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Suitability of Coal Fly Ash and Incineration Ashes as Raw Materials for Zeolite Synthesis

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The objectives of this study are to investigate the suitability of various coal fly ashes and incineration ashes for zeolite synthesis. Zeolite P and hydroxysodalite are produced from coal fly ash and paper sludge incineration ash. When soluble and acid-soluble materials in incineration fly ash are removed by the water washing or acid washing before hydrothermal synthesis, hydroxysodalite can be produced. The factors to make solid-liquid separation difficult are the calcium component and the unburned carbon in ash.

Keywords: Zeolite, Coal Fly Ash, Incineration ash, Hydrothermal Synthesis

Introduction

In Japan, the discharged amount of coal fly ash or various incineration ashes is enormously increasing with the reconsideration of a thermal power plant. The development of new technologies for recycling or reusing such ashes is strongly desired.

Many researchers[1,2,4-9] have reported that zeolite can be synthesized from coal fly ash and various incineration ashes by alkali hydrothermal treatment, and have suggested that these zeolites produced from various ashes are applicable to a water purification, a soil improvement and so on.

In this zeolitization technology, however, many engineering problems are still remained. For example, the engineering technologies to design the production equipment of zeolite or the optical overall process system for zeolite production, to reduce the production cost and to stabilize the quality of zeolite should be established. In many cases, these problems are caused by the nature of coal ash and incineration ash as raw materials of zeolite. Thus, to investigate the suitability of various ashes for zeolite synthesis is very important from the engineering viewpoint.

In this study, many kinds of coal fly ashes, paper sludge incineration ashes, municipal waste incineration fly ashes, RDF incineration ashes and swage sludge incineration ashes were used as raw materials for zeolite synthesis. The physical properties, such as cation exchange capacity (CEC), chemical composition, SEM observation and so on, of the products synthesized by the hydrothermal reaction were measured. Furthermore, the nature of solid-liquid separation after the hydrothermal reaction was investigated. The suitability of various ashes for zeolite synthesis was evaluated from these results.

Experimental

Hydrothermal Synthesis of Zeolite

Five kinds of coal fly ashes and various incineration ashes (three kinds of paper sludge ashes, three municipal waste incineration fly ashes, RDF incineration ash and swage sludge incineration ash) were used as raw materials for zeolite synthesis. 100-200g of dried ash and 400cm^3 of 1.5-2.0mol/dm^3 NaOH solution were prepared in an 800cm^3 autoclave. Alkali hydrothermal synthesis was carried out under the condition of 3hrs reaction time, 393K reaction temperature and 500-650rpm agitation speed. The slurry after hydrothermal reaction was separated between solid and liquid by vacuum filtration, and then the obtained cake was adequately washed by distilled water. The cake was dried in stationary dryer at 393K for 24hrs.

Physical properties of various ashes and products synthesized by alkali hydrothermal reaction

For coal fly ash, various incineration ashes and the products obtained by hydrothermal reaction, the analysis of chemical composition, the identification of crystalline materials and SEM observation of surface structure were respectively carried out by an energy dispersion type X-ray fluorescence analysis equipment (EDX), an X-ray diffraction equipment and a scanning electron microscope.

The measurement of cation exchange capacity (CEC) for the product by alkali treatment was carried out by the modified Harada-Aomine method[2]. The amount of cations exchanged by cation exchange operation was measured by using an atomic adsorption method, and CEC of the product was calculated as the amount of exchangeable cation per 100g of dry powder.

Removal of impurity in ash by water washing and acid washing treatment

Incineration ash containes many kinds of materials, which can not change into zeolite chemically, such as various metal oxides, soluble or acid-soluble salts, unburned carbon and so on. These impurity ingredients in the municipal waste incineration fly ash were removed by distilled water washing or HCl solution washing.

2.0g of dried municipal waste incineration fly ash and 50cm^3 of distilled water or 1.0mol/dm^3 HCl solution were mixed and agitated adequately, and the washed ash and the solution were separated by a centrifuge separator. A series of this operation repeated 10times, and then the residue material removed by washing was dried in stationary dryer. By using these ashes, zeolite synthesis was carried out in the same way mentioned above.

Results and Discussion

Physical and chemical properties of various ashes

Table 1 shows the chemical composition of various ashes determined by the EDX method. The chemical analysis indicates the weight percents of each component when all of the weight percent of metal ingredient over the eleventh of atomic number is assumed to be 100%. The ignition loss shows the weight decrease when the ash is placed in electric muffle at 1073K for 3hrs. The metal component in ash and the ignition loss respectively indicate % and wt% in this paper.

The amount of Si and Al is one of an aim for suitability as raw materials for zeolite synthesis. Though the chemical composition of coal fly ash differs from the production site to the production site, most of coal fly ashes contain 70-90% of Si+Al in all metal components. In the case of CFA-5, however, the amount of Si+Al and Ca is respectively 33% and 44% as an exception. The amount of Si+Al in paper sludge incineration ash is 40-70%. In fact, the chemical composition may change more widely than this range by the difference of an incineration method or the kind of paper sludge. Compared with coal fly ash, the content of alminosilicate in paper sludge ash is generally low. As shown in PSIA-1 and PSIA-3 in **Table 1**, the notice point is high content of Ca component. This is because the limestone or $CaCO_3$ are thrown into the incineration muffle in order to neutralize HCl gas occurred in incineration process. In the case of municipal waste incineration fly ash and RDF incineration ash, the content of Ca, Na and Cl (most of 'Others' in **Table 1**) is very large by the salt component in waste, such as $CaCl_2$ and NaCl. On the other hand, the swage sludge incineration ash contains 64.1% of Fe component, which is caused by the addition of ferric sulfide as the cohesion precipitant. Thus, many incineration ashes contain a large amount of impurity

Table 1 Chemical composition of various ashes used in this study

Unit: %(metal component), wt%(Ignition loss)

Ash*	Si	Al	Ca	Mg	Na	Fe	Ti	Others	Ignition loss
CFA-1(JIS)	50.4	20.3	7.5	2.9	5.4	8.2	1.8	3.5	3.4
CFA-2	47.5	33.8	4.2	0.2	2.7	7.9	1.9	1.8	6.8
CFA-3	69.1	17.4	1.6	1.1	0.3	5.8	0.3	4.4	4.1
CFA-4	53.4	21.6	3.2	0.4	0.4	5.8	1.9	13.3	14.6
CFA-5	23.1	10.1	40.8	0.8	1.9	13.4	1.1	8.8	9.2
PSIA-1	49.1	26.2	14.1	2.3	0.1	3.0	0.2	5.0	1.6
PSIA-2	44.7	25.4	8.7	10.0	<0.1	4.7	2.3	4.2	2.7
PSIA-3	25.9	20.2	44.0	5.7	0.2	1.2	1.7	1.1	2.3
MWIFA-1	21.8	14.8	32.3	3.8	3.7	18.1	1.2	4.3	4.7
MWIFA-2	4.7	2.7	34.1	2.4	11.6	0.5	0.4	43.6	11.7
MWIFA-3	10.6	8.4	38.6	3.9	12.9	4.6	9.2	11.8	5.3
RDFIFA-1	17.8	16.9	40.0	3.5	5.5	2.1	1.0	13.2	4.1
SSIA-1	6.4	5.1	7.7	0.3	0.2	64.1	<0.1	16.2	1.9

*CFA:Coal Fly Ash, PSIA:Paper Sludge Incineration Ash, MWIFA:Municipal Waste Incineration Fly Ash, RDFIFA:RDF Incineration Fly Ash, SSIA:Swage Sludge Incineration Ash.

ingredient, which can not be changed into zeolite, by the route of waste or the incineration method.

Physical properties of products obtained by alkali hydrothermal treatment

Many researchers[2,4] found that the CEC of zeolite generally increased with an extent of reaction time and an increase in alkali concentration. In this study, the effect of several reaction conditions such as reaction time and alkali concentration on not only the CEC and crystal type of the product but also the nature of solid-liquid separation were investigated.

Fig.1 shows the X-ray diffraction patterns of the products obtained by alkali hydrothermal reaction. In the case of the product from coal fly ash (CFA-1 in **Fig.1**), the peak patterns of zeolite P appear newly, whereas those of hydroxysodalite are confirmed in the case of paper sludge incineration ash. Any zeolite species is not produced from municipal waste incineration fly ashes, RDF incineration ashes and swage sludge incineration ashes.

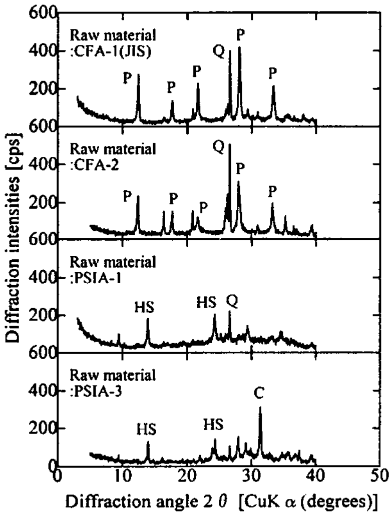

Fig.1 X-ray diffraction patterns of the products synthesized in various ashes

Table 2 shows the chemical composition and CEC for the products obtained from various ashes. Zeolites synthesized from coal fly ash have 150-350meq/100g of CEC in spite of very short reaction time of 3hrs. When the reaction time extends to 5hrs, the CEC value of zeolite increases by 20-30%. The products from paper sludge ash have 100-300meq/100g of CEC. The difference in CEC between zeolite from coal fly ash and that from paper sludge incineration ash is caused by the kind of synthesized zeolite crystal. In other word, zeolite P synthesized from coal fly ash has bigger CEC value than hydroxysodalite synthesized from paper sludge incineration ash. The CEC of the products from municipal waste incineration fly ashes, RDF incineration ashes and swage sludge incineration ashes are very low (below 30meq/100g), because zeolite species is not produced. On the other hand, Na content of all products which zeolite species can be synthesized, enormously increases over 10%. The increase in Na content originates in the Na^+ ion taken in zeolite crystal, and these results substantiate the formation of zeolite crystal too.

Table 2 Chemical composition and CEC for the products obtained from various ashes

Unit: %(metal component)

Material Ash	Si	Al	Ca	Mg	Na	Fe	Ti	Others	CEC*
CFA-1(JIS)	41.4	19.8	11.2	1.7	17.6	5.1	1.6	1.6	335 (Ca^{2+})
CFA-2	42.0	31.7	3.0	0.9	11.8	5.8	1.7	3.1	225 (Ca^{2+})
CFA-4	47.0	21.7	2.8	0.2	14.2	5.4	1.9	6.8	162 (Ca^{2+})
CFA-5	26.4	11.2	29.0	0.9	13.1	14.7	0.7	4.0	31 (Ca^{2+})
PSIA-1	40.5	21.3	10.6	2.1	12.3	2.2	0.2	10.8	298 (Na^+)
PSIA-3	29.4	20.6	30.7	3.4	13.7	0.9	1.0	0.3	106 (Na^+)
MWIFA-1	25.5	17.5	38.4	1.5	11.4	1.7	0.6	3.4	19 (Na^+)
RDFIFA-1	17.4	13.9	43.3	1.8	7.5	2.9	0.3	12.9	23 (Na^+)

*Unit: meq/100g, ( ) denotes the kind of exchangeable cation used for CEC measurement.

The relationship between calcium component in ash and the solid-liquid separation nature was investigated. It was found by our previous report[5] that the more the amount of calcium in ash is, the worse the solid-liquid separation is by the production of $Ca(OH)_2$. In the case of CFA-5, PSIA-3 and RDFIFA-1, the nature of solid-liquid separation aggravates conspicuously when these ashes are treated in alkali solution. Consequently, when the amount of calcium ingredient in ash is over 30%, the solid-liquid separation becomes very bad.

When coal fly ash or various incineration ashes are treated in alkali hydrothermal condition, the unburned carbon in ash affects the nature of solid-liquid separation. The ignition loss in **Table 1** originates in the unburned carbon in coal ash or the incineration residue of organic compound in incineration ash. The solid-liquid separation gradually declines with an increase in the amount of unburned carbon in the case of coal fly ash. This phenomenon is especially remarkable over 10wt% of unburned carbon. On the other hand, unburned organic compound or humus acid in incineration ash dissolves in NaOH solution, and at the same time decomposition gas breaks out. These circumstances make the reaction rate of zeolite slow, and the recycle of NaOH solution after hydrothermal reaction impossible. Thus, to reduce the amount of organic component, which can be dissolved by alkali solution, is very important in using incineration ash as raw materials.

Removal of impurity by water washing and acid washing treatments

Many incineration ashes such as the municipal waste incineration fly ash or RDF incineration ash generally contain a large amount of impurity component that can not be changed into zeolite. Tanaka[8] reported that hydroxysodalite was synthesized from the municipal waste incineration fly ash pre-treated by water washing. In this study, zeolite synthesis was tried for the municipal waste incineration fly ash, which contains extreme low amount of alminosilicate in ash, by the removal of soluble and acid-soluble materials.

Fig.2 shows the mass balance in distilled water washing or HCl solution washing processes. W, Si+Al, Na+Ca+Cl and Na+Ca respectively indicates the weight of dry powder, the content of Si and Al in ash, the content

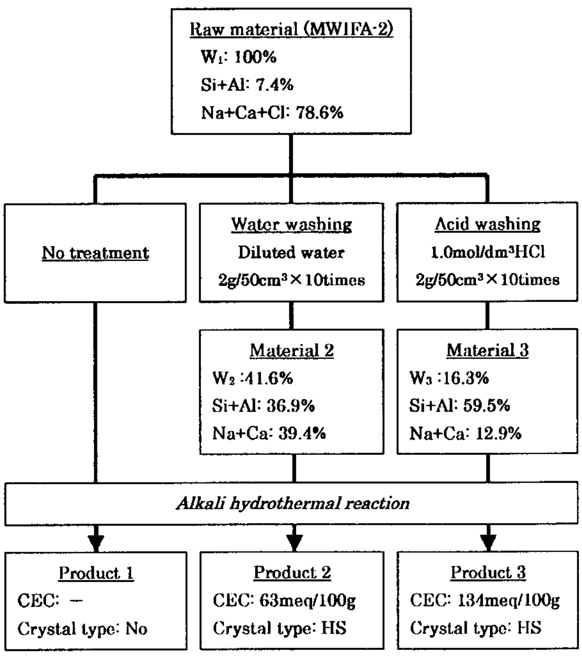

Fig.2 Material balance of impurity removal by water washing and acid washing of municipal waste incineration fly ash

amount of salt component in ash (most of 'Others' in **Table 1** can be considered as chlorine) before and after the washing operation.

When the municipal waste incineration fly ash is treated in alkali hydrothermal condition without removing the impurity component in ash, zeolite species can not be produced at all. In water washing treatment of the ash, 58.4% of ash dissolves in aqueous phase, and 41.6% of that remains as a solid phase, that is, a residue (Material 2 in **Fig.2**). At the same time, the amount of Si+Al in ash component is concentrated to 36.9%, whereas the amount of Na+Ca, which is impurity for zeolite, remains 39.4%. When the hydrothermal reaction is carried out for this treated ash, hydroxysodalite that has 63meq/100g of CEC is produced (Product 2). In acid washing treatment by 1.0mol/dm^3 HCl solution, 83.7% of ash dissolves in aqueous phase, and the amount of Si+Al in ash component is concentrated to 59.5% (Material 3 in **Fig.2**). A little amount of some heavy metals such as Zn, Pb, Cd, etc. is dissolved in HCl solution at the same time. When the hydrothermal synthesis is carried out for this acid-treated ash, hydroxysodalite that has 134meq/100g of CEC is produced (Product 3).

From the above results, it is possible to produce the zeolite that has adequate CEC by water washing or acid washing treatment from the municipal waste incineration ash, which has very low purity for alminosilicate.

Suitability evaluation of various ashes as raw materials for zeolite synthesis

Fig.3 shows the suitability of various ashes as raw materials for zeolite synthesis. Zeolitization reaction under the alkali hydrothermal condition consists of the three reaction steps, that is, the dissolution reaction of alminosilicate in ash, the deposition reaction of alminosilicate gel and the crystallization reaction from alminosilicate gel into zeolite[4]. When alminosilicate over 50-60% is contained in ash, the zeolite which has adequate CEC as well as the natural zeolite is synthesized in many cases. The impurity ingredients in ash, which cannot be converted into zeolite, are mainly calcium component and unburned carbon. The calcium component converts $Ca(OH)_2$ by a chemical change in alkali solution, and the produced of $Ca(OH)_2$ results in the decrease in the nature of solid-liquid separation. On the other hand, the unburned carbon in ash is fined or isolated from ash components under the heating and agitating conditions. These phenomena remarkably appear in the ash containing over 30% of calcium component or over 10wt% of unburned carbon, and it is impossible to separate zeolite cake and alkali solution because the floating nature of zeolite increases in the presence of $Ca(OH)_2$ or the fine particle of unburned carbon. For example, the filtration rate decreased from about $250kg/m^2hr$ to about $10kg/m^2hr$ in some experiments.

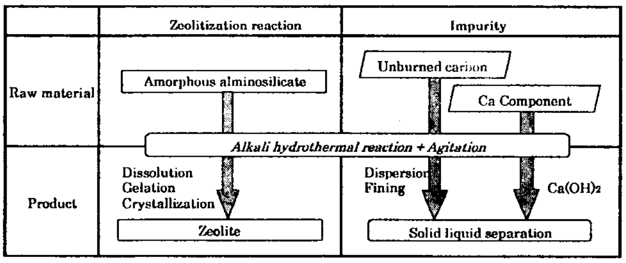

Fig.3 Effects of presence of unburned carbon and calcium component in ash on zeolitization reaction

Conclusion

In order to evaluate the suitability of coal ash or various incineration ashes as raw materials for zeolite synthesis, the hydrothermal reaction of zeolite was carried out by using several coal fly ashes, five kinds of incineration ashes. The properties, such as a cation exchange capacity (CEC), a chemical composition, crystal type, and the solid-liquid separation ability were measured for the products obtained by hydrothermal treatment.

When the impurity in ash is not removed before hydrothermal synthesis, zeolite species is produced from coal fly ash and paper sludge incineration ash. The kinds of zeolite are zeolite P and hydroxysodalite. When the soluble and acid-soluble materials in municipal waste incineration fly ash are removed by the water washing or acid washing before hydrothermal synthesis, the hydroxysodalite that has over 100meq/100g of CEC can be produced. On the other hand, the factors to make solid-liquid separation difficult are calcium component and unburned carbon in ash. This is caused by the chemical reaction of calcium component into $Ca(OH)_2$ or fining of the unburned carbon particle.

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