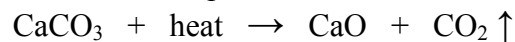


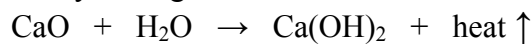
THE LIME INDUSTRY

"Lime" refers to both limestone (CaCO_3) and its derivatives burnt lime (CaO) and hydrated lime (Ca(OH)_2). These substances are of enormous importance to New Zealand industry: Ground limestone is one of the most important fertilizers. Burnt and hydrated lime are used in many industries to neutralise acid waste, and are used as causticisers in the pulp and paper industry and as flux in the steel industry. Lime is also used in road stabilisation and gold recovery and is exported around the South Pacific region.

Limestone occurs widely in New Zealand, but it needs to be quarried and processed before being ready for use. Burnt lime is produced from limestone by heating to 1100°C and allowing the following reaction to take place:



Hydrated lime is produced by adding water to calcium oxide in a continuous hydrator::



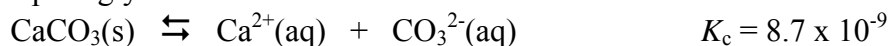
INTRODUCTION

The term lime is generally used to cover all aspects of the element calcium. In New Zealand, the term lime includes limestone (calcium carbonate - CaCO_3), burnt lime (calcium oxide - CaO), and slaked or hydrated lime (calcium hydroxide - Ca(OH)_2). All of these materials are used in large quantities both in New Zealand and overseas.

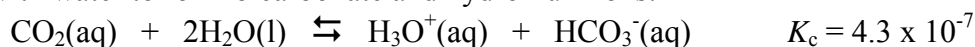
Lime is very important to the New Zealand economy because of its importance as a fertilizer. This use of lime is not new: in the second century BC the Roman Cato the Censor recommended the use of limestone to improve crop yields in acidic soils. Currently lime is one of the most common fertilisers used in New Zealand.

Lime is generally of marine origin - that is, it is formed under the sea as accumulations of the shelly marine organisms over long periods. For this reason, fossilized forms of sea life can be readily found in many limestones, although older limestones have generally been squeezed so much during their geological history that they have recrystallised into hard limestones or even marbles in which the remains of sea life are no longer recognisable. As most of the area now known as New Zealand has been covered by the sea at some time, limestones of varying purity are abundantly available in all areas of the country except central Otago and the centre of the North Island.

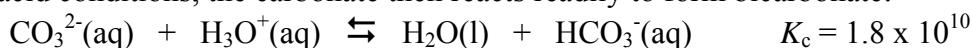
Limestone is sparingly water soluble:



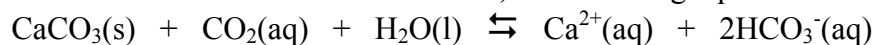
However, most natural water contains high levels of carbon dioxide. This increases the solubility of the limestone as follows. Firstly, the dissolved carbon dioxide reacts quite readily with water to form bicarbonate and hydronium ions:



In these acid conditions, the carbonate then reacts readily to form bicarbonate:



Thus when carbon dioxide is dissolved in the water, the following equilibrium exists:



Through these reactions, over time limestone is dissolved by rainwater and streams, giving limestone areas a rugged appearance and causing "sink-holes" where the surface has collapsed into caverns dissolved out by subterranean streams. However, another characteristic of limestone areas is caves with stalactites and stalacmites. Limestone caves have a relatively low carbon dioxide partial pressure (i.e. proportion of carbon dioxide in the atmosphere), so in caves the above equilibrium reaction is driven to the left, giving solid calcium carbonate. Each drip of water that lands on the ceiling or floor of a cave leaves behind it a minute quantity of lime, gradually building a pillar. By geological time scales these changes are comparatively rapid.

Uses

As stated earlier, the term 'lime' refers to three related substances: limestone, burnt lime and hydrated lime. These are each used for different purposes. Limestone is used as a fertiliser and in the manufacture of glass and cement. Burnt lime and hydrated lime are used in:

- the steel industry (as a flux)
- the pulp and paper industry (as a causticiser)
- gold mining
- road stabilisation
- water treatment
- wastewater treatment
- fellmongery (to treat hides)

By far the most important of these in New Zealand is the use of limestone in agriculture. Most New Zealand soils are naturally acid or become acid with plant growth and usage. This acidification results in certain ions such as aluminium and manganese being released in large amounts from the soil's silicate structure. With a low pH, ions of these elements are most toxic for plants. This results in poor growth because of the influence of these ions on plant metabolism. Lime application then raises the pH of the soil to 6 - 7 and also allows for the release of such elements as Mg, P and Mo for use by the plant. In general, 2½ - 5 tonnes per hectare is applied to virgin soils, with a further 2½ tonnes applied every four years. The pH of the soil is thought to be altered by the following reaction:



Lime also alters the physical characteristics of soils by altering both soil tilth and friability. Tilth refers to the depth of soil influenced by cultivation and a soil of good tilth means a depth of fine, crumbly soil. Friability refers to ease with which a soil is crumbled. Acid soils tend to pug like clay, whereas near neutral soils are light and crumbly.

The other uses of lime are covered in articles on those industries.

THE MANUFACTURE OF LIME

Step 1 - Quarrying

Formerly, limestone was quarried by blasting every day with explosives set in a series of short holes drilled behind the quarry face. In this method, the face was benched (terraced) so that the quarrymen could reach the drill sites. The drill holes were drilled vertically, six to twenty feet deep from each terrace, and a plug of gelignite was exploded at the bottom to form a chamber so that more explosive could be packed into the hole for the final blast, for which the chamber and the greater part of the stem of the hole were filled with explosive.

A newer method involves blasting only every few weeks. With this method there is a single high face; long holes are put down vertically behind the face, with tungsten carbide drill bits. When a line of these holes has been completed behind the face, the explosives are put in the holes and the blast is so arranged that each hole goes off just a fraction of a second later than the one next to it. The sound is like one big blast, but the fractional difference in timing between the explosion in each hole makes the vibration no more severe than if each were blasted separately.

In some quarries where the limestone is not too hard, entirely new methods have recently been used with great success. No explosives are needed; the same sort of earth-moving machinery as is used for road construction is employed.

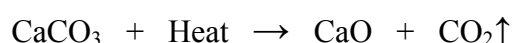
So, quarrying depends on the physical nature of the limestone which can range from soft to very hard. The quantity of moisture in the limestone is inversely proportional to the hardness. The lower the water content, the less energy has to be expended on drying the product prior to distribution. Once quarried, the large limestone blocks are crushed in rotary impactors. Then it is pulverised to reduce the particle size such that 95% can pass through a British standard sieve No. 8 (~ 2mm square hole) and 50% of the sample must pass through a British standard sieve No. 30. This is a sieve with 30 holes per inch across the sieve (hole ~0.5mm square). The coarse material is long acting, releasing lime over a considerable length of time. The very fine material is for quick action in redressing pH imbalance. The limestone is then applied either by ground spread vehicles or using an aeroplane.

Step 2 - Conversion

While most of the crushed lime is used as is, some is converted to either burnt or hydrated lime. These processes are covered below.

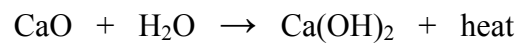
Burnt Lime

Burnt Lime is produced in New Zealand at three principle plants, in Otorohanga in the King Country, Havelock North and Dunback in Otago. High quality limestone (>95% CaCO₃) is calcined in a continuous process using rotary or vertical kilns at 1100°C, volatilizing off the carbon dioxide to leave the calcium oxide:



Hydrated lime

Hydrated lime is a derivative of burnt lime and is produced by reacting burnt lime with water in a continuous hydrator. During this process large amounts of heat are given off. The resultant micron-sized particles are then classified by air separators which reject coarse particles. The slaked material is light and "fluffy". The reaction proceeds as follows:



Both burnt lime and hydrated lime are delivered to end users in bulk via. truck and trailer, pneumatic tankers and in 25kg multiwall paper bags.

Article written by P.J. Brunt (Nelson Polytechnic) and R.C. Lawry (W.L. Lawry Ltd., Nelson). Revised for this edition by Peter Rolls (McDonald's Lime Ltd.) with editing by Heather Wansbrough.