JOURNAL OF
Materials
CHEMISTRY
Communication

Novel function for anionic clays: selective transition metal cation uptake by diadochy

Sridhar Komarneni,* Naofumi Kozai and Rustum Roy

Materials Research Laboratory and Department of Agronomy, The Pennsylvania State University, University Park, PA 16802, USA

Here we report for the first time, the extremely high and selective uptake of transition metal cations such as Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} by two anionic clays of nominal composition, $[Mg_6Al_2(OH)_{16}]^{2+}[CO_3{\cdot}4H_2O]^{2-}$ and $[Mg_2Al(OH)_6]^{+}[NO_3{\cdot}2H_2O]^{-}$. We postulate that the principal mechanism of this selective cation uptake is by substitution in the anionic clay structure for mainly Mg through a process known as diadochy. This newly discovered function for anionic clays is useful for the decontamination and immobilization of the above transition metals at room temperature and may find applications in the remediation of metal contaminated soils, filtration of drinking water as well as decontamination of waste waters.

This paper deals with transition metal cation uptake in anionic clays by a process known as diadochy. Copper, cobalt, nickel and zinc are some of the regulated metals which are of environmental concern because they are hazardous to humans and/or to other forms of life depending upon their concentration in drinking or irrigation water.[1] Remediation of the environment or decontamination of drinking water through filtration is possible with the use of a highly selective material for these metals. Inorganic exchange materials such as zeolites and cationic clays are frequently used in remediation. Minerals belonging to the anionic clay group have been reported by several researchers since the 1920s,[2–5] and CO_3^{2-} or NO_3^{-} hydrotalcites were first synthesized hydrothermally in these laboratories in 1952.[6] The term 'anionic clay' refers to natural or synthetic layered or lamellar double hydroxides with interlayers containing anionic species to balance the positive charge on the layers while the term 'cationic clay' refers to natural or synthetic layered structures whose interlayers contain cations to balance the negative charge on the layers[7] and these cations are exchangeable with other cations, *i.e.*, cation exchange. The process of cation exchange in natural and synthetic clays is well known.[8,9] Anionic clays are rare in nature while cationic clays are ubiquitous in all soils and sediments. Hydrotalcite, manasseite, pyroaurite, takovite, stichtite, honessite, meixnerite and sjögrenite, are some examples of minerals of the anionic clay family.[7] Anionic clays are a multifunctional group of materials with much research exploring their structural, chemical, ionic, catalytic, optical and electronic properties.[7,10–19] Anionic exchange, *i.e.*, exchange of interlayer anions with other anions in anionic clays has been studied previously.[20–23] However, to the best of our knowledge, no cation uptake studies by anionic clays have been reported. Here we report the extremely high and selective uptake of transition metal cations such as Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} by two anionic clays of nominal composition, $[Mg_6Al_2(OH)_{16}]^{2+}$-$[CO_3{\cdot}4H_2O]^{2-}$ and $[Mg_2Al(OH)_6]^{+}[NO_3{\cdot}2H_2O]^{-}$.

Two synthetic Mg–Al double hydroxide materials of the nominal composition given above were used in this study. The carbonate anion containing material was supplied by the Aluminum Company of America (ALCOA) while the nitrate anion containing material was synthesized hydrothermally at 200 °C for 4 h under saturated steam pressure in our laboratory according to the method described previously.[24] The carbonate and nitrate anion containing materials have surface areas of 9 and 54 $m^2\ g^{-1}$, respectively. We determined selective transition metal (M^{2+}) cation ($M^{2+}=Cu^{2+}$, Co^{2+}, Ni^{2+} and Zn^{2+}) uptake by using solutions containing 5×10^{-5}, 5×10^{-4}, 5×10^{-3} or 1×10^{-2} M M^{2+} in the presence of 0.5 M NaCl. The pH of the starting solutions except for 1×10^{-2} M $CuCl_2$ and 5×10^{-3} M $CuCl_2$ was adjusted to pH 5 with HCl and NaOH solutions. Because Cu precipitates at pH 5.0 in 10^{-2} M and 5×10^{-3} M solutions, the pH of these solutions was adjusted to 4.0 or used at their unadjusted pH (4.7). Each anionic clay (50 mg) was equilibrated by shaking with 25 ml of solution for 1 day. After equilibration the solid and solution phases were separated by centrifugation and the pH of the solutions were measured. The solutions were analyzed by atomic emission spectroscopy (AES) and the solid phases were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). Kinetics of uptake of Co and Ni were investigated using 5×10^{-4} M concentrations of these ions in 0.5 M NaCl at pH 5. The solutions and solids were separated and analyzed as above. All of the data points represent the average of triplicate runs.

Both anionic clays selectively removed 100% of all the transition metal (M^{2+}) cations from 5×10^{-4} and 5×10^{-5} M $M^{2+}Cl_2$ solutions in the presence of 0.5 M NaCl after equilibration for 24 h. When the concentration of metal cations was increased to 5×10^{-3} or 1×10^{-2} M the uptake of cations changed with the type of transition metal cation as well as the nature of the anionic clay, *i.e.*, whether the anionic clay contained carbonate anions or nitrate anions (Table 1). The commercial sample with lower charge density containing

Table 1 Transition metal cation uptake by two anionic clays [a]

transition metal cation	nominal starting concentration[b]/M	uptake (%) carbonate anion containing material	uptake (%) nitrate anion containing material
Co^{2+}	5×10^{-3}	22.9 ± 2.8	22.9 ± 1.6
Co^{2+}	1×10^{-2}	10.4 ± 3.0	8.1 ± 1.0
Ni^{2+}	5×10^{-3}	29.3 ± 3.8	21.2 ± 0.8
Ni^{2+}	1×10^{-2}	14.6 ± 2.2	9.3 ± 1.6
Zn^{2+}	5×10^{-3}	60 ± 3.6	50.6 ± 0.8
Zn^{2+}	1×10^{-2}	35.6 ± 4.8	24.9 ± 0.8
Cu^{2+} (pH 4.67)	5×10^{-3}	100 ± 0.05	78.3 ± 1.8
Cu^{2+} (pH 3.99)	5×10^{-3}	100 ± 0.05	79.4 ± 0.5
Cu^{2+} (pH 4.68)	1×10^{-2}	95.1 ± 1.1	38.9 ± 1.5
Cu^{2+} (pH 4.00)	1×10^{-2}	93.4 ± 0.7	37.1 ± 1.5

[a] Complete uptake occurred from 5×10^{-4} and 5×10^{-5} M concentrations of transition metals from 0.5 M NaCl by both anionic clays. [b] The transition metals are in the presence of 0.5 M NaCl.

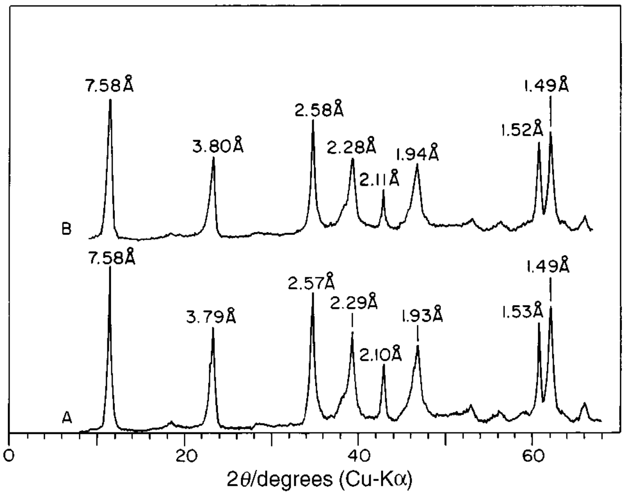

Fig 1 Powder XRD patterns of carbonate form of anionic clay: (A) untreated and (B) treated with 5×10^{-3} M Ni^{2+}

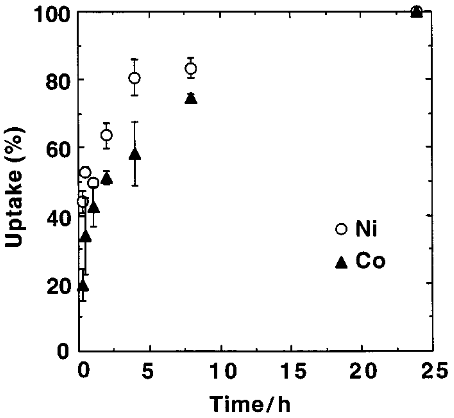

Fig. 2 Kinetics of uptake of Co and Ni from 0.5 M NaCl containing 5×10^{-4} M Co^{2+} or 5×10^{-4} M Ni^{2+}

CO_3^{2-} as the charge balancing ion reacted to take up higher percentages of all the transition metals compared to the hydrothermally synthesized higher charge density anionic clay with nitrate ions as the interlayer species even though the former sample has a larger particle size than the latter (SEM results not shown; see surface areas above). Powder XRD and scanning electron microscopy results showed that there were no changes in the patterns (Fig. 1) or morphology, respectively when the anionic clays were treated with 5×10^{-5} or 5×10^{-4} M Co^{2+}, Ni^{2+}, Zn^{2+} or Cu^{2+} and with 5×10^{-3} or 1×10^{-2} M Co^{2+} or Ni^{2+}. When the anionic clays were treated with 5×10^{-3} or 1×10^{-2} M Zn^{2+}, a small unidentified peak at *ca.* 2.70 Å appeared while the remainder of the pattern remained unchanged. For 5×10^{-3} or 1×10^{-2} M Cu^{2+} solution, the formation of botallackite, $Cu^{2+}(OH)_3Cl$ as an additional phase was observed. Solution analyses indicated more or less stoichiometric release of Mg^{2+} into the solution by the uptake of all the transition metals (Table 2) except at concentrations of 5×10^{-3} and 1×10^{-2} M for Cu^{2+} where precipitation of botallackite was observed. We have also tested calumite, $[Ca_2Al(OH)_6]^+[NO_3{\cdot}xH_2O]^-$ which is an analogue of hydrotalcite for Cd^{2+} and Pb^{2+} uptake using the same concentrations of these ions as the above transition metals in 0.5 M NaCl. The uptakes of Cd and Pb by calumite were determined to be very high but the amounts of Ca released into solution were in excess of stoichiometric exchange with Cd or Pb. The mechanism of uptake of these ions on calumite, however, is not clear. Because the equilibrium pH with calumite is very high, precipitation along with other mechanisms are possible (detailed results on calumite will be reported elsewhere).

The above results of transition metal cation uptake on Mg–Al anionic clays and the rapid kinetics involved (Fig. 2) suggest that the mechanism of transition metal ion uptake is by diadochy, *i.e.*, substitution for Mg^{2+} in the anionic clay crystal structure facilitated by the easy access for the cations through the interlayer spaces (Fig. 3). Diadochy is a well

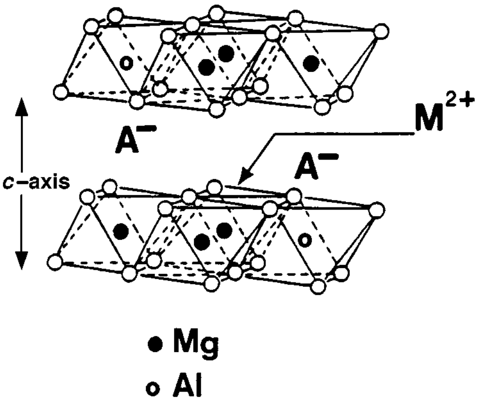

Fig. 3 Schematic of M^{2+}(=Cu, Ni, Co and Zn) substitution for Mg^{2+} in anionic clay structure through the interlayer space

Table 3 Theoretical capacities for metal cation uptake of some clays and zeolites in comparison to those of anionic clays

material	theoretical capacity for metal cation uptake/mequiv. $(100\ g)^{-1}$[a]
cationic clays	
montmorillonite	~100
vermiculite	~180
zeolites	
clinoptilolite	~220
zeolite, 4A	~540
anionic clays	
$[Mg_6Al_2(OH)_{16}]^{2+}[CO_3{\cdot}4H_2O]^{2-}$	~1990
$[Mg_2Al(OH)_6]^+[NO_3{\cdot}2H_2O]^-$	~1450

[a] Calculated from chemical formula.

Table 2 Uptake of transition metal (M^{2+}) cations from 0.5 M NaCl containing 5×10^{-3} M M^{2+} with concurrent stoichiometric (within experimental errors) release of Mg^{2+} from anionic clays

metal ion	pH after equilibration	carbonate anion containing material		nitrate anion containing material	
		M^{2+} uptake/mM	Mg^{2+} release/mM	M^{2+} uptake/mM	Mg^{2+} release/mM
Co^{2+}	7.1	1.17	0.83	1.17	1.18
Ni^{2+}	7.0	1.45	1.40	1.03	1.28
Zn^{2+}	6.3	2.77	2.52	2.33	2.32
Cu^{2+}	5.4	—	—	3.45	2.57

known reaction in calcite[1] and hydroxyapatites.[25] This mechanism is very likely because anionic clays with all these transition metals have been prepared by many researchers.[7] The kinetics of Co^{2+} and Ni^{2+} ion uptake are rapid as shown in Fig. 2 which is a very important consideration in certain applications such as waste water treatment or drinking water filtration. The new function discovered here for anionic clays is expected to have applications in remediation of metal contaminated soils and groundwater (for example, at superfund sites) and clean up of drinking as well as waste waters because of their very high theoretical capacities for transition metals compared to the existing cation exchange materials (Table 3). The anionic clay materials not only selectively remove transition metal cations but also lock them up in their structure leading to their immobilization. An additional advantage of these materials compared to synthetic zeolites and clays is that they can be inexpensively prepared at room temperature.[7]

This research was supported by the Materials Research Laboratory's Consortium on Chemically Bonded Ceramics.

References

1 J. R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990, p. 692.
2 N. S. Kurnakov and V. V. Chernykh, *Zap. Vserass. Mineral Ova.*, 1926, **55**, 118.
3 G. Aminoff and B. Broomé, *Kungl. Svenska. Vetensckaps Handel*, 1930, **9**, 23.
4 H. H. Read and B. E. Dixon, *Miner. Mag.*, 1933, **23**, 309.
5 C. Frondel, *Am. Mineral.*, 1941, **26**, 295.
6 D. M. Roy, R. Roy and E. F. Osborn, *Am. J. Sci.*, 1953, **251**, 337.
7 A. de Roy, C. Forano, K. El Malki and J. P. Besse, in *Expanded Clays and Other Microporous Solids*, ed. M. L. Occelli and H. E. Robson, Van Nostrand Reinhold, New York, 1992, p. 108.
8 W. J. Lay, *Ind. Eng. Chem.*, 1954, **46**, 1061; J. M. Kerr, *Bull. Am. Ceram. Soc.*, 1954, **38**, 374.
9 S. Komarneni and R. Roy, *Science*, 1988, **239**, 1286; W. J. Paulus, S. Komarneni and R. Roy, *Nature* (*London*), 1992, **357**, 571.
10 R. Allman, *Acta Crystallogr.*, *Sect. B*, 1968, **24**, 972.
11 H. F. W. Taylor, *Miner. Mag.*, 1969, **37**, 338.
12 K. Hashi, S. Kikkawa and M. Koizumi, *Clays Clay Miner.*, 1983, **31**, 152.
13 A. de Roy, J. P. Besse and P. Bondot, *Mater. Res. Bull.*, 1985, **20**, 1091.
14 K. El Malki, A. de Roy and J. P. Besse, *Eur. J. Solid State Inorg. Chem.*, 1989, **26**, 339.
15 A. de Roy and J. P. Besse, *Solid State Ionics*, 1991, **46**, 95.
16 M. Lal and A. T. Howe, *J. Solid State Chem.*, 1981, **39**, 368.
17 S. Miyata and T. Kumura, *Chem. Lett.*, 1973, 843.
18 S. Miyata, *Clays Clay Miner.*, 1975, **23**, 369.
19 J. G. Nunan, P. B. Himelfarb, R. G. Herman, K. Kleir, C. E. Bogdan and G. W. Simmons, *Inorg. Chem.*, 1989, **28**, 3868.
20 H. P. Boehm, J. Steinle and C. Vieweger, *Angew. Chem.*, *Int. Ed. Engl.*, 1977, **16**, 265.
21 D. L. Bish, *Bull. Mineral.*, 1980, **103**, 170.
22 S. Miyata, *Clays Clay Miner.*, 1983, **31**, 305.
23 T. Kwon, G. A. Tsigdinos and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 1988, **110**, 3653.
24 G. Fetter, F. Hernández, A. M. Maubert, V. H. Lara and P. Bosch, *J. Porous Mater.*, 1997, **4**, 27.
25 T. Suzuki, K. Ishigaki and M. Miyake, *J. Chem. Soc.*, *Faraday Trans. 1*, 1984, **80**, 3157.

Communication 8/01631C; *Received* 26th *February*, 1998