

Hazardous ions uptake behavior of thermally activated steel-making slag

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Abstract

This study concerns the utilization of waste steel-making slag, a by-product that contains mainly CaO, Fe₂O₃ and SiO₂. The as-received slag was ground and thermally activated by temperature treatment from 110 to 1000 °C for 24 h. Although the as-received slag was amorphous, it became partially crystallized during grinding. These crystalline phases were larnite and iron oxide but other crystalline phases also appeared in addition to larnite after calcination. The uptake of Ni²⁺, PO₄³⁻ and NH₄⁺ by the samples was investigated from solutions with initial concentrations of 10 mmol/l. The sample calcined at 800 °C showed the highest Ni²⁺ uptake (4.85 mmol/g) whereas the highest simultaneous uptake of PO₄³⁻ (2.75 mmol/g) and NH₄⁺ (0.25 mmol/g) was achieved by calcining the material at 700 °C. The principal mechanism of Ni²⁺ uptake is thought to involve replacement of Ca²⁺ by Ni²⁺. The mechanism of PO₄³⁻ uptake is mainly by formation of calcium phosphate while that of NH₄⁺ involves sorption by the porous silica surface of the samples.

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1. Introduction

Water pollution from municipal, industrial and agricultural sources is becoming a severe problem. Municipal water pollution is caused by wastewater from homes and commercial establishments, which contains relatively high concentrations of phosphorus, an element implicated in eutrophication. The characteristics of industrial wastewaters differ considerably both within and among industries. Wastewater discharged by enterprises that process ores and concentrates of non-ferrous metals is usually polluted with heavy metal ions, such as cadmium (Cd²⁺), lead (Pb²⁺), nickel (Ni²⁺), copper (Cu²⁺), and zinc (Zn²⁺) [1]. Many of the industries involved in metal finishing, mining and mineral processing, coal mining and oil refining, have problems associated with heavy metal contamination of process and runoff waters. Soils and groundwaters contain the residues of human agricultural practices (fertilizers, pesticides, etc.) and improperly disposed of industrial wastes. Ammonium and

phosphorus-containing solutions are used as the basic raw materials in many chemical and pharmaceutical industries. Eutrophication of surface water by algal bloom is due mainly to increased concentrations of nitrogen and phosphorus.

Many million tones of slag are generated as a by-product of steel making during the separation of the molten steel from impurities. Normally there is more residual iron in slag, which accounts for its darker color. This slag can be recycled into a range of useful products for building roads and pavements.

Both commercial and synthetic slags have been utilized in various ways including the use of commercial blast-furnace slags and synthetic-slugs for the preparation of calcium silicate hydrate and hydrotalcite by alkaline activation [2–5]. The environmental impact of ferrochrome slag has been studied and the leaching of metal ions from slag to ground water was found to be slight [6]. The removal of heavy metal ions, such as Pb, Ni, Cu, Zn and Cr from slag has been found to depend mainly on the replacement of Ca²⁺ by the target heavy metal ions [7–10]. The adsorption of ammonium and phosphate ions from seawater by acid-treated slag has been studied [11].

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In the present study, steel-making slag was activated by grinding and calcining at various temperatures. The uptake properties of Ni^{2+} by these samples, and their simultaneous uptake of NH_4^+ and PO_4^{3-} were investigated.

2. Experimental

2.1. Sample preparation and characterization procedure

The slag sample was obtained from the Oita factory of the Nippon Steel Co., Oita, Japan. Since the as-received slag was in the form of cm-sized chunks, it was first gently crushed in an iron mortar then reduced in an alumina mortar and pestle to 10–20 μm . Differential thermal analysis/thermogravimetry (DTA/TG) was carried out using a Thermoplus thermal analyser (TG-8120, Rigaku, Japan). This powder was thermally activated by temperature treatment from 110 to 1000 °C for 24 h. Powder X-ray diffraction (XRD) patterns were obtained using a diffractometer (XRD-6100, Shimadzu Japan) with monochromated $\text{Cu K}\alpha$ radiation. The specific surface area was calculated by the BET method using an automatic gas adsorption instrument (Autosorb-1, Quanta Chrome, USA). The chemical composition of the sample was analyzed by X-ray fluorescence (RIX2000, Rigaku, Japan).

2.2. Uptake experiments

All the calcined samples and an uncalcined sample were subjected to Ni^{2+} uptake experiments and simultaneous NH_4^+ and PO_4^{3-} uptake experiments under the following conditions; temperature: 25 °C, sample/solution ratio: 0.1 g/50 ml, initial concentration of Ni^{2+} (from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution) and NH_4^+ and PO_4^{3-} (from $\text{NH}_4\text{H}_2\text{PO}_4$ solution): 10 mmol/l, reaction time: 24 h. The pH values were measured immediately prior to placing the sample into the solution (initial pH) and after the reaction (final pH). The initial pH of the Ni^{2+} solution was 5.56 and that of $\text{NH}_4\text{H}_2\text{PO}_4$ solution was 4.72. The pH values were also measured for the reaction in de-ionized water. After the uptake experiments, the samples were centrifuged at 8000 rpm for 20 min, washed three times with de-ionized water and dried at 110 °C overnight. The separated solutions were chemically analyzed for Ni^{2+} , Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} and Si^{4+} by ICP-OES (Leeman Labs Inc., USA). The ammonium and phosphate ion concentrations were measured by ion chromatographs (IA-200, DKK·TOA, Japan). The uptake%, uptake (mmol/g) and distribution coefficient (K_d) were calculated using the following formulae:

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

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

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

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 composition of the slag is listed in Table 1. In addition to the major constituents, it also contains small amounts of P_2O_5 , TiO_2 and SO_3 . The specific surface area of slag sample is low (2 m^2/g). The DTA/TG curves of the as-received slag sample are shown in Fig. 1. The DTA curve revealed the formation of phases in between 400 and 500 °C and 650 and 700 °C. The XRD patterns of the samples are shown in Fig. 2. As-received slag sample is XRD amorphous. The uncalcined and ground sample contains larnite ($\beta\text{-Ca}_2\text{SiO}_4$, JCPDS Card No. 33-302) and plusite (FeO , JCPDS Card No. 6-615). The intensity of the larnite increases with higher treating temperature. With increasing treating temperature up to 400 °C the iron oxide decreases and kirschsteinite (CaFeSiO_4 , JCPDS Card No. 34-98) appears, possibly formed as a result of solid-state reaction between iron ox-

Table 1
Chemical composition (mass%) of slag

Sample	Slag
CaO	43.4
Al_2O_3	4.3
SiO_2	19.4
Fe_2O_3	19.6
MnO	6.0
MgO	4.0
P_2O_5	1.8
TiO_2	0.4
SO_3	1.0

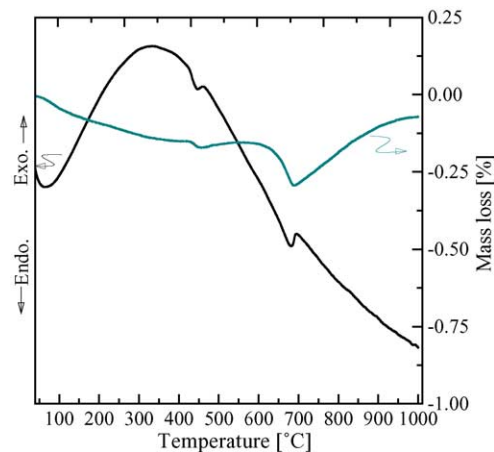


Fig. 1. DTA/TG curves of as-received slag sample.

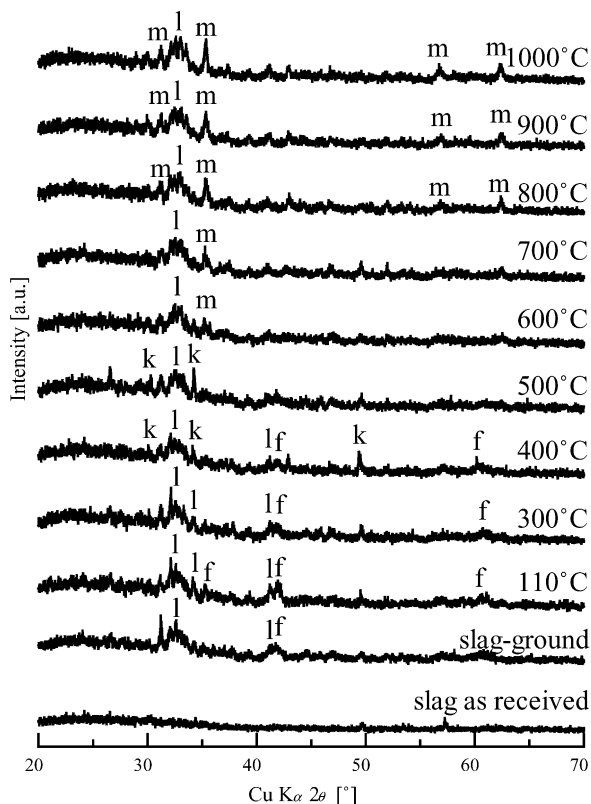


Fig. 2. XRD patterns of slag samples calcined from 110 to 1000 °C for 24 h, only ground and as-received slag. The symbols are as follows: (l) larnite, (k) kirschsteinite, (m) manganese oxide and (f) plustite.

ide and calcium silicate. Above 600 °C, manganese oxide (Mn₃O₄, JCPDS Card No. 13-162) is observed, in addition to larnite.

3.2. Ni²⁺ uptake properties

Ni²⁺ uptake as a function of temperature treatment is shown in Fig. 3 and Table 2. The Ni²⁺ uptake of the uncalcined and ground sample (1.8 mmol/g) increased upon treat-

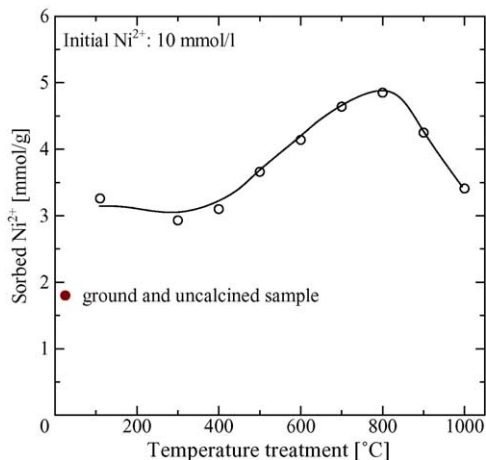


Fig. 3. Ni²⁺ sorption by slag samples as a function of temperature treatment.

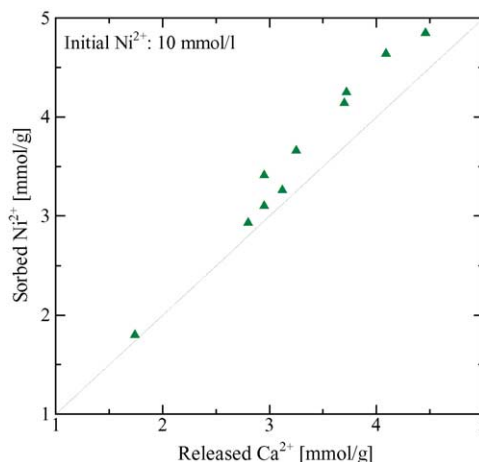


Fig. 4. Relationship between Ni²⁺ sorbed by the samples and Ca²⁺ released into solution.

ing at 110–400 °C to about 3 mmol/g. From 400 to 800 °C a further uptake increase was found but above 800 °C the uptake decreased. The maximum Ni²⁺ uptake by this material was 4.85 mmol/g, but the changes in Ni²⁺ uptake are not directly related to the changes in the XRD patterns shown in Fig. 2.

Ni²⁺ uptake from the solution is thought to occur with the dissolution of Ca²⁺ from the sample as reported for the CaO–Al₂O₃–SiO₂ system [12,13]. The data for the release of Ca²⁺ and sorption of Ni²⁺ by these samples, plotted in Fig. 4, are distributed about the line representing the ion replacement reaction (Ca²⁺-solid + Ni²⁺ → Ni²⁺-solid + Ca²⁺). Thus, the main uptake mechanism of Ni²⁺ by these samples involves ion replacement.

The effect of pH on Ni²⁺ uptake by the samples is illustrated in Fig. 5 together with the blank experiment with Ni²⁺ solution but no sample. In general, protons can compete with metal cations for sorption at pH-dependent, variably charged sites. Ni²⁺ sorption by the present samples increases steeply

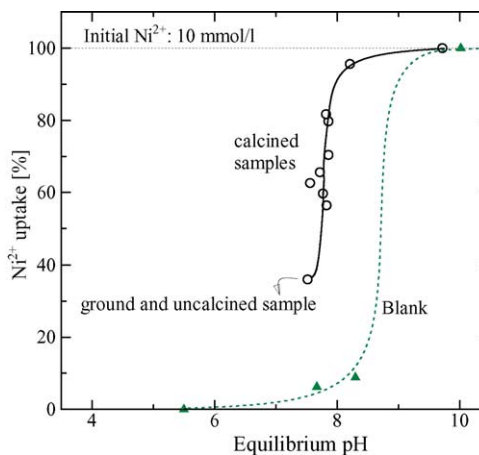


Fig. 5. Ni²⁺ uptake by slag and blank samples as a function of equilibrium pH.

Table 2
Ni²⁺ uptakes of slag samples treated at various temperatures

Calcining temperature (°C)	Ni ²⁺ uptake				Dissolved ions (mmol/l)		
	Final pH	mmol/g	%	K _d	Ca ²⁺	Mg ²⁺	Si ⁴⁺
Uncalcined	7.52	1.80	36.0	281	3.47	0.10	0.50
110	7.56	3.26	62.6	839	6.24	0.12	0.21
300	7.83	2.93	56.4	647	5.59	0.08	0.16
400	7.77	3.10	59.7	741	5.89	0.11	0.22
500	7.86	3.66	70.4	1188	6.49	0.15	0.13
600	7.86	4.14	79.7	1961	7.39	0.23	0.15
700	8.21	4.64	95.6	10924	8.18	0.12	0.16
800	9.72	4.85	100	∞	8.91	0.05	0.31
900	7.82	4.25	81.7	2225	7.44	0.22	0.16
1000	7.72	3.41	65.6	953	5.89	0.18	0.12

with pH at about pH = 8, which is lower than the value found in the blank test (pH = 9). The difference in the two pH dependence curves is due to the sorption mechanism by the slag samples. However, according to the solubility product, the principal mechanism of Ni²⁺ sorption at pH > 7 involves the precipitation of Ni(OH)₂. The slag samples are therefore thought to provide heterogeneous nucleation sites for hydroxide precipitation at lower pH. The sharp loss of mass% in TG curves shown in Fig. 6 of the slag sample calcined at 800 °C after Ni²⁺ uptake up to 500 °C in comparison to that of before uptake reveals the formation of hydroxide phase. The deviation of Ni²⁺ sorption as a function of Ca²⁺ release from the unity line in Fig. 3 is explained by this mechanism. On the basis of the relationships between the released Ca²⁺ and sorbed Ni²⁺, and the effect of pH on Ni²⁺ uptake by these samples, it is concluded that the mechanism of Ni²⁺ uptake involves the replacement of Ca²⁺ in the sample by Ni²⁺ from the solution. This uptake mechanism is, however, not an exchange reaction because the reverse reaction (Ni²⁺-solid + Ca²⁺ → Ca²⁺-solid + Ni²⁺) does not occur. This may mean that the sorbed Ni²⁺ does not occupy the Ca sites in the sample but forms a surface hydroxide as reported in amorphous KAlSiO₄ [14].

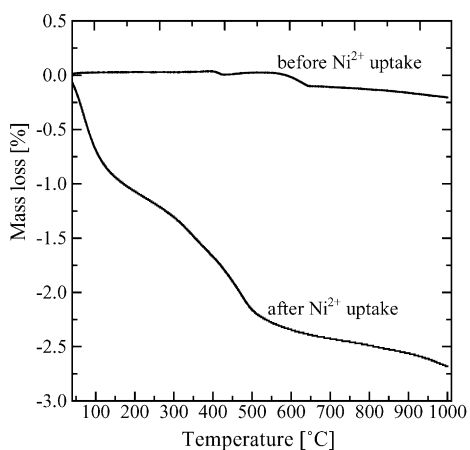


Fig. 6. TG curves of slag calcined at 800 °C before and after Ni²⁺ uptake.

3.3. NH₄⁺ and PO₄³⁻ uptake properties

NH₄⁺ and PO₄³⁻ uptake are shown in Fig. 7 as a function of temperature treatment. PO₄³⁻ uptake by the sample treated at 110 °C was 1.85 mmol/g, increasing only slightly to 2 mmol/g after treating at 600 °C. Treating above 600 °C increases the PO₄³⁻ uptake steeply to a maximum value of 2.75 mmol/g at 700 °C, above which temperature it decreases again. The temperature of maximum PO₄³⁻ uptake (700 °C) is 100 °C lower than that for Ni²⁺ uptake. By contrast, NH₄⁺ uptake remains almost constant irrespective of the calcining temperature.

During the NH₄⁺ and PO₄³⁻ uptake reaction, large amounts of Ca²⁺ and Si⁴⁺ are released from the sample (Table 3). The final pH values of the slag samples after reaction in de-ionized water are in the range 11.3–11.5 while samples treated with a solution containing 10 mmol/l NH₄H₂PO₄ have final pH values of 8.4–8.6. The high pH value of the slag sample in de-ionized water is due to dissolution of Ca²⁺ from the sample into the solution. This is a disadvantage of the present samples and it would be preferable to bring the solution pH back to approximately neutral by modifying the

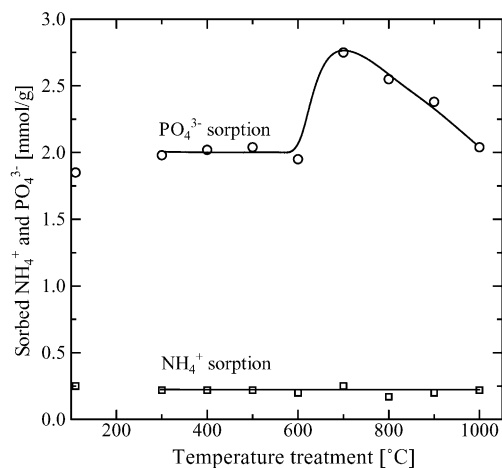


Fig. 7. Changes of the simultaneous NH₄⁺ and PO₄³⁻ sorption by slag samples as a function of temperature treatment.

Table 3
Simultaneous uptakes of NH_4^+ and PO_4^{3-} by slag samples treated at various temperatures

Calcining temperature ($^{\circ}\text{C}$)	NH_4^+ uptake			PO_4^{3-} uptake			Dissolved ions (mmol/l)		
	mmol/g	%	K_d	mmol/g	%	K_d	Ca^{2+}	Mg^{2+}	Si^{4+}
110	0.25	5.42	29	1.85	35.8	279	1.82	0.14	1.60
300	0.22	4.77	25	1.98	38.3	310	1.77	0.12	1.60
400	0.22	4.77	25	2.02	39.1	321	1.67	0.11	1.53
500	0.22	4.77	25	2.04	39.5	327	1.57	0.10	1.64
600	0.20	4.23	22	1.95	37.8	304	1.72	0.12	1.57
700	0.25	5.42	29	2.75	53.2	567	0.67	0.12	2.10
800	0.17	3.58	19	2.55	49.3	486	0.68	0.12	2.03
900	0.20	4.23	22	2.38	46.1	428	0.95	0.13	2.17
1000	0.22	4.77	25	2.04	39.4	325	1.67	0.18	2.07

samples. When $\text{NH}_4\text{H}_2\text{PO}_4$ solution is reacted with the slag, a large amount of calcium is removed from the sample and adsorbs phosphate, promoting the precipitation of calcium phosphate as observed in the XRD pattern shown in Fig. 8. The formation of calcium phosphate has the effect of suppressing changes in pH. Although some H^+ is taken into the sample in charge compensation, NH_4^+ is also taken into the sample from solution.

Although the maximum uptake of PO_4^{3-} by the slag sample is lower than Ni^{2+} uptake, it is much higher than reported 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) [15], alum (0.03 mmol/g) [16], γ -alumina (0.33 mmol/g) [17] and acid treated slag (1.05 mmol/g) [11]. Furthermore, the maximum NH_4^+ uptake by the present samples is higher than by sepiolite (0.1 mmol/g) [18] and acid treated slag (0.007 mmol/g) [11] but lower than for composites of γ -alumina/potassium aluminosilicate gel (3 mmol/g) [17], clinoptilolite (0.8 mmol/g) [19]. Unlike other reported adsorbents, the present samples have the ability to simultaneously take up NH_4^+ and PO_4^{3-} , giving them an added advantage for actual environmental applications.

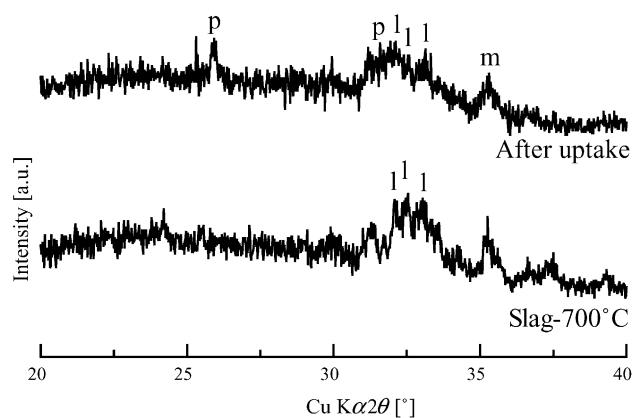


Fig. 8. XRD patterns of slag calcined at 700°C before and after $\text{NH}_4\text{H}_2\text{PO}_4$ uptake. The symbols are as follows: (l) larnite; (m) manganese oxide and (p) calcium phosphate.

4. Conclusion

The uptake of Ni^{2+} and the simultaneous NH_4^+ and PO_4^{3-} by steel-making slag samples thermally activated at various temperatures was investigated by a batch method. These activated materials show sorption ability for Ni^{2+} , NH_4^+ and PO_4^{3-} . The uptake of these ions is optimal in samples activated at 700 – 800°C . Slag is thus a cheap raw material for producing adsorbents with a high capacity for removing heavy metals, phosphate and ammonium ions. These materials appear to be extremely suitable for reducing environmental pollution caused by the presence of these common ionic contaminants of water.

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