

# CONVERTING WASTE MATERIALS FROM PVC AND PAPER PROCESSES TO MAKE PURE CALCIUM CARBONATE FOR THOSE INDUSTRIES

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## ABSTRACT

CalciTech Synthetic Minerals Ltd., a development company based in Geneva, Switzerland, has developed a unique, patented process for producing high purity, ***synthetic calcium carbonate*** (SCC) from impure, by-product raw materials. One such raw material is ***carbide lime***, a by-product of PVC polymer production by the acetylene process. China and India currently generate over 7 million tons<sup>1</sup> per year of waste carbide lime.

More recent research by CalciTech has shown that another potential raw material is ***paper sludge ash*** (PSA), a mineral by-product of paper recycling that can comprise a large fraction of the total weight of all recycled paper. With the rapid growth of paper recycling, millions of tons per year of this waste material are now being produced on a world wide basis.

Utilization of carbide lime and paper sludge ash as raw materials makes CalciTech SCC a truly “green” recycled mineral material. In addition, the manufacture of SCC from these waste mineral materials sequesters 44 tons of carbon dioxide gas for every 100 tons of end product produced.

## THE PRECIPITATED CALCIUM CARBONATE (PCC) PROCESS

Worldwide, almost 10 million tons of precipitated calcium carbonate (PCC) is produced annually for use in a wide range of end use applications. Roughly 70% of the total is consumed by the paper industry for the filling and coating of paper. Large amounts of PCC are also used in the filling of polymers, as a pigment in paint, and as a thixotrope in sealant and plastisol formulations. In addition, PCC with sufficient purity can be used for food and pharmaceutical applications.

PCC is manufactured by a series of chemical reactions beginning with high purity quicklime (calcium oxide), which is produced by the calcination of high calcium limestone. The quicklime is hydrated with water (slaked) to produce a suspension of calcium hydroxide, which is then reacted with gaseous carbon dioxide (CO<sub>2</sub>) to form microscopic crystals of calcium carbonate. The resulting suspension of PCC is screened to remove the larger impurity particles, and the

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<sup>1</sup> All “ton” quantities used in this paper refer to metric tons.

product is then used either as an aqueous slurry or as a dried and milled material depending on the intended end use.

However, the commercial PCC process suffers from the requirement that expensive, top quality, virgin quicklime be used as a raw material. Despite screening of the slaked lime slurry and the final PCC slurry to remove large contaminant particles, fine particles of various impurities are present during and after the carbonation step. These impurities can and do lead to a number of potential quality problems with commercial PCC products.

For example, impurities such as iron and manganese in the quicklime can lead to poor color and brightness in the final PCC product. Heavy metal impurities such as lead, arsenic and chromium can contaminate the final PCC product, thus rendering it unsuitable for food and pharmaceutical applications. Abrasive impurities such as fine silica particles can cause excessive wear to paper machine wires and polymer processing equipment when the PCC is used in paper and plastics applications.

In addition, certain quicklime impurities (as well as fluctuations in the water reactivity of the quicklime used in the PCC process) can lead to unwanted variations in the particle size, shape and crystal structure of the resulting PCC products. PCC manufacturers attempt to overcome these issues through tight raw material specifications and constant process monitoring, but the costs of this continual struggle are high production costs and frequent end product “excursions” that can result in poor PCC quality.

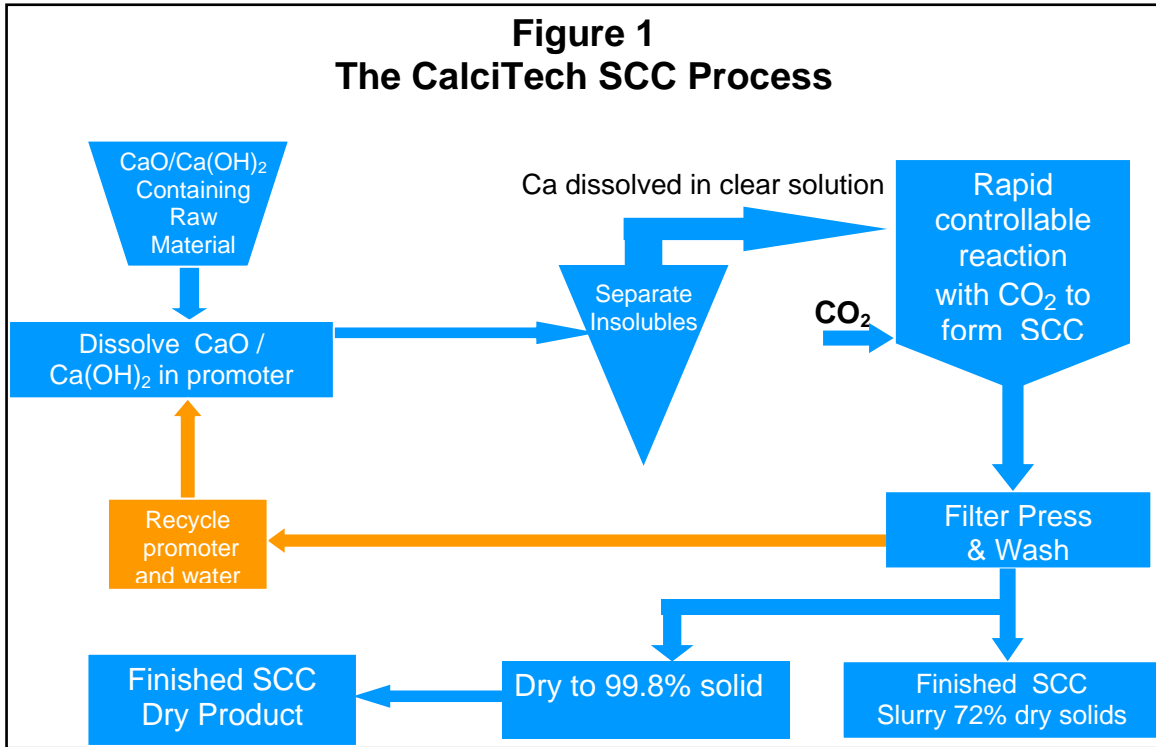
## **THE CALCITECH SYNTHETIC CALCIUM CARBONATE (SCC) PROCESS**

CalciTech Synthetic Minerals Ltd. is a development company based in Geneva, Switzerland that is about to start full scale production. Through years of laboratory and pilot scale effort, CalciTech has perfected a unique and patented process that allows microscopic calcium carbonate particles to be synthesized with unprecedented purity and consistency. Due to the fundamentally different nature of the CalciTech calcium carbonate process and product from existing PCC materials, the company has dubbed the new material “**Synthetic Calcium Carbonate**” or “**SCC**.”

Most remarkably, this superior form of synthesized calcium carbonate can readily be produced from inferior, by-product and waste raw materials. Virtually any material that contains significant amounts of calcium oxide and/or calcium hydroxide can be used as a raw material for the manufacture of SCC by the CalciTech process.

The core of the CalciTech SCC process involves the use of a proprietary chemical agent (known as a “*promoter*”) that greatly increases the solubility of calcium oxide and/or calcium hydroxide (and ONLY these materials) in water.

As shown in Figure 1, the calcium containing raw material is treated with the promoter and calcium oxide and/or calcium hydroxide is selectively dissolved into solution.



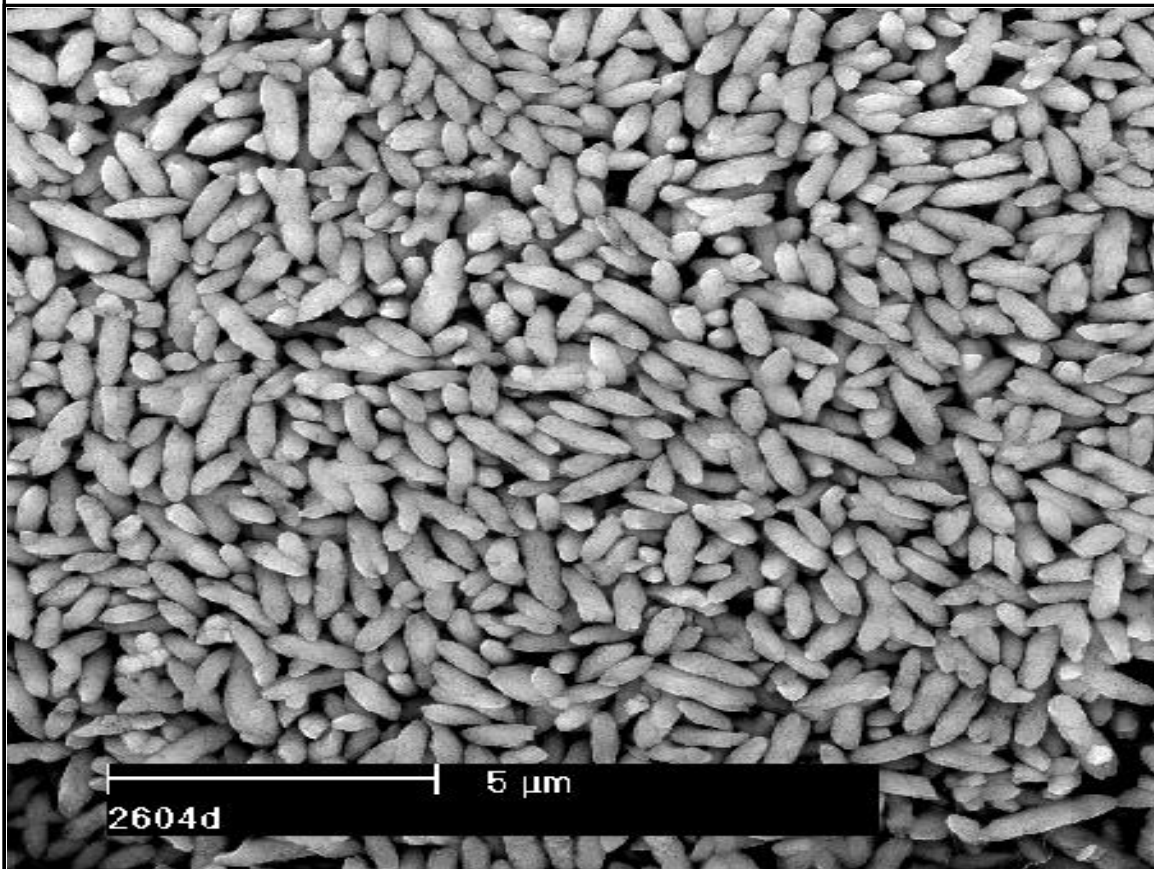
The insoluble (non-calcium) materials are then completely removed via solids separation techniques, and the crystal clear solution of  $\text{Ca(OH)}_2$  and promoter is then transferred to a carbonation reactor. At this point virtually all non-calcium materials have been removed from the reactants.

A  $\text{CO}_2$  containing gas is then introduced into the reactor in a fashion similar to the conventional PCC process. However, unlike the PCC process where the dissolution of solid calcium hydroxide introduces both a rate limiting step and a source of PCC crystal variability, in the SCC process all the calcium is already in solution awaiting reaction with the  $\text{CO}_2$  gas. The carbonation step, therefore, goes swiftly to completion and SCC crystals of outstanding uniformity and purity are produced.

The SCC product is then dewatered and washed to remove the promoter. Depending on the intended end use, the SCC may be concentrated and dispersed to a 72% solids slurry (if, for instance, paper coating is the intended application) or it may be processed further via drying and milling (if, for instance, it is intended for use in polymer, food or pharmaceutical applications). After suitable reprocessing, the promoter is recycled back to the beginning of the process and reused to solubilize additional calcium oxide/hydroxide from the incoming raw material.

The CalciTech process is capable of producing a variety of SCC particle shapes and sizes depending on the process conditions used. However, as shown in Figure 2, the prime product currently undergoing commercialization is a rice shaped, discrete calcite morphology with an average particle size of about one micron and a very narrow particle size distribution (as measured via the Micromeritics SediGraph instrument). The extreme uniformity of the SCC crystals is evident in this scanning electron microscope (SEM) image.

**Figure 2**  
**SEM Micrograph of CalciTech SCC**



Extensive applications testing has shown that this crystal morphology makes the most effective use of each SCC particle and produces an outstanding balance of properties and processing in such diverse end uses as paper coating, polymer filling and food and pharmaceutical formulations.

An additional advantage of CalciTech SCC is its extreme chemical purity. The removal of virtually all non-calcium contaminants prior to carbonation not only allows use of impure raw materials, but also produces a calcium carbonate

product that meets and exceeds all food and pharmaceutical purity requirements. Even magnesium, a close chemical cousin to calcium that is present in significant quantities in all PCC products, is virtually absent from CalciTech SCC. The outstanding purity of CalciTech SCC results in a product with very high whiteness and brightness and extremely low abrasivity.

Table 1 below shows a quantitative elemental impurity analysis for **CalciSP**, CalciTech’s food and pharmaceutical grade SCC, which was carried out at the Analytical Laboratory of the Geneva Institute of Technology using an ICP-MS instrument. The extremely low levels of such problematic elements as lead and arsenic make CalciTech SCC a very attractive material for use in food and pharmaceutical applications.

**Table 1**  
**Typical Elemental Impurity**  
**Content of CalciSP SCC**

<b>Chemical Element</b>	<b>Concentration [ppm] ± 10%</b>
Aluminium (Al)	<< 10
Arsenic (As)	< 0.3
Cadmium (Cd)	< 0.1
Chromium (Cr)	< 1.6
Copper (Cu)	< 0.3
Fluorine (F)	< 15
Iron (Fe)	<< 20
Lead (Pb)	<< 0.2
Mercury (Hg)	< 0.02
Mg and alkali salts	<< 0.1 %
Nickel (Ni)	< 3.7
Zinc (Zn)	< 1

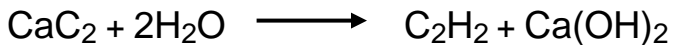
The single largest expense in the production of PCC by the current commercial process is the high quality, virgin quicklime that must be used as the calcium raw material source. For this reason, the ability of the CalciTech SCC process to use impure, by-product raw materials offers a significant process cost advantage.

In addition, the need to calcine limestone in order to produce “fresh” quicklime for production of PCC results in an overall addition of CO<sub>2</sub> to the environment for every ton of PCC manufactured. The CalciTech SCC process, however, requires no new quicklime to be produced. Therefore, the recycling of waste materials into high quality SCC leads to a truly “green” end product, whose manufacture results in the removal of 44 tons of CO<sub>2</sub> from the atmosphere for every 100 tons of SCC produced.

## CARBIDE LIME AS A CALCITECH RAW MATERIAL

CalciTech presently operates a pilot scale SCC plant in the town of Leuna, Germany and has plans to construct a 100,000 ton per year commercial plant at an adjacent industrial site. Carbon dioxide for these operations originates from a nearby oil refinery, while the calcium raw material source comes from a huge landfill of carbide lime located in the nearby town of Schkopau, Germany.

Carbide lime is one of the original calcium raw material sources evaluated for use in the CalciTech SCC process. This material is a waste by-product composed of impure calcium hydroxide that arises from the production of acetylene gas (C<sub>2</sub>H<sub>2</sub>) through the reaction of calcium carbide (CaC<sub>2</sub>) with water. The chemical equation for this reaction is as follows:



The calcium carbide is produced by heating coke and low quality quicklime to very high temperature in an electric arc furnace. The end product is typically only 80% pure with significant quantities of lime impurities and unreacted coke present. After the generation of acetylene gas, these calcium carbide impurities end up in the carbide lime, which, in turn, is usually disposed of in large landfills and lagoons.

In years past enormous quantities of acetylene gas were generated in Europe for use as a monomer in the production of various polymers. Although acetylene has now been replaced by petrochemical derived monomers, large landfills of carbide lime are still prevalent throughout Europe. Such sites offer abundant raw materials for future SCC production plants.

In Asia, explosive growth in PVC manufacturing has taken place in recent years. Most of this new PVC production capacity is based on the reaction of acetylene with hydrogen chloride to form vinyl chloride monomer. As a result, China alone is currently producing in excess of 7 million tons per year of carbide lime waste. This waste is presently used as a low cost additive in building materials or dumped into landfills. However, the Chinese Environmental Protection Administration is now requiring new PVC plants to recycle or treat the carbide lime waste.

In a fortunate coincidence, most PVC products are filled with up to 40% by weight of ground natural and/or precipitated calcium carbonate. Therefore, the production of SCC via the CalciTech process in Asia represents a unique opportunity to manufacture a critical component of the PVC polymer formulation out of the very waste that is generated in the production of the PVC resin. Studies of SCC in filled polymer systems have shown it to be an excellent mineral filler that imparts outstanding polymer properties while at the same time offering significant polymer processing benefits.

CalciTech has evaluated samples of Asian carbide lime waste and found that it can be used to produce pure SCC that is quite similar to that produced from the German carbide lime in Schkopau. Based on these findings, CalciTech is currently exploring the environmental benefits of SCC production from carbide lime waste with numerous Asian PVC manufacturers.

## **RECYCLED PAPER SLUDGE ASH (PSA) AS A CALCITECH RAW MATERIAL**

The recycling of paper products has grown tremendously throughout the world during the past few decades. This growth has been driven by environmental concerns about energy consumption, landfill usage and water and air pollution. Although the exact energy savings are subject to debate, studies by various governmental agencies have shown a savings of between 40% and 64% in energy for manufacture of recycled paper vs. virgin paper. Studies by the EPA claim a reduction of 35% in water pollution and 74% in air pollution for recycled paper manufacturing vs. production of virgin paper.

The quantity of paper currently being recycled is impressive. In Europe 64.5% of all paper products (excluding tissue) was recovered in 2007 (about 45.5 million tons), and the continent is on track to achieve its stated goal of 66% recycling during 2010. In the US 53.4% of all (non-tissue) paper used was recovered for recycling in 2006 (some 48.6 million tons), and the US paper industry has set a goal to increase the recovery rate to 55% by 2012.

A little known downside to paper recycling, however, is the fact that more than 20% of the total weight of paper recovered for recycling ends up as a waste material called recycled paper sludge. In the paper recycling process only the longer wood fiber component of the paper is recovered for reuse. Nearly all of the mineral based fillers and coating pigments (as well as starch, inks, and short paper fibers) end up in the recycled paper sludge waste stream.

These recycled paper sludge wastes amount to between 12 and 15 million tons per year in Europe (with a similar amount generated in North America), and they have been disposed of in landfills or used for low value applications in agriculture. However, since 2008 the EU has classified recycled paper sludge as a waste that is unsuitable for agricultural use, and environmental groups are increasingly opposed to such use in North America.

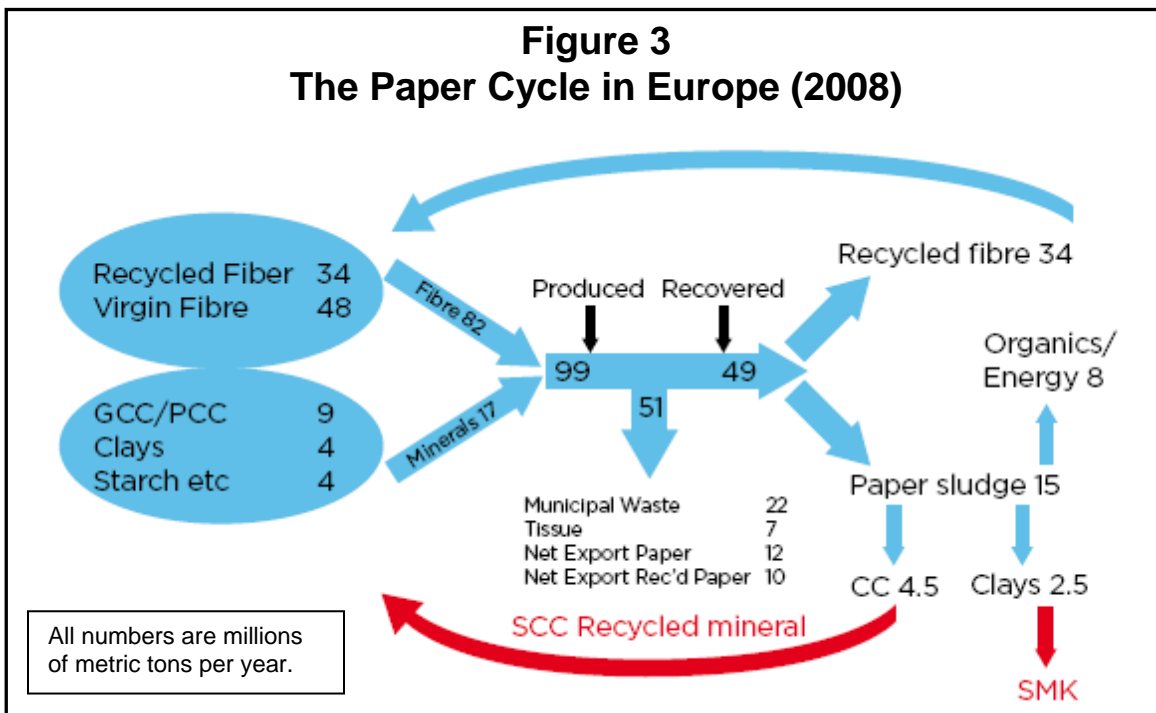
An alternative disposal method practiced by many recycled paper mills is to incinerate the sludge to extract energy from the organic components and to produce a solid paper sludge ash (PSA). This calcined ash has limited applications as a low value additive in construction materials and in agriculture, but, overall, the PSA constitutes a material of little or no value that is increasingly costly to dispose of. With landfill taxes projected to rise dramatically in coming

years, PSA will become a greater and greater problem for the recycled paper industry.

Fortunately, research by CalciTech has shown that PSA can be successfully used as a raw material for the production of high purity SCC using CalciTech's patented process. Production of SCC from PSA eliminates the need for the production and transport of ground calcium carbonate or for the manufacture of PCC from virgin quicklime for use in recycled paper. In addition, large quantities of waste carbon dioxide from the incineration of the recycled paper sludge (or from other sources) can be captured and used in the manufacture of SCC. The resulting recycled paper product is a truly 100% "green" material containing recycled wood fiber as well as recycled synthetic calcium carbonate.

As an added benefit, the removal of the calcium oxide component from the PSA during SCC production leaves behind another relatively pure material called *synthetic metakaolin* (SMK), a synthetic value-added mineral that finds applications in high strength cement.

Figure 3 below presents an overall view of the European paper cycle for 2008 and illustrates how production of SCC from PSA completes the cycle for the calcium carbonate component of recycled paper and also produces SMK as an additional useful synthetic mineral product.



Based on data from the Confederation of European Paper Industries (CEPI) on the volume of various grades of recovered paper, CalciTech estimates that approximately 4.5 million tons per year of SCC could theoretically be produced

from the European PSA waste stream. Approximately the same amount of SCC could in theory be produced from the similarly sized North American PSA waste stream.

By analyzing the process streams of known recycled paper mills, CalciTech has identified approximately 10 sites in Europe where dedicated SCC plants with capacities between 30,000 and 70,000 tons per year could be constructed using PSA as the sole raw material source. Even larger capacities could be attained if waste carbide lime or low grade quicklime were added to the raw material mix. Numerous recycled paper mills in North America offer similar opportunities for CalciTech SCC plants using PSA as a raw material.

As ever tighter environmental regulations are imposed on the polymer and paper industries throughout the world, the ability of CalciTech's unique SCC process to turn mineral-based industrial wastes into extremely useful and high purity end products will become increasingly valuable to these (and other) industries. For this reason, among many others, the future of CalciTech's Synthetic Calcium Carbonate is every bit as bright as the color of the product itself.

