

This article was downloaded by:

On: 25 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Simultaneous Removal of NH_4^+ and PO_4^{3-} in Aqueous Solution and Its Mechanism by Using Zeolite Synthesized from Coal Fly Ash

Norihiro Murayama^a; Shinsuke Yoshida^a; Yuko Takami^a; Hideki Yamamoto^a; Junji Shibata^a

^a Department of Chemical Engineering, Kansai University, Osaka, "JP" Japan

Online publication date: 24 February 2003

To cite this Article Murayama, Norihiro , Yoshida, Shinsuke , Takami, Yuko , Yamamoto, Hideki and Shibata, Junji(2003) 'Simultaneous Removal of NH_4^+ and PO_4^{3-} in Aqueous Solution and Its Mechanism by Using Zeolite Synthesized from Coal Fly Ash', Separation Science and Technology, 38: 1, 113 – 130

To link to this Article: DOI: 10.1081/SS-120016701

URL: <http://dx.doi.org/10.1081/SS-120016701>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 1, pp. 113–129, 2003

Simultaneous Removal of NH_4^+ and PO_4^{3-} in Aqueous Solution and Its Mechanism by Using Zeolite Synthesized from Coal Fly Ash

Norihiro Murayama, Shinsuke Yoshida, Yuko Takami,
Hideki Yamamoto, and Junji Shibata*

Department of Chemical Engineering, Kansai University, Osaka, Japan

ABSTRACT

The objective of this study is to investigate the cation exchange property of the product (zeolite P) synthesized from coal fly ash by alkali hydrothermal reaction, and to evaluate the water purification ability for simultaneous removal of NH_4^+ and PO_4^{3-} in aqueous solution.

Zeolite P crystal begins to be collapsed or to be dissolved with a decrease in aqueous pH. The cation exchange capacity of the product drastically decreases below pH 4. The simultaneous removal of NH_4^+ and PO_4^{3-} can be achieved when NH_4^+ is exchanged by CaP zeolite and an insoluble salt is formed by the reaction between Ca^{2+} released from zeolite and PO_4^{3-} in aqueous solution.

From the above results, the effect of pH on cation exchange property of the product and the mechanism of simultaneous removal of NH_4^+ and

*Correspondence: Junji Shibata, Department of Chemical Engineering, Kansai University, Suita, Osaka 567-8680, Japan. Fax: 81-6-6388-8869; E-mail: shibata@kansai-u.ac.jp.

PO_4^{3-} in aqueous solutions are considered, respectively. The CaP zeolite used in this study, which can simultaneously remove NH_4^+ and PO_4^{3-} , has advantages compared with the other removal methods.

INTRODUCTION

Recently, a coal-fired power plant was reconsidered as an energy source owing to the difficulty in establishing the nuclear power plant and the deficiency of petroleum resources. An increase in coal ash discharged from power plants results in another problem. The amount of overall discharged coal ash in Japan is extremely increased, which is estimated to be over 10 million tons per year. New methods for recycling of coal ash have to be developed under these circumstances.^[1]

Many researchers^[2–7] have found that various kinds of zeolite could be produced from coal ash by an alkali hydrothermal reaction, and suggested that the zeolite from coal ash could be used for various purposes such as water purification, soil improvement, various adsorbents, and so on. Many reports on the mechanism of zeolitization reaction from coal fly ash and the cation exchange property of the obtained zeolite were published.^[8–13] However, there are a lot of engineering problems and phenomena to be investigated in case of designing the manufacturing equipment for zeolite synthesis or commercializing the technology. It is very important to develop the new usage of the zeolite with a new advantage. As a part of the development of zeolite usage, the removal ability of the zeolite from coal fly ash for NH_4^+ and PO_4^{3-} in aqueous solution has been considered in some papers,^[13,14] but these kinds of reports are few. The mechanism of PO_4^{3-} removal by the zeolite has not been adequately clarified yet.

The zeolite would be an excellent water purification agent that can simultaneously remove both cation and anion in aqueous solution. For this purpose, the effect of pH on cation exchange properties of zeolite, the simultaneous removal of NH_4^+ and PO_4^{3-} in various solutions and the mechanism of simultaneous removal are investigated in this study.

EXPERIMENTAL

Zeolite Synthesis from Coal Fly Ash

Coal fly ash used in this study was supplied by Denpatsu Coal Tech. Co., Ltd. The quality of this coal ash satisfies Japanese Industrial Standard.

**Removal of NH_4^+ and PO_4^{3-}** **115**

A portion of dry powder of coal fly ash and 2.0 mol/dm^3 NaOH solution were put into in 800 cm^3 autoclave made of stainless steel at $100 \text{ g}/400 \text{ cm}^3$ of solid–liquid ratio. Zeolite synthesis from coal fly ash was carried out by an alkali hydrothermal treatment under heating and agitating conditions. Agitation speed, reaction temperature, and reaction time were adopted to be of 500 rpm, 393K, and 3 h, respectively.

The zeolite obtained by the above hydrothermal reaction (NaP zeolite) was used as a starting material for various cation exchange and ion removal experiments shown in the blow section. The surface structure of coal fly ash and NaP zeolite is shown in Fig. 1(a) and (b). The physical properties and chemical composition of these are shown in Tables 1 and 2. The cation exchange capacity of the product measured by the modified Harada–Aomine method^[12] was about 300 meq/100 g. This method consisted of a saturation substitution operation by Ca^{2+} and a saturation re-substitution by NH_4^+ . The obtained product was confirmed to be such complex material as coal fly ash particles covered with zeolite crystal. We reported details on the physical properties and chemical composition of the obtained zeolite in the previous papers.^[10,11]

Acid Resistance Test of NaP Zeolite

In order to confirm the acid resistance property of the zeolite synthesized from coal fly ash, 1.0 g of dried NaP zeolite was contacted with 40 cm^3 of various HCl solutions for 15 min by a vertical type shaker. The concentration of HCl solutions was chosen such that the pH of the slurries after shaking was in a range of pH 2 and pH 10 at 298K. After the above operation, the solid cake was separated by a centrifugal separator, washed by distilled water, dried in a stationary drier at 378K for 24 h.

Crystalline materials were identified by means of an x-ray diffraction (JDX-3530S, Nihon Denshi Co., Ltd.), and the chemical composition was analyzed by an x-ray fluorescence analysis (EMAX-3770, Horiba Co., Ltd.). Amounts of Al^{3+} , Na^+ , and Ca^{2+} were analyzed by an inductively coupled plasma atomic emissions spectrometry (ICPS-1000III, Shimadzu Co., Ltd.).

 NH_4^+ Exchange Test with NaP and CaP Zeolites

One gram of NaP zeolite and 40 cm^3 of CaCl_2 solutions were mixed and shaken in the pH values around 7. After the zeolite and CaCl_2 solution being separated, the new ion exchange cycle with fresh CaCl_2 solution were

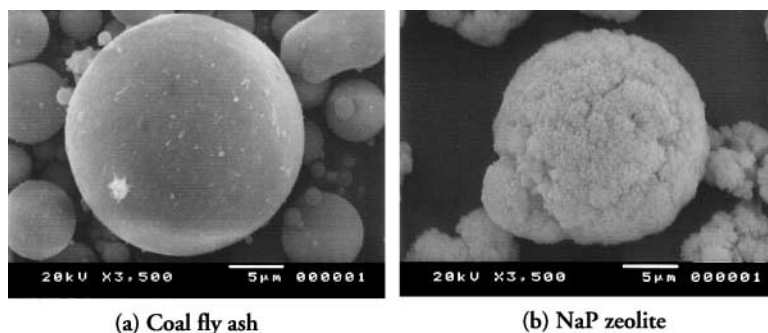


Figure 1. SEM photographs of coal fly ash and NaP zeolite.

repeated. A series of ion exchange operations were carried out six times, and the effect of the contact conditions on Ca substitution ratio of zeolite was investigated. The Na^+ and Ca^{2+} in the zeolite were re-exchanged by saturation substitution with NH_4^+ . This saturation substitution was carried out repeatedly with 1.0 mol/dm^3 NH_4Cl solution until Na^+ or Ca^{2+} were not released from the zeolite.

By using the NaP zeolite and the CaP zeolite obtained by the Ca substitution operation mentioned above, the NH_4^+ adsorption test was conducted at various pH values. The NH_4^+ solutions having various concentrations and pH values were prepared by changing the mixing ratio of NH_4Cl and NH_4OH . One gram of zeolite and 40 cm^3 of NH_4^+ solution were contacted under the same conditions mentioned above. The ion exchange amount of NH_4^+ was calculated from a decrease in NH_4^+ in solution. The concentration of NH_4^+ in solution was measured by an ion chromatograph (DX-500, Nihon Dionex Co., Ltd.). The CaP zeolite separated from solution was washed with distilled water and dried.

Table 1. Physical properties of product synthesized from coal fly ash.

Crystal type of zeolite	NaP zeolite
Cation exchange capacity	300 meq/100 g
Si/Al ratio	2.1
Specific surface area	$59 \text{ m}^2/\text{g}$
Median diameter	$25 \mu\text{m}$
Particle size distribution	1–100 μm

Removal of NH_4^+ and PO_4^{3-} **117****Table 2.** Chemical composition of coal fly ash and obtained product (NaP zeolite) [unit: wt%].

	Si	Al	Na	K	Ca	Fe	Ti	Mg
Coal fly ash	50.4	20.3	5.4	2.7	7.5	8.2	1.8	2.9
NaP zeolite	41.4	19.8	17.6	1.6	11.2	5.1	1.6	1.7

 PO_4^{3-} Removal Test with CaP Zeolite

One gram of CaP zeolite was put into 40 cm³ of PO_4^{3-} solutions in order to investigate the PO_4^{3-} removal with CaP zeolite. The PO_4^{3-} solutions were prepared by using H_3PO_4 , Na_3PO_4 , K_3PO_4 , or $(\text{NH}_4)_3\text{PO}_4$ as a phosphorus source. In case of $(\text{NH}_4)_3\text{PO}_4$ solution, simultaneous removal of NH_4^+ and PO_4^{3-} in solution with the CaP zeolite was intended. The contact condition, separation method, and various instrumental analyses were the same as shown in the former section.

The amounts of NH_4^+ and PO_4^{3-} exchanged or removed were calculated from a decrease in NH_4^+ and PO_4^{3-} concentration in the solution. The amount of PO_4^{3-} in the solution after solid–liquid separation was measured by an inductively coupled plasma atomic emissions spectrometry.

RESULTS AND DISCUSSION**Acid Resistance of NaP Zeolite**

When a cation exchange reaction with zeolite is carried out in aqueous solution, the cation exchange capacity of zeolite is not essentially dependent on pH. However, the crystal body of zeolite is broken by the action of proton in a low pH region. In other words, it is very important in practical use to investigate the effect of the acid resistance of the product on the cation exchange capacity.

Acid resistance of the NaP zeolite synthesized from coal fly ash is investigated. The natural pH of NaP zeolite slurry is over 10 when pH adjustment is not carried out. The amount of Al^{3+} eluted from zeolite and x-ray diffraction intensities of crystalline materials in the product are shown in Fig. 2 as a function of pH. The amount of Al^{3+} eluted in aqueous solution means a collapsed degree of zeolite crystal by proton. The amount of Al^{3+} eluted suddenly increases below the pH value of 4. The x-ray diffraction

intensity of zeolite P decreases with a decrease in pH value from 10 to 5, which indicates rapid decomposition of zeolite P in the pH region below 4. On the other hand, the x-ray diffraction intensities of quartz and mullite originally contained in coal fly ash increase slightly with a decrease in pH. An increase in diffraction intensities is explained by the relative increase of these materials due to the decomposition of zeolite species.

Surface structure of NaP zeolite after acid-washing treatment by various HCl solutions is shown in Fig. 3. The particle surface is covered with zeolite crystal above pH 9.6, while a part of zeolite crystal is exfoliated after the acid washing with pH 4.2. Almost all of zeolite crystal phase is dissolved by HCl solution below pH 3.8, and the fly ash core appears. These results of SEM observation are concordant well to the corresponding results shown in Fig. 2.

The crystalline degree of zeolite P gradually deteriorates with a decrease in pH in the pH range over 4, which does not lead to the dissolution of Al site in zeolite crystal. On the other hand, zeolite crystal itself begins to dissolve

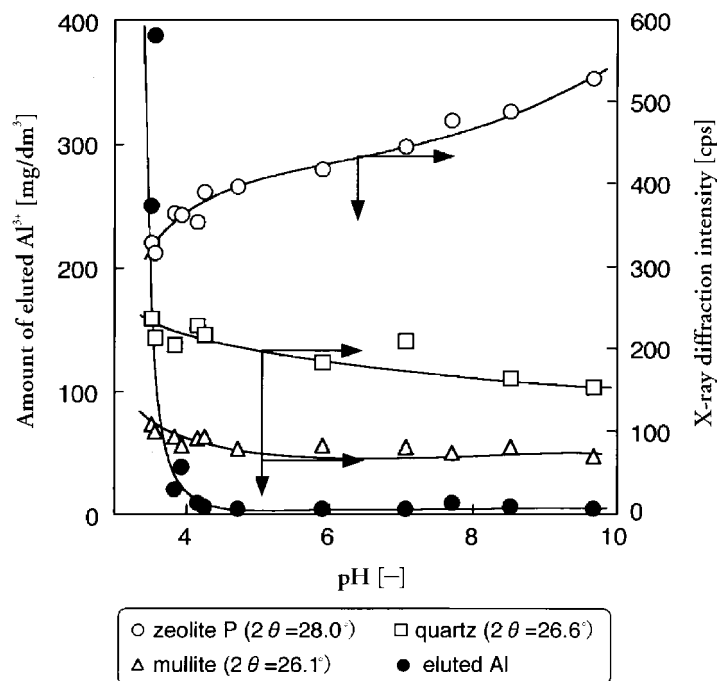


Figure 2. Amount of Al^{3+} eluted from zeolite and x-ray diffraction intensities of crystalline materials as a function of pH.

Removal of NH_4^+ and PO_4^{3-}

119

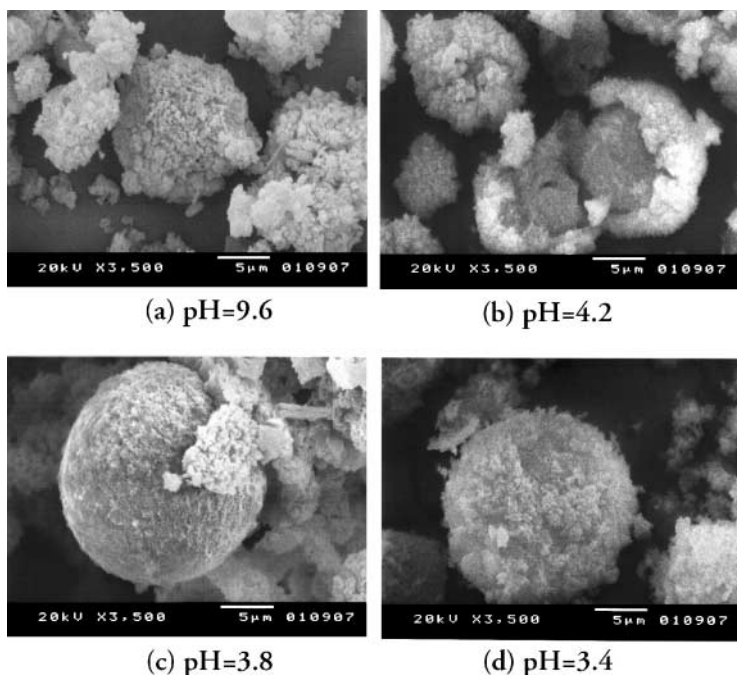
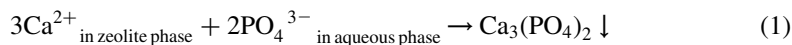


Figure 3. Surface structure of NaP zeolite after acid-washing treatment by various HCl solutions.

with a decrease in pH in the pH range below 4. Therefore, the NaP zeolite must be used up to pH4.

Production of CaP Zeolite as Water Purification Agent

Zeolite does not have generally anion exchange ability. In our previous report,^[13] NH_4^+ in solution is removed by a cation exchange reaction with zeolite, whereas Ca component in zeolite contributes to the removal of PO_4^{3-} in aqueous solution. For an example, the PO_4^{3-} removal with zeolite is achieved by the following chemical reaction,



In the simultaneous removal of NH_4^+ and PO_4^{3-} in aqueous solution, the CaP zeolite provides Ca^{2+} into the solution to remove PO_4^{3-} . However,

the products synthesized from coal fly ash are such NaP zeolites as containing Na^+ ion as an exchangeable cation, because the reaction of zeolitization is carried out by using NaOH as an alkali source. The Ca^{2+} exchange is required for the production of CaP zeolite.

The Ca substitution behavior between Ca^{2+} in solution and Na^+ in zeolite is shown in Fig. 4. In the case of 75 meq/dm^3 of initial Ca^{2+} concentration, the amount of Ca^{2+} in solution is equal to that of exchangeable Na^+ in zeolite. The Ca exchange ratio of zeolite increases with an increase in the number of substitution operation below 4 times. The five and six times substitution operations give constant results of about 73%. On the other hand, in the case of $1,000 \text{ meq/dm}^3$ of initial Ca^{2+} concentration, the Ca substitution ratio increases to about 94% with the number of substitution operations until five times. The substitution operations more than five times do not increase the Ca substitution ratio in spite of repeated substitution operations. Therefore, the Ca

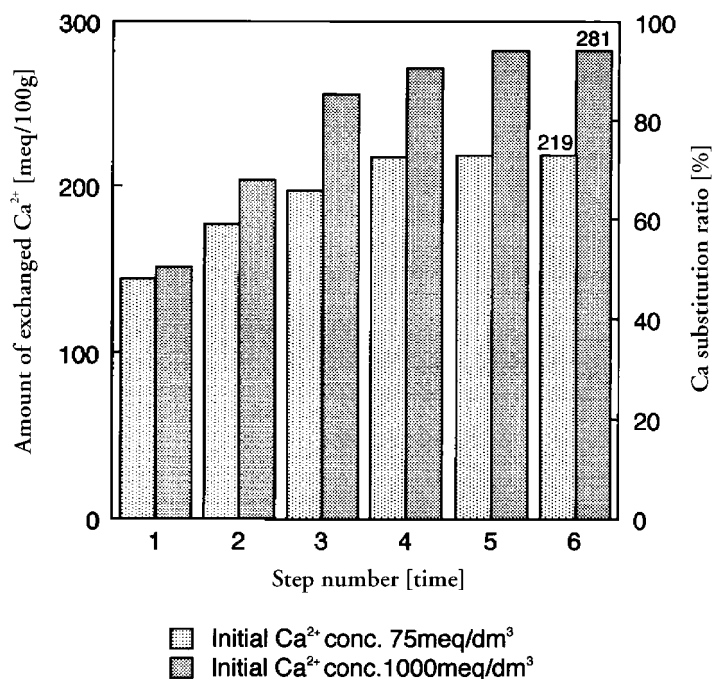


Figure 4. Ca substitution of product by cation exchange reaction between Ca^{2+} in solution and Na^+ in zeolite.

Removal of NH_4^+ and PO_4^{3-}

121

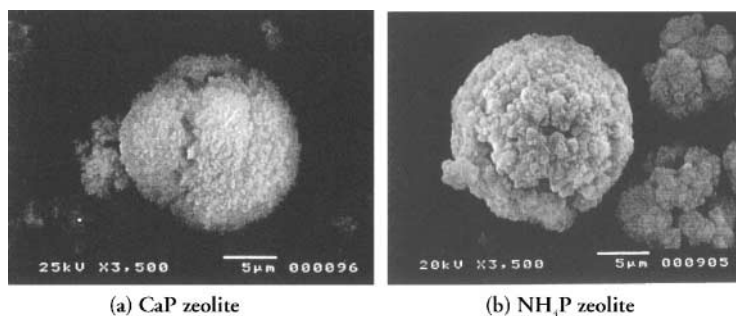


Figure 5. SEM photographs of products exchanged by Ca^{2+} and NH_4^+ .

substitution operation by high Ca^{2+} concentration should be adopted to obtain the zeolite with high Ca substitution ratio.

SEM photographs of the products exchanged by Ca^{2+} are shown in Fig. 5(a). Compared with the surface structure of NaP zeolite shown in Fig. 1(b), some cracks appear on the particle surface of the product treated by a Ca substitution operation, but generally speaking, the large difference is not recognized between both zeolites. This is because the zeolite is frequently brought into contact with proton in Ca^{2+} solution by repeated Ca substitution operations, and then the structure of zeolite crystal is slightly warped by the difference in ion radius or electric charge between Na^+ and Ca^{2+} .

Removal of NH_4^+ and PO_4^{3-} in Solution with Various Zeolites

The NaP zeolite or the 94% Ca substituted zeolite are respectively contacted with 1.0 mol/dm^3 NH_4Cl solution. These cation exchange reactions between Na^+ or Ca^{2+} in zeolite and NH_4^+ in solution are carried out at around pH 7. The results are shown in Fig. 6. NaP zeolite is superior to CaP zeolite in respect to both NH_4^+ exchange rate and exchange amount. NH_4^+ substitution ratio of about 95% and about 70% are respectively obtained from NaP and CaP zeolites in a cation exchange operation. The difference in NH_4^+ exchanged amount is due to the Coulomb force between the negative charge site of zeolite and cation. The Coulomb attractive force between the negative charge of zeolite and the divalent cation, Ca^{2+} , is greater than that between zeolite and the monovalent cation, Na^+ , and then the Na^+ in the zeolite P is easy to be exchanged with NH_4^+ compared with Ca^{2+} . When the contact operation with NH_4^+ solution is repeatedly carried out, NH_4^+ substitution

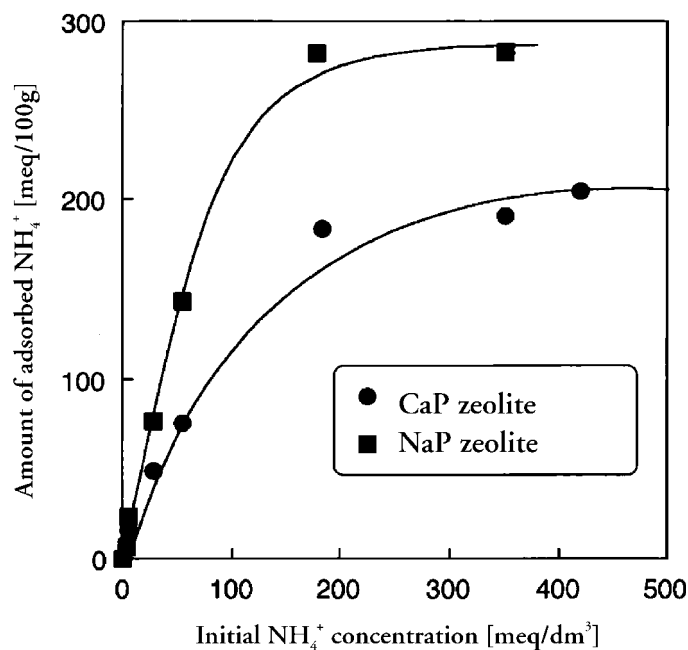


Figure 6. Removal of NH_4^+ in various solutions by NaP and CaP zeolites.

ratio reaches to near 100%. Almost all of Na^+ and Ca^{2+} in zeolite can be essentially exchanged by NH_4^+ in solution.

SEM photograph of the zeolite exchanged by NH_4^+ is shown in Fig. 5(b). Compared with NaP and CaP zeolites shown in Figs. 1(b) and 5(a), the surface structure of NH_4P zeolite changes from fine protruding material into such coarse flock as many fine particles coagulate each other. On the other hand, some x-ray diffraction peaks of NH_4P zeolite shift to the lower angle side due to the NH_4^+ intake compared with those of NaP zeolite.

The amounts of Al^{3+} eluted from zeolite and NH_4^+ exchanged in zeolite are shown in Fig. 7 as a function of pH. The amount of NH_4^+ exchanged in zeolite is large in the pH region from 4 to 10, but remarkably decreases below pH 4 and over pH 10. The exchange behavior is explained by the fact that zeolite crystal is broken by the action of proton in the lower pH region, whereas the amount of NH_4^+ in solution is very small in the higher pH region. In high pH, NH_4^+ in solution changes to NH_3 , because the dissociation constant (pKa) of NH_4^+ is 9.24. The suitable pH condition to remove NH_4^+ in aqueous solution with the zeolite is the pH from 4 to 10.

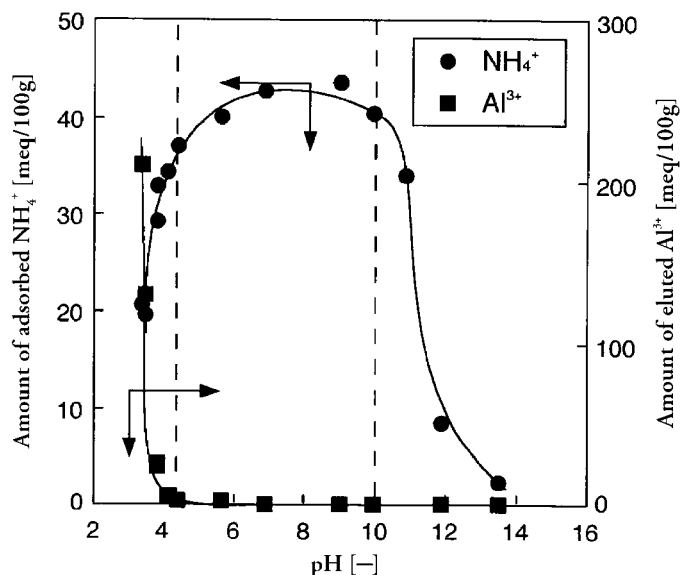


Figure 7. Amount of Al^{3+} eluted from zeolite and NH_4^+ adsorbed in zeolite as a function of pH.

The CaP zeolite is contacted with various PO_4^{3-} solutions of various concentration prepared by using phosphoric acid (H_3PO_4) and some orthophosphates (Na_3PO_4 , K_3PO_4 , $(\text{NH}_4)_3\text{PO}_4$). The removal of PO_4^{3-} in various solutions with CaP zeolite is shown in Fig. 8. In case of H_3PO_4 solution, the removal of PO_4^{3-} increases with an increase in initial PO_4^{3-} concentration. The removal amount is especially large over 3,000 mg/dm³ of initial concentration. The pH after removal operation for PO_4^{3-} in initial concentrations of 3,000 and 14,000 mg/dm³ becomes about 4 and 5, which results in zeolite crystal collapse. That is, in the right side of the broken line shown in Fig. 8, the removal of PO_4^{3-} merely seems to be achieved by Ca^{2+} supplied by the dissolution of zeolite crystal and inner coal fly ash.

In the case of Na_3PO_4 , K_3PO_4 , and $(\text{NH}_4)_3\text{PO}_4$ solutions of around pH 7, the removal of PO_4^{3-} increases with an increase in initial PO_4^{3-} concentration until initial PO_4^{3-} concentration of 5,000 mg/dm³. The removal amount of PO_4^{3-} already leads to the saturation state at 5,000 mg/dm³ of initial concentration. The removal of PO_4^{3-} is the largest in $(\text{NH}_4)_3\text{PO}_4$ solution in the same PO_4^{3-} concentration. Zeolite crystal is not disintegrated by the contact operation with Na_3PO_4 , K_3PO_4 , and $(\text{NH}_4)_3\text{PO}_4$ solutions.

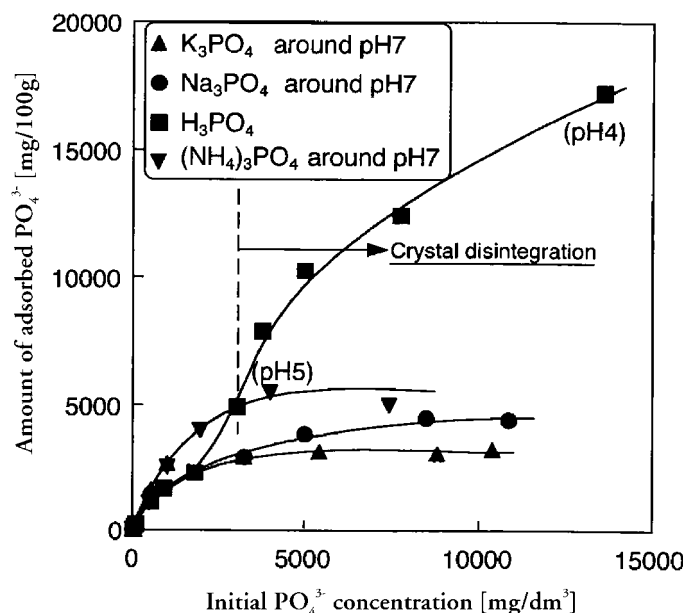


Figure 8. Removal of PO_4^{3-} in various solutions by CaP zeolite.

In these cases, Ca^{2+} is provided by the cation exchange reaction between exchangeable Ca^{2+} in zeolite and some cations like Na^+ , K^+ , and NH_4^+ in various orthophosphate solutions without collapsing the zeolite crystal.

Surface structure of CaP zeolite after PO_4^{3-} removal is shown in Fig. 9. The zeolite crystal phase is dissolved in H_3PO_4 solution at pH 4, and then inner fly ash phase appears on the particle surface. Though the surface structure of the products after PO_4^{3-} removal slightly differs among $(\text{NH}_4)_3\text{PO}_4$, Na_3PO_4 , and K_3PO_4 solutions at pH 7, the zeolite crystal phase is not dissolved by the PO_4^{3-} removal operation. On the other hand, though it is not shown in the figure, NaP zeolite does not essentially remove PO_4^{3-} in solution at pH around 7.

From the above results, Ca^{2+} is supplied in solution (1) by cation exchange of CaP zeolite, (2) by the disintegration of CaP zeolite, and (3) by the dissolution of inner coal fly ash.

In order to clarify the removal process of PO_4^{3-} , a change in the concentrations of various cations is investigated before and after the removal operation. Cation exchange behavior between NH_4^+ , Na^+ , K^+ in solution and Ca^{2+} in zeolite in various PO_4^{3-} solutions is shown in Fig. 10. All cations and Ca^{2+} in zeolite are exchanged and the amount of cation exchange is 100–

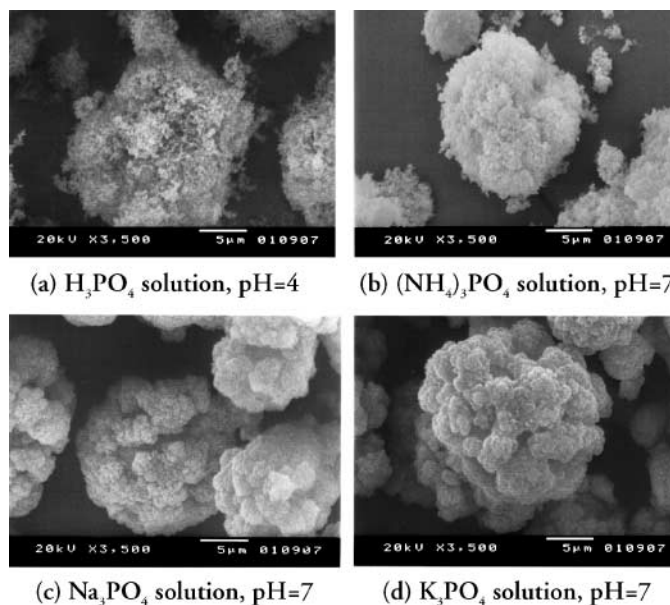


Figure 9. Surface structure of CaP zeolite after PO_4^{3-} removal.

190meq/100 g. The amount of cation exchange is the largest in the $\text{NH}_4^+ - \text{Ca}^{2+}$ system. The concentration of Ca^{2+} released from zeolite is $8.3 \times 10^{-3} - 1.7 \times 10^{-2} \text{ mol/dm}^3$ for these removal operations. The PO_4^{3-} in solution can be removed by the released Ca^{2+} without disintegrating zeolite crystal, and the removal amount of PO_4^{3-} is 3,000–6,000 mg/100 g. For example, about 90% of NH_4^+ and about 46% of PO_4^{3-} in solution can be removed simultaneously by the CaP zeolite from the mixed solution containing 5 mg/dm^3 NH_4^+ and PO_4^{3-} .

Mechanism and Advantages of Simultaneous Removal of NH_4^+ and PO_4^{3-}

The mechanism of simultaneous removal of NH_4^+ and PO_4^{3-} in solution with CaP zeolite is considered from the results obtained in the above section. The schematic diagram for simultaneous removal of NH_4^+ and PO_4^{3-} is shown in Fig. 11. In this consideration, the effect of competition by the other ions is not taken into account.

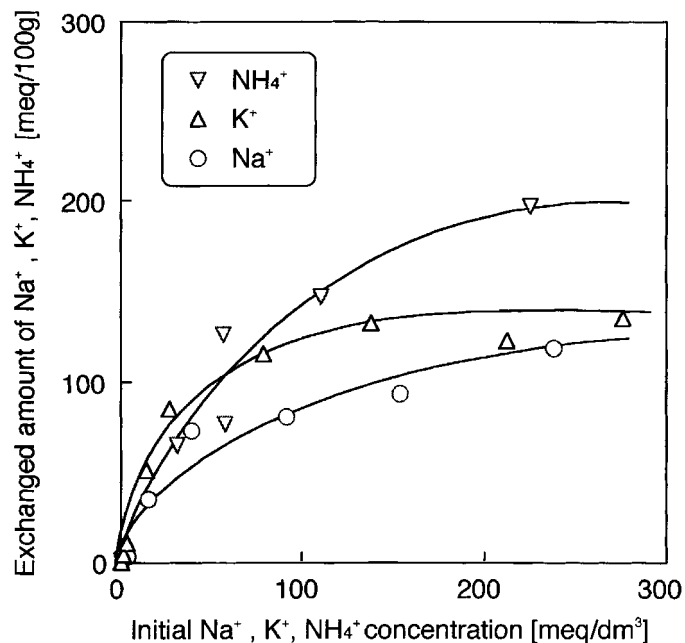


Figure 10. Cation exchange behavior of NH_4^+ , Na^+ , K^+ – Ca^{2+} systems in various PO_4^{3-} solutions.

At first, in case of pH over 5 (Case 1 in Fig. 11), the removal of NH_4^+ in solution with zeolite can be essentially achieved by a cation exchange reaction. In the pH over 10, zeolite has cation exchange ability, but almost all of NH_4^+ itself changes into NH_3 . On the other hand, zeolite crystal itself begins to collapse by the action of proton in pH below 5, and the removal of NH_4^+ cannot be achieved (Case 2).

The removal of PO_4^{3-} is accomplished by the formation of insoluble salt by CaP zeolite. In the region of pH below 5 (Case 3), Ca^{2+} is provided in solution and PO_4^{3-} is certainly removed, but CaP zeolite crystals itself are disintegrated by the action of proton. In this case, CaP zeolite does not essentially play a role as water purification agent. In the pH range from 5 to 10 (Case 4), Ca^{2+} is released from CaP zeolite by cation exchange, and the removal of PO_4^{3-} can be achieved without collapsing zeolite crystal structure. In the pH over 10 (Case 5), PO_4^{3-} is not removed because Ca^{2+} is not supplied from CaP zeolite.

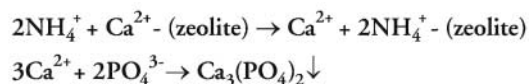
From these results, the simultaneous removal of NH_4^+ and PO_4^{3-} can be accomplished when the cation exchange between Ca^{2+} and NH_4^+ , and the

Removal of NH_4^+ and PO_4^{3-}

127

	pH condition			
	high	10	5	low
NH ₄ ⁺	Case 1		Case 2	
	Removable		Not removable	
Cation exchange	Isolation of NH ₃	Cation exchange	Disintegration and Dissolution of zeolite	
PO ₄ ³⁻	Case 5	Case 4	Case 3	
	Not removable	Removable		
Supply of Ca ²⁺	No supply of Ca ²⁺	Formation of insoluble salt	Disintegration and Dissolution of zeolite or Dissolution of inner coal fly ash	

<Typical example of chemical reaction>


Figure 11. Schematic diagram of simultaneous removal of NH_4^+ and PO_4^{3-} .

precipitation of insoluble salts, $\text{Ca}_3(\text{PO}_4)_2$ takes place at the same time (chemical reaction in Fig. 11). Consequently, the most important factor to remove NH_4^+ and PO_4^{3-} simultaneously is to provide Ca^{2+} into solution without disintegrating the zeolite crystal by keeping a suitable pH condition (pH 5–10).

Generally, two kinds of reagents must be applied for the removal of NH_4^+ and PO_4^{3-} in solution. For example, the combination of a cation exchanger and an anion exchanger, a cation exchanger and a high polymer cohesion agent, or a cation exchanger and an inorganic cohesion precipitant are considered. In any case, the cost is high for the use of these reagents, or the counter anion such as Cl^- and SO_4^{2-} remains in the solution as an impurity in the use of Fe^{3+} or Al^{3+} as a precipitant. On the other hand, the zeolite after removal of NH_4^+ and PO_4^{3-} should not be regenerated as a water purification agent, but be used as a soil improvement agent because this zeolite has both water-keeping ability and slow-releasing ability for P and N components. This may also make a contribution to

the promotion of the reuse of coal ash, and the coal combustion residue can be returned safely to the soil by this method. The CaP zeolite synthesized from coal fly ash, which can simultaneously remove NH_4^+ and PO_4^{3-} without releasing a counter anion, has advantages over the other ordinary methods from the viewpoints of water purification and the effective use of coal fly ash.

CONCLUSION

To investigate the simultaneous removal ability of the zeolite for NH_4^+ and PO_4^{3-} in solution, various cation exchange tests of NaP and CaP zeolites were carried out for the solution containing NH_4^+ and PO_4^{3-} at various of pH values. The effect of pH on cation exchange property of zeolite and the mechanism of simultaneous removal for NH_4^+ and PO_4^{3-} were investigated, respectively.

The NH_4^+ removal with zeolite is achieved by cation exchange reaction. Though the cation exchange property of zeolite is essentially independent of aqueous pH, zeolite crystal itself collapses or dissolves in the pH below 5, so that the amount of cation exchange in zeolite drastically is reduced as the result. On the other hand, the PO_4^{3-} removal is accomplished by Ca^{2+} supplied from zeolite into solution. Ca^{2+} source to remove PO_4^{3-} is supplied by the cation exchange of CaP zeolite, the disintegration and dissolution of zeolite and the dissolution of inner coal fly ash. The simultaneous removal for NH_4^+ and PO_4^{3-} can be achieved when NH_4^+ in solution is exchanged by exchangeable Ca^{2+} in CaP zeolite followed to form an insoluble salt between the released Ca^{2+} and the PO_4^{3-} in solution.

The CaP zeolite can simultaneously remove NH_4^+ and PO_4^{3-} without releasing a counter anion and has advantages compared with the other methods. However, the existence of the other competition ions should be considered in practical usage. We will investigate the effect of competition ions on cation exchange of the zeolite in detail.

REFERENCES

1. Japan Fly Ash Association. *Coal Ash Hand Book*, 2nd Ed.; 1995; Vol. II, 1–12.
2. Henmi, T. A physico-chemical study of industrial solid wastes as renewable resource—zeolitization of coal clinker ash and paper sludge incineration ash. *Memoirs Agric. Dept, Ehime Univ.* **1989**, 33 (2), 143–149.

**Removal of NH_4^+ and PO_4^{3-}** **129**

3. Henmi, T. Sangyouhaikibutu no zeolite-tenkanniyoru saishigenka yuukouriyu-gijyutukaihatu. *New Technol. Sci.* **1994**, 3–166.
4. Shigemoto, N.; Hayashi, H.; Miyake, K. Selective formation of Na-x zeolite from coal fly ash by fusion with sodium hydroxide prior to hydrothermal reaction. *J. Miner. Sci.* **1993**, 28, 4781–4786.
5. Biskup, B.; Subtic, B. Removal of heavy metal ions from solutions by means of zeolites. I. Thermodynamics of the exchange processes between cadmium ions from solution and sodium ions from zeolite A. *Sep. Sci. Technol.* **1998**, 33 (4), 449–466.
6. Querol, X.; Plana, F.; Alastuey, A.; Lopez-Soler, A. Synthesis of Na-zeolites from fly ash. *Fuel* **1997**, 76 (8), 793–799.
7. Sultan, A.; Shiraz, C.; Keane, M.A. The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y zeolite. *Sep. Purif. Technol.* **1998**, 13, 57–64.
8. Murayama, N.; Ishimoto, H.; Shibata, J. Hydrothermal synthesis and physical property evaluation of zeolite from paper sludge ash. *J. Mining Mater. Process. Inst. Jpn* **2000**, 116 (1), 31–36.
9. Murayama, N.; Yamakawa, Y.; Ogawa, K.; Shibata, J. Alkali hydrothermal synthesis of zeolite from coal fly ash and its cation exchange property. *J. Mining Mater. Process. Inst. Jpn* **2000**, 116 (4), 279–284.
10. Murayama, N.; Ogawa, K.; Nishikawa, Y.; Yamamoto, H.; Shibata, J. Reaction mechanism of zeolite synthesis from coal fly ash. *J. Mining Mater. Process. Inst. Jpn* **2000**, 116 (6), 509–514.
11. Murayama, N.; Yamamoto, H.; Shibata, J. Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. *Int. J. Miner. Process.* **2002**, 64 (1), 1–17.
12. Nishikawa, Y.; Murayama, N.; Yamamoto, H.; Shibata, J.; Ogawa, K. Hydrothermal synthesis of zeolite from coal fly ash by using NaOH/ Na_2CO_3 Solution. *J. Mining Mater. Inst. Jpn* **1999**, 115 (13), 971–976.
13. Takami, Y.; Murayama, N.; Ogawa, K.; Yamamoto, H.; Shibata, J. Water purification property of zeolite synthesized from coal fly ash. *J. Mining Mater. Process. Inst. Jpn* **2000**, 116 (9), 987–991.
14. Lee, D.B.; Lee, K.B.; Han, S.S.; Henmi, T. Granulation of artificial zeolite for the simultaneous removal of nitrogen and phosphorous from the wastewater. *J. Korean Soc. Soil Sci.* **1998**, 31, 67–71.

Received December 2001

Revised April 2002