Energy-efficient mineral carbonation of blast furnace slag with high value-added products

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A B S T R A C T

Large quantities of CO_2 and blast furnace (BF) slag are discharged in the iron and steel industry. Mineral carbonation of blast furnace slag can offer substantial CO_2 emission reduction and comprehensive utilization of the solid waste. An energy- and cost-efficient mineral carbonation technology combined with NH_3 capturing CO_2 and simultaneous power generation is presented in this article. In this process, blast furnace slag was leached with recyclable ammonium bisulphate (ABS) to extract Ca, Mg and Al. Gaseous ammonia, which is produced during ammonium sulphate (AS) roasting for ABS regeneration, was used to capture CO_2 in flue gases using a CO_2 mineralization cell (CMC) to simultaneously generate NH_4HCO_3 and electricity. The extracted $CaSO_4$ and $MgSO_4$ reacted with an NH_4HCO_3/NH_3 solution to realize stable CO_2 sequestration while the extracted Al was recovered in the form of aluminium ammonium sulphate, which is a high value-added product. The process parameters and efficiency of the leaching, mineralization and Al recovery were investigated in detail in the present study. The results showed that approximately 91% of Mg and 97% of Ca in the BF slag were converted into corresponding carbonates and 76% of aluminium was recovered in the form of $NH_4Al(SO_4)_2 12H_2O$ with a purity of 99.6 wt.%. 3802 kg of blast furnace slag was required for sequestration of 1000 kg CO_2. A preliminary energy analysis indicated that although the present process was somewhat energy intensive without a net reduction of CO_2 emission, an improved process, which combined the NH_3 capturing CO_2 and simultaneous generating of electrical energy with a mixed ammonium sulphate (AS)+ blast furnace (BF) slag roasting instead of the separated ammonium sulphate roasting and ammonium bisulphate aqueous leaching of the blast furnace slag, was energy-efficient with a 567 kg net reduction of CO_2 emission during the sequestration of 1000 kg of CO_2. An economic analysis of the process demonstrated that the sales revenue of the primary products after deducting the cost of raw materials reached up to $427 for sequestration of 1000 kg of CO_2.

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1. Introduction

Carbon dioxide capture (utilization) and storage (CCS/CCUS) is one of the important options to inhibit the increase of CO_2 concentration in the atmospheric for climate change mitigation (Thambimuthu. et al., 2005; Iacobescu et al., 2016). Although the geological and oceanic sequestration of CO_2 has a huge potential, it requires proper geological conditions (e.g., depleted oil or gas fields) and geographical conditions (e.g., close to deep sea for the CO_2 sources) as well as the inevitable use of expensive equipment to monitor the possible CO_2 escape into the atmosphere for a very
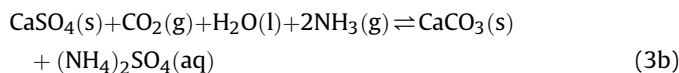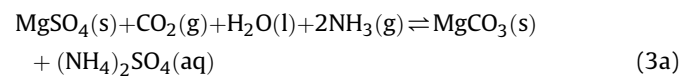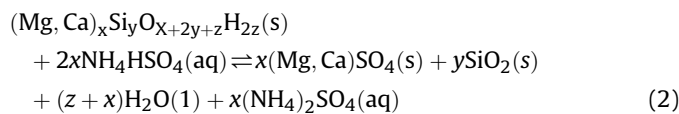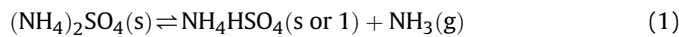
long time. CO_2 mineral sequestration mainly refers to isolation of CO_2 by carbonation of calcium and magnesium components in various minerals, especially in silicate minerals, forming stable carbonates. Silicate rocks are abundant in nature to the extent that, in theory, the potential for CO_2 storage by mineral carbonation is higher than of other CO_2 storage methods (Lackner, 2015).

Mineral sequestration is comprised of direct and indirect methods. The former simulates the process of nature weathering. Due to the slow reaction kinetics, a variety of strengthening methods, including activation pre-treatment of minerals (Santos et al., 2006), the use of high temperature and pressure (Huijgen et al., 2006; C.Y. Tai et al., 2006), and high-gravity methods (Chang et al., 2012), are used to accelerate the reaction process. However, the products of direct carbonation are generally low value-added mixtures. Indirect CO_2 mineralization ordinarily
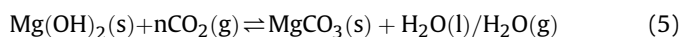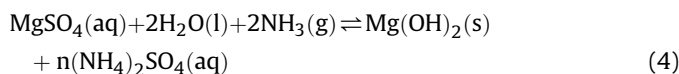
includes two successive steps: extraction of Ca and Mg components from minerals with an acidic or weakly acidic reagent and then carbonation of Ca- and Mg-rich solutions or solids with CO_2 in a basic or a weakly basic environment. Since the method has relatively mild reaction conditions, faster kinetics, high carbonation conversions of Ca and Mg, and purer, and thus more valuable, by-products (Teir et al., 2007, 2009; Zhao et al., 2015; Maroto-Valer et al., 2005; Said et al., 2013; Wang and Maroto-Valer, 2011; Sanna et al., 2013, 2014; Fagerlund et al., 2010, 2012; Eloneva et al., 2008; Kodama et al., 2008; Sanna et al., 2016; Ukwattage et al., 2017; Wang et al., 2018), it is now receiving widespread attention. The key issues faced with the method are how to elevate the energy efficiency and process economy. Up to now, many researches have chosen ammonium sulphate or ammonium bisulphate + NH_3 as the reagents (Wang and Maroto-Valer, 2011; Sanna et al., 2013, 2014), where these compounds firstly decompose minerals into Ca and Mg sulphates, and then are regenerated after the subsequent mineralization with the aid of NH_3 (Sanna et al., 2014). Equations (1)–(3) show the reactions.

$$(NH_4)_2SO_4(s) \rightleftharpoons NH_4HSO_4(s \text{ or } 1) + NH_3(g) \tag{1}$$

$$\begin{aligned}(Mg, Ca)_xSi_yO_{X+2y+z}H_{2z}(s) \\ + 2xNH_4HSO_4(aq) \rightleftharpoons x(Mg, Ca)SO_4(s) + ySiO_2(s) \\ + (z+x)H_2O(1) + x(NH_4)_2SO_4(aq)\end{aligned} \tag{2}$$

$$\begin{aligned}MgSO_4(s) + CO_2(g) + H_2O(l) + 2NH_3(g) \rightleftharpoons MgCO_3(s) \\ + (NH_4)_2SO_4(aq)\end{aligned} \tag{3a}$$

$$\begin{aligned}CaSO_4(s) + CO_2(g) + H_2O(l) + 2NH_3(g) \rightleftharpoons CaCO_3(s) \\ + (NH_4)_2SO_4(aq)\end{aligned} \tag{3b}$$

The extraction reaction (2) and mineralization reaction (3) are exothermic and thermodynamically spontaneous, while the regeneration reaction (1) is endothermic. Obviously, the energy consumption of the entire process can be significantly reduced by integration of the energy demands of these reactions. However, reaction (1) takes place usually between 250 and 300 °C, and reactions (3) proceed spontaneously only below 180 °C under standard conditions. Thus, the low-grade mineralization reaction enthalpy ($\Delta H^0_{20C} = -217$ kJ/mol-CO_2 for $MgSO_4$; $\Delta H^0_{20C} = -179$ kJ/mol-CO_2 for $CaSO_4$) cannot be utilized directly. Therefore, Ron Zevenhoven et al. divided the carbonation of $MgSO_4$ derived from serpentine into two steps (Fagerlund et al., 2012):

$$\begin{aligned}MgSO_4(aq) + 2H_2O(l) + 2NH_3(g) \rightleftharpoons Mg(OH)_2(s) \\ + n(NH_4)_2SO_4(aq)\end{aligned} \tag{4}$$

$$Mg(OH)_2(s) + nCO_2(g) \rightleftharpoons MgCO_3(s) + H_2O(l)/H_2O(g) \tag{5}$$

The changes in the enthalpy and Gibbs free energy as well as the maximal temperature for $\Delta G^0 < 0$ of reactions 3–5 were calculated

using HSC 5.0 (Autokumpu Company) and are listed in Table 1. Clearly, only the heat released in reaction 5 can be utilized directly by reaction 1 since the previous reaction might have a higher temperature than the latter. Therefore, they employed a fluidized bed to conduct reaction 5 under the conditions of 500 °C and 2 MPa. In theory, the maximum heat recovery is 22.6 kJ/mol-CO_2. However, this method needs to capture CO_2 from flue gases, compress it to > MPa, and can only be applied to magnesium silicate minerals since the reaction (3b) for carbonation of $CaSO_4$ from calcium silicate minerals can't be divided into two separate reactions similarly to the reactions (4) and (5).

Recently, Xie et al. proposed a CO_2 Mineralization Cell (CMC) to transform chemical energy, which is released during aqueous mineralization, into electrical energy, analysed the theory and conducted experimental verification (Xie et al., 2014, 2015). According to this approach, any chemical energy released during the carbonation reaction of a basic reactant (e.g., calcium hydroxide, sodium hydroxide and ammonia) using an acidic CO_2 can be transformed into electrical energy by the cell. However, the transformation cannot be completed since the reaction is a non-oxidation reduction reaction without an electron transfer. Hence, two hydrogen electrodes are designed in the CMC, and an ion exchange membrane is used to separate the cathode and anode areas. Basic reactants are introduced in the anode area, while CO_2 is injected into the cathode region. H_2 gas is consumed at the anode electrode and is equally regenerated at the cathode electrode to introduce electrons or a H_2-induced current in the external circuit of the cell. This design allows a stable current and electrical energy to be generated by the CMC cell. The CMC with NH_3 as a basic reactant is shown in Fig. 1.

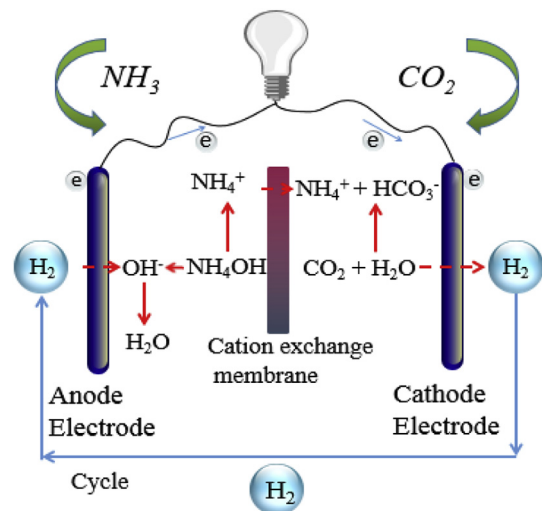Inspired by this research, reaction (3) in the present study can be designed as:

Fig. 1. Schematic illustration of the CMC described in this paper.

Table 1
Reaction enthalpies and thermodynamics calculated by the authors in the present study.

Reaction	$\Delta H^0_{25°C}$/(kJ/mol)	$\Delta H^0_{405°C}$/(kJ/mol)	Temperature for $\Delta G^0 < 0$ (°C)	$\Delta G^0_{25°C}$/(kJ/mol)
(3a)	−216.8	—	235	−75.0
(4)	−153.2	—	255	−53.6
(5)	−63.6(a)	−22.6(b)	495	−21.4
(7)	−132.4	—	200	−55.4
(8a)	−89.8	—	No limit	−54.0
(8b)	−51.6	—	No limit	−19.2