

Production of precipitated calcium carbonate from industrial by-product slags (Slag2PCC)

Saostetun kalsiumkarbonaatin tuotanto karbonaattivapaista kuonatuotteista

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Abstract

Significant CO₂ emissions reductions could be achieved by using steelmaking slags for mineral carbonation. Owing to their high calcium content, steelmaking slags could be very suitable for this method, which could safely store carbon dioxide for a very long time. If calcium could be extracted from the slags prior carbonation, a pure, and thus also marketable, calcium carbonate (PCC) could be produced.

The aim of this project is to investigate and develop a process for reduction of CO₂ emissions by producing calcium carbonate, pure enough to be suitable for the PCC market, from iron- and steelmaking slags. Focus is on the possibility to use acetic acid as a solvent for producing pure calcium carbonate from steelmaking slags.

Tiivistelmä

Merkittävät hiilidioksidipäästövähennemät voitaisiin saada käyttämällä teräksentuotannon kuonia mineraalien karbonointiin. Niiden suuren kalsiumpitoisuuden takia, teräksentuotannon kuonat voisivat hyvin sopia tähän menetelmään, joka pystyisi varastoimaan hiilidioksidia turvallisesti hyvin pitkän ajan. Jos kalsium pystyttäisiin erottamaan kuonista ennen karbonointia, voitaisiin tuottaa puhdasta ja siten myös myyntikelpoista kalsiumkarbonaattia (PCC).

Tämän projektin tavoitteena on tutkia ja kehittää prosessi vähentämään hiilidioksidipäästöjä tuottamalla kalsiumkarbonaattia, joka on riittävän puhdasta PCC:n markkinoille, raudan- ja teräksenvalmistuksen kuonista. Erityiskohteena on tutkia mahdollisuutta käyttää etikkahappoa liuottimena tuottamaan puhdasta kalsiumkarbonaattia teräksentuotannon kuonista.

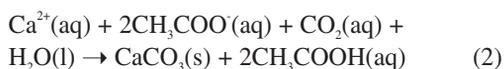
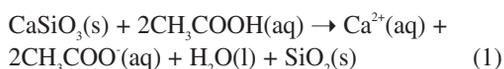
1 Background

To achieve the reduction of CO₂ emissions required for climate change mitigation, it seems that carbonation of silicate minerals could be one of the solutions with most potential. More importantly, it seems to be the only CO₂ capture and storage (CCS) option for Finland (Koljonen et al. 2004), at least inside the Finnish borders. Calcium oxide (CaO), the reactive component of calcium silicates, can be found in industrial waste materials and by-products besides its natural sources (Huijgen and Comans 2003). The CaO content of iron- and steelmaking slags can be even higher than the CaO content of natural calcium silicates (Stolaroff et al. 2005). More significantly, the price of iron- and steelmaking slags is significantly lower than that of natural calcium silicates (Teir et al. 2005a). All this makes iron-

and steelmaking slags attractive raw materials for carbonation.

The product from carbonation of iron- and steel-making slag, a calcium carbonate, could possibly be marketed as precipitated calcium carbonate (PCC) if the purity requirements were fulfilled. PCC is mainly consumed by the paper industry, where it is used as a filler and coating pigment in paper. The potential for producing a commercial carbonate product by mineral carbonation could allow for higher process costs than what the CO₂ reduction compensates for when calculated as CO₂ emission allowances costs (Teir et al. 2005b).

We have previously studied a potential manufacturing option for producing calcium carbonates from calcium silicates (Teir et al. 2005b; Kakizawa et al. 2001). It uses an aqueous solution of acetic acid to extract calcium from natural calcium silicates (Equation 1), after which the produced calcium acetate solution reacts with CO₂, producing calcium carbonate which precipitates from the solution (Equation 2):



If the global production of steelmaking slags was used as feedstock for carbonate production using this process method, 70–180 Mt of CO₂ could possibly be sequestered annually. If the process replaced the current PCC manufacturing process, additional CO₂ emissions reductions could be achieved. Iron- and steelmaking slags would also be refined into more valuable products. However, very little experimental data was found on the process (Kakizawa et al. 2001; Fujii et al. 2001).

Preliminary laboratory scale batch experiments showed that calcium is rapidly extracted from blast furnace- and basic oxygen furnace-slugs in aqueous acetic acid solutions. Complete dissolutions of slags were reached at high acid concentrations and silica was removed as a gel by keeping the dissolution temperature at 70 °C (Teir et al. 2005a).

2 Objectives

The primary research goal of this project was to research and develop a process for reduction of CO₂ emissions by producing calcium carbonate from iron- and steelmaking slags. Secondary goals included developing the process to produce a calcium carbonate material pure enough for the PCC market and to find out whether similar processes could be suitable for carbonating magnesium silicates for magnesium carbonate production as a large-scale carbon dioxide sequestration method in Finland. The main academic goal was to produce a licentiate thesis by post-graduate researcher Sanni Eloneva.

3 Project work programme

Duration of the project	Funding of the project
1.8.2005–31.10.2007	Total 133,000 €, of which Tekes funding 104,000 €
Project partners	Helsinki University of Technology
Participating companies	Rautaruukki, UPM Kymmene, Wärtsilä
International co-operation	Nordic Energy Research

The project was originally planned to run for twenty-four months, August 2005 – July 2007. However, due to various setbacks project completion was delayed till October 2007. The original timetable for the project is presented in figure 1.

The research consisted of experimental research, model calculations and process simulations. The focus shifted towards experimental research, which was needed for determining the feasibility of the process. Experiments were carried out in the Laboratory of Energy Engineering and Environmental Protection with batch reactors. Model calculations and process simulations were performed using Outokumpu HSC 5.1 and Aspen Plus software. Atomic Absorption Spectrophotometry (AAS) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) analyses were provided by the Laboratory of Physical

	2005												2006												2007					
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6
Batch experiments: solubility of the slags																														
Atmospheric batch experiments: carbonation																														
Design and construction of the pressurised reactor																														
Pressurised batch experiments: carbonation																														
Process modelling																														
Reporting																														
Extraction techniques																														
Quality of produced carbonate																														
Financial analysis																														
Continuous process																														

Figure 1. Original timetable of the project.

Chemistry and Electrochemistry, while X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD) analyses were provided by Ruukki. Scanning Electron Microscope (SEM) imaging, particle size distribution and ISO brightness measurements were carried out by Specialty Minerals.

Members of the research group took part in many national and international conferences, and gave oral presentations in most of them. Please see the list of publications for an extensive overview.

4 Project results

Unless otherwise mentioned, text here is based on the publications and reports listed in section 6.

First, thermodynamic calculations were carried out to verify the theoretical possibility to produce calcium carbonate from steelmaking slags using the acetic acid process route proposed by Kakizawa et al. (2001). The solution equilibrium was calculated using Outokumpu HSC 5.1. The Gibbs free energy calculations of the extraction reaction showed that the extraction of Ca^{+2} -ions from CaSiO_3 is thermodynamically feasible at temperatures lower than 156 °C. Gibbs free energy calculations of the carbonation reaction showed that the carbonation of Ca^{+2} ions proceeds already at temperatures over 45 °C. The calculations also show that the extraction reaction is exothermic ($\Delta H < 0$), while the carbonation reaction is endothermic ($\Delta H > 0$). However, the net (overall) reaction of calcium silicate carbonation is exothermic.

To predict the precipitation of CaCO_3 from a calcium-rich acetic acid solution, the thermodynamic equilibrium of the species and products participating in reaction Equation 2 was calculated. According to the calculations adding a surplus of acetic acid to the system inhibits the formation of calcium carbonates. A 100% conversion to CaCO_3 would require that practically all surplus of acetic acid is neutralized with a base, e.g. NaOH (as done in this work) (Figure 2).

The extraction of calcium from steelmaking slags and wollastonite in aqueous solutions of acetic acid was studied using batch experiments. The experiment set-up is displayed in figure 3. Experiments showed that dissolution was faster and a higher conversion was achieved with the tested steelmaking slags than with wollastonite (Figure 4). While only 50% of the calcium in wollastonite dissolved in an aqueous solution of acetic acid (33.3 wt-% CH_3COOH) at 50 °C, 80–100% of the calcium in steelmaking slag was extracted under similar conditions. Other elements, such as silicon, iron, aluminium, and magnesium, dissolve as well. No connection between the dissolution rates of the calcium silicates and the crystal structure of the material was found.

The effect of various process parameters upon the dissolution step was tested using blast furnace slag. Experiments showed that for complete dissolution of blast furnace slag 15–18 mol of acetic acid was required per mole of calcium in slag (at 50 °C) (Figure 5), which is 8–9 times the theoretical requirements for extracting calcium (Equation 1). One reason for the large requirement of acid is that other elements in slag react with the

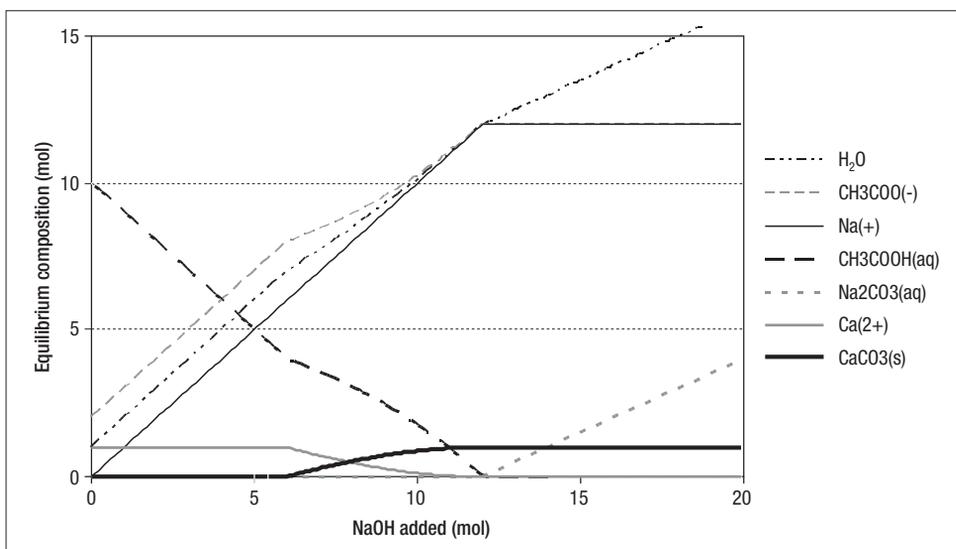


Figure 2. Effect of NaOH presence in a system at thermodynamic equilibrium at 25 °C consisting of 1 mol Ca²⁺, 2 mol CH₃COO⁻, 1 mol H₂O, 100 mol CO₂ (at 1 bar) and 10 mol CH₃COOH.

acid as well. However, when the dissolution was complete, the pH of the solutions was still about 3–4, which indicates that not all acid had been consumed. By raising the temperature of the solution, the conversion was lowered, but could be compensated for by using higher concentrations of acid. At 70 °C and 80 °C (and large concentra-

tions of dissolved slag) almost all the dissolved silicon precipitated as gel and was successfully removed by filtration. However, other separation measures will be needed to remove aluminium, iron, magnesium and other elements released from the slag or to prevent these elements from ending up in the carbonate product.

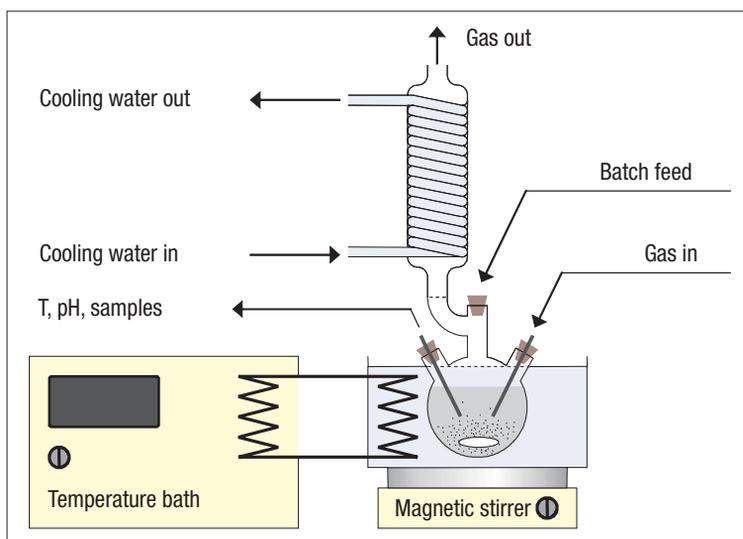


Figure 3. Experimental set-up.

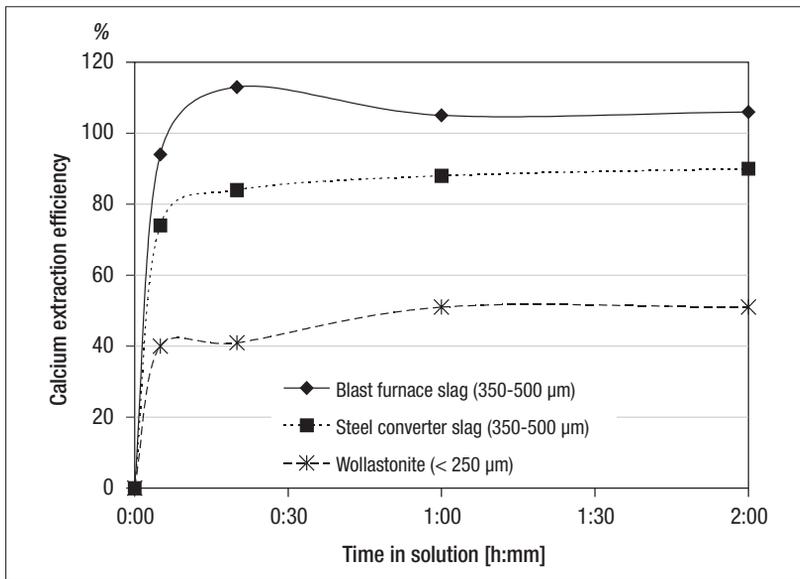


Figure 4. Extraction of calcium from steelmaking slags and wollastonite in aqueous solutions of acetic acid (33.3 wt-% CH_3COOH).

Thermodynamic calculations indicated that precipitation of carbonates from acetate solutions would be favorable at temperatures above 45 °C. However, experiments with carbonating solutions of dissolved blast furnace slag and acetic acid produced no carbonate precipitate during 4 h at 30–70 °C. Thermodynamic calculations veri-

fied that the solution was too acidic to allow for carbonate precipitation. While addition of sodium hydroxide raised the solution pH resulting in formation of precipitate containing carbonates, a considerable amount of sodium hydroxide was required, which also reduces the amount of acetic acid that can be recovered for re-use. By evapo-

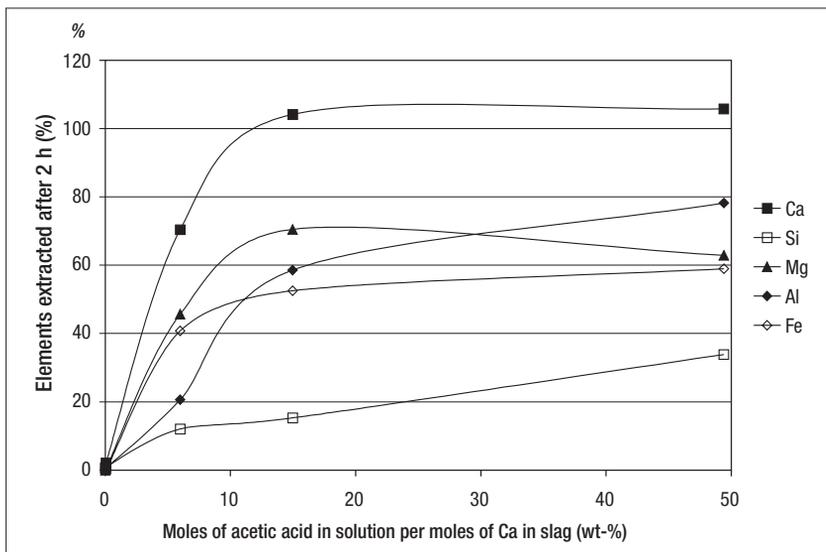


Figure 5. Effect of concentration of acetic acid (0–33 wt-%) upon dissolution of blast furnace slag.

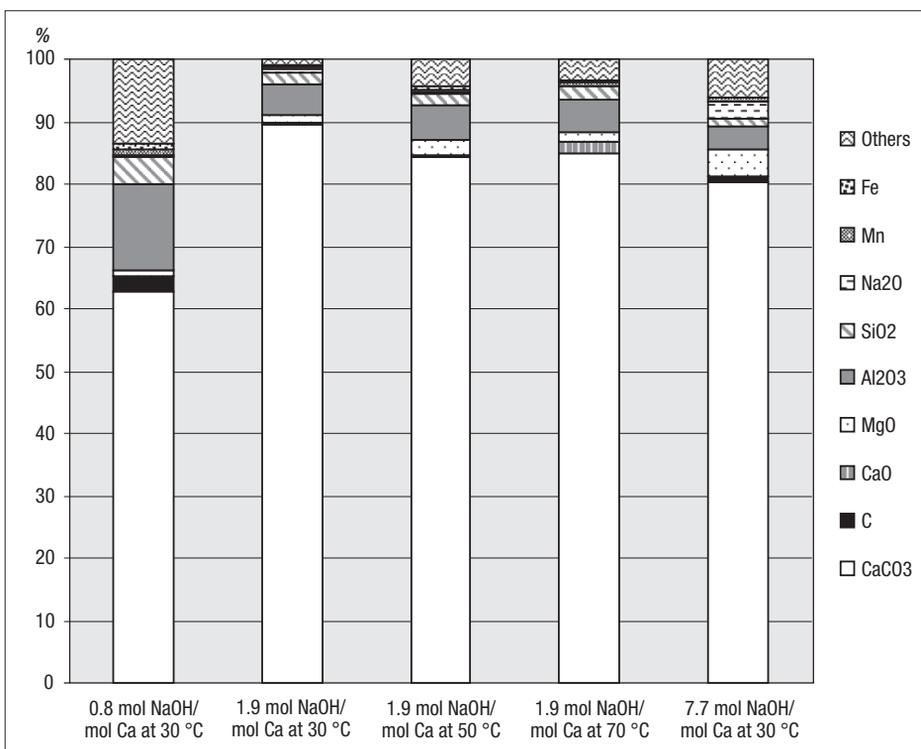
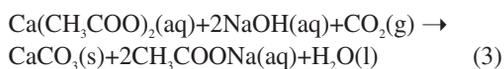


Figure 6. Elemental compositions of the dried and washed precipitates from the carbonation experiments with slag-derived acetate solutions as determined by XRF and total carbon content analyses (units wt-%).

rating the solution containing dissolved slag, and mixing the precipitated acetate with water prior to carbonation the sodium hydroxide requirements were reduced to the stoichiometric requirements (of Equation 3). Bubbling CO₂ gas through the acetate solution precipitated relatively pure (80–90%) calcium carbonate (Figure 6).



Preliminary feasibility calculations showed that the heat requirement for evaporation of the acetic acid is large, but could be covered for by using low-grade waste heat (120 °C) from other industrial processes. The requirements for sodium hydroxide and make-up acetic acid were also relatively large (Figure 7), requiring recovery and processing of the produced sodium acetate solution. Carbon dioxide emissions from the production or regeneration of the chemicals would ex-

ceed the amount of carbon dioxide stored by the carbonation step, and the large amount of dissolved impurities would probably make recovery of the solution difficult. Purchasing the sodium hydroxide and make-up acetic acid would make the process very expensive. Since the precipitate produced contained a large amount of impurities (10–20%) the product would probably not have a high market value. Therefore, the use of acetic acid does not seem to be a feasible option for producing carbonates from blast furnace slag. Besides this, other uses for blast furnace slag exist.

The possibility to dissolve calcium selectively from steel converter slag by using acetic acid was investigated also. It was found that weak acetic acid solutions (30% or less of the acid stoichiometrically required to dissolve all the calcium) dissolve only lime (calcium oxide) and calcium hydroxide from the slag, forming a solution that

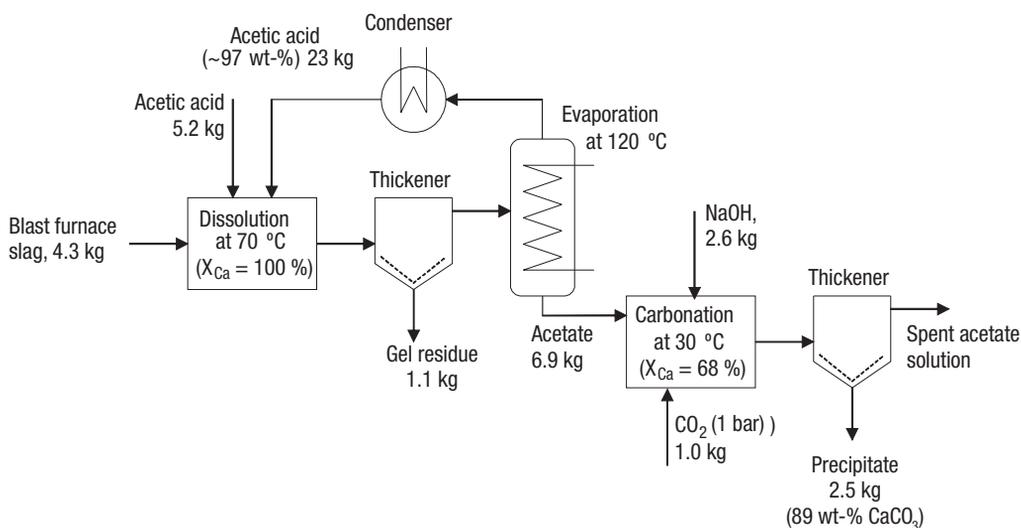


Figure 7. Process scheme for producing calcium carbonate from blast furnace slag. Numbers based on experimentally verified results.

contains mostly calcium acetate. Stronger solutions dissolve more calcium, but also significant amounts of iron and silicon, as well as small concentrations of Mn, Mg, V and Al from the steel converter slag. This is undesirable, because a commercial calcium carbonate product should contain as little impurities as possible. Solution temperature was found not to have a significant effect on the dissolution of steel converter slag, but a longer leaching time was found to promote silicon gel formation, allowing for the mechanical removal of the silica.

Precipitation of any substantial amount of calcium carbonate from the solution of acetic acid and dissolved steel converter slag was found to require addition of sodium hydroxide (Figure 8). When calcium carbonate precipitates from a calcium acetate solution, acetic acid is formed, which acidifies the solution and prevents further precipitation of calcium carbonate. Addition of sodium hydroxide converts calcium acetate into calcium hydroxide and sodium acetate, which prevents the formation of acetic acid and favors the formation of calcium carbonate. Calcium conversion from the solution into the precipitate was then as high as 86% and the purity of the precipitate was 99.5–99.8%.

Solution temperature was found to have effect both on the precipitates' particle shape and size (Figure 9), while sodium hydroxide addition effected mainly the shape of the particles and amount of the added sodium hydroxide for the particle size of the precipitate. With sodium hydroxide addition the particles have a rhombohedral particle shape, very high brightness and small particle size at low temperatures.

Carbon dioxide concentration did not effect the amount or quality of calcium carbonate formed, indicating that probably flue gases can be used right away as a source of carbon dioxide without a need for CO₂ separation from the gas. While the lowest concentration increased the stabilization time of the solution pH, indicating that a longer precipitation time was needed, it was decreased by both a temperature increase and a higher gas flow. Therefore, it seems that low carbon dioxide concentration in flue gases can be compensated for by an increase in solution temperature or gas flow. (However, in flue gases there may exist also NO_x, SO_x, Hg and other trace elements, as well as fly ash, which probably would reduce the PCC quality unless separated before using the flue gas.)

The studied production method could in the best case produce 42 kt/a of ~ 99 % pure calcium car-

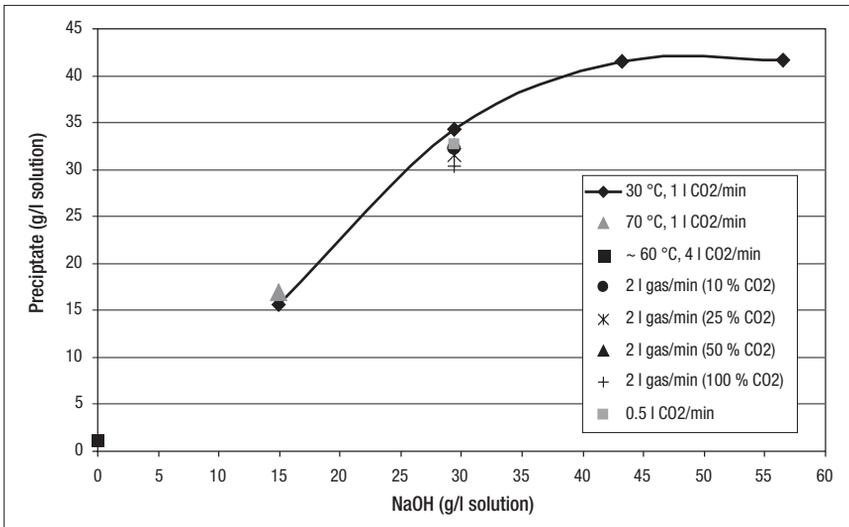


Figure 8. Amount of precipitate formed in relation to amount of sodium hydroxide used.

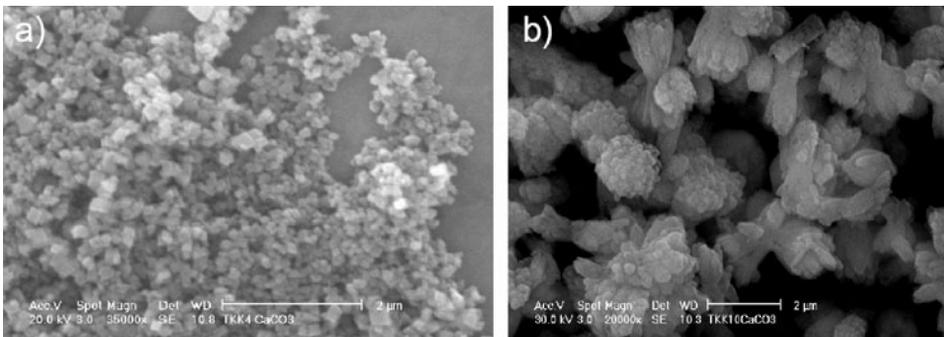


Figure 9. SEM pictures of the precipitates from the experiments with 1 l/min CO_2 flow and 14 g NaOH/l solution of dissolved steel converter slag and acetic acid at a) 30 °C and b) 70 °C.

bonate from the Raahе Works annual steel converter slag production, covering approximately 10% of Finland’s PCC market. While the residual slag produced could possibly be used better as construction material, because undesired free lime (Monshi and Asgarani 1999; Mäkikyrö 2004) was removed, this needs further investigation. Although the process could be suitable for any other steel work, producing steelmaking slags that contain free lime or calcium hydroxide, the consumption of sodium hydroxide and acetic acid makes the route studied here too expensive to be economically reasonable.

5 Impact of the results and plans for the future

Although the results from this project demonstrate that it is possible to produce relatively pure calcite (80–90%) from blast furnace slag and very pure (> 99%) calcite from steel converter slag, the process concept at its current development stage is not suitable for reducing CO_2 emissions. The main obstacles are the large requirements for sodium hydroxide and acetic acid that cannot be recovered and re-used.

A solvent that extracts calcium selectively from slags and allows for spontaneous precipitation of carbonates would eliminate the requirement for sodium hydroxide. Finding a suitable solvent is the key issue for significantly lowering the process costs for carbonate production from slags. The follow-up new project, “Slag2PCC Plus” (2007–2009), is based on the findings in “Slag2PCC” and focuses on significantly improving the process requirements for carbonate production from steelmaking slags by making use of more suitable solvents. Also, the acetic acid recovery using an extraction method will be tested, which may solve at the same time the problem of pH stabilization. Separation methods that lead to PCC product quality improvement will be tested as well.

6 Publications and reports

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