



# CALIX CATALYTIC CALCINATION

## TECHNICAL SUMMARY

Calix is a start-up company that acquired the rights to intellectual property for a minerals processing technology, called calcination. The application for which the technology has been developed is the calcining of lime, dolomite or magnesite (metal carbonate minerals) to their respective oxides, such as lime, dolime and magnesia. There are other minerals processing applications that have been identified. Calcined materials have many well established markets, and the generic competitive advantage of the Calix Calcination is the lower capital cost for a plant, the higher reactivity of the product. The process also allows the production of new materials, such as Semidolime™, which can be used as a new controlled release fertiliser, and more importantly as the basis for new building materials. This application is considered in the Green Paper "Calix Building Materials". The market for lime is ~US\$10 billion, and for cement it is ~US\$110 billion.

The compelling long term advantage of Calix Calcination is that the process captures pure carbon dioxide (CO<sub>2</sub>), which the industry presently releases to the atmosphere. The calcination of lime, principally by the cement industry, is responsible for 2.5% of the anthropogenic emissions of CO<sub>2</sub>, and the industry is under very strong political pressure to reduce these emissions because of its contribution to global warming. A Calix plant can sell the pure CO<sub>2</sub> into certain markets (dry ice, industrial gas, food grade), or it can compress and sequester the CO<sub>2</sub> to take advantage of carbon credits<sup>1</sup>. This application is considered in the Green Paper "Calix Carbon Capture".

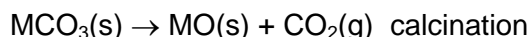
A second advantage of the Calix process is that the Calix calciner is based on low maintenance modules that have a capacity of 50,000 tonnes pa (of lime) produced. Plants having a capacity comparable to those used by the industry today (100,000 to 800,000 tonnes pa) can be assembled using a number of modules. These modules are portable, allowing for relocation to meet customer needs.

## TECHNOLOGY AND PRODUCTS

### WHAT IS CALCINATION?

Calcination is one of the oldest minerals processes, used and developed over a period of 3,000 years, for converting limestone (calcium carbonate) to lime (calcium oxide). It is now a generic process which can be applied to processing dolomite, magnesite and other materials to their oxide form, more generally from carbonates through heating to produce the oxide, driving off the CO<sub>2</sub>.

In Calcination granules or rocks of the metal carbonate (MCO<sub>3</sub>) are heated to release the CO<sub>2</sub> in a gas stream, leaving the metal oxide. The chemical reaction is



With calcium (M=Ca), the existing industrial process for producing lime from limestone uses large kilns, in which rocks of limestone, typically >20mm in diameter, are heated for many hours. The

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<sup>1</sup> The Calix process can be used as the basis for a regenerable dry sorbent approach to carbon capture, which is described elsewhere in the Green paper Calix Carbon Capture.



lime properties can be controlled by the temperature and residence time – from dead burned lime that has been sintered at high temperatures and is inert because of its smaller surface area, to burned lime that reacts readily, for example, with water, because it has a high surface area and porosity. For limestone  $\text{CaCO}_3$ , the calcination temperature is  $\sim 895^\circ\text{C}$  to produce lime  $\text{CaO}$ , and for magnesite  $\text{MgCO}_3$  it is  $\sim 385^\circ\text{C}$  to produce magnesia ( $\text{MgO}$ ), and for dolomite  $\text{MgCO}_3 \cdot \text{CaCO}_3$  the initial calcination  $\sim 414^\circ\text{C}$ , where the magnesium site decomposes to give “Semidolime<sup>TM</sup>”, ie  $\text{MgO} \cdot \text{CaCO}_3$ , and at  $895^\circ\text{C}$  the calcium site decomposes to give dolime, ie  $\text{MgO} + \text{CaO}$ . Generally dolime produced in a slow kiln is a mixture of magnesia and lime crystallites, due to an irreversible phase separation. That is, the reverse process does not reform dolomite. Partially calcined dolime is not produced on an industrial scale because standard kiln calcination is not effective.

Modern lime kilns are large vertical calciners that hold  $\sim 100$  tonnes of rock to obtain the economies of scale for such a slow process. Thus the capital expenditure for a kiln is very high, in the range of \$20-40 million for reasonable throughput. Best practice since the 1980's has produced kilns that are very energy efficient, consuming  $\sim 3.6$  GJ per tonne of lime produced. This is quite close to the minimum energy required, of 3.18 GJ per tonne, from thermodynamics, with the difference being the efficiency of recuperation of heat from the products through heat exchangers. Great attention has been given to optimise the recuperation. Kilns available today burn coal or natural gas with air, giving an exhaust gas that is a mixture of  $\text{CO}_2$ , steam, unburnt oxygen and, predominantly, nitrogen.

Calcination of limestone is the first process in the production of cement clinker. The second process is the sintering of the lime with the other components, generally silica and clay, at very high temperatures, typically above  $1500^\circ\text{C}$ . In the mid-20<sup>th</sup> century, these processes were combined into a single process, but with the high cost of energy, there is now a trend to separate the calcination and sintering processes to optimise the process. The Calix Calcination technology is applicable in such an optimized process, to produce the lime. It is the potentially very large cost reductions in capital plant, combined with the potential to generate zero greenhouse emissions (discussed below), which will position Calix in this market. Engaging with the cement industry is a longer term objective. It is the community expectation of zero emissions that may facilitate the uptake of a new approach in a very conservative industry.

### **WHAT IS THE CALIX CALCINATION PROCESS?**

The Calix Calcination process uses the following processes:-

- Grinding the limestone rocks to granules of  $\sim 100\mu$  mesh size. There is an energy and maintenance cost to this, compared to grinding calcined lime rocks, which are more friable. This is accounted for in the costs of manufacturing. By grinding, the rate of the calcination process becomes determined by the rate of the chemical reaction, rather than the transport of  $\text{CO}_2$  out of the rocks in the conventional process.
- Calcining the granules in the presence of steam. The steam catalyses the reaction so that it is complete within a time of less than 3 seconds. The steam accelerates the chemical reaction rate, and this reduces the time for calcination because granules are used instead of rocks.

There is a large body of scientific literature for the calcination of limestone that enables the process to be numerically modelled as a function of granule size, temperature,  $\text{CO}_2$  and steam partial pressures. The reverse reaction, called carbonation, is also well studied, and the rate of reaction is linked to that of calcination at the microscopic scale. The complexity arises because the reaction is heterogeneous, and takes place at pores in the initial material and as these evolve



during the course of the reaction as the CO<sub>2</sub> is released from the particle interior. In addition, the particles begin to sinter at high temperature, and the surface area, and the distribution of micropores and mesopores change. The kinetic data for magnesite and dolomite are less well established. Generally, the scientific results for these materials, without steam catalysis, demonstrate that calcination in these materials is more strongly affected by the transport of CO<sub>2</sub> than for limestone, under the same conditions. There are compelling published reports, on a pilot scale, which demonstrate that the effect of steam is considerable in inducing rapid calcination, but the kinetic data are not available.

However, it is the results obtained by Calix in its 16m high Test Calciner that provide the most compelling evidence for rapid steam calcining of magnesite, dolomite and limestone granules. The test calciner demonstrated high conversion efficiency in 1-2 kg batches.

The important innovation that takes advantage of the fast reaction is the design of the calciner. It adopts the Downer reactor design that is used extensively by the petroleum industry for catalytic cracking to take advantage of gravity feed. This is a low cost, compact, low footprint design. The very efficient heat transfer from the calciner walls is created by the viscosity of the granular flow. The collective acceleration of the particles leads to an efficient heat transfer. This heat transfer mechanism does not operate in conventional kilns, in which the heat must be supplied by combustion of gasses within the kiln. This generates a mixture of CO<sub>2</sub> from both the combustion of the fuel and the calcination process, such that the gas emitted into the atmosphere is principally a mixture of CO<sub>2</sub> and nitrogen. The cost of capture of the CO<sub>2</sub> is currently too expensive, so that the conventional approach will continue to pollute the atmosphere.

The Calix Calciner process allows for external heating of the calciner. The exhaust produces a mixture of CO<sub>2</sub> and steam, and is readily converted into a pure CO<sub>2</sub> stream by condensing the water. The CO<sub>2</sub> can be compressed. The CO<sub>2</sub> can be sold as a chemical in gas or solid form (eg dry ice) for many industrial processes – as diverse as flavour extraction from foods to extraction of natural gas. If the CO<sub>2</sub> is stored by sequestration, then carbon credits can be obtained. If carbon credits are, say, US\$20 per tonne, and it costs US\$6 per tonne for transportation, sequestration and monitoring, then the process can be profitable. This depends, of course, on the development of a sequestration industry that would undertake this task. Such an industry would be clustered near power stations that adopted a Carbon Capture and Sequestration process. Such power stations are predicted to be put into service from 2015, most likely in the USA or Europe. By using a C3 reactor and a small fraction of the power station energy output, the CO<sub>2</sub> from the external combustion to heat the walls of the calciner can also be captured, giving a true zero-emissions process. The systems to capture CO<sub>2</sub> from calcination, as well as the C3 plant to capture CO<sub>2</sub> from combustion, can, in principle, be retrofitted to the Calix calciner. Thus the plant can be initially sold without CO<sub>2</sub> capture but is “CO<sub>2</sub> capture ready”. This will allow customers to take advantage of CO<sub>2</sub> trading credits, tax credits, and other incentives/opportunities when their local CO<sub>2</sub> capture market is ready.

With the seed funding, engineering designs will be completed and fully costed to give a clear understanding of the bottom line performance of the calciner – both the capex costs and the fuel costs to generate the heat and the steam required.

## **CALIX PRODUCTS**

It is well established that the reactivity of calcined materials depends on the production process. The reactivity of lime is measured, for example, by the rate of dissolution in acids and water. A long sintering of the lime produces an unreactive material (dead-burned lime), whereas a fast process generates a reactive material, and an incomplete reaction reduces the reactivity. The



reactivity of lime is a product of two effects – the best known effect is that the reactivity scales with the surface area of the material. This can be greater than 20 times that of the limestone, and sintering results in a decrease of the surface area. The second effect arises from the presence of reactive chemical defects on or near the surface, and these occur when the calcination process is sufficiently fast such that these defects do not have time to be reduced by a relaxation of the granule structure. In general terms, Calix will produce a more reactive product than in conventional kilns, but controlled annealing outside of the calciner can be undertaken for applications for a low reactivity material. It is noted that high temperature steam and CO<sub>2</sub> promote annealing.

The calcination of dolomite MgCO<sub>3</sub>.CaCO<sub>3</sub> at ~420°C produces the partially calcined material MgO.CaCO<sub>3</sub>, that Calix calls Semidolime™. Calix believes that the partially calcined material has not separated into crystals of MgO and CaCO<sub>3</sub> during the very short time in the reactor at these temperatures, so that the Mg and Ca ions are in close contact. Calix has recognised that this leads to a strong building material when combined with fillers, including bauxite tailings, pulverised car tyres, and biomass. These materials can be produced to have a very low solubility in water, thereby overcoming a major hurdle for such materials. They are lightweight, and have a very low heat thermal conductivity and are inflammable. It is stressed that the calcined material cannot be made using any other known calcination process, and that materials made from, say, mixtures of MgO and CaCO<sub>3</sub> do not have the strength of the Calix material.

## MARKETS

The global markets for lime are about US\$10 billion comprising about 80 market segments. Lime is used as a fertiliser, for waste treatment of water, gold extraction, paper manufacturing etc. The entry into the lime markets depends on regional demand and opportunities. For example, the high capex kilns are large, but this means that transport costs can raise the price above that required for those opportunities that do not have enough long term demand to warrant a lime manufacturer setting up a local plant. The modular Calix technology can expand the markets for lime.

The largest use of lime is as the active binding ingredient in the manufacture of Portland cement clinker. This is a separate industry, with a market of US\$110 billion. The cement market is very well established and dominated by a few large companies, with minimal competition. If the Calix sintering plant is used to produce the lime, and can be integrated into a low cost sintering process, then new markets for cement will emerge based on small portable production units. Again, this can be important, particularly as transport costs rise. Currently, cement factories are large and expensive, and this has led to large regional monopolies that can pass on spiralling costs to customers. The factories are also large carbon dioxide polluters, and are under pressure from communities, and ultimately the market through carbon taxes and trading systems. The Calix process offers a route to zero carbon emissions for the cement industry. It is stressed that the Calix process is not yet “available technology” to the cement industry, and Calix plans to enter a strategic partnership to develop it, and make it available to the industry.

The markets for Semidolime™ are not established. This new material can be the basis for new quick release/controlled release fertilisers that have the optimum calcium/magnesium ratio with a controlled rate of release determined by the degree of calcination. This material can also be used as the basis for new composite building products. The market for composite building materials is large and fragmented. There is a growing realisation that the costs of building materials will increase as their traditional feedstocks become depleted and energy costs rise. Calix has acquired the Intellectual Property that will enable these markets for building materials to be explored.



There are major emerging markets for lime calcination in the carbon capture industry, in which a  $\text{CaO}/\text{CaCO}_3$  cycle to capture  $\text{CO}_2$  from the flue gases of fossil fuel power plants, cement plants and steel plants. The emerging market is difficult to quantify. Using a target of US\$20 per tonne of  $\text{CO}_2$ , the market from new coal plants installed with this technology from 2015, is expected to exceed US\$100 billion by 2025. This application cannot be met using conventional lime kilns, and is the basis of the C3 project described elsewhere.

## STATE OF DEVELOPMENT OF THE CALIX PROCESS

The inventor of the Calix process had previously spent some \$2 million in taking it to a pilot plant stage with batch processing. This unit is 16 m high and has a single throat, and acquired by Calix while decommissioned. A number of provisional patent applications were submitted as a result of the success at batch processing, with the first having a priority date of October 2005. These patents have been further developed, and full specifications have been submitted into the PCT examination process.

The batch processing plant has calcined samples of dolomite, limestone and magnesite from around the world, with independent laboratory analysis of the product. Calix has researched the requirements for continuous processing, and is now in a position to specify the engineering parameters for a system. Calix has identified that its process can be viewed as a variant of the well known Downer process catalytic processing of petroleum, so that there will be a wide body of engineering expertise and ancillary equipment available. The scaling properties of the process are very simple through the use of modules, allowing for plants that have a capacity of 50,000 tonnes pa to 500,000 tonnes pa.

The inventor of the Calix process researched the application of Semidolime™ as the basis for a new range of building products, and made many demonstration products with different additives. This product is the active component for a new class of composite materials, leading to novel products for building and road construction. The Calix process is the only known method of producing this material. The composites are mechanically strong, lightweight, water resistant, fireproof and thermally insulating. There is a wide range of additives that can be used for different products – biomass, bauxite waste, car tyres etc to make the composites.

## RISKS

The principal risk in this project will be the engineering of the calciner to be efficient under continuous processing. The heat transfer efficiency through the calciner walls to the granules is important, as are the suppression of the back reaction with  $\text{CO}_2$ , and the optimisation of the steam pressure and gas pumping systems. As previously stated, Calix will be able to adapt designs and materials handling processes that are found in the petrochemical industry, and this will reduce many engineering risks. There is a wide body of expertise in steam handling systems from the power industry.

## COMPETITIVE ADVANTAGES

### Process:

Conventional kilns take ~5 hours to process limestone rocks to lime. Calix reduces this to ~ 3 seconds by using limestone granules of 50-150  $\mu$  mesh size. The science behind the Calix process is well understood through international research over 80 years, but has not previously been put into industrial application. The missing ingredient is the realisation that a fast process of



less than 3 seconds enables a very simple gravity feed process to be used. Some researchers have adapted fluid bed reactor systems to this process, but the throughputs required for industrial processes are such that this approach does not scale well. The very large change in the processing time from hours in kilns to seconds has many implications, but the major impact lies in the potential capital cost savings of a plant. Rather than a kiln that weighs 100 tonnes, the Calix calciner is a vertical retort that weighs less than 2.5 tonnes, and is transportable in a container. The potential for reduction in capex is an order of magnitude. The energy cost of producing lime in the best available plant is about 3.6 GJ/tonne of lime produced, which is close to the thermodynamic limit of 3.17 GJ/tonne. The Calix process will be comparable, even including the costs of grinding.

A competitive advantage of the Calix Calcination process is that the calciner is a compact module that can be transported in standard shipping containers, rapidly assembled and disassembled. It is very likely that this will lead to new markets. Limestone is plentiful, and there will be local markets for fertilizers and eg for waste treatment, and these are affordable from large regional plants because of the high cost of transportation. Fuel is more readily transported to installations, and is usually readily available. There are communities, for example in Africa that could not afford a large scale conventional plant, but could afford a smaller plant.

### **Calcined Materials:**

The lime produced by the Calix process is more reactive because it has not had time to be sintered to a dead-burned oxide. This has been demonstrated in a pilot plant for batch processing using dolomite, magnesite and limestone. This is a more valuable product for almost all lime applications, with the exception of some fertilizer products. For applications in carbon capture described below, research has shown that the most important feature of the lime particles is the surface area of the mesopores created by calcination. Calix is confident that its process will produce a highly reactive material.

### **Materials made from Calcined Products:**

The Semidolime™ cannot be produced by any other process, and this provides a very significant competitive advantage. A preliminary analysis based on general building materials prices and cost of inputs indicates that the Calix materials will be competitive in both cost and performance. This is considered in detail in the Green paper "Calix™ Building Materials".

### **Carbon Capture:**

There are daily newspaper reports dealing with the importance of reducing greenhouse gas emissions. Calix will enter this market through its C3 process. However, it is recognised that the Calix Calciner can capture the pure CO<sub>2</sub> from the calciner, without needing to use the C3 reactor system. The C3 process could be used to capture the CO<sub>2</sub> from the combustion process used to provide the heat to the calciner.

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