



# CALIXO™ MATERIALS

## TECHNICAL SUMMARY

Calix has developed a new binder material, Semidolime™ that can be used as the basis for a range of new products that will be marketed under the CalixO™ brand. These products include cements and coatings, as well as fertilizers. This paper will focus on the application of the material as a building product.

A first competitive advantage of the material is that it is manufactured by Catalytic Calcination from a plentiful mineral dolomite in a single step process. The starting material costs are comparable to cement, and the processing costs are ~50% less from both energy consumption and capital requirements. The binder retains 50% of the CO<sub>2</sub> and reduces greenhouse gas emissions compared to cement, and it can be produced from a zero-emissions calcination process.

A second competitive advantage is that the binder itself sets as an hydraulic cement to give a high strength material (unlike cement) and that it sets with a wide range of fillers. Cement has only one application, the product of concrete, and concrete gets its strength from the interaction of the cement with its fillers (sand and aggregate), which in turn requires very high standards to meet in the production of concrete. CalixO™ building materials can be made from waste fillers, which can often be obtained at almost zero cost. These can range from rice husks, desert sand, red mud, silt and municipal waste. Unlike concrete, these products are impermeable to water.

## TECHNOLOGY AND PRODUCTS

### INNOVATION

Cements, generally hydraulic cements, can be formulated using a novel material MgO.CaCO<sub>3</sub>, called herein Semidolime™, as the cementitious component. Semidolime™ is produced rapidly by calcining dolomite in steam at about 414°C in reactor with a short residence time of seconds to inhibit sintering and phase separation, followed by rapid quenching. This commercial development of this reactor is the subject of the project described in the paper "Calix Catalytic Calcination".

Cement formulations which can be made using Semidolime™ include composites with other cementitious materials, binders such as Pozzolans, fillers and other additives such as accelerants, polymers and resins to give the desired properties. The cements, depending on the compositions, have a fast setting time, high strength, low density, high water resistance, and a low thermal conductivity, inflammable and low thermal expansion. Calix has acquired the formulations of these cements.

These properties make this unique material an ideal basis for a low cost building material, because the price of the feedstock is low (dolomite is a common mineral found worldwide) and the Calix calcination process is a low cost manufacturing process.

These cements are differentiated from traditional calcium and magnesium cements because they are pre-carbonated, and the energy used to produce the cementitious Semidolime™ is reduced to a level compatible with the needs for formation of the bonding network in the cement. This means not only lower manufacturing costs (energy consumption reduced by ~50% on a volume basis), but also the strength of the cement is fully realised upon setting (ie no long term



carbonation) and the temperature rise from hydration is also reduced compared to cements with the same cementitious composition and setting time.

## BACKGROUND

Most calcium based cements are formed with calcium as the elemental basis for cementitious component, generally in the form of lime, CaO. These cements include Portland cement, and Portland type blended cements such as Portland-slag cements and Portland limestone cements. Formulations for a range of these cements are set out in the European Prestandard for Common Cements (Env 197-1:1992). Cements should preferably have uniform hydration rates of their components to avoid the building up of stresses during setting, and these rates can be controlled by using accelerants that include alkaline materials, acidic materials, organic materials, and can be modified by the degree of sintering of the cementitious materials. Volume change on setting should be minimised so that stresses do not develop, and it is the use of either calcium or magnesium that largely bestows this important property on the cement. Additives to the cement can include natural and artificial Pozzolans that participate in the formation of the bonding network that gives strength. Pozzolans are materials that include those that contain silicon and aluminium that react with or are activated by an alkali, and in the presence of water form stable silicon and aluminium compounds. Pozzolans include waste materials such as fly ash, burnt rice husks, flue wastes, certain mine tailings, and mineral extraction wastes such as red mud from alumina production. Cement additives include fillers, which are materials that do not greatly participate in the network, and these include sawdust, unburnt rice husks, biomass, shredded car tyres. Some fillers compensate for volume changes to the cementitious materials as they set, thereby reducing the development of macroscopic stresses. Calcium based Pozzolan cements are formed by activating the Pozzolans, often with heat or alkali, and reacting with hydrated lime.

Other cements are formed with magnesium as the elemental basis of the cementitious component. Sorrel cements, are based on the use of magnesium oxychloride, but they have undesirable properties, such as inducing corrosion of iron, and degradation by water. Magnesium cements based on reactive magnesia MgO can be made with additives such as phosphates, chromites, etc to give desirable properties. Magnesium based Pozzolan cements are formed by activating the Pozzolans as above, and reacting with hydrated magnesia, and which requires a reactive magnesia that has not been sintered. Generally speaking, for each calcium based formulation of cement, there is an analogous magnesium based formulation (where the concept of formulation accounts for reactivity of the materials). Cement formulations such as the Sorrel cements were developed before the production of reactive magnesia was developed. Calcination of magnesium carbonate yields a highly sintered material with a low reactivity similar to that of the mineral Periclase.

An important difference between calcium based cements and magnesium based cements is associated with the higher solubility of the calcium in water compared to magnesium at typical pH values of the water. The leaching of calcium in limestone by magnesium in ground and sea water is well documented, and is believed to be the mechanism of formation of dolomite through this slow process on geological timescales. Generally, a magnesium cement will have a lower leaching rate with water than a calcium cement of the same formulation (all other things being equal). Otherwise, there are many similarities. Thus many cements can be made that are based on mixtures of magnesium and calcium cementitious materials.

In calcium, magnesium and mixed calcium/magnesium based cements, the granules of the cementitious materials (CaO and MgO granules) are preferably reactive, ie unsintered and with a high surface area, to facilitate the formation of an extended network of chemical bonds formed during setting. This network provides the necessary strength for characterisation as a cement.



The high reactivity also enhances the rate at which the cement sets. Thus granules that have been extensively sintered have a reduced surface area and a low reactivity, and form poorer cements in contrast to those that use unsintered materials. Different applications require different setting times, and the rate of setting can be enhanced by accelerants of various types, including acids and bases. In some applications, the setting time is preferably slowed, and this can be controlled by the degree of sintering. Direct comparisons of magnesium and calcium based formulations is often difficult because the surface areas/reactivity of the starting materials are often not comparable.

Another common feature of calcium and magnesium based cements is that they chemically absorb carbon dioxide from the atmosphere, through a portion of the sites being converted to the carbonate. In most cases, this carbonation is beneficial, and leads to a further strengthening of the material. The cement industry is now subject to carbon taxes, and the offsets associated with such sequestration are not readily available to the industry as the reaction occurs well after the cement is set, it is sufficiently slow that the carbon dioxide released to the atmosphere during manufacture of the cement has participated in global warming, and the extent of carbonation depends on factors that are outside the control of the manufacturer.

Despite the many common properties of calcium and magnesium based cements, there are very few cement formulations that are produced from calcined dolomite. Dolomite is a plentiful mineral, with a crystalline structure based on units of  $MgCO_3 \cdot CaCO_3$ . That is, the calcium and magnesium ions are in close proximity. Dolomite can be calcined to give a material, dolime ( $MgO + CaO$ ), which is comprised of microcrystallites of magnesia  $MgO$  and lime  $CaO$ . The phase separation of  $MgO$  and  $CaO$  is a consequence of thermodynamics, namely that crystals of  $MgO$  and  $CaO$  have a lower free energy than a crystal  $MgO \cdot CaO$ . Cements based on dolime are not very satisfactory because the magnesia microcrystals become unreactive during the calcination, so that the magnesium is precluded from contributing to the extended network of chemical bonds that give cements their strength. The  $MgO$  then hydrates very slowly, and this leads to the development of stresses over time. Simply put, the temperature required to calcine the calcium site is more than  $895^\circ C$ , and at this temperature the material produced by calcination of the magnesium site has the energy and time to restructure, and phase separation occurs. Furthermore, in conventional kilns, the  $MgO$  reacts with the magnesia-based insulating materials commonly used as liners in kiln. For these reasons, dolomite and magnesite are generally avoided as feedstock impurities in the calcination of limestone, and dolomite is not commercially calcined in conventional lime kilns. Dolime is produced for applications where the lack of reactivity is important, similar to dead burned magnesia. But dolime based cements are very poor. The Calix Catalytic Calcination process treats dolomite in a way that confers a beneficial effect on its cementitious properties. Cements that use a mixture of lime and active magnesia are known, and have good properties. It is Calix' experience that Semidolime<sup>TM</sup> will produce a better product.

## **CALIX BUILDING MATERIALS**

Calix can manufacture using a novel material, namely Semidolime<sup>TM</sup>  $MgO \cdot CaCO_3$ , as the basis of its cementitious properties. The Semidolime<sup>TM</sup> is produced at temperatures of  $\sim 495^\circ C$ , at which temperature the calcium site is thermodynamically stable and does not calcine. However, even at these low temperatures, there is a propensity of  $MgO$  and  $CaCO_3$  to phase separate and sinter during a prolonged calcination process. The Semidolime<sup>TM</sup> of this invention has the desirable cementitious properties by using a process in which the degree of phase separation and sintering is minimised. At low temperatures, the Semidolime<sup>TM</sup> is a stable substance with identifiable chemical and physical properties. The calcium and magnesium sites in the Semidolime<sup>TM</sup> have retained their close spatial correlation that pre-existed in the dolomite, and its chemical and



physical properties are unlike those of the mixture of MgO and CaCO<sub>3</sub> formed in standard kilns. This correlation exists when the Semidolime™ is hydrated as slurry.

There are immediate benefits that arise from the use Semidolime™ as a cementitious material. Recall that most hydraulic cements capture significant CO<sub>2</sub> from the atmosphere, and this slow carbonation gradually strengthens the cement. When Semidolime™ is used, the CO<sub>2</sub> is already in situ, and is uniformly dispersed, so that the material generates its maximum strength early during the setting process. This retention of CO<sub>2</sub> is not the same as using a partially calcined cementitious material, because the distribution of CO<sub>2</sub> is non-uniform in the calcined granule. Calcination is a heterogeneous chemical reaction that occurs on the surfaces of the micropores and mesopores of the granule, and works its way from the outside of the granule inwards. Partially calcined granules retain their carbonate deep inside the granules, and these are not greatly involved in the setting process in cements. Semidolime™ has a uniform distribution of carbonate ions throughout the granule, and when used in cement, this leads not only to a network in which the carbonate ion is uniformly distributed, but also to a hydration rate that is spatially uniform. In effect, the semi-calcined dolomite has created a carbonated cement at the outset, and has a greater strength that is little changed by exposure to the atmosphere.

As energy costs increase, there is an energy saving that results in the use of Semidolime™. If the subtle differences between magnesium and calcium cements of the same formulation are overlooked, then the energy cost per unit volume of Semidolime™ compared to lime is reduced by greater than 50% because only 50% of the CO<sub>2</sub> is removed. A more accurate estimate is made using the enthalpies of calcination and densities. Conceptually, for example, calcium based cements consume considerable energy to remove all the CO<sub>2</sub>, and over time this energy is recovered by the cement through the very slow carbonation, and is dissipated as heat. The Semidolime™ process bypasses the long term process leading to reductions in energy costs and CO<sub>2</sub> pollution. Of course, there are differences between calcium and magnesium based cements of the same formulation, and these differences lead to standards for particular formulations.

The benefits disappear if another high temperature process is introduced. For example, Semidolime™ would not be useful as an alternative to lime in a clinker based process, because the Semidolime™ would consume energy and calcine to dolime. Therefore, the cements that will benefit from Semidolime™ are those that do not require an additional sintering process. Cements that use an activated Pozzolan as an additive to introduce silica and alumina would greatly benefit from the use of Semidolime™.

The surfaces of cements formed using Semidolime™ are already carbonated and are inert, so that the effect of weathering is greatly reduced. The combined effects of the low solubility magnesium and the carbonation result in an excellent stability. Semi-calcined dolomite is non-toxic. In addition, the presence of magnesium confers upon the cement the benefits of a low thermal conductivity, and a mechanical stability to large temperature variations. There are characteristics of magnesium cements. Even with a high percentage of flammable fillers, such as biomass, the cement is inflammable and stable.

The acceleration of the setting rate of cements based on Semidolime™ can be managed using the same principles that apply to calcium and magnesium cements. Some formulations can set so quickly that the build up of heat from the hydration can cause unwanted stresses when the material sets. The setting time can be controlled by a limited degree of sintering (without engendering significant phase separation), or by reducing the surface area by changing the calcination conditions.



Mineral dolomite is often mined with impurities of limestone and/or magnesite. Using the preferred manufacturing process for Semidolime™, any limestone granules do not calcine, and they become fillers in the cement. Magnesite granules present calcine to magnesia at a slightly lower temperature, of 495°C than that at which dolomite calcines to Semidolime™. Because these calcining temperatures are quite similar, the magnesia is also formed as a reactive high surface area granule. The cementitious components in mixtures of dolomite and magnesite calcined according to the preferred process are the Semidolime™ and magnesia, and the good quality cements are formed using such mixtures, and there is a significant tolerance to variations in the feedstock composition.

Mineral dolomite is also often mined with impurities of silica, particularly near weathered areas. If the silica is present as silica granules, these also become a Pozzolan/filler in the cement, without deleterious effects. If incorporated into the dolomite granules as an impurity, the calcination rate can be significantly reduced as the silica impacts on the change in morphology of the granules during the reaction, and this slows down the calcination reaction. If present in small amounts, this is not a problem, and the silica is incorporated into the network structure of the cement.

The preferred means of producing Semidolime™ is to use a steam catalysed calcination of dolomite that has been ground to ~100µ diameter, at a temperature of about 414°C in a calciner that has a residence time of several seconds. The steam catalyses the chemical reaction, and also affects the change in the morphology of the granule. The calcination of dolomite granules in the absence of steam and a high carbon dioxide partial pressure is limited by the transport of CO<sub>2</sub> from the particle. The conditions for rapidly calcining dolomite require a reduction of the CO<sub>2</sub> partial pressure during calcination to suppress the back reaction, and this occurs through the combined effects of steam injection, the natural exhaust processes, and pumping of the calciner by the effects of steam condensation and mechanical pumping of the calciner.

## SUMMARY

Calix has a manufacturing process that uniquely creates a new material, Semidolime™, from one of the most abundant minerals on earth, dolomite, using a low cost manufacturing process. The Semidolime™ has unique properties in that it forms the basis for a novel pre-carbonated cement. These will be stronger than their uncarbonated equivalents because of the stronger network bonds (ie stronger than the hydrates initially) and the fact that the carbonation is uniform in the material. The energy costs of calcination are reduced compared to lime on a volume/volume basis because only 50% of the CO<sub>2</sub> is calcined, and the temperature rise on setting is also reduced. In effect, the energy required on a volume basis to calcine Semidolime™ is better matched to the energy needs for formation of the cement, whereas lime and magnesia have excess energy. The uniformity of the chemical composition is essential in transferring this benefit to the cement.

Furthermore, the CO<sub>2</sub> is captured in a pure stream, and when sequestered, would allow for the payment of carbon credits. It is a "green" building material. It forms composite cements with a very wide range of Pozzolans, fillers etc to give the desired properties, and many of these materials are waste materials that are causing environmental hazards – from car tyres, alumina tailings, biowaste etc.

The surfaces of cements formed using Semidolime™ are already carbonated and are inert, so that the effect of weathering is greatly reduced. The combined effects of the low solubility magnesium and the carbonation result in an excellent stability. Semi-calcined dolomite is non-toxic. In addition, the presence of magnesium confers upon the cement the benefits of a low thermal conductivity, and a mechanical stability to large temperature variations. There are



characteristics of magnesium cements. Even with a high percentage of flammable fillers, such as biomass, the cement is inflammable and stable. It can be used to safely solidify volatile materials, such a low level radioactive waste, and heat generated by the radioactivity does not degrade the material.