



## Experiment and kinetic modeling for leaching of blast furnace slag using ligand



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### ABSTRACT

Blast furnace (BF) slag is recognized as an excellent source of precipitated calcium carbonate (PCC) and CO<sub>2</sub> sequestering agents because it contains a significant amount of calcium. The pH-swing method is a promising process for commercialization of the slag carbonation process among the other indirect carbonation methods due to the high selectivity of calcium extraction and production of high quality PCC. In this study, ligand-based solvents, such as acetic acid, gluconic acid, and citric acid, were examined as new leachates for the extraction step in the pH-swing process. Citric acid showed the highest efficiency, and the extraction efficiencies were estimated based on particle size distribution, concentration of solvent, solid-to-liquid ratio, stirring speed, and temperature. The calcium extraction rate increased with decreasing particle size and S/L ratio and with increasing concentration of solvent and stirring speed. However, extraction efficiency decreased significantly at high temperature because calcium-citrate complexes were precipitated. Along with the experiments, a kinetic study based on the shrinking core model was carried out at temperatures lower than 30 °C. Our results demonstrated that the extraction process was controlled by a surface chemical reaction, and the activation energy was estimated to be 50.74 kJ mol<sup>-1</sup>.

### 1. Introduction

Industrial waste can reduce the cost of CO<sub>2</sub> mineralization by reducing mining and raw materials and because these wastes are much more reactive than natural minerals [1]. Slag is a by-product of the steelmaking industry and contains around 40% calcium oxides, which are produced at a rate of about 0.13–0.20 ton per ton of steel manufactured. Since slag is abundant, and 1.97 tons of CO<sub>2</sub> are emitted from steel production facilities for every ton of crude steel manufactured, it is considered to be a suitable material for ex situ CO<sub>2</sub> mineralization [2]. The reaction of aqueous CO<sub>2</sub> and calcium ions leached from the slag can produce precipitated calcium carbonate (PCC), which is used in various industries including paper and plastics [3]. Thus, CO<sub>2</sub> mineralization by the PCC process with steel slag has been actively studied recently because it produces a valuable product and reduces the amount of CO<sub>2</sub> generated from the steelmaking industry [4].

The pH-swing process enhances PCC production from slag by maintaining a low pH in the extraction step and a relatively high pH in the carbonation step. Many researchers have attempted to exploit pH-swing processes using various types of solvents with slag [5–11]. Strong acids are not appropriate as leaching agents because they require large

amounts of base materials, typically 2.4 tonne consumed per tonne of CO<sub>2</sub> sequestered [12]. The extraction efficiency of ammonium salt-based solvents is roughly 50% with 1 M solvent and 20 g solid-to-1 L liquid conditions, as shown in Table 1. Despite the existing studies on the pH-swing process with ammonium salt-based solvents, the key issues of the overall process (decreasing consumption of chemicals and increasing calcium extraction rate) still need to be investigated to commercialize the slag carbonation process [13].

Alternative solvents appropriate for pH-swing can be found in hydrometallurgy, wherein ligand solvents are chosen as chelating agents for leaching heavy metals from industrial wastes or ores in the aqueous phase because of their good efficiency and high selectivity for the target metal ion. Vuyyuru et al. and Chauhan et al. used ethylenediaminetetraacetic acid (EDTA) as a chelating agent to selectively extract cobalt/molybdenum and nickel, respectively, from spent catalyst [14,15]. They suggested that the particle size distribution of spent catalyst, stirring speed, temperature, concentration of ligand in the solvent, and solid to liquid ratio are major variables that influence selective extraction. Zhang et al. found that dissolution of Fe ions is greatly enhanced by gluconic acid because ligand ions in chelating agents (gluconate) form a thermodynamically stable metal-ligand complex with

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Nomenclature		PCC	precipitated calcium carbonate
BF	blast furnace	PTFE	polytetrafluoroethylene
$C_i$	molar concentration of component $i$ ( $\text{mol L}^{-1}$ )	$R$	gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
$\text{Cit}^{3-}$	fully dissociated citrate anion in aqueous phase	$R^2$	coefficient of correlation (adjusted R-squared)
$E_a$	activation energy ( $\text{kJ mol}^{-1}$ )	$S$	solid-to-liquid ratio
$k$	apparent reaction rate constant ( $\text{min}^{-1}$ )	SCM	shrinking core model
$k_0$	pre-exponential factor ( $\text{min}^{-1}$ )	$t$	residence time in a reactor (min)
$k_c$	apparent reaction rate constant of surface chemical reaction-controlled process ( $\text{min}^{-1}$ )	$T$	temperature (K)
$k_d$	apparent reaction rate constant of diffusion-controlled process ( $\text{min}^{-1}$ )	$V$	volume of solution (liter)
		$W_i$	mass fraction of component $i$
		$X$	reaction conversion
		$\rho_i$	molar density of component $i$ ( $\text{mol L}^{-1}$ )

**Table 1**  
Performance of ammonium salt-based solvents for the pH-swing process in the literature.

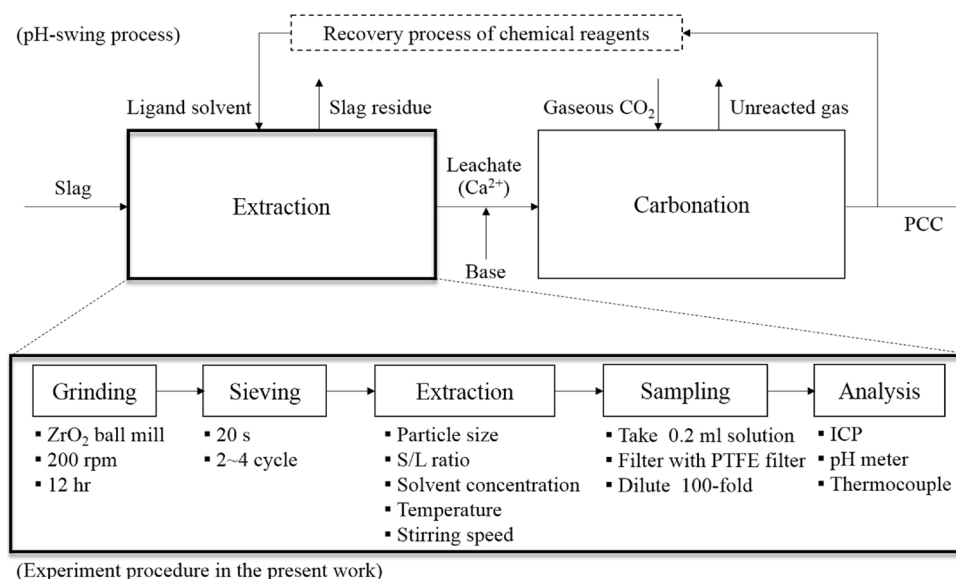
Slag type	Solvents	Particle size ( $\mu\text{m}$ )	S/L ratio ( $\text{g L}^{-1}$ )	Solvent concentration (M)	Stirring speed (rpm)	T ( $^{\circ}\text{C}$ )	Extraction time (h)	Ca extraction efficiency (%)	
Mixture of BF and steelmaking slag	$\text{NH}_4\text{Cl}$	< 63	62.925	1	300	80	1	59.5	[5]
Steel slag	$\text{NH}_4\text{Cl}$ $\text{NH}_4\text{NO}_3$	125–250	20	0.5	150–200	30	2	–	[6]
Steel making slag	$\text{NH}_4\text{Cl}$	38–250	100	2	–	60	2	52.47	[7]
Steel making slag	$\text{NH}_4\text{Cl}$	< 150	100	2	600	30	2	34.2	[8]
Granulated slag	$\text{NH}_4\text{NO}_3$	–	10	1	600	30	0.5	37	[9]
	$\text{NH}_4\text{Cl}$							11.4	
	$\text{CH}_3\text{COONH}_4$							11	
	$(\text{NH}_4)_2\text{SO}_4$							12.7	
Steel making slag	$\text{NH}_4\text{NO}_3$	74–125	20	1	100	RT	2	16.9	[10]
	$\text{NH}_4\text{Cl}$							50–80	
	$\text{CH}_3\text{COONH}_4$							54	
Steel making slag	$\text{NH}_4\text{NO}_3$	74–125	20	1	–	–	2	50	[11]
	$\text{CH}_3\text{COONH}_4$							54	
	$\text{NH}_4\text{Cl}$							45	

target metal ions [16]. Fredd and Fogler investigated the mechanism of calcium dissolution from calcium carbonate by chelating agents, and they demonstrated that calcium dissolution is caused by hydrogen attack and chelating effects [17].

Hydrogen attack is expected to improve the rate of slag leaching in acidic conditions, and chelating effects will intensify the selective leaching even in moderate pH conditions. Therefore, the pH at the end

of the extraction reaction shifts to a more basic region. This can be a remedy for reducing consumption of chemicals in the overall process. In this study, extraction experiments of several ligand candidates were carried out, and leaching characteristics of the most efficient solvent among the candidates were investigated to evaluate the usage of ligand solvents for slag carbonation to produce PCC.

Acetic acid, gluconic acid, and citric acid are ligand solvent



**Fig. 1.** Schematic diagram of the pH-swing process and the overall procedure used in the present work.

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