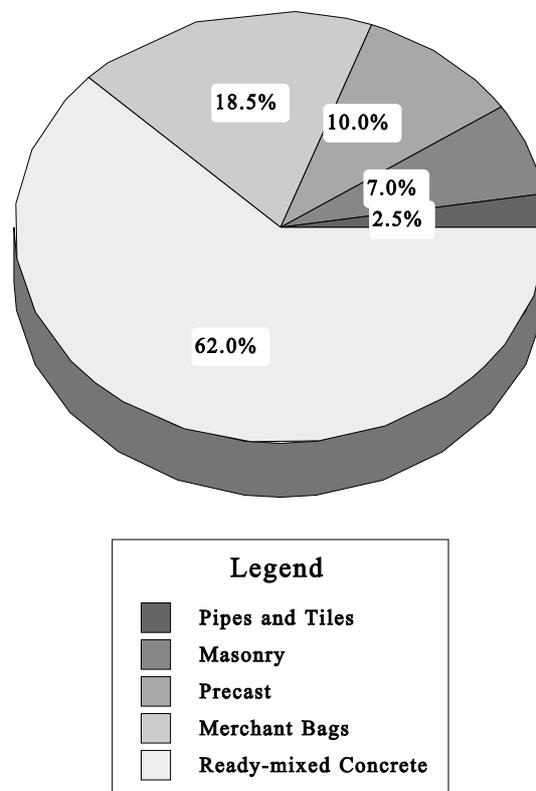


Figure 1 - New Zealand Cement Market Sector
Source: 100 years - Helping Build a Nation. Milburn Cement

THE MANUFACTURING PROCESS

Portland cement is made by heating raw materials rich in oxides of silicon, calcium, aluminium and iron to temperatures of around 1200 - 1400°C. The chemical reactions that occur within the partially molten mass result from the formation of the four main cement materials (**Table 1**).

²A colloid is a dispersion of very small particles in a continuous medium.

Table 1 - Major mineral constituents of Portland Cement

Compound*	Abbreviation	Chemical formula	Typical concentration/%
Tricalcium silicate	C ₃ S	3CaO•SiO ₂	60-70
Dicalcium silicate	C ₂ S	2CaO•SiO ₂	10-20%
Tricalcium aluminate	C ₃ A	3CaO•Al ₂ O ₃	5-10%
Tetracalcium alumino-ferrate	C ₄ AF	4CaO•Al ₂ O ₃ •Fe ₂ O ₃	3-8%

Of these compounds, C₃S and C₃A are mainly responsible for the strength of the cement. High percentages of C₃S (low C₂S) results in high early strength but also high heat generation as the concrete sets. The reverse combination of low C₃S and high C₂S develops strengths more slowly (over 52 rather than 28 days) and generates less heat. C₃A causes undesirable heat and rapid reacting properties, which can be prevented by adding CaSO₄ to the final product. C₃A can be converted to the more desirable C₄AF by the addition of Fe₂O₃ before heating, but this also inhibits the formation of C₃S. C₄AF makes the cement more resistant to seawater and results in a somewhat slower reaction which evolves less heat.

The balance of the formed compounds versus the performance characteristics required from the cement is a chemically controlled parameter. For this reason considerable efforts are made during the manufacturing process to ensure the correct chemical compounds in the correct ratios are present in the raw materials before introduction of the materials to the kiln.

The cement manufacturing process involves four distinct stages, and these are outlined below.

Step 1 - Quarrying

The raw material for cement manufacture is a rock mixture which is about 80% limestone (which is rich in CaCO₃) and 20% clay or shale (a source of silica, alumina and Fe₂O₃). These are quarried and stored separately. The lime and silica provide the main strength of the cement, while the iron reduces the reaction temperature and gives the cement its characteristic grey colour.

Step 2 - Raw material preparation

The steps involved here depend on the process used. There are two main cement manufacturing processes currently used in New Zealand: the dry process (used by Golden Bay) and the wet process (used by Milburn). The dry process uses more energy in grinding but less in the kiln, and the wet process has lower overheads than the dry process. The two processes are discussed separately below.

The dry process

The quarried clay and limestone are crushed separately until nothing bigger than a tennis ball remains. Samples of both rocks are then sent off to the laboratory for mineral analysis. If necessary, minerals are then added to either the clay or the limestone to ensure that the correct amounts of aluminium, iron etc. are present. The clay and limestone are then fed

together into a mill where the rock is ground until more than 85% of the material is less than 90 μ m in diameter.

The wet process

The clay is mixed to a paste in a washmill - a tank in which the clay is pulverised in the presence of water. Crushed lime is then added and the whole mixture further ground. Any material which is too coarse is extracted and reground. The slurry is then tested to ensure that it contains the correct balance of minerals, and any extra ingredients blended in as necessary.

Step 3 - Clinkering

This is the step which is characteristic of Portland cement. The finely ground material is dried, heated (to enable the sintering reactions to take place) and then cooled down again. While it is being heated various chemical reactions take place to form the major mineral constituents of Portland cement.

The powder from the dry process doesn't contain much moisture, so can be dried in a pre-heater tower. As it falls through the tower (which takes 30 seconds) it is heated from 70 to 800°C. The moisture evaporates, up to 20% of the decarbonation (loss of CO₂) occurs and some intermediate phases such as CaO•Al₂O₃ begin to appear. The mixture is then fed into the kiln.

The slurry from the wet process contains too much moisture to be successfully dried in a preheater tower. Instead, the slurry is fed directly into the kiln where it is formed into dry balls by the heat and rotation of the kiln. Because of this extra role of the kiln, wet process kilns are generally longer than dry process kilns: e.g. Milburn's kiln is more than 100 m in length, whereas that used by Golden Bay is only 60 m long. The kilns used in both processes are inclined on a shallow angle and lined with heat-resistant bricks.

The kiln

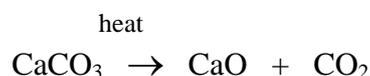
The kiln shell is steel, 60m long and inclined at an angle of 1 in 30. The shell is supported on 3 roller trunions and weighs in at over 1100 T. The kiln is heated by injecting pulverised coal dust into the discharge end where it spontaneously ignites due to the very high temperatures. Coal is injected with air into the kiln at a rate of 9 - 12 T hr⁻¹.

The reaction processes occurring within the kiln are not easily understood due to the wide variations in raw-mix chemistry, raw-mix physical properties and kiln operating conditions, and the physical difficulties of extracting hot materials from the process for investigation before they cool.

Breaking the reaction processes into a number of simple zones means we can make some approximations about the cement formation process.

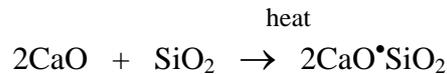
Zone 1: 0 - 35 min, 800 - 1100°C

Decarbonation. Formation of 3CaO•Al₂O₃ above 900°C. Melting of fluxing compounds Al₂O₃ and Fe₂O₃.



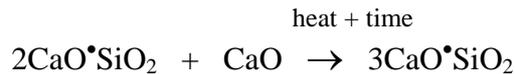
Zone 2: 35 - 40 min, 1100 - 1300°C

Exothermic reactions and the formation of secondary silicate phases as follows:



Zone 3: 40 - 50 min, 1300 - 1450 - 1300°C

Sintering and reaction within the melt to form ternary silicates and tetracalcium aluminoferrates:



Zone 4: 50 - 60 min, 1300 - 1000°C

Cooling and crystallisation of the various mineral phases formed in the kiln.

The cooler

Immediately following the kiln is a large cooler designed to drop the temperature of the clinker (as the fused material is now called) from 1000°C to 150°C. This is achieved by forcing air through a bed of clinker via perforated plates in the base of the cooler. The plates within the cooler slide back and forth, shuffling the clinker down the cooler to the discharge point and transport to a storage area.

At this point in the process the materials have been formed into all the required minerals to make cement. Like cement, the clinker will react with water and harden, but because it is composed of 1-3 cm diameter fragments it is too coarse to be used.

Step 4 - Cement milling

To produce the final product the clinker is mixed with gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), which is added as a set retarder, and ground for approximately 30 minutes in large tube mills. The cement flows from the inlet to the outlet of the mill (a rotating chamber), being first ground with 60 mm then 30 mm diameter steel balls. The first grinding breaks up the material and the second grinds it to a fine powder. The amount of grinding is governed by the volume of cement fed into the mill: the greater the volume the coarser the grind. This has practical limits, with too much cement clogging up the mill and not enough actually increasing the particle size. The particle size is measured by laser diffraction analysis, and the quantity of material entering the mill adjusted accordingly. Over time the charge (steel grinding balls) wear out, so when they reach a certain size they fall through a sieve and then are replaced.

The cement grinding process is highly energy intensive. The largest mill at Golden Bay Cement is some 11 m in length, weighs over 230 T, is driven by a 2100 kW motor and can produce over 60 T hr⁻¹. The rotating mill generates significant quantities of energy and water is added to both the inlet and outlet ends of the mill to cool the product and the mill itself.

THE ROLE OF THE LABORATORY

The laboratory forms an integral part of the control systems on site with testing from raw materials to finished product. The laboratory operates a 24 hour facility in line with a continuous manufacturing facility responsible for the following aspects:

- Testing raw materials prior to blasting in the quarry and assisting with development of quarrying strategies forms the first step in the process.
- Analysing rock samples from the raw mill at regular intervals during the day and night and fine tuning the process to ensure chemical control is maintained.
- Analysing clinker at the end of the cooler (before grinding) to ensure that the manufactured process meets specification.
- Checking that cement mills are undertaking grinding correctly and that customers receive the right product.
- Checkings despatched materials for quality and compliance with NZ Standards requirements. Certificates of conformance are issued to customers based on these analyses.
- Product development.

Testing work within the laboratory ranges from simple air permeability measurements to high technology X-ray fluorescence analysis (see air pollution article). Qualifications within the laboratory reflect this wide range of testing and skills requirement with university qualified staff working alongside others with minimal formal qualifications.

ENVIRONMENTAL IMPLICATIONS

Many of the aspects of the cement making process are potentially environmentally damaging, although these risks can be minimised. The areas of potential concern are listed below.

Dust emissions

The manufacture of cement generates large quantities of dust. These must be prevented (both on environmental and economic grounds) from escaping to the atmosphere. The two areas where dust has the potential to escape are *via* air streams that have been used to carry cement (e.g. the mills or kiln) and directly from equipment used to transport cement (e.g. the various conveyor belts). Thus to prevent dust emissions all transport equipment is enclosed, and the air both from these enclosures and from the kiln and mills is treated in an electrostatic precipitator to remove its load of dust. Here dust-laden air passes between an electrode carrying 50 000 volts and an earthed collection plate. The electrostatic discharge between the electrode and the plate forces the dust onto the plates, from which it is removed.

The current emission limit from the main stack at Golden Bay is 250 mg m^{-3} and at Milburn is 150 mg m^{-3} , while in Europe emission limits of down to 50 mg m^{-3} are becoming common. This poses a significant challenge to the manufacturing operation both in capital cost to

reduce emissions and monitoring of emissions to ensure compliance with existing resource consents.

CO₂

Cement manufacture is an energy intensive process. One of the most significant challenges facing the industry into the 21st century is a requirement to reduce CO₂ emissions. CO₂ is produced during the calcination phase of the manufacturing process and also as a result of burning fossil fuels. Opportunity to reduce emissions through increased energy efficiency is only possible on the latter of the CO₂ emissions.

Quarry and plant water runoff

Runoff of storm water and treatment of waste water from quarries is a problem for almost all quarry operations. Usually this is trapped in wetland areas where the water is treated in a controlled manner. Within the factory runoff can be contaminated by oils and lubricants, but the runoff is monitored and training programmes are regularly undertaken to ensure this does not happen.

Chrome bricks

Kiln bricks used to be made of hexavalent chrome, which is a carcinogen and causes dermatitis in some people. Since the problems associated with its use were identified both Milburn and Golden Bay (along with almost all cement manufacturers internationally) replaced these bricks with environmentally-sound magnesium-spinel bricks.

Article written by Heather Wansbrough from the article in the previous edition by G. Slocombe (Tikipunga High School) and D. Gallop (Wilson's (N.Z.) Portland Cement Ltd.) with advice from Martyn Compton (Golden Bay Cement), Murray Mackenzie (Milburn New Zealand Ltd.) and Tim Mackay (The Cement and Concrete Association of New Zealand) and with reference to:

- *The Manufacture of Portland Cement*, The Cement and Concrete Association of New Zealand; 1989
- *100 years helping build a nation*; Milburn Cement; 1988
- Bogue, Robert Herman; *The Chemistry of Portland Cement (2nd. edition)*; Reinhold Publishing Corporation; 1955
- Lea, F. M.; *The Chemistry of Cement and Concrete (3rd edition)*; Edward Arnold (Publishers) Ltd.; 1970