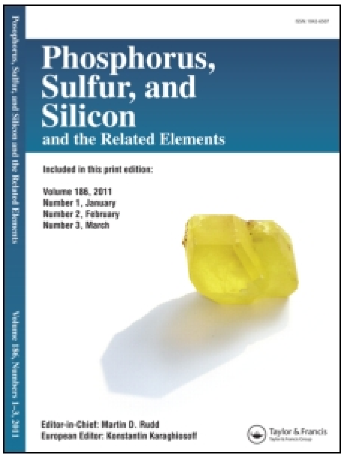

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Hydrotalcite from Seawater and Its Application to Phosphorus Removal

Tomohito Kameda[a b]; Toshiaki Yoshioka[a]; Miho Uchida[a]; Akitsugu Okuwaki[a]
[a] Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Sendai, Japan [b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

To cite this Article Kameda, Tomohito , Yoshioka, Toshiaki , Uchida, Miho and Okuwaki, Akitsugu(2002) 'Synthesis of Hydrotalcite from Seawater and Its Application to Phosphorus Removal', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1503 — 1506

To link to this Article: DOI: 10.1080/10426500212285

URL: http://dx.doi.org/10.1080/10426500212285

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1503–1506

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290093469

SYNTHESIS OF HYDROTALCITE FROM SEAWATER AND ITS APPLICATION TO PHOSPHORUS REMOVAL

Tomohito Kameda,[a,b] *Toshiaki Yoshioka,*[a] *Miho Uchida,*[a]
and Akitsugu Okuwaki[a]
Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba 07, Aoba-ku, Sendai 980-8579, Japan[a] *and Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 1,1 Katahira, 2-Chome, Aoba-ku, Sendai 980-8577, Japan*[b]

(Received July 28, 2001; accepted December 25, 2001)

*10.0 wt% milk of lime was added to seawater containing $AlCl_3$ at Mg/Al molar ratio of 3.0 until pH 10.5 with stirring, and kept at 25°C for 1 h. Hydrotalcite (HT) was precipitated as a single phase, and Mg^{2+} and Al^{3+} were quantitatively precipitated. The chemical composition was $[Mg_{0.75}Al_{0.25}(OH)_2][(SO_4)_{0.06}(Cl)_{0.02}(OH)_{0.11}{}^{*}]\cdot 0.27H_2O^{*}$ (*Balance). A 100 mg-P/L Na_2HPO_4 solution and the HT were shaken at 25°C. Phosphate removal increased with increasing time and the HT quantity, and was the highest at pH 7–9. Phosphate ion could be quantitatively removed, adding 8 times the stoichiometric quantity of the HT at pH 8.7 for 6 h.*

Keywords: Anion exchange; hydrotalcite; milk of lime; phosphorus removal; seawater; synthesis

INTRODUCTION

In order to prevent eutrophication, it is considered to reduce the load of phosphorus to water environment. One method is the removal of phosphate ion by HT ($[Mg^{2+}{}_{1-x}Al^{3+}{}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O{:}0.20 \leqq x \leqq 0.33$), which is a layered double hydroxide with anion exchange property;[1,2] however, HT is an expensive material used as antacid, etc.,[3] and it is necessary to develop new process for inexpensive HT. In this study, HT was synthesized using seawater and milk of lime in consideration for the utilization of plant-producing $Mg(OH)_2$, and the characteristic of phosphate removal by the HT was examined.

Address correspondence to T. Kameda. E-mail: kameda@tagen.tohoku.ac.jp

TABLE I The Compositions of Seawaters (mM)

Seawater	Na^+	K^+	Mg^{2+}	Ca^{2+}	$SO_4{}^{2-}$	Cl^-	Br^-
Artificial	466	0	53	10	28	536	0
Natural	424	9	48	11	25	500	1

EXPERIMENTAL

1. Synthesis of HT from Seawater (Seawater-Milk of Lime Process)

Table I shows the compositions of seawaters. 0.7–10.0 wt% $Ca(OH)_2$ slurry or $Ca(OH)_2$ powder were added to artificial or natural seawater containing $AlCl_3$ at Mg/Al molar ratio of 1.0–5.0 until pH 10.5 or stoichiometric amounts with stirring and kept at 25°C or 60°C for 1 h. Precipitates were filtered, washed with water, dried at 105°C for 24 h, and then identified by X-ray diffraction (XRD). Chemical composition of filtrates and precipitates was determined by ICP-AES and ion chromatography.

2. The Application of HT Prepared with the New Process to Phosphorus Removal

The $[Mg_{0.75}Al_{0.25}(OH)_2][(SO_4)_{0.06}(Cl)_{0.02}(OH)^*_{0.11}]\cdot 0.27H_2O^*$ ($HT_{(SW)}$) was applied to phosphorus removal. $HT_{(SW)}$ of 1–8 times the stoichiometric quantity were added to a 100 mg-P/L Na_2HPO_4 solution (15 ml) according to eq. (1) at pH 7.1–13.3, and they were shaken at 25°C for 6 h:

$$\begin{aligned}&[Mg_{0.75}Al_{0.25}(OH)_2][(Cl)_{0.02}(SO_4)_{0.06}(OH)_{0.11}] + 0.125HPO_4{}^{2-}\\&\quad\rightleftarrows [Mg_{0.75}Al_{0.25}(OH)_2][(HPO_4)_{0.125}] + 0.02Cl^-\\&\quad + 0.06SO_4{}^{2-} + 0.11OH^-.\end{aligned}\tag{1}$$

After the filtration, chemical composition of filtrates was determined by ion chromatography.

RESULTS AND DISCUSSION

1. Synthesis of HT from Seawater (Seawater-Milk of Lime Process)

1-1. The Effect of Mg/Al Molar Ratio in Solution (Artificial Seawater, 0.7 wt% $Ca(OH)_2$ Slurry, 60°C)

HT was precipitated as a single phase at Mg/Al molar ratio of 2.0–4.0, although a small amount of $Al(OH)_3$ was precipitated at 1.0 and a small amount of $Mg(OH)_2$ was precipitated at 4.5–5.0. As increasing Mg/Al molar ratio in solution, Al^{3+} precipitated increased and Mg^{2+} precipitated decreased. Mg^{2+} and Al^{3+} were quantitatively precipitated at 2.4–3.0.

1-2. The Effect of $Ca(OH)_2$ Slurry Concentration (Artificial Seawater, Mg/Al Molar Ratio of 3.0 in Solution, 25°C)

HT was precipitated as a single phase using 0.7–10.0 wt% $Ca(OH)_2$ slurry and even $Ca(OH)_2$ powder. Mg^{2+} and Al^{3+} were quantitatively precipitated.

1-3. Synthesis of HT from Natural Seawater (Mg/Al Molar Ratio of 3.0 in Solution, 10.0 wt% $Ca(OH)_2$ Slurry, 25°C)

HT ($HT_{(SW)}$) was also precipitated as a single phase from natural seawater, as well as from artificial seawater, and Mg^{2+} and Al^{3+} were quantitatively precipitated. The chemical composition of $HT_{(SW)}$ was $[Mg_{0.75}Al_{0.25}(OH)_2][(SO_4)_{0.06}(Cl)_{0.02}(OH)_{0.11}{}^*] \cdot 0.27H_2O^*$ (*Balance). The ratio of $SO_4{}^{2-}$ to Cl^- in the interlayer was high. This is because the charge density of $SO_4{}^{2-}$ is larger than that of Cl^-. Anion is easily intercalated into HT, as the charge density is larger.[4]

2. The Application of HT Prepared with the New Process to Phosphorus Removal

Figure 1 shows the effect of $HT_{(SW)}$ quantity on phosphate removal. Phosphate removal increased with increasing the $HT_{(SW)}$ quantity, and

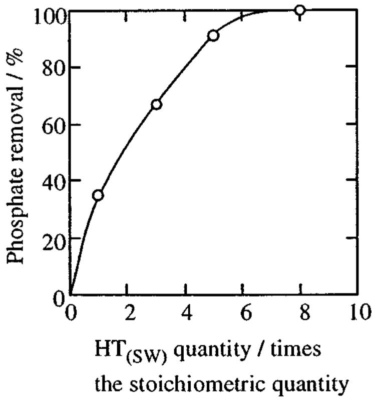

FIGURE 1 Effect of $HT_{(SW)}$ quantity on phosphate removal (pH 8.7).

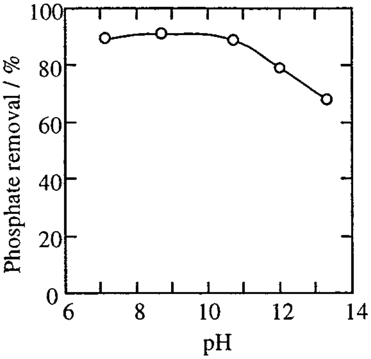

FIGURE 2 Effect of pH on phosphate removal using $HT_{(SW)}$ of 5 times the stoichiometric quantity.

phosphate ion could be quantitatively removed by adding 8 times the stoichiometric quantity of $HT_{(SW)}$; however, phosphate ion was not quantitatively removed at the stoichiometric quantity. The ionic species of phosphate at pH 8.7 are mainly HPO_4^{2-}. Because the anion size of HPO_4^{2-} is almost close to that of SO_4^{2-},[5] it is supposed that HPO_4^{2-} was not much exchanged for SO_4^{2-} in $HT_{(SW)}$. Figure 2 shows the effect of pH on phosphate removal. Phosphate removal was the highest at pH 7–9 and decreased with increasing pH. The ionic species of phosphate at pH 13.3 are mainly PO_4^{3-}. Although the charge density of PO_4^{3-} is larger than that of SO_4^{2-}, the phosphate removal was the lowest. Because of the large amounts of OH^- at the pH, it is supposed that OH^- was mainly intercalated into $HT_{(SW)}$, and the intercalation of PO_4^{3-} was prevented. In contrast, although the existence ratio of HPO_4^{2-} was low since the ionic species at pH 7.1 were a mixture of HPO_4^{2-} (44%) and $H_2PO_4^-$ (56%), the phosphate removal at pH 7.1 was almost as same as that at pH 8.7. This is attributable to the increase in the HPO_4^{2-} in solution with the deintercalation of OH^- in $HT_{(SW)}$.

REFERENCES

[1] A. Kawamoto, A. Ookubo, T. Sato, and T. Suzuki, *Mizukannkyougakkaishi*, **22,** 875 (1999).
[2] H. Shin, M. Kim, S. Nam, and H. Moon, *Water Sci. Tech.*, **34,** 161 (1996).
[3] F. Cavani, F. Trifiro, and A. Vaccari, *Catal. Today*, **11,** 173 (1991).
[4] S. Miyata, *Clays Clay Miner.*, **31,** 305 (1983).
[5] T. Sato, T. Wakabayashi, and M. Shimada, *Ind. Eng. Chem., Process Des. Dev.*, **25,** 89 (1986).