

# Utilization of steel-making slag for the uptake of ammonium and phosphate ions from aqueous solution

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Received 5 June 2007; received in revised form 4 December 2007; accepted 4 December 2007

Available online 14 December 2007

## Abstract

Steel-making slag, a waste by-product of the Steel Industry, constitutes a major disposal problem. In the present study, excellent adsorbent materials for reducing eutrophication in wastewaters have been prepared from this slag. Heated samples of acid-treated slag and mixtures of slag with kaolinite and  $\text{Al}(\text{OH})_3$  were examined to determine their uptake capacities for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  from aqueous solutions. In general, the equilibrium pH of the solution increased in comparison to initial pH with the uptake of target ions, the sample activated slag- $\text{Al}(\text{OH})_3$  showing the smallest change. The highest  $\text{PO}_4^{3-}$  uptake capacity was obtained with the slag- $\text{Al}(\text{OH})_3$  mixture heated at 900 °C whereas the highest uptake of  $\text{NH}_4^+$  was found in the slag- $\text{Al}(\text{OH})_3$  mixture heated at 800 °C. The uptake rates for  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  by the slag- $\text{Al}(\text{OH})_3$  mixture heated at 900 °C were 2.91 and 0.65  $\mu\text{mol}/(\text{g min})$ , respectively. It was shown that heating slag composites prior to incorporation into wastewater treatment filters resulted in an increased degree of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake.

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**Keywords:** Acid-treated slag; Slag- $\text{Al}(\text{OH})_3$ ; Slag-kaolinite;  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake

## 1. Introduction

The aim of the present research is to conserve natural resources by increasing the usefulness of industrial by-products in protecting the environment, improving its quality, protecting human health and guaranteeing the cautious and efficient use of natural resources.

Several million tonnes of dried sewage sludge, paper sludge, fly ash, construction and demolition waste; slag and other mineral wastes are produced every year. These wastes are mostly disposed of by burning with only a small amount used as a soil conditioner [1]. During the last few decades, the disposal of waste has become a problem of increasing importance. In densely populated industrial countries, regulations to protect the environment and the potential risk to groundwater quality have led in recent years to a reduction in the amount of avail-

able landfill space and a rise in the cost of land disposal of waste.

Since surface water sources are becoming widely polluted, groundwater is becoming increasingly important as a fresh water source for various purposes. Consequently, some areas have faced ground subsidence as a result of over-withdrawal of groundwater. Surface water contains considerable quantities of organic matter, nitrogen, and phosphorus, which degrade the water quality. Lake eutrophication results from nutrient enrichment from natural and anthropogenic sources and has an unfavorable impact on water quality. High concentrations of biologically available P often increase primary production and may favor the dominance of cyano-bacteria, with negative economic impacts on in-lake fisheries or recreational use [2]. It is therefore apparent that appropriate wastewater treatment processes are needed.

A number of physical, chemical, and biological methods have been applied to wastewater treatment. Solid removal is accomplished by sedimentation, sand filtration, or mechanical filtration. Biological processes such as submerged biofilters, trickling filters, rotating biological contactors and fluidized bed reactors are employed for oxidation of organic matter, nitrification, or denitrification [3]. Column experiments to study

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phosphorus removal by slag under dynamic conditions and the mathematical modeling of these systems have been reported [4].

Slag is a by-product of many industries, including metal melting and coal processing. Steel-making slag is produced during the separation of the molten steel from impurities in steel-making furnaces. The slag occurs as a molten liquid and is a complex solution of silicates and oxides that solidifies upon cooling. There are several types of steel-making slag produced during the steel-making process. These different slags are referred to as furnace or tap slag, raker slag, synthetic or ladle slags, and pit or cleanout slag. Because of the variations in the grade of steel products and differences in the furnaces of steel producing plants, the chemical composition of all steel-making slags are not the same. Steel-making slag is mainly composed of the oxides of calcium, silicon, iron and manganese. Though steel-making slag is considered to be essential in the production of iron, it has little or no use after serving its purpose in the metal refining process. Both commercial and synthetic slags have been utilized in various other ways, including cement manufacturing, road building applications, and in the preparation of calcium silicate hydrate and hydrotalcite by alkaline activation [1,5–7]. The environmental impact of ferrochrome slag has been studied and the leaching of metal ions to ground water was found to be slight [8]. The removal of heavy metal ions such as Pb, Ni, Cu, Zn and Cr from slag have been found to depend mainly on the replacement of  $\text{Ca}^{2+}$  by the target heavy metal ions [9–13]. The adsorption of ammonium and phosphate ions from seawater by acid-treated slag [14] and from water by thermally activated as-received steel-making slag [11] have been studied. The sorption of phosphorus from aqueous solutions by crystalline and amorphous blast furnace slags have found pseudo-second-order type reactions and followed the Langmuir adsorption isotherm [15].

Potassium aluminosilicate prepared from kaolinite and KOH is reported to have the ability to simultaneously take up both ammonium and phosphate ions at pH conditions from 5 to 10 [16]. It has been reported that the alumina surface of the porous material is preferable for the uptake of oxyanions such as  $\text{PO}_4^{3-}$  while a porous silica surface enhances the uptake of ammonium ions by capturing them in the silica framework [16,17].

The present study is an attempt to prepare silica, silica and alumina, and alumina-rich samples from steel-making slags by acid treatment and mixing with either kaolinite (from Georgia, USA) or synthetic  $\text{Al}(\text{OH})_3$  (from Wako, Japan). These samples were activated by grinding and heating at various temperatures. Their simultaneous uptake of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  was then investigated as a function of heating temperature, initial concentration and reaction time.

## 2. Experimental

### 2.1. Sample preparation and characterization

The slag was obtained from the Oita factory of the Nippon Steel Co., Oita, Japan in the form of cm-sized chunks which were first gently crushed in an iron mortar then ground in an

alumina mortar and pestle to a size of 10–20  $\mu\text{m}$ . The slag was treated with HCl in two ways: 1 g of slag was treated with 100 ml 0.1 M HCl (slag-0.1 HCl) and with 1 M HCl for 24 h, maintaining the final pH at 7 (slag-HCl-pH7) using NaOH solution in titrator (716 DMS Metrohom-Shibata, Japan). All the samples were washed separately, oven-dried and heated at 800 °C for 24 h. In other experiments the as-received slag was mixed with either kaolinite or  $\text{Al}(\text{OH})_3$  (1:1 and 4:3 mass ratios, respectively) and heated at 800 °C for 24 h (the use of heating temperatures of 700–1000 °C was carried out on the mixture of slag and  $\text{Al}(\text{OH})_3$  because of its superior phosphate uptake performance). The mixing ratios of kaolinite and  $\text{Al}(\text{OH})_3$  with slag were selected so as to produce silica-alumina and alumina-rich samples. The final pH of the slag-0.1 HCl-800, slag-HCl-pH7-800, slag-kaolinite-800, slag- $\text{Al}(\text{OH})_3$ -800 treated with distilled water was measured using a pH meter.

Powder X-ray diffraction (XRD) patterns were obtained using a diffractometer (XRD-6100, Shimadzu, Japan) with monochromated Cu  $\text{K}\alpha$  radiation. The chemical composition of the sample was analyzed by X-ray fluorescence (RIX2000, Rigaku, Japan).

### 2.2. Uptake experiments

The simultaneous  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake experiments, the slag-0.1 HCl-800, slag-HCl-pH7-800, slag-kaolinite-800 and slag- $\text{Al}(\text{OH})_3$ -800 samples, were performed under the following conditions; temperature: 25 °C, sample/solution ratio: 0.1 g/50 ml, initial concentration of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  (from  $\text{NH}_4\text{H}_2\text{PO}_4$  solution): 10 mmol/l, reaction time: 24 h. In order to determine the final pH of the water in which these samples had been immersed in the absence of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ , the samples were placed separately in distilled water with a sample/water ratio of 0.1 g/50 ml at room temperature and stirred for 24 h. The final pH of these samples in water was determined separately. Simultaneous  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake experiments were carried out on the slag- $\text{Al}(\text{OH})_3$  sample at temperatures ranging from 700 to 1000 °C. Simultaneous  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake experiments with variations of initial  $\text{NH}_4\text{H}_2\text{PO}_4$  concentration 2, 4, 6 and 10 mmol/l and reaction time 10, 20, 30, 40 and 60 min were also carried out on one slag- $\text{Al}(\text{OH})_3$  sample heated at 900 °C.

The pH values were measured immediately after placing the sample into the solution (initial pH) and after the reaction (the equilibrium pH). After the uptake experiments, the samples were centrifuged at 8000 rpm for 20 min, washed several times with de-ionized water. The solid samples were dried in an oven at 110 °C overnight and XRD patterns were taken. The separated solutions were chemically analyzed for  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  by ion chromatograph (IA-200, DKK TOA, Japan). The  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake data were separately determined three times and the average values are reported here. The uptake %, and uptake (mmol/g) were calculated using the following formulae:

$$\text{Uptake (\%)} = \frac{C_i - C_f}{C_i} \times 100,$$

Table 1  
Chemical compositions (mass%) of samples acid-treated slags and mixtures of slag with kaolinite and Al(OH)<sub>3</sub> heated at 800 °C whereas this is not done for the rest of the tables

Sample	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	TiO <sub>2</sub>
Slag-Al(OH) <sub>3</sub> 800 °C	22.4	53.5	9.4	8.7	2.7	1.3	0.8	0.8	0.2	0.2	–
Slag-0.1 HCl-800	38.5	5.4	23.9	17.8	5.9	5.0	2.1	–	–	0.3	1.1
Slag-HCl-pH-7–800	29.5	5.7	26.0	22.5	6.8	4.9	2.8	–	0.1	0.2	1.5
Slag-kaolinite 800 °C	14.1	36.0	39.1	6.2	1.9	0.6	0.4	0.3	0.1	0.2	1.1

$$\text{Uptake (nmol/g)} = \frac{(C_i - C_f)V}{M}$$

where  $C_i$ ,  $C_f$ ,  $V$  and  $M$  are the initial concentration (mmol/l), final concentration (mmol/l), volume of solution (l) and mass of sample (g), respectively.

### 3. Results and discussion

#### 3.1. Characterization of the samples

The average chemical compositions of the acid treated slags and mixtures of slag with kaolinite and Al(OH)<sub>3</sub> are listed in Table 1. In addition to the major constituents, the samples also contain small amounts of P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and SO<sub>3</sub>.

The XRD patterns of these samples are shown in Figs. 1 and 2, respectively. All the samples contain larnite (β-Ca<sub>2</sub>SiO<sub>4</sub>, JCPDS Card No. 33-302) and manganese oxide (Mn<sub>3</sub>O<sub>4</sub>, JCPDS Card No. 13-162). In addition, the slag-kaolinite sample heated at 800 °C contained a small amount of calcium manganese oxide (CaMn<sub>2</sub>O<sub>4</sub>, JCPDS Card No. 19-236). The larnite was present initially in the steel-making slag while the manganese oxide is the result of the crystallization of amorphous manganese oxide on heating to >600 °C [11]. The weak peak of calcium manganese oxide is thought to be due to the solid-state reaction of calcium and manganese oxides originally present in the slag sample.

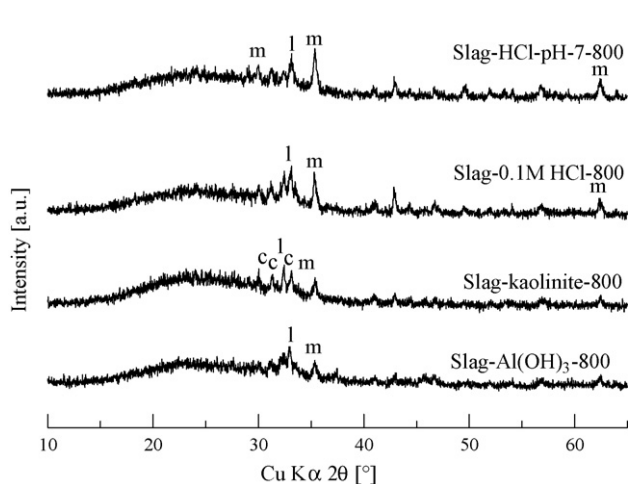


Fig. 1. XRD patterns of the acid-treated slags and mixtures of slag with kaolinite and Al(OH)<sub>3</sub> heated at 800 °C. The symbols are as follows: c: CaMn<sub>2</sub>O<sub>4</sub>; l: β-Ca<sub>2</sub>SiO<sub>4</sub> and m: Mn<sub>3</sub>O<sub>4</sub>.

#### 3.2. NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> uptake properties

##### 3.2.1. Equilibrium pH of solution and uptake capacity

The final solution pH resulting from 0.1 g of sample in 50 ml of distilled water at room temperature was measured separately and found to lie in the range 10.60–11.25. The slag-0.1HCl, slag-HCl-pH7, slag-kaolinite and slag-Al(OH)<sub>3</sub> samples heated at 800 °C were treated with aqueous NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution and their NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> uptake capacities were evaluated. The NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> uptake capacities, the equilibrium pH and released Ca<sup>2+</sup> and Mg<sup>2+</sup> contents are tabulated in Table 2. Though the present samples were found to be poor for removing ammonium ions, the NH<sub>4</sub><sup>+</sup> uptake capacity is the highest (0.30 mmol/g) in the slag-Al(OH)<sub>3</sub> mixture heated at 800 °C while the PO<sub>4</sub><sup>3-</sup> uptake capacity is the highest (2.55 mmol/g) in the slag-0.1 HCl sample heated at 800 °C. The equilibrium pH of the slag-0.1 HCl sample heated at 800 °C in NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution was higher (8.40) than the other samples while the equilibrium pH of the slag-Al(OH)<sub>3</sub> sample heated at 800 °C in NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution was lower (8.16). The higher pH is favorable for the uptake of phosphate ions while a lower pH is favorable for ammonium ion uptake. Although the lowest equilibrium pH was found for the slag-kaolinite sample, this did not show the maximum NH<sub>4</sub><sup>+</sup> uptake capacity due to the lower ion exchange capacity of the kaolinite clay. No characteristic relationship among the uptakes of NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> as functions of the released Ca<sup>2+</sup> and Mg<sup>2+</sup> was found with these samples. This was expected to be due to the formation of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O and Mg(OH)<sub>2</sub> precipitates. The

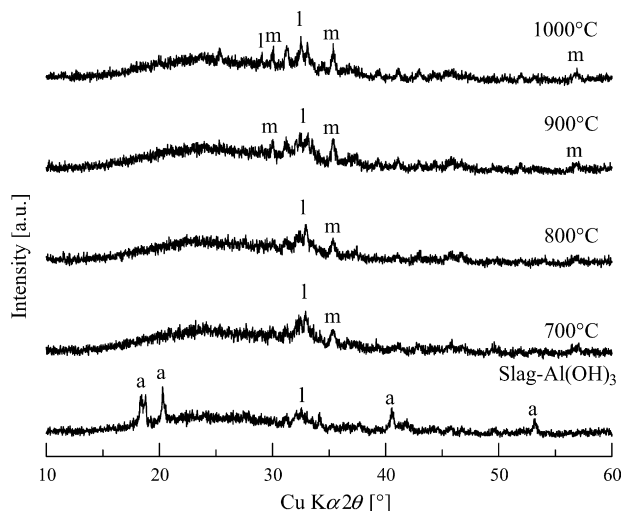


Fig. 2. XRD patterns of the slag-Al(OH)<sub>3</sub> samples heated at various temperatures. The symbols are as follows: a: Al(OH)<sub>3</sub>; l: β-Ca<sub>2</sub>SiO<sub>4</sub> and m: Mn<sub>3</sub>O<sub>4</sub>.

Table 2

Equilibrium pH ( $\text{pH}_{\text{equi}}$ ),  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake capacities and released divalent ions of the present samples heated at  $800^\circ\text{C}$  (Initial  $\text{NH}_4\text{H}_2\text{PO}_4$  concentration 10 mmol/l)

Sample	$\text{pH}_{\text{equi}}$	Uptake capacity				Released ions (mmol/g)	
		$\text{NH}_4^+$		$\text{PO}_4^{3-}$		$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
		(mmol/g)	(%)	(mmol/g)	(%)		
Slag- $\text{Al}(\text{OH})_3$	8.16	0.30	7.20	1.99	38.40	0.86	0.07
Slag-0.1 HCl	8.40	0.06	1.44	2.55	49.20	0.21	0.07
Slag-HCl-pH-7	7.96	0.03	0.72	1.41	27.21	1.20	0.15
Slag-kaolinite	7.24	0.14	3.36	0.80	15.44	1.13	0.09

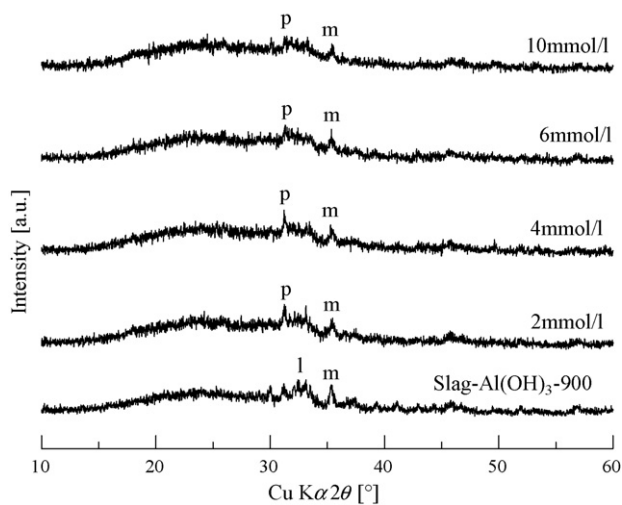


Fig. 3. XRD patterns of before and after  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake of the slag- $\text{Al}(\text{OH})_3$  sample heated at  $900^\circ\text{C}$ . The symbols are as follows: l:  $\beta\text{-Ca}_2\text{SiO}_4$ ; m:  $\text{Mn}_3\text{O}_4$  and p:  $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ .

presence of  $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$  was observed in the XRD patterns of samples after the uptake experiment (Fig. 3).

### 3.2.2. Effect of heating temperature

In a previous report we have shown that  $\text{PO}_4^{3-}$  uptake by steel-making slag increases with increasing heating temperature above  $600^\circ\text{C}$ , thereby attaining a maximum uptake of 2.75 mmol/g at  $700^\circ\text{C}$ . With a further increase in the heating temperature, the  $\text{PO}_4^{3-}$  uptake decreased. By contrast, no appreciable change was observed in the  $\text{NH}_4^+$  uptake capacity upon changing the heating temperature of steel-making slag [11]. Further, from the experimental data for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake shown in Table 2, the slag- $\text{Al}(\text{OH})_3$  sample heated at  $800^\circ\text{C}$  had the highest  $\text{NH}_4^+$  uptake capacity while the  $\text{PO}_4^{3-}$

uptake was also comparatively higher for this sample. Hence,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake experiments were carried out on slag- $\text{Al}(\text{OH})_3$  samples heated at  $700\text{--}1000^\circ\text{C}$  and the results are listed in Table 3. Although little change in the uptake of  $\text{NH}_4^+$  was observed with changes in heating temperature,  $\text{NH}_4^+$  uptake is very much smaller than  $\text{PO}_4^{3-}$  uptake. The  $\text{PO}_4^{3-}$  uptake by the sample heated at  $700^\circ\text{C}$  is 1.94 mmol/g, and increases with heating temperature, the maximum uptake being 2.11 mmol/g at  $900^\circ\text{C}$ . Further increase in the heating temperature results in a decrease of  $\text{PO}_4^{3-}$  uptake capacity. This is expected to be due to a greater degree of crystallization with heating temperature, thereby reducing the dissolution of  $\text{Ca}^{2+}$  in solution. The maximum  $\text{PO}_4^{3-}$  uptake by the slag- $\text{Al}(\text{OH})_3$  samples is related to the chemical composition ( $\text{CaO} + \text{Al}_2\text{O}_3$ ) since the presence of  $\text{CaO}$  enhances the formation of precipitates of  $\text{Ca}_3(\text{PO}_4)_2$ , and  $\text{Al}_2\text{O}_3$  is favorable for the uptake of oxy-anions [16].

### 3.2.3. Kinetics of $\text{NH}_4^+$ and $\text{PO}_4^{3-}$ uptake

It was established in the above experiments that the slag- $\text{Al}(\text{OH})_3$  sample heated at  $900^\circ\text{C}$  has the maximum  $\text{PO}_4^{3-}$  uptake capacity. Thus, a kinetic study was carried out of the simultaneous  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake by a single slag- $\text{Al}(\text{OH})_3$  sample heated at  $900^\circ\text{C}$  at various reaction times from 10 to 60 min. The data are shown in Table 4. No change in the  $\text{NH}_4^+$  uptake is observed up to 40 min, but the uptake of this ion increases after this time. By contrast, the  $\text{PO}_4^{3-}$  uptake increases steeply to 40 min but becomes constant at longer reaction times. This phenomenon can be explained on the basis that with the dissolution of  $\text{Ca}^{2+}$  from the sample, the pH increases, favoring the precipitation of calcium phosphate and the formation of water molecules. Thus, the pH of the solution decreases after calcium phosphate precipitation, facilitating the uptake of  $\text{NH}_4^+$ .

In order to investigate the rate law of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  sorption, the kinetic data obtained from batch experiments were

Table 3

$\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake of slag- $\text{Al}(\text{OH})_3$  samples heated at various temperatures (initial concentration of  $\text{NH}_4\text{H}_2\text{PO}_4 = 10$  mmol/l)

Treating temperature ( $^\circ\text{C}$ )	$\text{pH}_{\text{equi}}$	$\text{NH}_4^+$ uptake		$\text{PO}_4^{3-}$ uptake		Released ions (mmol/g)	
		(mmol/g)	(%)	(mmol/g)	(%)	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
700	8.47	0.25	5.0	1.94	37.4	0.93	0.15
800	8.40	0.30	7.2	1.99	38.4	0.86	0.07
900	8.42	0.20	3.9	2.11	40.6	0.83	0.10
1000	8.27	0.20	3.9	1.87	36.1	0.90	0.13

Table 4  
 $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake and released divalent ions of the sample slag-Al(OH)<sub>3</sub> heated at 900 °C with the change of reaction time (initial concentration of  $\text{NH}_4\text{H}_2\text{PO}_4 = 10 \text{ mmol/l}$ )

Reaction time (min)	Final pH	$\text{NH}_4^+$ uptake		$\text{PO}_4^{3-}$ uptake		Released ions (mmol/g)	
		(mmol/g)	(%)	(mmol/g)	(%)	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
10	6.64	0.03	0.6	0.12	2.3	0.97	0.0
20	6.80	0.03	0.6	0.51	10.1	0.89	0.0
30	6.83	0.03	0.6	0.75	14.9	0.70	0.0
40	7.01	0.03	0.6	1.11	22.1	0.58	0.0
60	7.15	0.06	1.1	1.16	23.1	0.66	0.05

analyzed using two kinetic equations. These are the first order equation proposed by Lagergren and Svenska [18] and the pseudo-second order equation proposed by Ho et al. [19]. The equations are rearranged into the linear form as follows:

$$\log_{10}(Q_e - Q_t) = \log_{10} Q_e - \frac{K_1}{2.303} t \quad (1)$$

$$\frac{t}{Q_t} = \frac{1}{(K_2 Q_e^2)} + \frac{t}{Q_e} \quad (2)$$

where  $Q_e$  (mmol/g) is the amount absorbed at equilibrium,  $Q_t$  the amount of sorption (mmol/g) at time  $t$  (minutes),  $K_1$  and  $K_2$  are rate constants of respective Eqs. (1) and (2).  $Q_e$  is taken from Table 3 for the sample slag-Al(OH)<sub>3</sub> heated at 900 °C. The plots of  $\log_{10}(Q_e - Q_t)$  and  $t/Q_t$  as a function of reaction time, shown in Fig. 4, suggest that the first order rate expression is more appropriate to the present experiment. The  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  uptake rates, calculated from first order rate expression, were found to be 2.91 and 0.65  $\mu\text{mol}/(\text{g min})$ , respectively.

### 3.2.4. Sorption isotherms

$\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake experiments were carried out on a single slag-Al(OH)<sub>3</sub> sample heated at 900 °C at four initial  $\text{NH}_4\text{H}_2\text{PO}_4$  concentrations of 2, 4, 6 and 10 mmol/l. This sample was chosen because it showed the maximum  $\text{NH}_4^+$  uptake capacity of all the present samples while  $\text{PO}_4^{3-}$  uptake was also comparatively higher. The uptake of  $\text{PO}_4^{3-}$  initially increased sharply with increasing initial  $\text{NH}_4\text{H}_2\text{PO}_4$  concentration and

finally slowly reaching towards saturation. This can be explained on the basis of the observed decrease in the equilibrium pH with increasing  $\text{NH}_4\text{H}_2\text{PO}_4$  concentration. The large amount of released  $\text{Ca}^{2+}$ , which increased the pH of the solution, favors the precipitation of calcium phosphate. With increasing calcium phosphate precipitation the pH of the solution decreases. At a relatively low pH, the sorption of phosphate ions on alumina surface occurs. As a  $\text{PO}_4^{3-}$  is sorbed at alumina surface of the sorbent, this site is saturated for further interactions with other sorbate molecules and a monolayer is formed. The higher  $\text{PO}_4^{3-}$  uptake was observed at equilibrium concentration of 6.2 mmol/l in Fig. 5, which may be due to multilayer formation of  $\text{PO}_4^{3-}$  on alumina surface of the sample during uptake process (deviation from monolayer concept). Table 4 shows that the dissolved  $\text{Ca}^{2+}$  decreases with increasing  $\text{PO}_4^{3-}$  uptake and the formation of calcium phosphate phase are confirmed by XRD (Fig. 3).

The  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  sorption behavior can be simulated by the use of mathematical equations. In this work, Langmuir and Freundlich models were used to simulate the isotherm data. The Langmuir model assumes that the uptake of metal ion occurs on a homogenous surface by monolayer sorption with no interaction between adsorbed ions. The model takes the following form [20]:

$$\frac{C_e}{Q_e} = \left( \frac{1}{Q_0} \right) C_e + \left( \frac{1}{Q_0 b} \right) \quad (3)$$

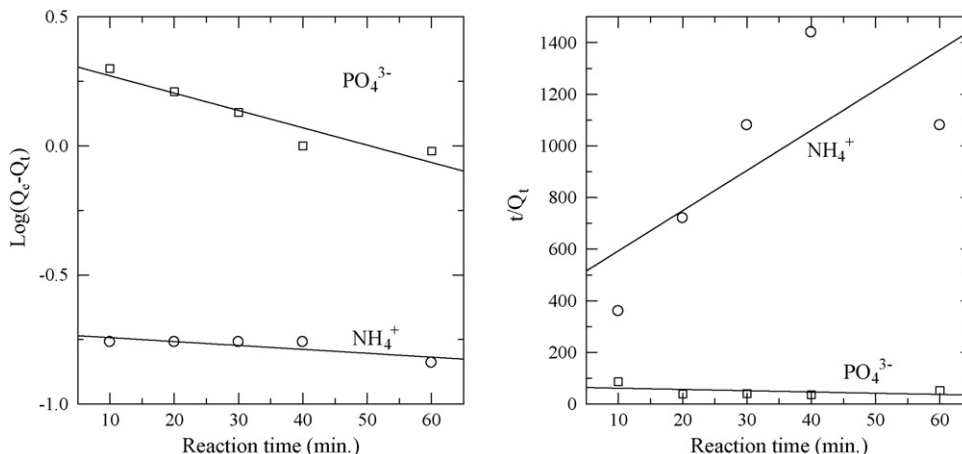


Fig. 4. First and pseudo second order kinetic plots of  $\log_{10}(Q_e - Q_t)$  and  $t/Q_t$ , respectively as a function of reaction time for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake by the slag-Al(OH)<sub>3</sub> sample heated at 900 °C.

Table 5

Langmuir and Freundlich parameters, correlation coefficient ( $r$ ) and sorption energy ( $\Delta G$ ) for the sorption of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  by the slag- $\text{Al}(\text{OH})_3$  sample heated at  $900^\circ\text{C}$

Sorbent ion	Langmuir constants				Freundlich constants		
	$Q_0$ (mmol/g)	$b$ (l/mol)	$r$	$\Delta G$ (J/mol)	$K_f$ (mmol $^{1-1/n}$ l $^{1/n}$ /g)	$n$	$r$
$\text{NH}_4^+$	0.15	10600	0.9751	-23.0	1.46	1.47	0.9416
$\text{PO}_4^{3-}$	2.27	1630	0.9979	-18.3	1.09	3.32	0.9693

where  $C_e$  is the equilibrium concentration (mmol/l),  $Q_e$  the amount sorbed at equilibrium (mmol/g),  $Q_0$  (mmol/g) and  $b$  (l/mol) are the Langmuir constants related to the sorption capacity and free energy change of adsorption ( $\Delta G$ ; J/mol) according to the following formula:

$$\Delta G = -RT \ln b \quad (4)$$

where  $R$  is the gas constant [8.314 J/(mol K)] and  $T$  is the temperature (K).

The Freundlich model assumes that the uptake of metal ion occurs on a heterogeneous surface by monolayer sorption. The model is described by the following Eq. [21]:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where  $K_f$  and  $n$  are the Freundlich constants.

The parameters calculated for the Langmuir and Freundlich equations are listed in Table 5. The equilibrium data fitted to Langmuir ( $r=0.9751$  and  $0.9979$  for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ ) model better than Freundlich model ( $r=0.9416$  and  $0.9693$  for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ ) indicating surface homogeneity of the adsorbent and monolayer adsorption onto a surface of identical sites. The sorption isotherms are shown in Fig. 5 and the solid curves are derived from the calculated parameters.

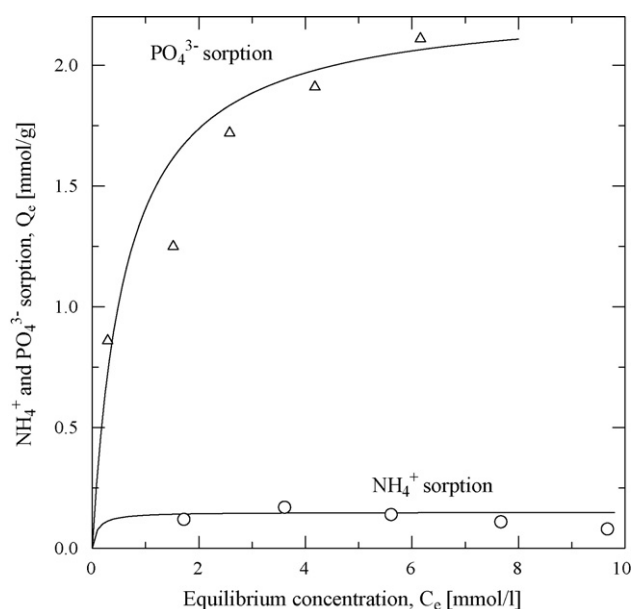


Fig. 5.  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  sorption isotherms of the slag- $\text{Al}(\text{OH})_3$  sample heated at  $900^\circ\text{C}$ .

Although the maximum uptake of  $\text{PO}_4^{3-}$  by the present samples is lower than previously reported for as-received slag heated at  $700^\circ\text{C}$  (2.75 mmol/g) [11], it is much higher than the reported data for fly ash (0.009 mmol/g), shale (0.007 mmol/g), bauxite (0.0064 mmol/g), burnt oil shale (0.006 mmol/g), limestone (0.007 mmol/g), zeolite (0.005 mmol/g), lightweight expanded clay aggregates (0.0044 mmol/g) [22], alum (0.03 mmol/g) [23],  $\gamma$ -alumina (0.33 mmol/g) [16] and acid treated slag (1.05 mmol/g) [14]. Though the present samples show poor uptake of ammonium ions, the possibility of simultaneous uptake of ammonium ions together with phosphate ions from same solution is an advantageous feature. The maximum  $\text{NH}_4^+$  uptake by the present samples is higher than for sepiolite (0.1 mmol/g) [24] and acid treated slag (0.007 mmol/g) [14] but lower than for clinoptilolite (0.8 mmol/g) [25] and composites of  $\gamma$ -alumina/potassium aluminosilicate gel (3 mmol/g) [16]. Unlike other reported sorbents, the present samples have the ability to simultaneously take up  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ , giving them an added advantage for actual environmental applications.

#### 4. Conclusion

The simultaneous uptake of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  by acid treated slag, mixtures of slag with kaolinite and  $\text{Al}(\text{OH})_3$  samples thermally activated at various temperatures were investigated by a batch method. These activated materials show simultaneous sorption ability for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ . The samples consisting of a mixture of slag and  $\text{Al}(\text{OH})_3$  heated at  $700$ – $900^\circ\text{C}$  have proved to be the best of all the present samples due to their higher simultaneous  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  uptake behavior from aqueous solution. Slag is thus a cheap raw material for producing sorbents with a high capacity for removing phosphate and ammonium ions which are extremely suitable for reducing environmental pollution caused by the presence of these common ionic contaminants of water.

#### Acknowledgements

VKJ thanks the Ministry of Education, Culture, Sports, Science and Technology, Japan for an award of a graduate fellowship (Monbukagakusho Scholarship) under which the present study was carried out. A part of this study is financially supported by The Steel Industrial Foundation for the Advancement of Environmental Protection Technology. We thank the Oita Factory, Nippon Steel Co., Oita, Japan for providing the slag. We are also thankful to Professor Dr. K.J.D. MacKenzie of Victoria University of Wellington, Wellington, New Zealand for critical reading and editing of the manuscript.

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