Hydrothermal synthesis of potassium-type zeolite from coal fly ash and evaluation of its physical properties

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Abstract

Hydrothermal syntheses of potassium-type zeolite from coal fly ash were carried out under various KOH concentrations and reaction temperatures, and crystal structure and cation exchange capacity (CEC) of the reaction products were investigated. Both acid resistance and heat resistance of the reaction products were considered, as these are important for use as a cation exchanger, a catalyst or an absorbent.

When hydrothermal synthesis from coal fly ash is conducted at a reaction temperature of 393K, potassium chabazite (K-CHA) begins to form for 5h of reaction time. K-CHA and K-H zeolite are formed as zeolite species at 393K and 453K, respectively. Both K-CHA and K-H zeolite are synthesized simultaneously at 433K. CEC values of the obtained K-CHA and K-H zeolite are 208meq/100g and 104meq/ 100g, respectively. The CEC of reaction products decreases with increasing reaction temperature, and this phenomenon dictates the kind of formed zeolite.

X-ray diffraction intensities of K-CHA gradually decrease with decreasing pH in the range above pH4. Whereas, in the range below pH 4, this intensity decreases rapidly and the elution amount of Al^{3+} from K-CHA with proton increases remarkably. In the case of heat treatment below 873K, the X-ray diffraction intensity of K-CHA decreases with increasing calcined temperature, but thermal decomposition of K-CHA and production of new crystalline materials do not take place in these treatments. With a heat treatment of 1273K, the K-CHA peaks disappear in the XRD pattern, and those of leucite generate anew.

Keywords : hydrothermal synthesis, zeolite, coal fly ash, cation exchange capacity

1. Introduction

The exhaustion of petroleum as a primary resource poses a great problem for mankind. Switching back from petroleum to coal is being widely investigated, and, as a result, usage of coal is increasing in electric power plants. A huge amount of coal ash is discharged in the combustion process, because coal originally contains a 5%~20% of ash component. The amount of coal fly ash in Japan is estimated to be about 8 million tons per year, and the amount discharged is likely to increase in the future. About 70 percent of coal ash produced in electric power plants is recycled as a raw material of cement or as an additive in concrete. However, the rest is mainly treated in landfill[1]. It is difficult both to increase the

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demand for coal fly ash in the cement and concrete industries and to build new reclamation spaces. Therefore, the development of new recycling technology for coal ash is needed in Japan[2].

Zeolitization from coal fly ash has been proposed by many researchers[3]-[6] as one type of utilization technology. Zeolite is an excellent functional material having cation exchange, adsorption and catalyst abilities. Potassium-type zeolite can be used as an excellent soil improvement agent with both water and fertilizer-keeping abilities[7]. We have previously reported on the formation behavior of potassium-type zeolite[8][9]. However, the effect of reaction temperature and KOH concentration on the zeolitization reaction or the physical properties of zeolite have not yet been clarified.

In this study, the characterization of potassium-type zeolitic materials obtained from coal fly ash was investigated under various KOH concentrations and reaction temperatures. Physical properties, such as cation exchange capacity, acid resistance and heat resistance, were measured for the obtained product.

2. Experimental

2.1 Hydrothermal synthesis of potassium-type zeolite

Coal fly ash made by Denpatsu Coal Tech Co. Ltd., was used in this study. One hundred grams of coal fly ash and 400cm^3 of 1.0~4.0mol/dm^3 KOH solutions were put into an autoclave (Taiatsu Glass Industries Co. Ltd., TAS-08). Hydrothermal syntheses were carried out under heating and stirring conditions. Agitation speed and reaction temperatures were set at 500rpm and 393K~453K, respectively. Reaction products are washed with distilled water and then dried at 378K for 12h. Identification of crystal structure and analysis of the chemical composition of the reaction products were carried out with an X-ray diffraction equipment (Nihon Denshi Co. Ltd., JDX-3530) and an energy-distributed fluorescence X-ray analysis equipment (Nihon Denshi Co. Ltd., JED-2110), respectively. Concentration of metal ions in alkali solution through hydrothermal synthesis of zeolite was measured with an inductively-coupled plasma spectrometer (Shimazu Co. Ltd., ICPS-1000Ⅲ) and an atomic adsorption dispersion spectrometer (Shimazu Co. Ltd., AA-6800).

2.2 Evaluation of reaction products

The measurement of cation exchange capacity (CEC) was applied using the Harada and Aomine method[10]. In order to substitute Ca^{2+}, 2.0g of dried sample was contacted three times with 20cm^3 of 0.5mol/dm^3 calcium acetate solution. The substitute operation of NH$_4^+$ took place six times using 20cm^3 of 1.0mol/dm^3 ammonium chloride solution. The total amount of Ca^{2+} was measured with an inductively-coupled plasma spectrometer, and the CEC value of the reaction product was expressed as milliequivalent per 100g of powder.

To evaluate the acid resistance of reaction products, 1.0g of dried sample was contacted with 40cm^3 of hydrochloric acid for 30 min. The Al^{3+} concentration dissolved from reaction products by the proton was measured with an inductively-coupled plasma spectrometer.

For evaluation of heat resistance, the reaction product was calcined in a tube-type electric furnace (Kouyou Thermosystems Corp. KTF030N) for 1h in air. The calcination temperature was set in the range 473K~1273K. The reaction products after heat treatment were measured with an X-ray diffraction equipment.

3. Results and Discussion

3.1 Hydrothermal synthesis of potassium-type zeolite

Chemical compositions of coal fly ash and the reaction products synthesized at various temperatures are shown in Table 1. The coal fly ash contains about 47 percent silicon and about 26 percent aluminum as metal base. These components exist as a form of amorphous aluminosilicate. A trace amount of potassium component is contained in the coal fly ash. The Si/Al ratio of the coal fly ash is 1.82. In the case of the reaction products, Si/Al ratios seem to increase with an increase in reaction temperature. Thus, the Si/Al ratio of reaction products synthesized at 393K, 433K and 453K are 1.43, 1.78 and 2.04, respectively. The various reaction products contain 5~7 times the potassium amount as compared with the coal fly ash. This increases with an increase in reaction temperature because of the formation of potassium-type zeolite.

Table 1. Chemical composition of coal fly ash and reaction products
obtained in 3.0mol/dm^3 KOH solution for 12h

			Reaction temp. [K]		
		Coal fly ash	393K	433K	453K
	Si	47.0	45.5	47.3	45.5
Content [%]	Al	25.8	31.9	26.6	22.3
	K	3.2	17.3	19.6	22.5
Si/Al ratio [-]		1.82	1.43	1.78	2.04

The X-ray diffraction pattern of the coal fly ash is shown in Fig.1 (a). The pattern is that of a typical amorphous material. Quartz and mullite ($3Al_2O_3 \cdot 2SiO_2$) are confirmed as crystalline material in the coal fly ash. The X-ray diffraction patterns of reaction products obtained in 3.0mol/dm^3 KOH solution at various temperatures are also shown in Fig.1. The reaction product synthesized at 393K is identified to be potassium-chabazite (K-CHA), a kind of zeolite materials. The reaction product synthesized at 433K shows XRD patterns based on both K-CHA and potassium aluminum silicate hydrate (K-H zeolite). On the other hand, only K-H zeolite is formed at a reaction temperature of 453K. K-CHA and K-H zeolite have about 0.3nm micro-pores and potassium ions as an exchangeable cation[11].

The time course of X-ray diffraction intensities of the coal fly ash and the reaction products synthesized at 393K in 3.0mol/dm^3 KOH solution is shown in Fig.2. X-ray diffraction intensity of K-CHA appears at 5h for the first time, and it becomes a constant value after 25h. Although the intensity of quartz does not change in the heating process, it
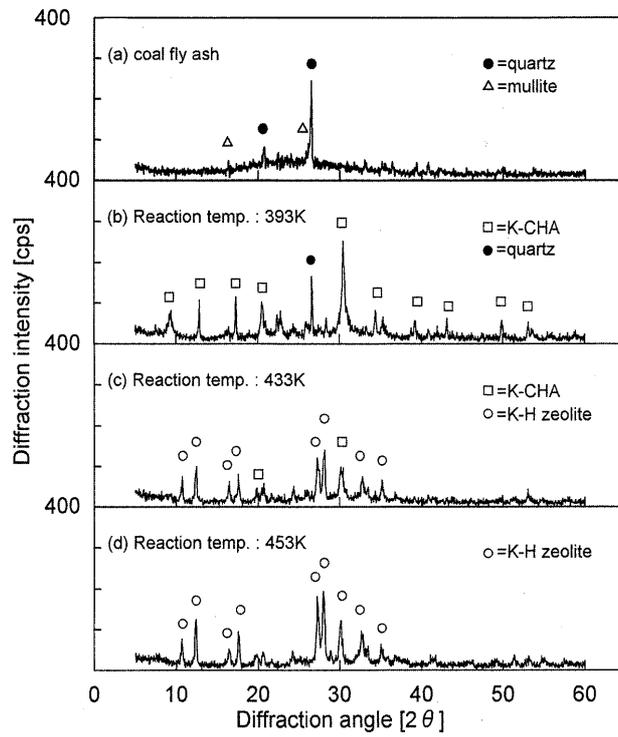
Fig.1 X-ray diffraction patterns of coal fly ash and reaction products
Alkali source : 3mol/dm³ KOH
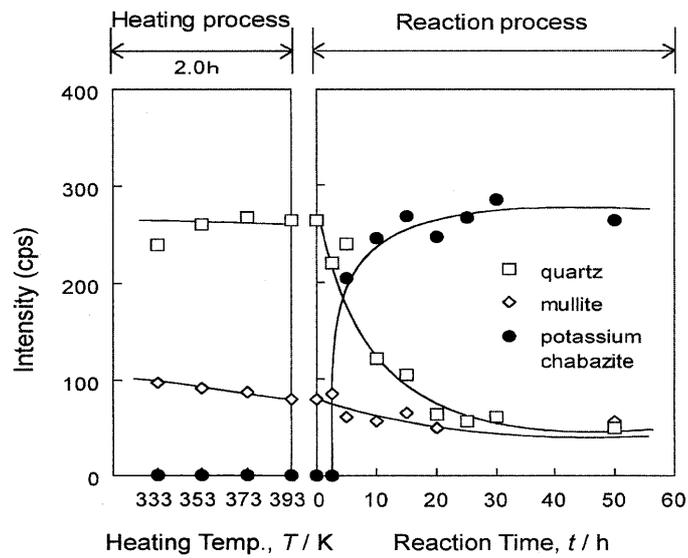Reaction time : 12h

Fig.2 Change in X-ray diffraction intensities of K-CHA products obtained in 3.0mol/dm³
KOH solution as a function of reaction temperature and time

rapidly decreases with the deposit of K-CHA on the particle surfaces. The intensity of quartz gradually decreases after 25h. On the other hand, X-ray diffraction intensity of mullite gradually decreases during the heating process, and it becomes constant after 25h.

The time course of several metal ion concentrations in the mother liquor is shown in Fig.3. The Si^{4+} concentration rapidly increases during the heating process, but it increases gradually in the reaction process. The Al^{3+} concentration increases until 353K during the heating process, and then decreases over 353K. The amount of K^+ gradually decreases with increasing reaction time. About 45% of the initial potassium ion is consumed at 50h of reaction time. Three reaction steps can be classified for the formation of zeolitic materials from coal fly ash[8)12)13)] : the dissolution process of silicon and aluminum in coal fly ash using an alkali, the gelation process through a deposit of aluminosilicate on the un-reacted coal fly ash, and lastly the crystallization process from the above deposit material into zeolite crystals.
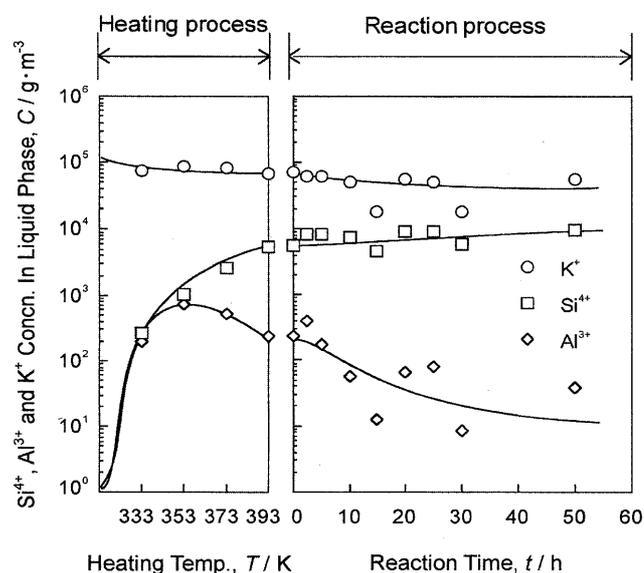

Fig.3   Change in Al^{3+}, Si^{4+} and K^+ concentrations in 3.0mol/dm^3 KOH solution as a function
of reaction temperature and time

In order to shorten the reaction time of potassium-type zeolite formation, it is very important to investigate the effects of alkali concentration and reaction temperature on the properties of obtained potassium-type zeolite. Changes in X-ray diffraction intensity of K-CHA and quartz, and the CEC value in 1.0~4.0mol/dm^3 KOH solution are shown in Fig.4. Reaction temperature and reaction time are 393K and 12h, respectively. Although K-CHA is not formed as zeolitic species in 1.0mol/dm^3 KOH solution, K-CHA may be synthesized in a KOH solution of 2.0~4.0mol/dm^3. X-ray diffraction intensity of quartz rapidly decreases in 1.0mol/dm^3 and 2.0mol/dm^3 KOH concentrations, and this value almost reaches a constant in the region of over 2.0mol/dm^3 KOH. The CEC value of the reaction product obtained in 1.0mol/dm^3 KOH solution shows about 58meq/100g. Under this condition, K-CHA is not
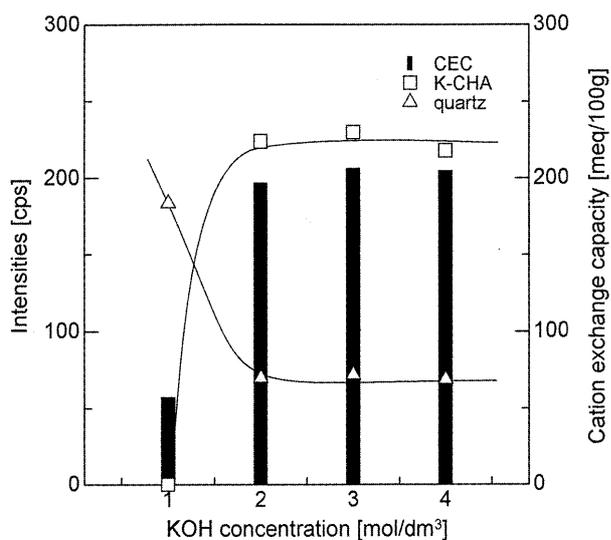
Fig.4 Change in XRD intensities and cation exchange
capacity with KOH concentration
Reaction temp. : 393K
Reaction time : 12h

formed from coal fly ash. This CEC value is not particularly high, but the CEC of the
product is higher than that of the coal fly ash. This phenomenon is caused by the deposit
materials on the surface of un-reacted coal fly ash having a slight cation exchange capacity.
On the other hand, the CEC values are almost the same, 210meq/100g, in the case of 2.0~
4.0mol/dm³ KOH solution.

Effects of reaction temperature on the potassium zeolite species and CEC are shown in
Fig.5. The KOH concentration and reaction time are set at 3.0mol/dm³ and 12h, respectively.
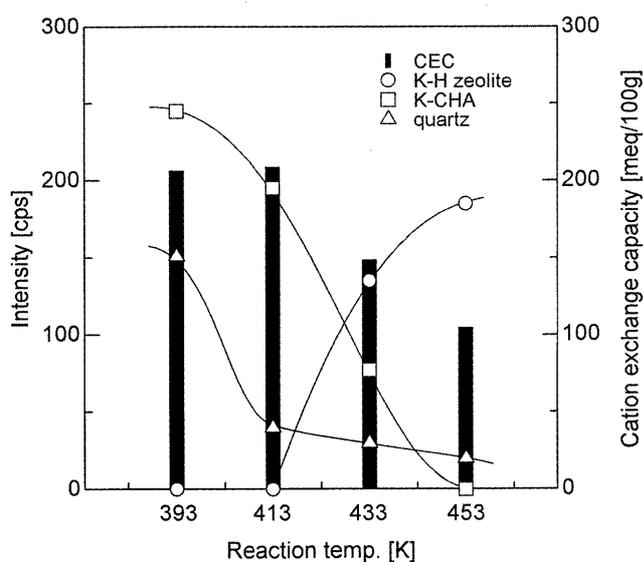

Fig.5 Change in XRD intensities and cation exchange capacity with reaction temperature
Alkali source : 3mol/dm³ KOH
Reaction time : 12h

The reaction products show the highest X-ray diffraction intensity value for K-CHA at 393K. The K-CHA formation amount decreases with increasing reaction temperature, and K-CHA peaks are not recognized at a reaction temperature of 453K. K-H zeolite can be synthesized at 433K, and the intensity of K-H zeolite increases with increasing reaction temperature. On the other hand, the X-ray diffraction intensity of quartz rapidly decreases from 393K to 413K: thereafter, it gradually decreases with increasing reaction temperature. The intensity of quartz is almost the same as the background of X-ray diffraction in Fig.1. It is thought that the coating percent of potassium-type zeolite on the surface of coal fly ash increases with an increase in reaction temperature. The CEC values of K-CHA products synthesized at 393K and 413K are the same value, about 200meq/100g, but the CEC of reaction products decreases with increasing reaction temperature above 433K. From the results illustrated in Table 1 and Fig.5, it is thought that the exchangeable potassium ion in the reaction products decreases in high reaction temperatures such as 433K or 453K. The larger the formation amount of K-CHA, the bigger the CEC value of potassium-type zeolite in this temperature range.

3.2 Evaluation of the properties of reaction products

Acid resistance and heat resistance are both evaluated for the reaction products obtained in 3.0mol/dm³ KOH solution at 393K for 50h. This product has the highest cation exchange capacity, 220meq/100g. Acid resistance of reaction product is an important property if using the potassium-type zeolite as a cation exchanger or a catalyst[11)14)]. Amount of Al^{3+} dissolved and X-ray diffraction intensity of K-CHA are shown in Fig.6 as a function of pH. The obtained suspension pH is about 10.5 without pH adjustment with hydrochloric acid. In the range of 4 to 10 pH, the X-ray diffraction intensity of K-CHA gradually decreases as the pH of the suspension decreases. On the other hand, the diffraction intensity
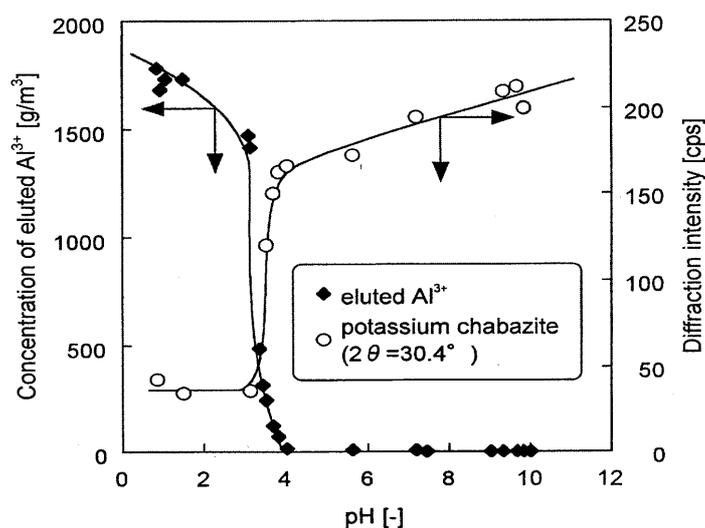

Fig.6   Acid-resistance property of reaction product
obtained in 3.0mol/dm³ KOH at 393K for 50h

rapidly decreases in the range of acidic pH 3 to 4. The aluminum ion dissolved from K-CHA zeolite does not appear above pH 4. But the amount of Al^{3+} rapidly increases at pH 3. It is thought that the crystal structure of K-CHA is disintegrated by acid dissolution below pH 4, and the aluminum component in K-CHA products is dissolved as a result. When K-CHA products are used as a cation exchanger, the condition of zeolite is adjusted to be above pH 4.

The dehydration behavior of zeolitic water is important for the evaluation as an absorbent of various gases[11]. For example, the heat resistance of zeolite materials is required, because catalytic reaction is ordinarily conducted at high temperature in the range 600K~800K[11)14]. The X-ray diffraction intensity of K-CHA for various calcination temperatures is shown in Fig.7. Below a calcination temperature of 1073K, the X-ray diffraction intensity of K-CHA decreases linearly with increasing calcined temperature. The X-ray diffraction pattern of reaction products at 873K and 1273K is shown in Fig. 8 (b),(c). The structure of K-CHA is maintained at 873K, although its intensity decreases before and after heat treatment (Fig.8 (b)). On the other hand, the K-CHA X-ray diffraction peak disappears through thermal decomposition, with the peak of leucite newly appearing at 1273K (See Fig.8 (c)). As our previous report[15] mentioned, a large part of the moisture in zeolite materials can be removed by calcination at about 600K. The structure of K-CHA does not disintegrate at calcination temperatures of below 1073K. It is possible to apply K-CHA products to an absorbent or a catalyst.
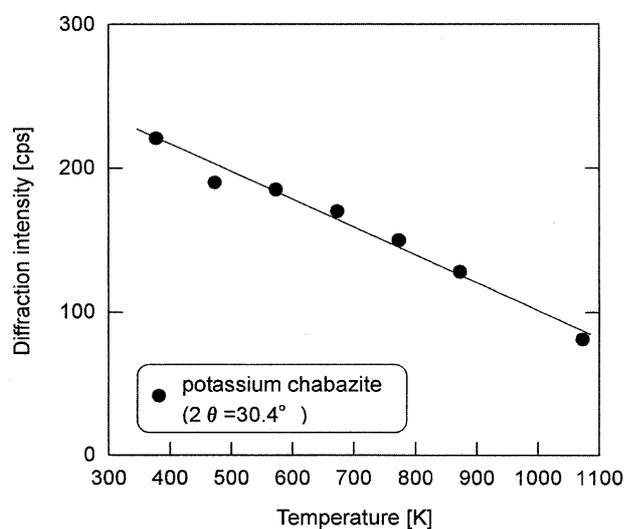

Fig.7 Change in diffraction intensity of product after
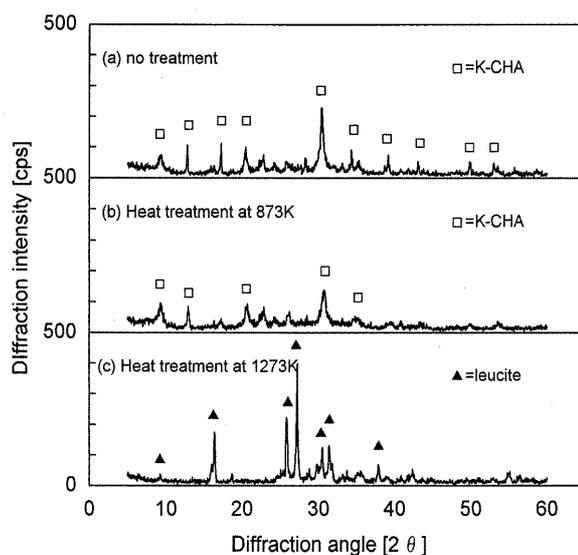heat treatment at various temperatures

Fig.8 X-ray diffraction patterns of reaction products
before and after heat treatment

4. Conclusions

In this study, the characteristics of the potassium-type zeolitic materials obtained from coal fly ash under various KOH concentrations and reaction temperatures was evaluated. Their physical properties, such as cation exchange capacity, acid resistance and heat resistance, were evaluated in order to use as soil improvement material, catalyst or absorbent.

The structure of K-CHA is formed from coal fly ash by synthesis in a $3.0mol/dm^3$ KOH and 393K. Both K-CHA and K-H zeolite are formed at 433K. K-H zeolite is formed at a reaction temperature of 453K. The CEC values of K-CHA and K-H zeolite are 208meq/100g and 104meq/110g, respectively.

K-CHA products synthesized at 393K are formed for the first time after 5h, and the X-ray diffraction intensity of K-CHA becomes constant after 25h. Although zeolitic materials are not formed in a $1.0mol/dm^3$ KOH solution, the X-ray diffraction intensity of K-CHA appears to be in the region of $2.0 \sim 4.0mol/dm^3$ KOH concentrations. The CEC values of these reaction products is almost the same : about 200meq/100g.

With regard to the acid resistance of K-CHA products, the X-ray diffraction intensity of K-CHA decreases with decreasing pH in a suspension above pH 4. In this region, disintegration of K-CHA does not take place completely. When K-CHA products are used as a cation exchanger, the pH condition of zeolite is set to be above pH 4. With regards to the heat resistance of K-CHA products, at calcination temperatures below 1073K, the X-ray diffraction intensity of K-CHA decreases linearly with increasing calcinations temperature. On the other hand, the X-ray diffraction peak of K-CHA disappears through thermal decomposition, and the peak of leucite appears at 1273K. The structure of K-CHA is not disintegrated at calcination temperatures below 1073K.

References

1) Nihon Furaiasshu Kyokai and Kankyo Gijyutu Kyokai: *Sekitanbai Handobukku, 2nd. edition,* (Tokyo, 1995), pp. II 1- II 12.

2) T. Owada, H. Hanasaka, K. Ozasa and Y. Sakurai: Proc. Int. *Workshop on Nobel Products from Combustion Residues,* (Morella, 2001), pp.53-58.

3) T. Henmi and E. Sakagami: *Jinko Zeoraito ga Chikyu wo Sukuu,* (Japan Times, Tokyo, 1998), pp.35-47.

4) M. Meguro, J. Haruna, T. Noda and T. Kanamaru: *Haikibutu Gakkai Ronbunsyu,* 8 (1997), 280-287

5) X. Querol, F. Plana, A. Alastuey and A.L. Soler: *Fuel,* 76 (1997), 793-799.

6) C.L. Choi, M. Park, D.H. Lee, J.E. Kim, B.Y. Park and J. Choi: *Environ. Sci. Technol.,* 35 (2001), 2812-2816

7) J. Shibata, N. Murayama, and H. Yamamoto: *Proc. TMS Annual Meeting, EPD Congress 2002,* (Seattle, 2002), pp-241-249.

8) J. Shibata, S. Yoshida, N. Murayama and H. Yamamoto: *Shigen-to-Sozai,* 118 (2002), 419-424

9) N. Murayama, H. Yamamoto, J. Shibata: *Int. J. Miner. Process.,* 65 (2002), 1-17

10) Y. Nishikawa, N. Murayama, H. Yamamoto and J. Shibata: *Shigen-to-Sozai,* 115 (1999), 971-976

11) N. Hara and H. Takahashi: *Zeoraito,* (Koudansha, Tokyo, 1975), pp.58-218

12) N. Shigemoto, K. Shirakami, S. Hirano and H. Hayashi: *Nippon Kagaku Kaishi,* 5 (1992), 484-492

13) N. Murayama, K. Ogawa, Y. Nishikawa, H. Yamamoto and J. Shibata: *Shigen-to-Sozai,* 116(2000), 509-514

14) H. Tominaga: *Zeoraito no Kagaku to Oyo,* (Koudansha, Tokyo, 1987), pp.117-156

15) N. Murayama, M. Tanabe, S. Yoshida, H. Yamamoto and J. Shibata: *Shigen-to-Sozai,* 119 (2003), 125-129