

Publication V

Sanni Eloneva, Arshe Said, Carl-Johan Fogelholm, and Ron Zevenhoven. 2010. Feasibility study of a method utilizing carbon dioxide and steelmaking slags to produce precipitated calcium carbonate (PCC). In: Proceedings of the 2nd International Conference on Applied Energy (ICAE 2010). Singapore. 21-23 April 2010. Pages 169-178.

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Feasibility Study of a Method Utilizing Carbon Dioxide and Steelmaking Slags to Produce Precipitated Calcium Carbonate (PCC)

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Abstract

The increasing atmospheric carbon dioxide concentration has led to concerns about global warming. One of the options that can contribute to the reduction of carbon dioxide emissions is the so-called CO₂ sequestration by mineral carbonation. Steel manufacturing which is one of the biggest industrial sources of CO₂ emissions could benefit from this option by utilizing its own by-products, i.e. steelmaking slags to combine with CO₂. Additional benefit would be achieved if the end-product was a pure and marketable calcium carbonate. We have recently studied a method, where aqueous solution of ammonium salt (e.g. ammonium acetate, ammonium nitrate and ammonium chloride) is used to extract calcium selectively from the steel converter slag, followed by precipitation of pure calcium carbonate by bubbling CO₂ through the formed solution. The ammonium salt solution is recovered and re-used.

The purpose of this research reported here was to investigate the feasibility of the studied method. Grain size of the steel converter slag was found to have a clear effect on the rate and extent of calcium extraction from the slag with the ammonium salt solvent. Solid to liquid ratio experiments revealed that ratios over 100 g/l should be avoided. The method was calculated to have economical potential and clearly negative CO₂ emissions.

Keywords: mineral carbonation, steelmaking slag, CO₂, ammonium salt, PCC

1. Introduction

Carbon dioxide capture and storage (CCS) is recognized as one option to tackle increase of atmospheric concentration of CO₂ for climate change mitigation [1]. While geological storage of CO₂ is the only storage option that has been fully demonstrated [2], storage of CO₂ as mineral carbonate has a larger storage potential [3] and does not require use of expensive monitoring equipment to ensure that CO₂ does not escape into the atmosphere. In mineral carbonation, carbon dioxide is fixed with magnesium or calcium oxide of a certain mineral forming solid and stable carbonate as an end product [4].

Steel manufacturing which is one of the biggest industrial sources of CO₂ emissions [5] could benefit from this option by utilizing its own by-products, steelmaking slags for sequestering CO₂. Steelmaking slags such as steel converter slag and blast furnace slag have a high calcium content and are therefore suitable raw material for carbonation. While steelmaking slags can be utilized for many purposes, there is not always an economically reasonable way to utilize them or they do not fulfill increasingly tight environmental regulations.

Few studies concerning utilization of steelmaking slags as raw material for carbonation have been made [6, 7, 8, 9, 10], but none of the mineral carbonation methods has yet been commercialized. Indirect mineral carbonation methods, where reactive component is extracted from the mineral prior carbonation seem attractive; the end product can then be a pure carbonate having a high market value. The reactive component of steelmaking slag is

calcium, thus end product of indirect carbonation of steelmaking slags could be pure calcium carbonate. Natural calcium carbonate, i.e. limestone has wide markets, while very pure synthetic calcium carbonate has a much higher price. This precipitated calcium carbonate (PCC) is mainly used as a filler and coating pigment of paper [11].

The main challenge in mineral carbonation is the slow reaction kinetics. In indirect carbonation, an acidic environment enhances the extraction of reactive compound like calcium, the following carbonation reaction step, on the other hand, is dependent on a basic environment [12, 13, 14, 15]. Specifically, while acidic conditions can be neutralized by base addition, this prevents efficient recycling of the chemicals making the method expensive. In our previous research the possibility to dissolve calcium selectively from the steel converter slag was investigated using various different solvents [16]. We found that ammonium salt solutions were the most promising solvents amongst the tested ones. Besides the two weak base-strong acid salts (ammonium chloride and ammonium nitrate) studied also by [10], ammonium acetate, which is a salt of a weak base and weak acid dissolved calcium efficiently and selectively. After removal of the slag residue, carbon dioxide was introduced into these solutions resulting in precipitation of pure calcium carbonate (99.8 wt-%). These ammonium salt solvents were found to be recyclable [17], although losses of ammonia were noted.

The objective of the research reported here is to evaluate the feasibility of the studied method, which enables production of pure calcium carbonate from steel converter slag by using ammonium salts as a solvent (Figure 1). Additionally, the effects of the slag's grain size, and solid to liquid ratio on dissolution of calcium from the slag were experimentally investigated. Finally, costs of the method's chemical consumption and its CO₂ emissions reduction potential were calculated.

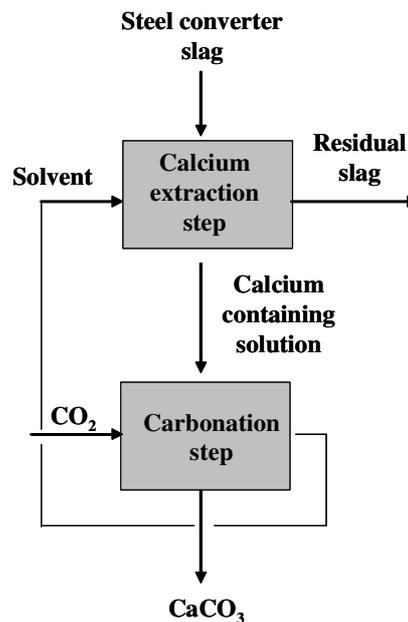


Figure 1. Process schematic of the idea of using recyclable solvent for production of calcium carbonate from steelmaking slags.

2. Methods

2.1. The effects of the slag's grain size

Slags are removed from the steel manufacturing process in their molten stage and then cooled down. After cooling, steel slag is processed to remove all free metallics, after which the grain size of the steel converter slag is generally less than 10 μm [18]. Grain size of the steel converter slag in our earlier experiments [16] was 74-125 μm . Consequently, it is important to find out how large particle size can be used in the carbonation method based on steelmaking slags and ammonium salt solutions as slag grinding is expected to be a quite energy intensive process.

The effect of grain size was tested by dissolving 10 g of steel converter slag (0-125, 125-250, 250-500, 500-1000, 1000-2000 and 2000-3000 μm) provided by Ruukki's Raahe Works in 500 ml solution of ammonium nitrate (2 M) at 30 °C. A round bottom flask equipped with the magnetic stirrer was used as a reaction vessel (Figure 2). It was surrounded by an open water bath, which was heated using a separate, temperature controlled water bath. The vessel was also equipped with a condenser cooled with tap water in order to avoid evaporation losses. The pH and temperature of the solution was measured using electrodes (± 0.1 °C, ± 0.1 pH), allowing for real-time monitoring and logging of data. Dissolution of calcium was monitored by taking 5 ml samples of the solution 2, 5, 10, 20, 40 and 60 minutes after addition of the slag. The solution samples were immediately filtered and analyzed for Ca with Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). Calcium content of the steel converter slag fraction used was analyzed by total digestion and ICP-AES.



Figure 2. Photo of the test facility.

2.2. Solid to liquid ratio

A solid to liquid ratio of 20 g/l was used in the earlier experiments [16]. Nevertheless, the higher solid to liquid ratio, the less water and smaller reactor size can be used. For this reason, dissolution of calcium from the steel converter slag in different solid to liquid ratios was tested. Sample (1, 2, 3, 5, 10, 15, 20 and 30 g) of the steel converter slag (125-250 μm) was added into 50 ml of 2 M ammonium salt solution (NH_4NO_3 , NH_4Cl or $\text{CH}_3\text{COONH}_4$) at 30 °C. The solution was stirred for one hour with a magnetic stirrer at 500-1000 rpm, after

which a solution sample was taken. A sample was filtered and analyzed for Ca by using ICP-AES. Calcium content of the steel converter slag fraction used was analyzed by total digestion and ICP-AES.

3. Results and discussion

3.1. The effects of the slag's grain size

As expected, calcium dissolved most efficiently (~60 % in 1 hour) and quickly from the slag that had the smallest grain size (0-125 μm) (Figure 3). Most of the calcium that dissolved had already dissolved from the slag five minutes after the slag was added into the ammonium nitrate solution. Likewise, calcium dissolved quite well from the slag samples that had the second and third smallest grain sizes (125-250 and 250-500 μm) (~55 in 1 hour). On the other hand, dissolution of calcium was somewhat slower as it took an about 30 to 40 minutes before most of the dissolving calcium had dissolved. When grain size of the slag increased above 500 μm , dissolution of calcium weakened significantly (only about 30, 20 and 15 % with 500-1000, 1000-2000 and 2000-3000 μm respectively in an hour). In conclusions, the smaller the steel converter slag's grain size, the higher the amount and rate of calcium extracted. Additionally, in order to avoid poor calcium extraction the grain size of the steel converter slag should not be increased to above 500 μm .

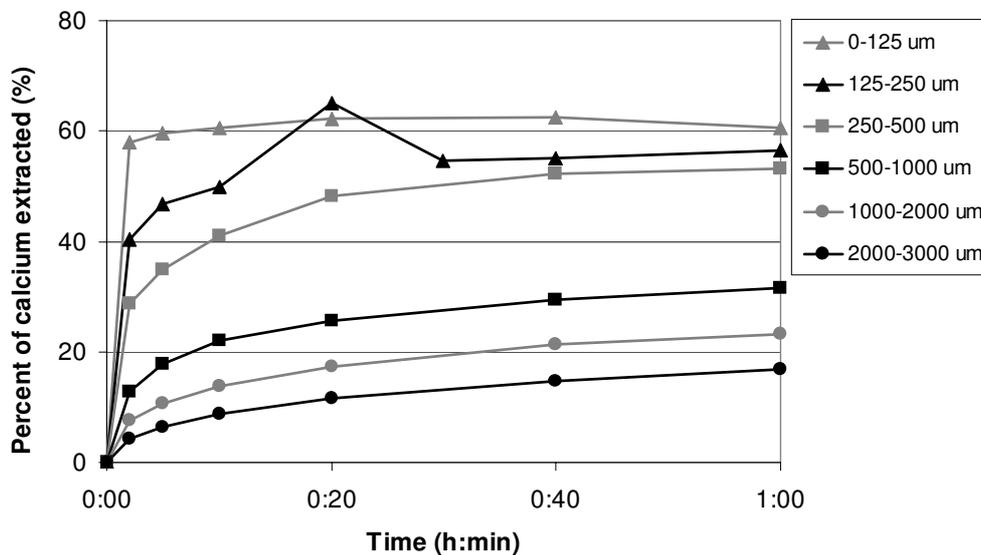


Figure 3. The effect of grain size on dissolution of calcium from steel converter slag in aqueous solution of ammonium nitrate.

Solution pH and temperature rose (~2.5-3.8 pH units and 0.1-0.4 $^{\circ}\text{C}$, respectively) immediately after the slag had been added into the solution (Figure 4 & Figure 5). The temperature curve indicates clearly that an exothermic reaction occurred shortly after the slag was added. The smaller the particle size of the slag, the higher the pH of the formed solution and the clearer the temperature increase.

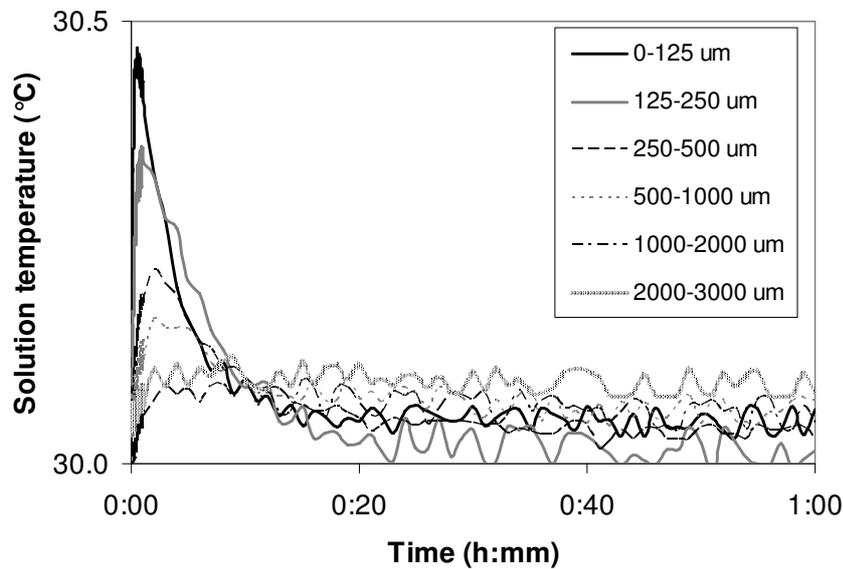


Figure 4. Inline solution temperature recordings of the experiments where the effect of the grain size of steel converter slag on dissolution of calcium was tested.

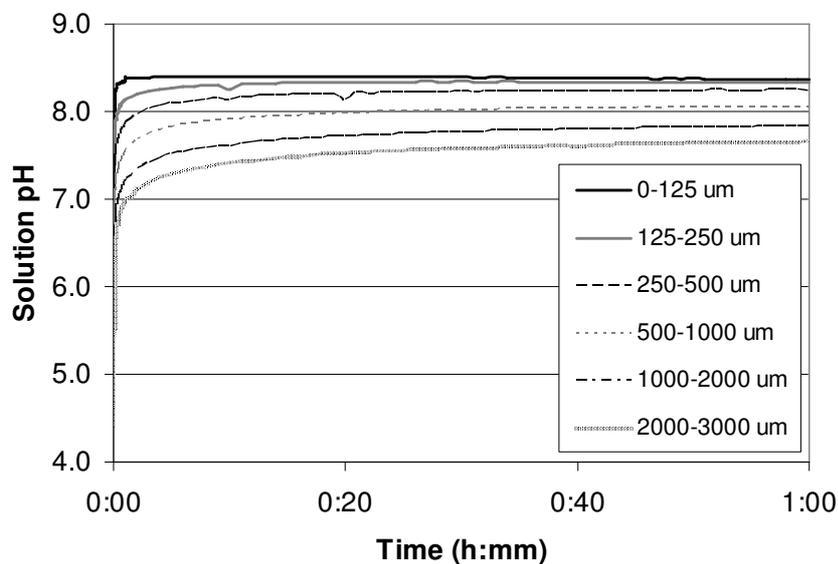


Figure 5. Inline solution pH recordings of the experiments where the effect of the grain size of the steel converter slag on dissolution of calcium was tested.

3.2. Solid to liquid ratio

The best calcium extraction efficiency (~55 %) was reached with the smallest solid to liquid ratio (20 g slag/l of solvent) (Figure 6). Dissolution of calcium was somewhat better in aqueous solution of ammonium nitrate than in ammonium acetate or -chloride, but the difference was quite insignificant (0-3 %-unit). The extraction efficiency decreased quite sharply (7-10 %-unit) as solid to liquid ratio increased until the ratio was 60 g/l, after which the decrease was slightly milder but steady. With the highest solid to liquid ratio (600 g/l),

only 15-18 % of the slag's calcium was dissolved. Consequently, low solid to liquid ratios (~ 20 g/l) in the extraction reactor should be favored and over 100 g/l should be avoided.

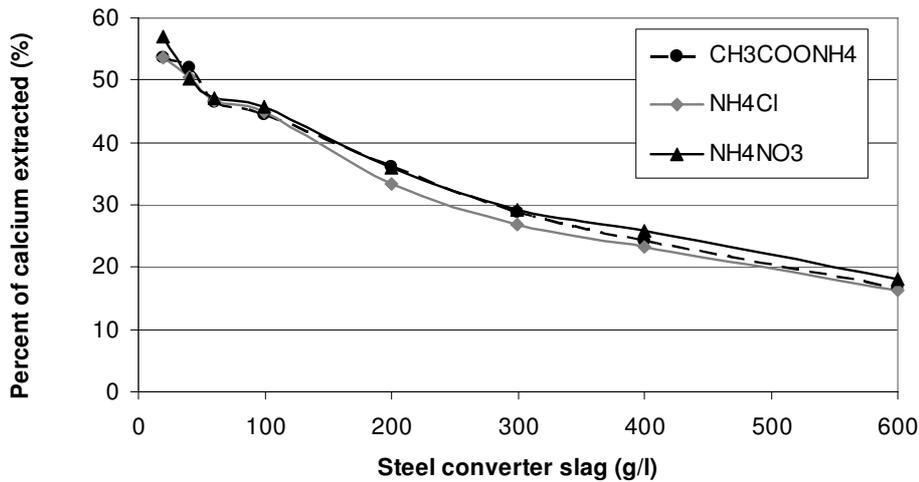


Figure 6. The effect of the solid to liquid ratio of the steel converter slag and used solvent on dissolution of calcium.

As the solid to liquid ratio increased from 20 g/l up to 100 g/l, the calcium concentration in the formed solution increased into about four fold (Figure 7). However, when the solid to liquid ratio increased from that up to 400 g/l, calcium concentration only doubled, after which the concentration increased only 1-2 g/l when the solid to liquid ratio was increased to 600 g/l (in total 43 g Ca/l at maximum). Calcium concentration seems to start stabilizing around 40 g calcium per l of solution, which corresponds to 1 mol of calcium per 2 moles of ammonium.

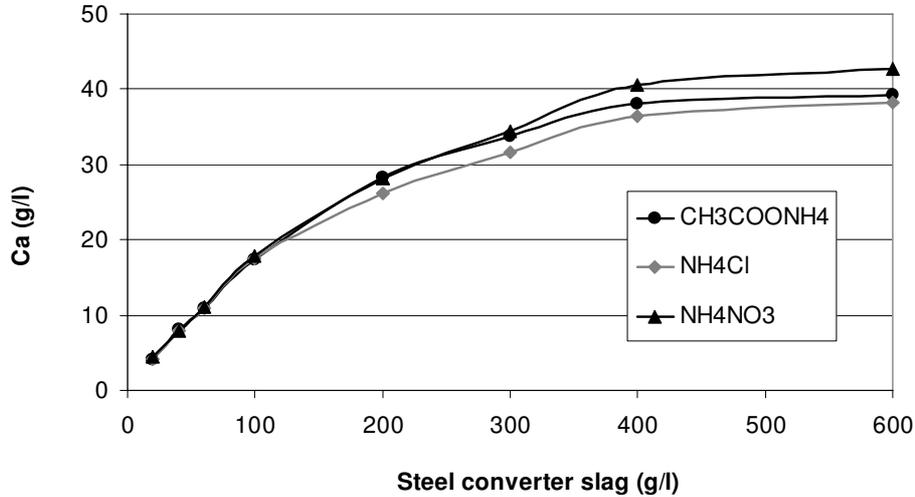


Figure 7. Calcium concentrations as function of solid to liquid ratio of the steel converter slag and used solvent.

4. Economical evaluation and CO₂ balance

Based on the solid to liquid ratio experiments, a 2 M aqueous solution of ammonium nitrate, acetate or chloride is able to hold about 40 g calcium per liter of solution. Assuming that at least 60 % of the steel converter slag's calcium can be dissolved (Figures 5 and 6 for example), if the slag is recycled enough many times and that CaO content of the slag is 45 wt-%, then 19 g calcium dissolves per 100 g slag. If we have 1 liter of 2 M solution, then 208 g slag is needed to form solution containing 40 g calcium per liter of solution. This amount should bind 44 g CO₂ and produce 100 g CaCO₃. Consequently, in order to bind 1 t of carbon dioxide, 4.7 t of steel converter slag is consumed, and 2.3 t CaCO₃ as well as 3.4 t residual slag is produced (Figure 8). Although the solvent is recycled, some make-up is needed [17]. Assuming that 5 % of the ammonium would be lost despite of the recycling, 39 kg of NH₃, 122 kg NH₄Cl, 182 kg of NH₄NO₃, or 175 kg of NH₄CH₃COO is consumed per ton of CO₂ sequestered in the carbonation step.

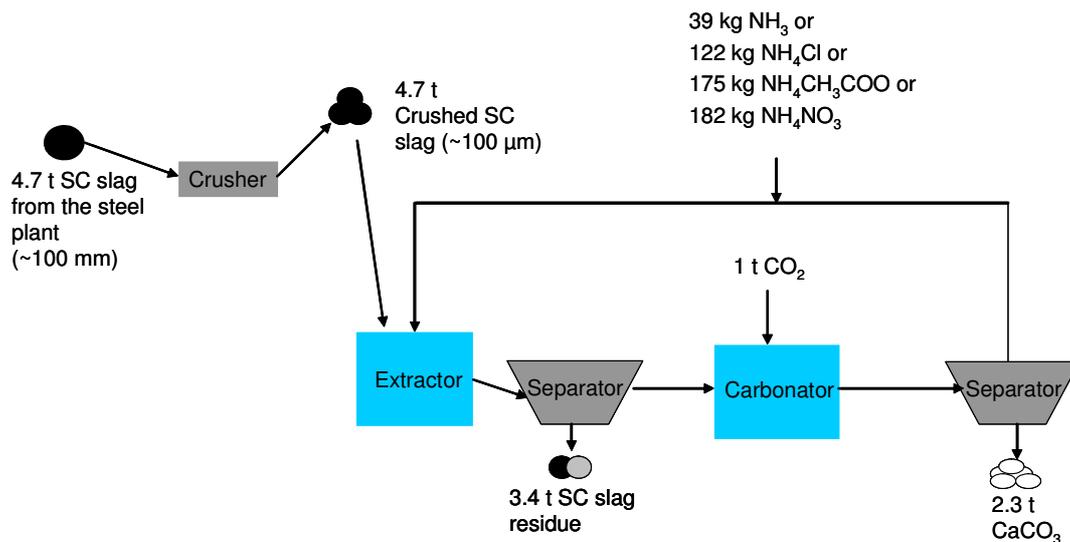


Figure 8. A process scheme for sequestering 1 t of CO₂ by producing pure calcium carbonate from steel converter (SC) slag using aqueous solution of ammonium salt as a solvent.

Based on the experiments where the effect of the slag's grain size was tested, the extraction rate was very fast (~5 min) with the smallest grain size (0-125 μm) and took about 40 minutes with 250-500 μm slag. With solid to liquid ratio of ten fold to these experiments, extraction could then roughly assumed to take about 50 minutes for 100 μm slag and about 400 minutes with 500 μm slag. At room temperature (20 °C) approximately 1 W of power is required to mix 200 g slag in 1 liter depending on the slag's particle size. Power requirement of the extraction step varies depending on the particle size, solution viscosity, solution density, impeller, and reactor dimensions for example [19]. Energy uptake of the extraction step can be estimated roughly to be within 5 to 200 kWh for 4.7 t slag depending on the particle size.

The power required to crush the slag can be calculated using Bond's equation (Eq.1):

$$W = W_i \left(\frac{10}{\sqrt{W_{P80}}} - \frac{10}{\sqrt{W_{F80}}} \right) \quad (1)$$

where W_{F80} and W_{P80} are the 80 % passing size of the feed and product, respectively, and W_i is the work index of the slag. By using the same work index for the slag as that in [10] (30.4 kWh/t), the power consumption for crushing 4.7 t slag is 140 kWh when slag is crushed to 100 μm and 60 kWh when crushed to only 500 μm .

The solution pH of the reported precipitation experiments [16] stabilized in about 50 minutes. Assuming that power requirements for mixing the formed calcium containing ammonium salt solution in the carbonation reactor would be similar to that of mixing the slag and the solvent, it can be roughly calculated that stirring 2.3 kg CaCO_3 in the carbonation reactor would require ~5 kWh of power.

Experimental results indicate that both reactions, i.e. extraction of calcium from the slag and carbonation of the formed calcium containing solution, are exothermic. As a result, no external heating should be needed. In addition, both reactions operate at low temperatures and at atmospheric pressure, and there seem to be no benefits of using elevated pressures.

CO_2 emissions from electricity generation in Finland are about 200 g/kWh on average [20]. Thus power required for crushing the slag, stirring the slag and solvent in the extraction reactor (at 20 °C), and for stirring the calcium carbonate particles and used solvent in the carbonation reactor (at 20 °C) in order to bind 1 ton of carbon dioxide, would generate 30 kg CO_2 if the slag is crushed to 100 μm and 50 kg CO_2 if slag is crushed to 500 μm . This method would therefore have clearly negative CO_2 emissions. In addition, if the produced CaCO_3 precipitate was used to replace conventionally manufactured PCC, then extra CO_2 emissions reductions were gained (0.22 t/t CaCO_3 replaced), as PCC is conventionally produced from limestone with a process that produces carbon dioxide [21].

By using price data collected for the ammonium salts in [22] and assuming that the price for a larger purchase of ammonium acetate is inline with the prices of smaller purchases, then it can be roughly calculated that use of NH_4Cl would cost 26 €/t CO_2 , use of NH_4NO_3 and use of $\text{NH}_4\text{CH}_3\text{COO}$ 40 €/t CO_2 (based on 5 % NH_3 losses/cycle). On the other hand, 227 €/t CO_2 could be earned by selling the produced calcium carbonate as PCC [23]. CO_2 emission allowance cost is ~13 €/t CO_2 in European CO_2 emission trading system [24], thus if allowances could be sold correspondingly to the sequestered CO_2 then an additional 13 €/t CO_2 were gained. Accordingly, the method has clear economical potential.

5. Conclusions

Grain size of the steel converter slag has a clear effect on the rate and extent of calcium extraction from the slag with the ammonium salt solvent. In order to avoid poor calcium extraction the grain size of the steel converter slag should not be increased to above 500 μm . A low solid to liquid ratio (~ 20 g/l) in the extraction reactor dissolves calcium efficiently. Further, solid to liquid ratios over 100 g/l should be avoided. The capacity of aqueous solution of ammonium salt to hold calcium can be described as molar ratio 2:1.

This method, which enables production of pure calcium carbonate from steel converter slag by using ammonium salts as a solvent, was calculated to have clearly negative CO_2 emissions. Therefore it can be used for storing CO_2 . In order to bind 1 t of carbon dioxide, 4.7 t of steel converter slag is consumed and 2.3 t CaCO_3 as well as 3.4 t residual slag is produced in this method. Storage capacity depends on the amount of steel converter slag available, thus this method has potential only for minor scale, yet significant, CO_2 storage. A clear advantage is, however, that it uses low value by-product as raw material and has

economical potential. Additional advantage is gained if the produced calcium carbonate precipitate is used to replace conventionally manufactured PCC. Future work will concentrate on finding the best equipment for ammonia vapor recovery, and the most suitable reactors and separators for the method.

Acknowledgement:

We thank Kimmo Kinnunen and Rita Kallio at Ruukki, Nigel Sanders at Specialty Minerals, as well as Hannu Revitzer at Aalto University School of Science and Technology, Department of Chemistry, for generously providing us with analysis services, and valuable discussions. We also thank Justin Salminen at Outotec for his contribution. We acknowledge the Finnish Funding Agency for Technology and Innovation (TEKES), Academy of Finland, The Graduate School for Energy Science and Technology (EST), Ruukki Productions, Specialty Minerals, and Fortum for financial support.

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