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# Case study for production of calcium carbonate from carbon dioxide in flue gases and steelmaking slag

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ABSTRACT

In this work, a concept for producing calcium carbonate from argon oxygen decarburisation (AOD) slag was further developed. In addition, its economic and environmental feasibility was evaluated. In the studied case, a stainless steel plant generating AOD slag and a paper plant requiring calcium carbonate are situated at a relatively close distance. The studied concept uses ammonium chloride as solvent for extracting calcium from the slag. In a subsequent step, the extracted calcium reacts with $CO_2$ in lime kiln flue gas and precipitates as calcium carbonate. First, an industrial application of the concept was designed including the following units: a reverse osmosis unit enabling better recovery of ammonium chloride, an evaporator for removing excess water from the process, and a scrubber for removing ammonia vapours from the flue gases. The process was modelled, after which the investment costs and operational costs were estimated, and its environmental footprint was assessed. The results indicate that the process could in its current stage of development be economic for producing calcium carbonate for replacing ground calcium carbonate used by paper mills. If the net annual profit would be used as payment on the investment, the payback period would be 2.2 years. As the process consumes $CO_2$ the process would have negative $CO_2$ emissions, avoiding 0.3 t $CO_2$ per tonne calcium carbonate produced.

## 1. Introduction

Steelmaking slags are rock-like by-products of the steelmaking industry, consisting principally of calcium, magnesium, and aluminium silicates, as well as iron and manganese. Depending on the steel production process, different slag types are produced. These slags are further refined into various types of slag products that are mostly applied in road construction. In Europe, over 60% of the steel slag produced is being utilised [10]. Still, almost 8 million tonnes per year is either put to interim storage or landfilled. Some slag types, such as ladle slag and slag from the argon oxygen decarburisation (AOD) process, primarily used in stainless steel making, consist of fine particles and contain chrome and other heavy metals, which makes these slag types more difficult materials to utilise [5,31].

Treating these materials with $CO_2$ has been studied, since these slag types contain high concentrations of calcium oxides and silicates that form calcium carbonate at relatively mild process conditions, offering a route for simultaneous valorisation of slag and storage of $CO_2$ [11,12,1]. However, the carbonation process affects the leaching behaviours differently depending on the type of slag, and in the case of AOD slag carbonation seems to increase the leachability of chromium ions [1].

In addition to treatment through direct carbonation with $CO_2$, various multi-step processes have been proposed and studied for extracting calcium from slags, ashes and wastes for capturing $CO_2$ by precipitation of calcium carbonate [21]. Calcium carbonate, both natural and synthetic, is the most commonly used filler material in papermaking [20]. The global consumption of filler grade calcium carbonate was 74 Mt in 2011, of which 60 Mt was ground calcium carbonate (GCC) and 14 Mt precipitated calcium carbonate (PCC) [23]. Of this, 39% was consumed in papermaking. GCC is mostly used as a pigment as an externally applied coating in coated papers. It is manufactured by simply grinding high quality limestone to small particle sizes. Therefore, GCC has a broad distribution of particle shapes and sizes, which reduces the optical performance of the material [4]. Synthesising calcium carbonate via precipitation reaction allows for control of the shape and size of the carbonate crystals, which optimises their optical properties for use in papermaking. PCC is normally brighter than GCC, since

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organic impurities and some metal oxides can be separated during the PCC production process [20]. In conventional production of synthetic, i.e. precipitated, calcium carbonate, flue gas containing $CO_2$ is bubbled though a hydrated lime slurry (calcium hydroxide), from which calcium carbonate precipitate. PCC production binds $CO_2$ as carbonate, but $CO_2$ is also emitted when limestone is calcined for providing lime for the process. The fuel required for calcination increases the $CO_2$ emissions, causing an average net emission of 0.2 t $CO_2$ per tonne $CaCO_3$ [18,9]. Also the production of GCC causes greenhouse gas emissions due to the energy required for mining and pulverisation of limestone (0.12 tonne $CO_2$ equivalent per tonne of ground calcium carbonate with a particle size $<22\,\mu m$; [25]. Both GCC and PCC production requires relatively pure limestone. For PCC manufacturing, the lime produced from limestone should typically contain more than 92% CaO, less than 2% MgO, less than 0.2% $Fe_2O_3$ and less than 0.05% sulphur [4]. PCC products typically used in the paper industry include scalenohedral calcite with an average diameter of 0.7–2 μm, which gives a high opacity.

An alternative production concept for PCC is under development that omits the need for fresh limestone and its calcination [6,15]. This concept has the potential to reduce $CO_2$ emissions and simultaneously utilize steelmaking slag. Similarly to the concept presented by Kodama et al. [13], calcium is first selectively dissolved from steelmaking slag in ammonium salt solutions in the extraction step:

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq) \tag{1}$$

$$CaO(s) + 2NH_4^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + 2NH_3(aq) \tag{2}$$

$$Ca(OH)_2(s) + 2NH_4^+(aq) \rightarrow Ca^{2+}(aq) + 2H_2O(l) + 2NH_3(aq) \tag{3}$$

$$Ca_2SiO_4(s) + 2NH_4^+(aq) \rightarrow Ca^{2+}(aq) + CaSiO_3(s) + H_2O(l) + 2NH_3(aq) \tag{4}$$

Kodama et al. [13] focuses on $CO_2$ capture and uses therefore a $CO_2$ absorption tower. However, carbonate precipitation is likely to be problematic in a spray tower (and especially in a packed bed column). In the present concept the focus is on PCC production, with careful control of temperature, residence time, and pH necessary for producing a PCC of certain shape and size [6,18]. Therefore, calcium carbonate is subsequently precipitated in a bubbling-type reactor (carbonator) by bubbling $CO_2$-containing flue gas through the solution:

$$2NH_3(aq) + Ca^{2+}(aq) + H_2O(l) + CO_2(g) \rightarrow CaCO_3(s) + 2NH_4^+(aq) \tag{5}$$

The calcium carbonate is separated by filtration and the solvent is returned to the extractor, as the ammonium salt is regenerated in the carbonator (Fig. 1). Both the calcium carbonate and the unreacted part of the slag from the extractor (slag residue) are washed in order to remove solvent remnants (ammonium salt). Laboratory experiments have shown that very pure $CaCO_3$ can be produced with main impurities being sulphur (0.02–0.08 wt-% S), magnesium (0.02–0.03 wt-% MgO), sodium (<0.03 wt-% $Na_2O$), silicon (<0.02 wt-% $SiO_2$) and iron (<0.02 wt-% $Fe_2O_3$; Mattila [18]). Similarly, the particle shape can be adjusted—both rhombohedral and scalenohedral calcite can be produced, as well as aragonite [17,18,32]. A laboratory pilot rig of the concept was recently completed, enabling production 5–10 kg batches of calcium carbonate [24].

In this work, a techno-economic assessment for producing calcium carbonate from steelmaking slag was made. The studied case consisted of a stainless steel plant generating slag and a paper plant consuming both PCC and GCC (ground calcium carbonate) situated at a relatively close distance. First, an industrial application of the concept was designed. The process was modelled, after which the investment costs and operational costs were estimated, and its environmental footprint was assessed. The process was modelled using Outotec HSC Chemistry software. The environmental footprint of the process was calculated with GaBi software.

## 2. Definition of the studied case

In this study, the cost and environmental impact of a new plant that would produce calcium carbonate from steelmaking slag for use in a paper mill were evaluated. The paper mill of this case study produces fine paper, for which it requires annually 60,000 t fine-ground (60% <1 μm, aragonite) GCC for coating purposes and 80,000 t scalenohedral PCC (1–2 μm median particle size, narrow distribution) as filler material. Steelmaking slag is produced at a stainless steel plant, which is located 40 km away from the paper mill. The steel plant produces ~280,000 t per year of air-cooled AOD slag and ladle slag that would be readily available for use for calcium carbonate production.

Work with the above-mentioned laboratory pilot has so far demonstrated production of rhombohedral calcite and aragonite from steelmaking slag, but attempts to produce scalenohedral calcite with the pilot has so far been unsuccessful [32,24]. Also, the calcium carbonate produced has a broad particle size distribution (<100 μm). Therefore, the case study targeted replacement of the GCC required by the paper mill with calcium carbonate produced from AOD slag.

Since the distance between the two plants is relatively short, previous calculations have shown that the cheapest alternative considering logistics is to build the process next to the steel mill and transport the produced calcium carbonate by trucks to the paper mill [26]. A lime kiln is currently available at the steel mill site, which provides a suitable $CO_2$ source for the new calcium carbonate production process (22% vol-$CO_2$, 80–120 °C, 100,000–140,000 t $CO_2$ per year). The current steel mill plant layout was

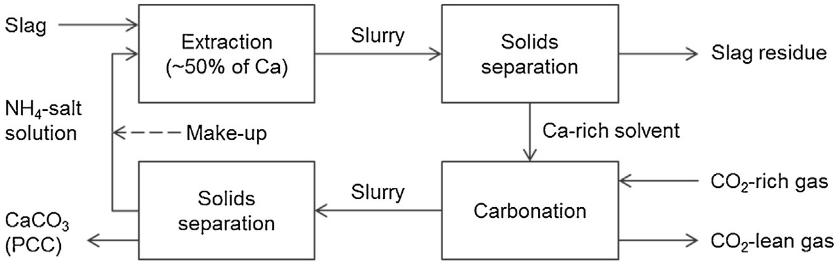

**Fig. 1.** The studied concept for producing calcium carbonate from $CO_2$-rich gas and slag.