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Phase diagrams of the $MgSO_4$-$Al_2(SO_4)_3$-$(NH_4)_2SO_4$-H_2O system at 25 and 55 °C and their application in mineral carbonation

Weizao Liu [a], Fanqi Meng [a], Guanrun Chu [a], Liming Wang [b], Hairong Yue [a], Bin Liang [a], Chun Li [a], *

[a] *School of Chemical Engineering, Sichuan University, Chengdu, 610065, China*
[b] *Sichuan University, Hi-Tech Group Co., Ltd., Chengdu, 610065, China*

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ABSTRACT

A route for the indirect mineral carbonation of blast furnace slag using $(NH_4)_2SO_4$ as a recyclable reagent has recently been proposed. The main challenges associated with this route are reducing its energy consumption and improving its cost-efficiency. In this process, the recycling of $(NH_4)_2SO_4$ by evaporation of the carbonation liquor make up a large proportion of the total energy consumption. Thus, controlling the water dosage during leaching of the products of roasting the blast furnace slag with $(NH_4)_2SO_4$, which are mainly various sulfates of Ca, Mg, Al, and NH_4^+, is of great importance. In this study, the solubilities of the quaternary $MgSO_4$-$Al_2(SO_4)_3$-$(NH_4)_2SO_4$-H_2O system were measured at 25 and 55 °C using the isothermal method. The resulting phase diagrams are instructive for determining the lowest liquid-to-solid ratio required for leaching and for recovery of the value-added byproduct, ammonium alum, from the leachate. The results show that the crystalline region of $NH_4Al(SO_4)_2 \cdot 12H_2O$ dominates in the phase diagrams, indicating that it is easily crystallized out and that the use of this route for the separation of aluminum as ammonium alum is feasible. The liquid-to-solid ratios for the leaching unit were calculated to be 4.55 and 1.97 mL/g at 25 and 55 °C, respectively. The liquid-to-solid ratio at 55 °C was reduced by 56.7% compared to the ratio at 25 °C.

1. Introduction

The anthropogenic emission of greenhouse gases, especially CO_2, is among the greatest hazards to Earth's climate and ecosystems [1]. It is estimated that the CO_2 concentration will have risen from 280 ppm in the 1750s to over 450 ppm in the 2050s. Thus, mitigating the increase in the atmospheric CO_2 concentration is imperative. Carbon dioxide capture, utilization, and storage (CCUS) is one of the main strategies to reduce CO_2 emissions, and consists of geological storage, oceanic storage, and mineral storage. However, geological storage is a very location-dependent technology and entails high post-storage monitoring costs, and oceanic storage may destroy the marine ecosystem. CO_2 mineral storage [2–4] mainly utilizes the reactions of carbon dioxide with calcium and magnesium silicate minerals to form stable carbonates ($CaCO_3$ and $MgCO_3$), and thus can permanently store CO_2. Compared with other storage methods, mineral storage not only avoids long-term and expensive CO_2 leak monitoring, but also produces value-added byproducts.

CO_2 mineral storage processes can be divided into direct and indirect mineral carbonation methods. In the latter processes, an acidic or weakly acidic reagent is usually used to digest the minerals. The extracted Ca^{2+} or Mg^{2+} is then reacted with CO_2 in a basic or a weakly basic environment to achieve the sequestration of CO_2. The extractants ammonium sulfate (AS) and ammonium bisulfate (ABS) + NH_3 have demonstrated excellent recyclability [5–8], and have been reported to be very effective in the mineral carbonation of serpentine [9], olivine [10], amphibole [10], pyroxene [10], concrete aggregate [11], and blast furnace slag [12,13].

Fig. 1 shows a schematic flowchart of the indirect mineral carbonation of blast furnace slag with $(NH_4)_2SO_4$ in our previous study [12]. In this process, blast furnace slag was roasted together

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* Corresponding author.
E-mail address: lic@scu.edu.cn (C. Li).

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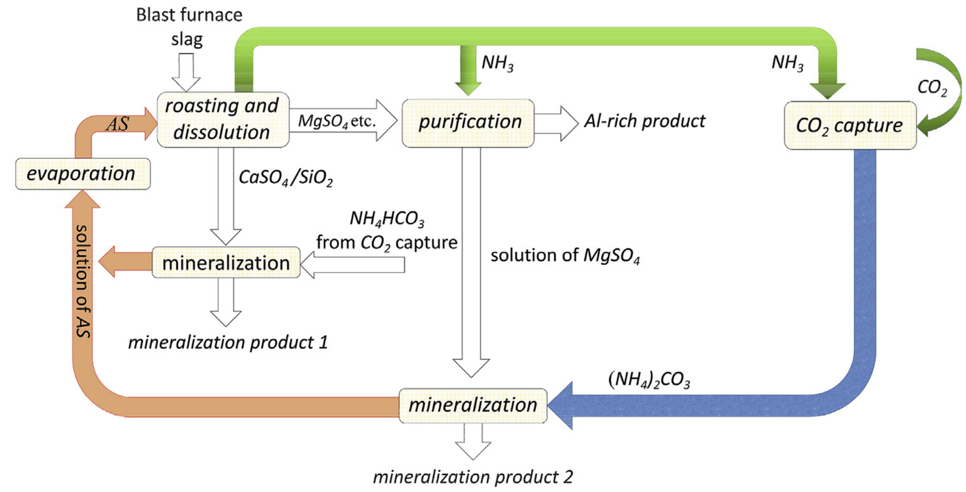

Fig. 1. Schematic illustration of mineral carbonation with blast furnace slag.

Table 1
Chemicals, source, CAS number, and purity.

Chemical name	Purity	Source	CAS number
Magnesium sulfate heptahydrate	>99 wt.%	Chron Chemicals	10034-99-8
Ammonium sulfate	>99 wt.%	Chron Chemicals	7783-20-2
Aluminum sulfate octadecahydrate	>99 wt.%	Chron Chemicals	7784-31-8
Sulfuric acid	95–98 wt.%	Chron Chemicals	7664-93-9
Sodium hydroxide	>98 wt.%	Chron Chemicals	1310-73-2

with AS at 300–400 °C. The main reactions in this process can be expressed as follows:

$$Ca_2MgSi_2O_7\ (s) + 3.5(NH_4)_2SO_4\ (s) \rightarrow 2CaSO_4\ (s) + 0.5(NH_4)_2Mg_2(SO_4)_3(s) + 2SiO_2\ (s) + 6NH_3\ (g) + 3H_2O\ (g)$$

$$Ca_2Al_2SiO_7\ (s) + 6(NH_4)_2SO_4\ (s) \rightarrow 2CaSO_4\ (s) + 2NH_4Al(SO_4)_2\ (s) + SiO_2\ (s) + 10NH_3\ (g)$$

The roasted slag was then leached in water, yielding a complex leachate solution consisting of $MgSO_4$, $Al_2(SO_4)_3$, and $(NH_4)_2SO_4$ and a leaching residue containing $CaSO_4$ and SiO_2. The NH_3-containing flue gas emitted during the roasting was bubbled into the leachate to precipitate aluminum, yielding a 44% content of the Al-rich byproduct of Al_2O_3. The mother liquor thus obtained, which is rich in $MgSO_4$ and $(NH_4)_2SO_4$, and the leaching residue were carbonated separately with NH_4HCO_3. Finally, the Mg-depleted mother liquor was evaporated to recover and recycle the $(NH_4)_2SO_4$. The main challenges associated with this route are reducing its energy consumption and improving its cost-

Table 2
Solubility data for the ternary systems $Al_2(SO_4)_3$-$(NH_4)_2SO_4$-H_2O, $MgSO_4$-$(NH_4)_2SO_4$-H_2O, and $Al_2(SO_4)_3$-$MgSO_4$-H_2O at 55 °C and 0.095 ± 0.001 MPa.[a]

$Al_2(SO_4)_3$-$(NH_4)_2SO_4$-H_2O			$MgSO_4$-$(NH_4)_2SO_4$-H_2O			$Al_2(SO_4)_3$-$MgSO_4$-H_2O		
Composition of the liquid phase/wt.%		Equilibrium solid phase[b]	Composition of the liquid phase/wt.%		Equilibrium solid phase[b]	Composition of the liquid phase/wt.%		Equilibrium solid phase[b]
$(NH_4)_2SO_4$	$Al_2(SO_4)_3$		$(NH_4)_2SO_4$	$MgSO_4$		$MgSO_4$	$Al_2(SO_4)_3$	
0	30.86	A16	0.00	34.07	M6	34.07	0	M6
0.37	30.37	A16 + AN	2.60	33.30	MN + M6	28.08	5.68	M6
0.54	25.6	AN	4.03	28.75	MN	24.03	10.42	M6
1.34	18	AN	4.83	26.15	MN	20.40	15.06	M6
3.53	12.33	AN	6.64	21.77	MN	19.02	16.41	M6 + M22
6.69	8.42	AN	8.33	18.22	MN	17.48	17.60	M22
9.83	6.53	AN	11.65	12.77	MN	15.76	19.09	M22 + A16
13.73	5.26	AN	18.10	7.20	MN	14.06	20.43	A16
17.11	4.81	AN	24.89	4.02	MN	10.10	22.46	A16
20.89	4.49	AN	31.99	2.39	MN	5.65	25.65	A16
23.11	4.25	AN	36.88	1.58	MN	0.00	30.86	A16
26.06	4.13	AN	41.26	1.10	MN			
33	3.75	AN	45.89	0.76	MN + N			
38.9	3.69	AN	46.23	0.00	N			
42.95	3.58	AN + N						
46.23	0	N						

[a] Standard uncertainties (abbreviated as u) for temperature and pressure are $u(T) = 0.2$ °C and $u(P) = 0.001$ MPa; standard uncertainties $u(w(X)) = 0.18$ wt.%, where X can be $MgSO_4$, $Al_2(SO_4)_3$, or $(NH_4)_2SO_4$.
[b] A16 = $Al_2(SO_4)_3 \cdot 16H_2O$, AN = $NH_4Al(SO_4)_2 \cdot 12H_2O$, M6 = $MgSO_4 \cdot 6H_2O$, MN = $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, M22 = $MgAl_2(SO_4)_4 \cdot 22H_2O$, N = $(NH_4)_2SO_4$.