



In-Situ CO₂ Capture in Magnesium Production Industrial Processes

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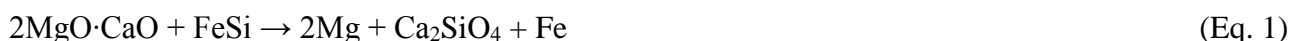
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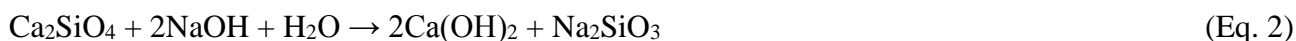
Abstract

The world's current primary magnesium production is mainly delivered via the Pidgeon Process. This process consists of the reaction of calcined dolomite ore (CaO·MgO) with FeSi as reductant at the reaction temperature of ~1200 °C and under a maximum of 1 mbar vacuum atmosphere (Eq. 1). As a result of this reaction, metallic magnesium and a reduction slag phase are obtained as a product of the process and as waste material, respectively [1-4]. Reduction slag is an inert waste material, consisting mainly of Ca₂SiO₄ (80-85% by wt.) with minor amounts of MgO and Fe₂O₃ [5]. In a primary magnesium production plant, dolomite calcination is one of the most important CO₂ sources along with other reduction units [6]. The global warming potential of a modern plant was calculated to be between 15.3 kg CO₂ and 23.6 kg CO₂ for per kg of produced Mg, where dolomite calcination is responsible for 3.5 kg CO₂ [7].



In this study, the valorisation of waste reduction slag from the Pidgeon Process was investigated for the first time as a potential route to obtain sorbent materials that could be used for in-situ CO₂ capture in the process, so the global warming potential of the plant could be reduced. The used slag contained 56.00% CaO, 12.95% MgO, 25.13% SiO₂ and 5.80% Fe₂O₃ by weight. The X-ray diffraction (XRD) pattern of the slag indicated that CaO and SiO₂ were in the form of Ca₂SiO₄. Because of the stable structure of Ca₂SiO₄, two different leaching routes under alkaline and acid conditions were applied in order to activate the slag and to obtain Ca(OH)₂-Mg(OH)₂ phases that could be used for CO₂ capture. The block diagrams of applied leaching routes are presented in Figure 1. For both routes, leaching experimental conditions and CO₂ capture capacities of derived sorbent materials were optimised.

In the alkaline media leaching route (route A, Figure 1), the slag phase (average particle size 41.6 µm) was reacted in NaOH media according to Eq. 2. Different stoichiometries from 1 to 5 times excess of NaOH, leaching times from 30 min to 540 min and leaching temperatures (50°C and 70°C) were investigated. Leaching conditions were optimised on basis of the maximum weight uptake of the filter cakes and were found to be 70°C, 360 minutes and 3 times excess NaOH stoichiometry. A Ca(OH)₂ phase was confirmed by XRD to be present in the filter cakes derived from the leaching protocol. The CO₂ uptake of the obtained filter cakes was tested by Thermogravimetric Analysis (TGA, TA Q500). For the optimum filter cake sample a maximum, i.e. equilibrium, capture capacity of 8.88 wt.% was measured at 650°C and under 92.4% (v/v) CO₂ atmosphere.



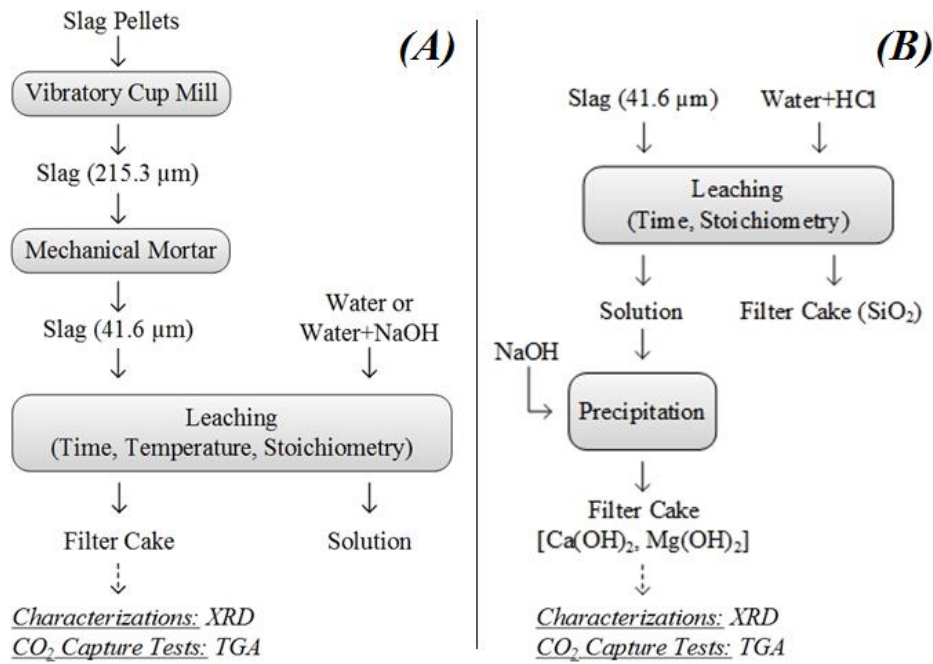
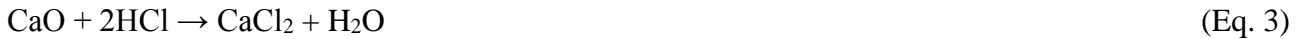


Figure 1. Investigated leaching routes; (A) alkaline media and (B) acid media.

In the acid media route (route B, Figure 1), Ca and Mg in the slag (average particle size 41.6 µm) were leached out into the solution by using HCl (Eq. 3 and Eq. 4).



Filter cakes mainly consisted of SiO_2 and, it is anticipated that they can be used as a source material for other syntheses such as those yielding Si-containing sorbents for CO_2 capture applications. On the other hand, Ca and Mg were precipitated from the pregnant solution by means of NaOH addition to filtered solutions (Eq. 5 and Eq. 6). Precipitates were characterised by using X-ray diffraction and, it was determined that the precipitate phase consisted of Ca(OH)_2 and Mg(OH)_2 . Optimum leaching conditions were determined as 1.3 times excess HCl stoichiometry and leaching duration of 15 minutes. The highest precipitation efficiency (90.98%) was obtained for the experiment conducted with a 1.1 times excess NaOH stoichiometry and duration of 60 minutes. The CO_2 capture capacity of the precipitated phases was also evaluated by TGA. The highest equilibrium CO_2 uptake of 45.00 wt.% was obtained at 700 °C under 92.4% (v/v) CO_2 atmosphere.

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