

An abstract, colorful geometric pattern composed of overlapping, translucent shapes in shades of blue, purple, orange, and yellow, resembling a crystalline or mineral structure. The pattern is set against a dark blue background.

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# Success story on mineral carbonation of CO<sub>2</sub>



**Aalto University**  
School of Engineering

# Success story on mineral carbonation of CO<sub>2</sub>

Pushing academic research towards industrial scale through advanced modelling and piloting

At Aalto University's Department of Energy Technology, Professor Mika Järvinen's Energy Engineering and Environmental Protection research group is conducting pioneering research on biomass combustion, carbon capture and storage (CCS) by mineral carbonation, circulating fluidised bed gasification of waste, and advanced modelling of industrial processes, mainly for energy and metallurgical applications. To foster good industrial collaboration, the group carries out laboratory-, pilot- and full-scale research to avoid problems in scaleup and provide sustainable and economically feasible solutions for companies.

The latest process that has been developed deals with CO<sub>2</sub> sequestration by mineral carbonation using steel slag (a by-product of steelmaking) as a raw material. The principle of the carbonation process is simple. We first dissolve calcium (Ca) selectively from the steel slag with an ammonium salt solvent, and then bubble a CO<sub>2</sub>-containing gas through the Ca-rich solution.

In 2011 the Aalto University Foundation, together with Abo Akademi University and SSAB (formerly Ruukki) Raahе Works, successfully secured a patent for a technique that produces calcium carbonate (CaCO<sub>3</sub>) from alkaline by-products [1]. This CCS approach aims to reduce CO<sub>2</sub> emissions by using alkaline industrial waste materials and flue gas rich in CO<sub>2</sub> to produce a valuable CaCO<sub>3</sub> product that is marketable to, for example, the paper, pharmaceutical or plastics industries. The conventional production of this precipitated calcium carbonate (PCC) requires limestone to be mined, transported and subjected to a very energy intensive calcination processes that also emits CO<sub>2</sub>. However, by substituting limestone as the raw material with industrial Ca-rich wastes (e.g. steel slag), our method reduces waste, saves energy and reduces CO<sub>2</sub> emissions.

Here, we present the principles of our concept and address the latest developments and findings and most importantly, search for new partners to push this technology commercially.

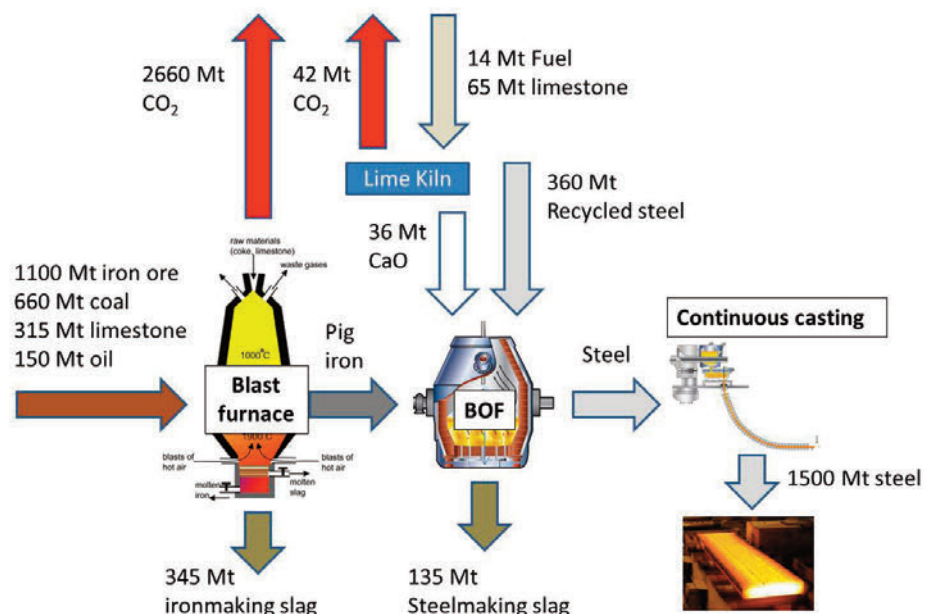


Figure 1. Simplified diagram of a typical integrated steel manufacturing process indicating major material flows [5]

### Steelmaking (BOF)

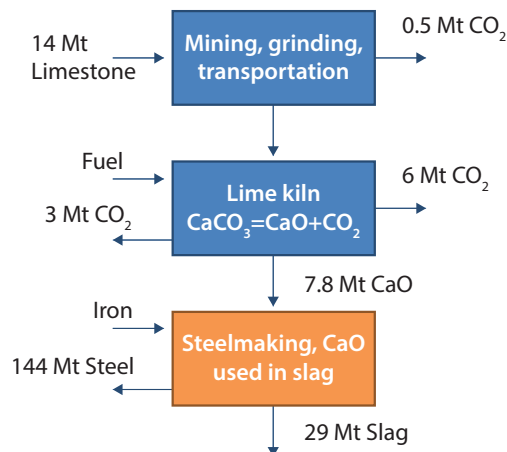


Figure 2. CO<sub>2</sub> and calcium flows in BOF steelmaking process

### Traditional PCC making

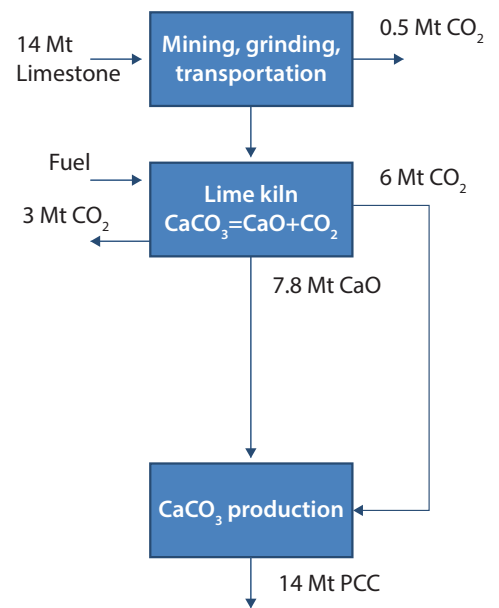


Figure 3. Traditional PCC production

### The roles of CO<sub>2</sub> and Calcium in Steel Production

Almost 1500 Mt of steel are manufactured globally every year and on average 1.8 t of CO<sub>2</sub> are produced per tonne of steel [2]. The production of steel is a very energy and material intensive process based predominantly on fossil fuels, thus the iron and steel industry is a significant source of anthropogenic CO<sub>2</sub> accounting for around 6.7% of global emissions [3]. In the coming decades there will be continued growth in the volume of steel produced, thus CO<sub>2</sub> emissions from the iron and steel industry as a whole will increase unless efforts are made to reduce them. In Finland, more than 3.8 Mt of steel were produced in 2012, corresponding to around 6-7 Mt of total CO<sub>2</sub> emissions annually [4]. Figure 1 presents a typical combined iron and steel production process, in terms of annual global amounts.

In addition to the direct and indirect emissions of CO<sub>2</sub>, the production of steel also generates about 400 Mt/y of a solid waste by-product known as slag, 50 Mt/y of which comes from Europe. Slag is formed from species in pig iron such as Si, Mn, Mg, some Fe and also valuable Cr that are oxidised during steelmaking [6]. One major component in slag formation is CaO that is fed to the top of the slag to remove silicon and sulfur and improve flowability. Slag is also essential for the process as it protects the steel from further oxidation and acts as a thermal insulation while the ladle is transported between different process stations in the steel mill. After the processing of the steel is complete, the slag is removed from the top of the ladle and the clean steel is then cast.

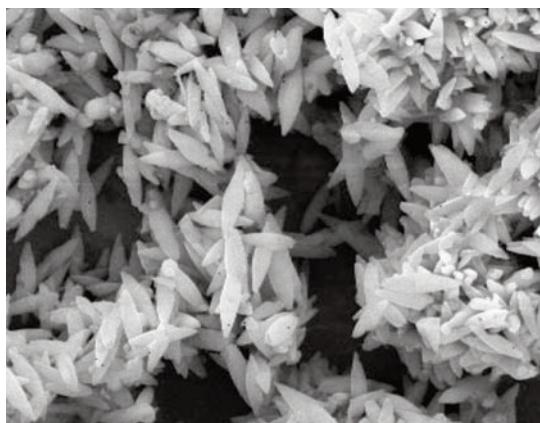
There are several different types of slag produced at different stages of the steelmaking process in varying quantities which depend on the chemistry, raw materials and other factors particular to the production method used. The different slag by-products are generally named for the furnace from where they originate e.g. blast furnace (BF) slag, basic oxygen furnace (BOF) slag and electric arc furnace (EAF) slag. The EAF process is another method of steel production which is used for recycled steel. Together, BOF slag and EAF slag are commonly referred to as steel slag or steel converter slag. BF slag is already very effectively used as a raw material in the cement industry [6]. In addition, it is not suitable for our process by its chemical composition. Figure 2 presents the BOF process with respect to calcium processing. As can be seen, the slag is rich in calcium and if not further treated, it is wasted. Steel converter slag is very well suited for Slag2PCC process as it contains a large amount of free calcium that can be effectively extracted. Steelmaking slag finds applications in road construction as well as the cement industry, however, about 13% is unusable for these purposes and is generally landfilled [7].

### Production of precipitated calcium carbonate (PCC)

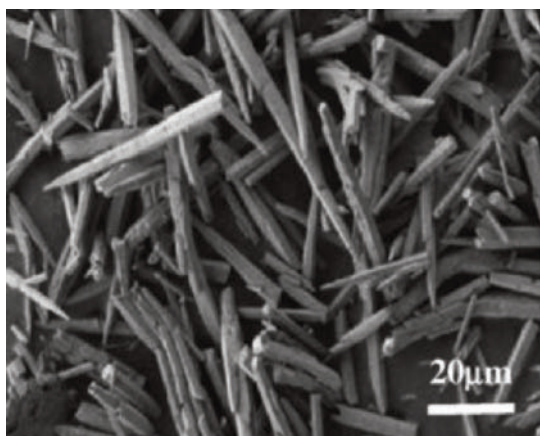
CaCO<sub>3</sub> is a very versatile mineral that is used in many industries. The most common source of CaCO<sub>3</sub> is limestone, a hard sedimentary rock composed primarily of CaCO<sub>3</sub> and magnesium carbonate (MnCO<sub>3</sub>) with varying levels of impurities. It is found in mineral deposits all over the world, although only a few can be economically mined and an even smaller number contain CaCO<sub>3</sub> deposits of sufficiently high quality to be



**Figure 4.**  
**Scalenohedral calcite structure used in paper industry, particle size 1-3 micron**



**Figure 5.**  
**Aragonite crystals used as paper coating, particle size 1-10 micron**



used in industries other than the construction industry. Only if the purity, whiteness, and homogeneity are acceptable is commercial extraction for high quality applications considered worthwhile. After quarrying, further treatment is required to produce natural  $\text{CaCO}_3$  of the highest quality, known generically as ground calcium carbonate (GCC) [7].

When very high quality  $\text{CaCO}_3$  is produced synthetically in an industrial precipitation process then the product is known as precipitated calcium carbonate (PCC). The quality of industrially-produced PCC generally surpasses that of even the highest quality natural GCC as the process can be tailored and controlled to produce a wide variety of PCC products with very high purity and different crystal properties. For this reason PCC can be sold at a higher price. A typical production process of PCC is presented in Figure 3

The global consumption of PCC increased from 10 Mt in 2004 to 14 Mt in 2011 and is expected to continue to grow. There are many requirements for the PCC properties including particle size, purity, brightness and crystal morphology, and these vary depending on the application.

$\text{CaCO}_3$  exists as the three polymorphs of calcite, aragonite and vaterite [14]. Of these three crystal forms only aragonite and calcite have major commercial applications and are

produced on an industrial scale [8]. Figure 4 and 5 show just a couple of examples of the crystal morphologies that can be produced. Different applications require different crystal structure and therefore, there is a need to better understand how these can be produced in a robust manner.

### **New concept – Steelmaking combined with PCC production**

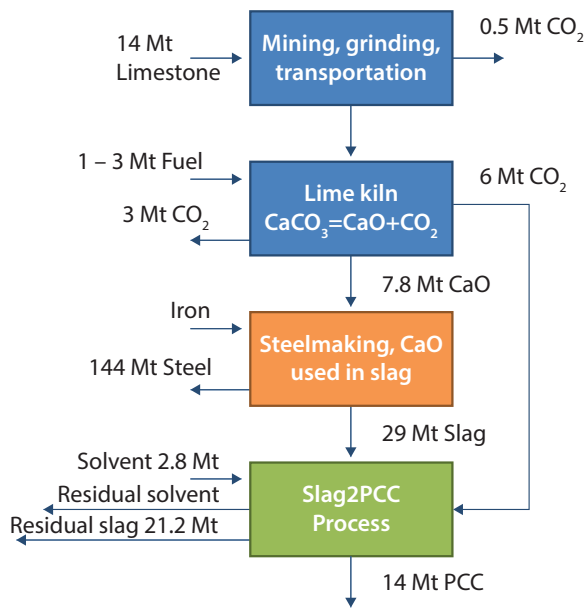
Producing PCC from steelmaking slag has been proposed as a potential method of reducing part of the the  $\text{CO}_2$  emissions from the steel industry by locking-up  $\text{CO}_2$  in a stable mineral form, whilst at the same time turning steel slag waste into a valuable product [5, 7]. Figure 6 presents a basic schematic of how a Slag2PCC process could be integrated with the steelmaking process.

In the Slag2PCC process, a solution of an ammonium salt is used to extract calcium from steelmaking slag. The resulting Ca-rich solution is bubbled with  $\text{CO}_2$  gas which reacts to form PCC. This PCC could replace limestone used in the production of steel reducing virgin material consumption and associated  $\text{CO}_2$  emissions or, if the PCC can be produced at sufficiently high quality, it could be sold at a higher price as a commodity chemical to several other industries. In addition to the steel industry, the pulp and paper industry has a significant presence in Finland and is a major consumer of PCC [4]. The presence of both these industries in close proximity in Finland therefore presents an excellent opportunity to develop mutually beneficial synergies between the two, at a time when both are being confronted with environmental and economic challenges.

### **Benefits from the new process concept**

To give an even better idea of the potential of the new Slag2PCC concept, we give here some simple material balance calculations. Traditional PCC production globally produces roughly 3 Mt  $\text{CO}_2$ , mainly from burning fossil fuels in a lime kiln. Considering only the production of CaO for the steelmaking process (not overall steel production), traditional steel production generates 3 Mt  $\text{CO}_2$  (lime kiln fuel) as well as 6 Mt  $\text{CO}_2$  (calcination), giving a total of 9 Mt  $\text{CO}_2$  annual. Theoretically, our proposed integrated system produces only 3 Mt of  $\text{CO}_2$ , resulting in more than 6 Mt less  $\text{CO}_2$  – a 73% reduction. In an optimal case, where waste heat could be used for evaporation processes, this would also mean that global PCC requirement could be obtained from the Slag2PCC process combined with steelmaking. While the potential  $\text{CO}_2$  savings are relatively small in terms of global emissions, the amount of avoided  $\text{CO}_2$  is twice the annual production of  $\text{CO}_2$  at Ruukki, Raahe works, the biggest single  $\text{CO}_2$  emitter in Finland.

## Steelmaking combined with PCC production



**Figure 6. New Slag2PCC process concept combined with converted steelmaking**

### Latest research results

The feasibility of PCC production from steelmaking slag has been successfully demonstrated at the pilot scale. Although further work has to be done in order to better control the morphology and particle size of the PCC produced by the Slag2PCC process, we can successfully produce rhombohedral calcite and aragonite of various sizes. We are also currently working on developing alternative PCC products based on the particular advantages of the Slag2PCC process for potential high value niche applications. Recovery of the ammonium salt solvent is a critical aspect of the process and how to best achieve this at minimal energy cost is a major challenge.

We are also investigating ways to improve the filtration system so that all Ca-rich or carbonated solution can be recovered easily under either batch or continuous operation. Filtration at the micrometer scale is also very challenging so other methods of collecting the PCC solids and recycling the solvent are also under investigation.

### Future work

Before we can begin to think about scale-up to an industrial-sized plant, it is imperative that the processes are first understood at every level in the pilot plant. We need to test all the process parameters to have a robust recipe for different types of PCC morphology. This way we will find out the actual energy consumption, expected chemical consumption, the quality of the steel slag residue's, the quality of the product PCC, and the amount of CO<sub>2</sub> that can be fixed by the process considering all direct and indirect emissions. Once the process has been

optimised at every level, we can begin to translate the method to a larger scale. We are currently looking for the best ways of achieving this as well as new partners to grow towards production on a commercial scale.

### Funding

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