

Uptake properties of Ni^{2+} by $n\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ($n = 1-4$) prepared from solid-state reaction of kaolinite and calcite

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Abstract

A series of $n\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ samples ($n = 1-4$) were prepared by solid-state reaction of mechanochemically treated mixtures of kaolinite and calcite fired at 600–1000 °C for 24 h. All the samples were X-ray amorphous after firing at 600–800 °C but had crystallized by 900 °C. The main crystalline phases were anorthite ($n = 1$), gehlenite ($n = 2$ and 3) and larnite ($n = 4$). The uptake of Ni^{2+} by $n\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ samples fired at 800 and 900 °C was investigated at room temperature using solutions with initial Ni^{2+} concentrations of 0.1–50 mmol/l. Amorphous samples (fired at 800 °C) showed a higher Ni^{2+} uptake capacity than crystalline samples (fired at 900 °C). Ni^{2+} uptake was found to increase with increasing of CaO content. Amorphous $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ showed the highest Ni^{2+} uptake capacity (about 9 mmol/g). The Ni^{2+} uptake abilities of the present samples are higher than those of other materials reported in the literature. Since the sorbed Ni^{2+} /released Ca^{2+} ratios of these samples are close to unity, ion replacement of Ni^{2+} for Ca^{2+} is thought to be the principal mechanism of Ni^{2+} uptake by the present samples.

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1. Introduction

Water pollution is rapidly increasing with industrialization and urbanization and becoming a global environmental problem. Wastewater discharged by industries that process ores and concentrates of non-ferrous metals is usually polluted with heavy metal ions such as Cd, Pb, Ni, Cu, Zn, etc. Many industries involved in metal finishing, mining and mineral processing, coal mining and oil refining, have problems arising from heavy metal contamination of the runoff water. The development of new approaches and technologies is therefore required to assist in both the removal and recovery of valuable metals from the wastewater associated with these processes.

For the removal of heavy metal ions from wastewaters, ion exchange, chemical precipitation, electro deposition, filtration and adsorption are used [1,2]. Cation exchange materials such as zeolites are candidates because of their high cation exchange capacities [3]. However, zeolites have higher selectivity for alkali and alkaline earth ions than for heavy metal ions. This results in the deterioration of their heavy metal uptake properties under actual environmental conditions, in which alkali and alkaline earth ions are normally present. Ion exchange is feasible when an exchanger has a high selectivity for the metal to be removed and the concentration of competing ions is low. In certain cases, special resins with a very high selectivity for a particular heavy metal ion are available [4]. The metal may then be recovered by incinerating the metal-saturated resin but the cost of such a process limits its application to valuable metals. Such resins are not used for the uptake of less-valuable metals or for the separation of metal ion mixtures with components of similar chemical character.

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New materials have been sought for a long time because the availability of high-performance adsorbents may provide an economical means of removing and separating mixtures of heavy metal ions from effluents.

Sorption of heavy metal ions by modified kaolinites [5], montmorillonites [6–11], bentonite [12,13] and zeolite-bearing volcanoclastic rock [14] has already been reported. By contrast, we have investigated the functional materials prepared from kaolin group minerals. The products include microporous silica [15], mesoporous γ -alumina [16], mesoporous mullite fiber [17] formed by selective leaching methods, mullite whiskers [18] formed by solid–gas reaction and amorphous cation uptake material formed by solid-state reaction. In the course of these studies, we have prepared amorphous KAlSiO_4 [19], amorphous $\text{BaAl}_2\text{Si}_2\text{O}_8$ [20], amorphous $\text{CaAl}_2\text{Si}_2\text{O}_8$ [21] and both amorphous and crystalline $\text{Ca}_2\text{Al}_2\text{SiO}_7$ [22] by solid-state reaction of kaolinite with carbonates and have examined their uptake capacity for various cations. The amount of nickel uptake by amorphous $\text{Ca}_2\text{Al}_2\text{SiO}_7$ was 7.6 mmol/g [22], much greater than the other materials mentioned above. These materials showed high uptake selectivity for transition metals but low uptake of alkali and alkaline earth ions. This characteristic property makes this class of material an effective candidate for the uptake of heavy metal ions from actual wastewaters in which both alkali and alkaline earth ions are always present. We have confirmed this in uptake experiments using actual river water [21].

From a structural point of view, layered structures are thought to be more suitable than framework structures as host materials for cation uptake because the release of the host cations may occur more readily and efficiently from the layered structures. This is confirmed by the higher uptake ability of amorphous $\text{Ca}_2\text{Al}_2\text{SiO}_7$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ with a layered structure [21,22]. In this study, both amorphous and crystalline forms of $n\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ($n = 1\text{--}4$) were prepared by solid-state reaction of kaolinite with CaCO_3 because these starting materials are already used in the preparation of $\text{CaAl}_2\text{Si}_2\text{O}_8$ [21] and $\text{Ca}_2\text{Al}_2\text{SiO}_7$ [22]. The Ni^{2+} uptake ability by these compounds was examined to elucidate the effect of composition on the overall uptake efficiency of the system, compare with the reported sorbents and achieve the best performance.

2. Materials and methods

2.1. Sample preparation and characterization

The starting materials were kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2$) from GA, USA (Albion Co.), and CaCO_3 (special grade, Wako Pure Chemicals, Japan). A series of the mixtures of kaolinite and CaCO_3 in 1/1–1/4 molar ratios was prepared by wet milling using an alumina pot (80 ml) with 300 alumina balls (5 mm \emptyset) using a planetary ball mill (LA-PO.1, Ito Seisakusho Ltd., Japan) operating at 300 rpm for 12 h.

After milling, the slurry was dried at 110 °C for 24 h and fired at 600–1000 °C for 24 h at a heating rate of 10 °C/min. The samples are designated $n\text{--}m$, where n and m represent the molar ratio of CaO in $n\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and the firing temperature, respectively.

Powder X-ray diffraction (XRD) patterns were obtained using a diffractometer (XRD-6100, Shimadzu, Japan) with monochromated $\text{Cu K}\alpha$ radiation. The presence of residual carbonate was determined using FTIR spectroscopy (FTIR-8600PC, Shimadzu, Japan). The specific surface area was calculated by the BET method using an automatic gas adsorption instrument (Autosorb-1, Quanta Chrome, USA). The chemical compositions of the samples were analyzed by X-ray fluorescence (RIX2000, Rigaku, Japan).

Solid-state ^{29}Si and ^{27}Al MAS NMR spectra of all the amorphous samples were obtained at 11.7 T using a Varian Unity 500 spectrometer operating at ^{29}Si and ^{27}Al frequencies 99.294 and 190.242 Hz with a 5 mm Doty MAS probe spun at 10–12 kHz. The ^{29}Si MAS spectra were obtained with a 7 ms 90° pulse and a delay time of 60 s and the ^{27}Al MAS spectra with a 1 ms 15° pulse and delay time of 1 s. The ^{29}Si and ^{27}Al spectra were referenced to tetramethylsilane (TMS) and $\text{Al}(\text{H}_2\text{O})_6^{3+}$, respectively.

2.2. Ni^{2+} uptake experiment

All samples ($n = 1\text{--}4$) fired at 800 and 900 °C for 24 h were subjected to Ni^{2+} uptake experiments by a batch method under the following conditions; temperature 25 °C, solid/solution ratio 0.1 g/50 ml, initial Ni^{2+} concentration 0.1–50 mmol/l and duration 24 h with stirring. The pH values were measured just before placing the sample into the solution (initial pH) and after the reaction (final pH) using a pH meter (Toa D.K.K., Japan). 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 concentrations of the various cations in the separated solutions were analyzed by ICP-OES spectrometer (Leeman Labs Inc., USA). The uptake% and uptake (mmol/g) were calculated using the formulae,

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

$$\text{uptake} \left(\frac{\text{mmol}}{\text{g}} \right) = \frac{(C_i - C_f)V}{m}$$

where C_i , C_f , V and m are the initial concentration (mmol/l), final concentration (mmol/l), volume of solution (ml) and amount of sample (g), respectively.

3. Results and discussion

3.1. Characterization of the products

The XRD patterns of the samples fired at 800 and 900 °C for 24 h are shown in Fig. 1. All the samples fired

between (C_e/Q_e) and C_e .

$$\left(\frac{C_e}{Q_e}\right) = \left(\frac{C_e}{Q_0}\right) + \left(\frac{1}{Q_0b}\right) \quad (1)$$

where C_e (mmol/l) is the equilibrium concentration, Q_e (mmol/g) the amount adsorbed at equilibrium and Q_0 (mmol/g) and b (l/mmol) are the Langmuir constants related to adsorption capacity and energy of adsorption (ΔG ; kJ/mol) represented by the following formula:

$$\Delta G = -RT \ln(1000b) \quad (2)$$

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

The Freundlich model assumes that the removal of metal ion occurs on a heterogeneous surface by monolayer adsorption. The model describes a linear relation between $\log(Q_e)$ and $\log(C_e)$.

$$\log(Q_e) = \log(K_F) + \left(\frac{1}{n}\right) \log(C_e) \quad (3)$$

where K_F and n are the Freundlich constants.

The Ni^{2+} sorption isotherms of the samples are shown in Fig. 4. The parameters calculated from the Langmuir and Freundlich equations based on the experimental data are listed in Table 1. As clear from the correlation coefficients (r) in Table 1, better fits are obtained from the Langmuir calculations. The solid curves in Fig. 4 are calculated from the obtained Langmuir parameters. The sorption isotherms show very large differences between the samples. The Q_0 values are in the following order: 112-800 < 212-800 < 312-800 < 412-800 for the 800 °C samples and 112-900 < 212-900 < 312-900 < 412-900 for the 900 °C samples. Thus, the Q_0 values increase with increasing values of n in $n\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ for both the amorphous and crystallized samples. The relationships between Ni^{2+} uptake capacities of the samples and their basicities ($=(\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3)/\text{SiO}_2$) are shown in Fig. 5. The Ni^{2+} uptake capacity of the amorphous samples (fired at 800 °C) increases linearly with the basicity whereas the increase of Ni^{2+} uptake of the crystallized samples (fired at 900 °C) is gradual at low basicity but becomes steeper at higher basicity. This indicates that the presence of CaO in

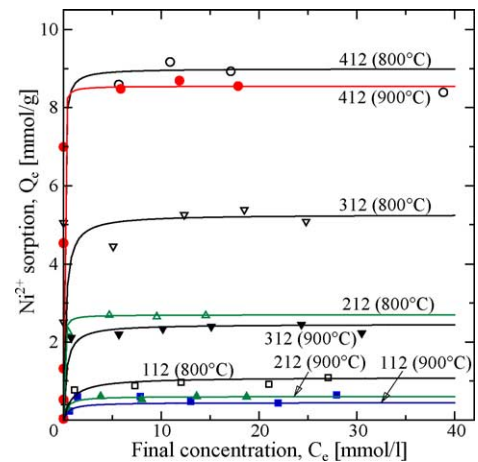


Fig. 4. Adsorption isotherms of Ni^{2+} by $n\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ samples. The lines in the figure are based on the resulting Langmuir parameters. The symbols in the figure are as follows: (□) 112-800; (■) 112-900; (▲) 212-800; (▲) 212-900; (▼) 312-800; (▼) 312-900; (○) 412-800; (●) 412-900.

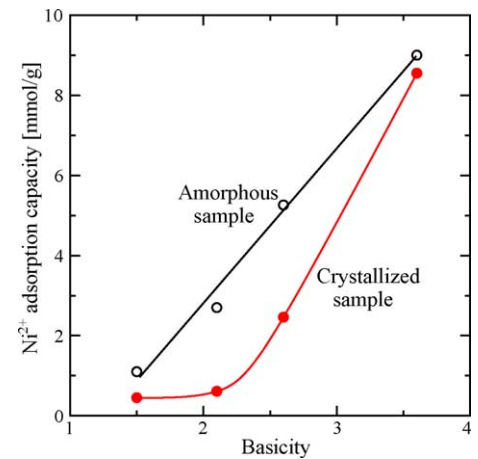


Fig. 5. Change of adsorption capacities of amorphous (800 °C) and crystallized (900 °C) samples as a function of sample basicity.

the layered structure of the samples plays a major role in the uptake of Ni^{2+} from an aqueous environment. The steep increase of Q_0 in the crystallized samples is attributed to the crystalline phase, i.e. of higher Ca_2SiO_4 content. All the

Table 1

Langmuir and Freundlich parameters, correlation coefficient (r) and adsorption energy (ΔG) for the adsorption of Ni^{2+} by the samples together with their specific surface area

Sample			Langmuir parameters				Freundlich parameters			S_{BET} (m^2/g)
Ratio	Firing temperature (°C)	Structure	Q_0 (mmol/g)	b (l/mmol)	r	ΔG (kJ/mol)	K_f	n	r	
112	800	Amorphous	1.10	1.13	0.9974	-17.4	0.68	6.76	0.9817	31
212	800	Amorphous	2.70	23.12	1.0000	-24.9	2.40	20.0	0.9405	13
312	800	Amorphous	5.26	4.75	0.9983	-21.0	3.50	6.7	0.9805	19
412	800	Amorphous	9.00	19.14	0.9996	-24.4	8.10	25.0	0.6935	19
112	900	Crystalline	0.45	1.96	0.9932	-18.8	0.59	43.5	0.9010	3
212	900	Crystalline	0.61	3.00	0.9978	-19.8	0.38	6.3	0.8576	2
312	900	Crystalline	2.46	3.38	0.9996	-20.1	2.10	22.7	0.9466	3
412	900	Crystalline	8.55	65.00	1.0000	-27.5	8.00	30.3	1.0000	6

Table 2
Comparison of the adsorption capacity of Ni^{2+} on various adsorbents

Adsorbent	Q_0 (mmol/g)	Reference
Fly-ash	0.01	[33]
Granular activated carbon	0.03	[35]
Clinoptilolite	0.04	[34]
Ca-bentonite	0.11	[37]
Clay treated with HCl	0.19	[37]
Natural clay	0.21	[38]
Clay treated with NaCl	0.25	[37]
Red mud	0.26	[39]
Na-bentonite	0.41	[37]
$\text{CaAl}_2\text{Si}_2\text{O}_8$ (amorphous)	0.50	[22]
Acid-treated carbon	0.57	[41]
Blast furnace slag	0.95	[40]
Coirpith carbon	1.06	[36]
$\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7$ (gehlenite)	2.64	[22]
$\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7$ (amorphous)	7.57	[22]

amorphous samples show higher Q_0 values compared with the crystallized samples, with the exception of 412-900. The Ni^{2+} uptake capacities of the samples were examined in relation to their specific surface area values. The Ni^{2+} uptake capacity of the crystallized samples increases sharply with specific surface area but no clear relation was found for the amorphous samples, suggesting that the specific surface area has little effect on their Ni^{2+} uptake capacity (Table 2).

Since the uptake of Ni^{2+} from solution is thought to be accompanied by the release of Ca^{2+} from the sample, the data for released Ca^{2+} and sorbed Ni^{2+} are plotted for these samples in Fig. 6. The data are distributed about the straight line representing the replacement reaction (Ca^{2+} -sample + $\text{Ni}^{2+} \rightarrow \text{Ni}^{2+}$ -sample + Ca^{2+}), indicating that the uptake of Ni^{2+} by these samples occurs by replacement of Ca^{2+} cations. The scattering of data to lower than the straight line in the low Ca^{2+} concentration region is due to the excess dissolution of Ca^{2+} after complete uptake of Ni^{2+} from solution. This uptake mechanism is, however,

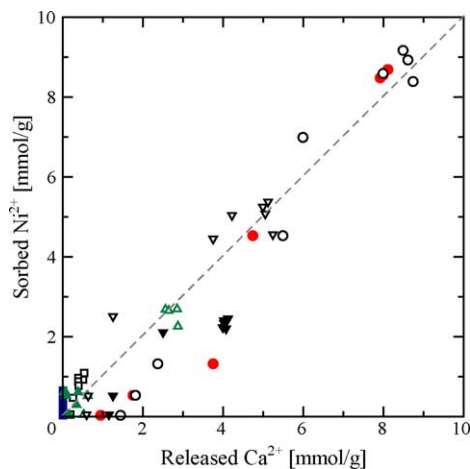


Fig. 6. Relationship between Ni^{2+} sorbed by the samples and Ca^{2+} released to the solutions. The symbols in the figure are as follows: (□) 112-800; (■) 112-900; (△) 212-800; (▲) 212-900; (▼) 312-800; (▼) 312-900; (○) 412-800; (●) 412-900.

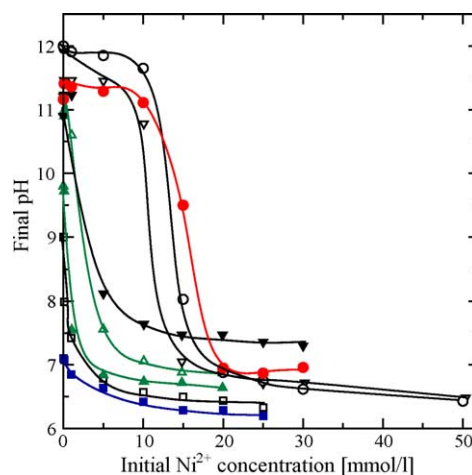
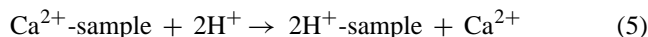
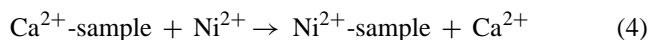


Fig. 7. Final pH of the solution as a function of initial concentration. The symbols in the figure are as follows: (□) 112-800; (■) 112-900; (△) 212-800; (▲) 212-900; (▼) 312-800; (▼) 312-900; (○) 412-800; (●) 412-900.

not an exchange reaction because the reverse reaction (Ni^{2+} -sample + $\text{Ca}^{2+} \rightarrow \text{Ca}^{2+}$ -sample + Ni^{2+}) does not occur.

Fig. 7 shows the final pH of these samples as a function of the initial Ni^{2+} concentration of the solutions. All the samples show pH values between 6 and 7.5 at high initial concentrations and are not different from the initial pH values (5–6). The pH values, however, increase steeply at lower initial Ni^{2+} concentrations. This pH change is thought to result from the following reaction accompanying the complete uptake of Ni^{2+} from solution.



This uptake of H^+ , coming from solution, by the samples brings about an increase in the final pH. The difference in maximum sorption Q_0 of these samples is thought to correspond with differences in their release of Ca^{2+} . In the present study, we did not examine about the selectivity of the present materials for heavy metals but high selectivity for heavy metals is expected to these materials because the uptake mechanisms are same with the previously reported $\text{CaAl}_2\text{Si}_2\text{O}_8$ [21] and $\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7$ [22], which have high selectivity for heavy metals.

4. Conclusion

The uptake of Ni^{2+} by amorphous and crystalline $n\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($n=1-4$) samples prepared by mechanochemical treatment and firing of kaolinite–calcite mixtures, was investigated. The following results were obtained:

- (1) All samples showed very good Ni^{2+} uptake with sorption isotherms in better agreement with the Langmuir model than the Freundlich model.

- (2) Ni²⁺ uptake increased with increasing basicity of the samples.
- (3) Ni²⁺ uptake was highly influenced by the structural state of the adsorbent, and was higher in amorphous compounds than in the corresponding crystalline materials.
- (4) A Ni²⁺ uptake capacity of 9 mmol/g was achieved in an amorphous sample of 4CaO·Al₂O₃·2SiO₂ (sample 412-800).
- (5) The principal mechanism of Ni²⁺ uptake is the replacement of Ca²⁺ in the solid by Ni²⁺ from the solution.

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