

Studies on the Production of Artificial Zeolite from Coal Fly Ash and Its Utilization in Agro-Environment

Deog-Bae Lee¹⁾, Teruo Henmi²⁾, Kyung-Bo Lee¹⁾, Jae-Duk Kim¹⁾

¹⁾National Honam Agricultural Experiment Station, RDA, 381 Songhak Dong Iksan, Korea, 570-080

²⁾Faculty of Agriculture Ehime University 3-5-7 Tarumi Matsuyama Japan, 790-0905

ABSTRACT :

1. Production of the artificial zeolite from coal ash

Coal fly ash is mainly composed of several oxides including SiO₂ and Al₂O₃ derived from inorganic compounds remained after burning. As minor components, Fe₂O₃ and oxides of Mg, Ca, P, Ti (trace) are also contained in the ash. These components are presented as glass form resulting from fusion in the process of the combustion of coal. In other word, coal ash may refer to a kind of aluminosilicate glass that is known to easily change to zeolite-like materials by hydrothermal reaction. Lots of hot seawater is disposing near thermal power plants after cooling turbine generator periodically. Using seawater in the hydrothermal reaction caused to produce low price artificial zeolite by reduction of sodium hydroxide consumption, heating energy and water cost. As coal ash were reacted hydrothermally, peaks of quartz and mullite in the ash were weakened and disappeared, and new Na-P1 peaks were appeared strengthily. Si-O-Si bonding of the bituminous coal ash was changed to Si-O-Al (and Fe³⁺) bonding by the reaction. Therefore the produced Na-P1 type zeolite had high CEC of 276.7 cmol⁺·Kg⁻¹ and well developed molecular sieve structure with low concentration of heavy metals.

2. Utilization of the artificial zeolite in agro-environment

The artificial zeolite(1g) could remove 123.5 mg of zinc, 164.7 mg copper, 184.4 mg cadmium and 350.6 mg lead in the synthetic wastewater. The removability is higher 2.8 times in zinc, 3.3 times in copper, 4.7 times in cadmium and 4.8 times in lead than natural zeolite and charcoal powder. When the heavy metals were treated at the ratio of 150 Kg·ha⁻¹ to the rice plant, various growth inhibition were observed; brownish discoloration and death of leaf sheath, growth inhibition in culm length, number of panicles and grains, grain ripening and rice yield. But these growth inhibition was greatly alleviated by the application of artificial zeolite, therefore, rice yield increased 1.1~3.2 times according to the metal kind. In addition, the concentration of heavy metals in the brown rice also lowered by 27~75%. Artificial Granular Zeolites (AGZ) was developed for the purification of wastewater. Cation exchange capacity was 126.8 cmol⁺·Kg⁻¹. AGZ had Na-P1 peaks mainly with some minor C₃S peaks in X-ray diffractogram. In addition, AGZs had various pore structure that may be adhere the suspended solid and offer microbiological niche to decompose organic pollutants. AGZ could remove ammonium, orthophosphate and heavy metals simultaneously. Mixing ratio of artificial zeolite in AGZs was related positively with removal efficiency of NH₄⁺ and negatively with that of PO₄³⁻. Root growth of rice seedling was inhibited severely in the mine wastewater because of strong acidity and high concentration of heavy metals. As AGZ(1 Kg) stayed in the wastewater(100L) for 4days, water quality turned into safely for agricultural usage and rice seedlings grew normally.

Key words : Coal Fly Ash, Artificial zeolite, Heavy metals, Rice growth, Wastewater purification, Granulation

Introduction

1. Occurrence and disposal of coal ash

Combustion of coal produces a variety of residues, including fly ash, bottom ash, flue gas desulfurization waste(scrabbler sludge), flueidized bed boiler waste, and coal gasification ash.

Fly ash is the largest portion of the waste that is collected by mechanical filters or electrostatic precipitator from the combustion of fuel in modern coal-fired power plant. The proportion of fly ash reached up to 84% of total coal ash, fly and bottom ash(Adriano and Brisbin, 1978; Elseewi *et al.*, 1980). Bottom ash is the residue from coal combustion that

remained in the boiler. It is composed of both fine- and coarse-grained materials, and is generally a combination of ash and slag.

In Korea, about 3.6 million tons of coal ash was generated from 10 thermal power plant in 1998. In spite of the massive occurrence, only about 32% of total fly ash is being reused; land reclamation, brick production, manufacture of cements and concrete, but most coal ashes are disposing into the dumping site(Cha et al., 1999). So it is important to utilize the fly ash more effectively in environmental aspect. The ash disposal on terrestrial ecosystems has three major adverse impacts. Firstly, leaching of potentially toxic substances from the ash into soils and groundwater. The potential for groundwater contamination due to leachate from coal combustion residue disposal sites is based on the elevated concentrations of soluble salts and potentially toxic trace elements, including As, Ba, Cd, Cr, Pb, Hg, and Se, present in coal combustion wastes. The groundwater contamination at disposal sites, however, appears to be localized in the immediately vicinity of the disposal site(Thesis *et al.*, 1978; Cherkauer, 1980; Sakata, 1987; Spencer and Drake, 1987).

Secondary impact is the limiting vegetation establishment on ash disposal sites and changes in plant elemental composition are: (I) lack of essential nutrients, usually N and P; (II) toxicity caused by high pH and/or high soluble salt concentrations, high boron, and high concentration of other potentially toxic trace elements; and (III) the presence of compacted and/or cemented layers in the ash(Hodgson and Townsend, 1973; Townsend and Hodgson, 1973; Hodgson and Buckley, 1975; Townsend and Gillham, 1975; Bradshaw and Chadwick, 1980).

Thirdly, inputs to aquatic systems from ash disposal sites can affect both water quality and the biota that occupy receiving lakes and streams. Addition of ash effluents can increase the electrical conductivity, turbidity, and water temperature of receiving surface waters(Guthrie and Cherry, 1976; Forbes and Magnuson, 1980; Cherry *et al.*, 1984; Van Hassel and Wood, 1984).

Another potential impact of ash disposal on the aquatic environment is sedimentation and smothering of benthic fauna due to the release of large amounts of suspended solids. To reduce these impacts on the environment, we should be find out recycling way to decrease the disposal of fly ash.

2. The mineralogical characteristics of ash

The physical, chemical, and mineralogical characteristics of

bottom and fly ashes depend upon a variety of factors, including the composition of the parent coal combustion conditions, the efficiency and type of emission control devices, and the disposal methods used(Van Hook, 1979; Adriano *et al.*, 1980). Consequently, it is difficult to generalize about the composition of ashes, or their behavior in the environment. However, certain characteristics are fairly uniform for most ashes.

Fly ashes are composed predominantly of small, glassy, hollow particles, with particle sizes ranging from 0.01 to 100 μ m and specific gravity of 2.1 to 2.6(Adriano *et al.*, 1980). Fly ash is a complex heterogeneous material consisting of both amorphous and crystalline phases(Page *et al.*, 1979; El-Mogazi *et al.*, 1988; Mattigod *et al.*, 1990). Fly ash is mainly composed of several oxides such as SiO₂ and Al₂O₃ derived from inorganic materials remained after burning. As minor components, Fe₂O₃ and oxides of Mg, Ca, P, Ti(trace) are also included in the ash(Nozaki 1982). Coal ash can referred to as a kind of aluminosilicate glass containing some impurities, and its chemical composition is similar to volcanic glass of volcanic ash in nature. Volcanic glass is known to easily change to zeolite-like materials by hydrothermal reaction(Sudo and Matsuoka 1958).

In aluminosilicate, the aluminum ion may exist in either 4-fold or 6-fold coordination as contrasted to silicon, which is always 4-fold coordinated in aluminum. In zeolite, the aluminum is 4-coordinated with oxygen and these structures have higher ease of crystallization than aluminosilicates in which the aluminum ions are located in either ordered structure or in 6-fold coordination.

3. Production of artificial zeolite from coal ash

Schafhautele attempted to synthesize zeolite under hydrothermal conditions. In 1845, he reported the preparation of quartz by heating gel silica with water in an autoclave. After this, additional syntheses of several "zeolite" were reported in succeeding years. Over many decades, geologist and mineralogist have been extremely interested in reproducing the formation of minerals simulated natural processes. In addition, early investigators were interested in the interpretation of the conditions for mineral formation as they were related to geological process(Breck, 1974)

Production of zeolites from coal ash also needs hydrothermal treatment for substitution of Al (and Fe³⁺) for Si in its framework tetrahedra. The CEC of a zeolite is primarily a function of the degree of the substitution. In practice, the

ion-exchange behavior of a zeolite also depends on many factors: (i) framework topology(Channel configuration and dimensions), (ii) size and shape(polarizability) of the ions, (iii) charge density in the channel and cages, (iv) valence and charge density of the ions, and (v) electrolyte composition and concentration in the external solution(Barrer, 1978).

Henmi(1987a; 1987b), and Henmi and Narita(1987) found that alkali treatment of fly ash caused to increase in cation exchange capacity from 8 to 30 times according to the kinds of fly ash. After that, many researches began to study on the NaOH concentrations and kinds of fly ash as a raw materials (Okada, 1991; Shin *et al.*, 1993; Park and Choi, 1995; Moon and Kim, 1995; Tamura *et al.*, 1997).

Because lots of cost is required for the production of artificial zeolite by the consumption of heating energy and sodium hydroxide, it is necessary to find out the economic production way of the artificial zeolite. Most researchers used distilled water for the preparation of sodium hydroxide solution(Henmi, 1987a; 1987b; 1989; Henmi *et al.*, 1990; Okada, 1990; Shin *et al.*, 1993; Moon and Kim, 1995; Tamura *et al.*, 1997; Henmi, 1997; Kim *et al.*, 1998; Lee *et al.*, 1997; Lee *et al.*, 1998a; 1998b). In factory of artificial zeolite, tap water is used for preparation of sodium hydroxide solution. Therefore, it is necessary to find out alternative water to distilled water or tap water.

In general, most thermal power plants are located near seashore for some reasons: (i) easy importation of coal from abroad, (ii) easy disposal of coal fly ash into artificial sea pond, (iii) utilization of much seawater to cool periodically turbine generator. Therefore much hot seawater are disposing to near seashore. Additionally, the seawater contain much of cations and anions like sodium, magnesium, calcium, chloride, sulfate and so on. The chemical composition of the alkali solution is known to affect the zeolite formation(Aiello *et al.*, 1989; Ankia *et al.*, 1991; Hawkins *et al.*, 1978; Warzywoda and Thompson, 1991). Namely, utilization of seawater in the hydrothermal reaction could save consumption of heating energy, water cost and sodium hydroxide.

4. Utilization of the artificial zeolite for agro-environment

With industrial development over the 150 years, there has been increased release of metals by human-related activities. Campbell *et al.*(1983) compared natural and anthropogenic quantities of the trace metals emitted to the atmosphere and showed that around 15 times more Cd, 100 times more Pb, 13 times more Cu, and 21 times more Zn are emitted by man's

activities than those by natural processes.

Phytotoxic responses by heavy metals may be determined by a number of factors, which govern both availability and the relative toxicity of the metal contamination, such as pH, clay content, organic matter content and nutritional status(Clark and Clark; 1981; Deuck *et al.*, 1987; Dickinson *et al.*, 1988). Therefore, primary in situ methods for reducing soil heavy metals availability to plant is sorption, ion exchange, precipitation, and attenuation (Johnson *et al.*, 1977; Sopper, 1989). Increasing soil pH also has been evaluated(Schuman, 1986; Sims and Kline, 1991).

Artificial zeolite had high cation exchange capacity, large surface area and porous structure. So it was also proposed as an effective purifier of ionic pollutants such as heavy metals and ammonium by many researchers(Henmi 1987a; 1987b; Henmi and Narita, 1987; Henmi, 1989; Okada 1991; Shin *et al.*, 1993; Moon and Kim, 1995; Park and Choi, 1995).

Most of mine tailings are managing poorly after construction of embankment because mines are mostly located secluded places. Mine wastewater contains high concentration of heavy metals with high acidity because much spoils and wastes are high in pyrite(FeS_2 which is oxidized to form sulfuric acid(Adams *et al.*, 1971; Fail and Wochok, 1977; Capp, 1978; Jastrow *et al.*, 1981). When the wastewater flow into stream, it will have detrimental impact on agro-environment such as growth damage to plants, contamination of agricultural land and products. The high heavy metal concentration in agro-environment can ultimately jeopardize human and animal due to food chain transfer, ingestion of wind-blown dusts, or direct ingestion of soil. But little information has been known with regard to soil improver and to purify mine wastewater.

In case of animal wastewater, concentration of ammonium and phosphate are so high that it caused to eutrophication and oxygen depletion in the water. In order to purify animal wastewater, facilities and management techniques are necessary for separation of sludge and additional purifying materials to remove phosphate.

There were some researches on granulation of zeolite in Korea to increase additive value of natural zeolite as soil improving material(Choi *et al.*, 1995). And Kim *et al.*(1995) also investigated on the production of bed soil using artificial zeolite, but there are few reports to develop artificial granular zeolite for the simultaneous removal of nitrogen and phosphate, and purification of mine wastewater.

Conclusively, most of the coal ash is disposed into the settling ponds and landfills, and amount of coal ash will

increase worldly in the near future by the thermal power plant expanding plan. Therefore, recycling technique on fly ash is indispensable. This study was focused on the conservation of agro-environment by using artificial zeolite and on the development of economic production way of artificial zeolite.

Utilization of Seawater in the Production of Artificial Zeolite from Coal Fly Ash

1. X-ray diffractogram

Figure 1 shows the results of the X-ray diffractogram of artificial zeolite which were obtained by various concentration of NaOH at 100°C for 72 hours reaction. The main peaks of artificial zeolite were at the following angles(2θ): 12.4, 17.7, 21.7, 28.2, and 33.4. These patterns were very similar to Na-P1 type synthetic zeolite (Treacy *et al.*, 1996). It represented that the peaks of artificial zeolite were increased with increasing the concentration of NaOH up to 3 M, but rather slightly decreased at 3.5 M NaOH.

On the contrary, the peaks of quartz at the 2θ angles of 20.9, 26.6, 36.6 and 39.4 were disappeared, and the peaks of mullite at the 2θ angles of 16.5, 26.0, 33.5 and 35.3 were strengthened with hydrothermal treatment because the characteristic d spacing of both mullite and Na-P1 should be superimposed at this point. Although the reaction time maintained for 72hours, the other zeolite except for the Na-P1 was not detected. The baseline of Na-P1 around 2θ 5° became somewhat stabilized by reaction with 2.0 M, 2.5 M and 3.0 M NaOH, but the baseline became unstable by reaction with 3.5 M NaOH.

Considering the presence of anions could affect the type of zeolite crystallization in the synthesis of zeolite with silica and aluminum (Breck, 1974), anions in NaOH solution from seawater such as sulfate and chloride could play in a role in crystallization of Na-P1 from coal fly ash. Therefore, it is required for more study on influence of ions on the development of artificial zeolite.

2. Cation Exchange Capacity and element analysis

The CEC of the product is due to the formation of alumino-silicate species possessing the framed structure of Si-O-Al(Fe). The framework has been known to be formed from supersaturated $\text{Si}(\text{OH})_4$ and $\text{Al}(\text{OH})_4^-$ or $\text{Fe}(\text{OH})_2^-$ in hot alkaline solution (Bing and Muniton, 1989). As pointed out by Alexander *et al.* (1954), the solubility of Si increases rapidly

Table 1. CEC value of hydrothermal products as influenced by sodium hydroxide concentration in seawater for 24, 48, and 72 hour

NaOH concentration	24hr	48hr	72hr
	c mol (+) Kg ⁻¹		
2.0M	244.5	226.6	237.0
2.5M	259.8	257.5	263.4
3.0M	263.4	265.5	276.7
3.5M	179.8	164.9	191.6

above pH 9 due to the ionization of monosilicic acid; Al solubility increases above pH 8 where the $\text{Al}(\text{OH})_4^-$ ion predominates (Marion *et al.* 1976) so substitution of Al for Si occurs actively by increasing pH above 8. The greater the substitution, the more alkali or alkali earth cations needed to maintain electrical neutrality, leading to the higher CEC.

The change in CECs of the fly ash and artificial zeolite were examined with the function of NaOH concentrations (Table 1). The CEC of artificial zeolite was increased by increasing NaOH concentration up to 3.0M, but drastically decreased with NaOH concentration over 3.5M. This result showed that preparation of alkali solution using seawater could save more sodium hydroxide in synthesis of artificial zeolite from coal fly ash than those other investigations (Henmi 1987a, b; Park and Choi 1995; Shin *et al.*, 1993). Reaction time did not affect the CEC value between 24 and 48 hours, but the CEC value was the greatest in 72hour reaction than other reaction times observed in this experiment. From the reported CEC value of pure Na-P1, 515 $\text{cmol}^+ \cdot \text{Kg}^{-1}$ (Kato *et al.*, 1986), it can be estimated that the CEC of the synthesized Na-P1 by hydrothermal reaction with 3.0M NaOH, from 263.4 to 276.7 $\text{cmol}^+ \cdot \text{Kg}^{-1}$, represents about from 51.1 to 53.7% conservation.

3. IR spectrum

The infrared (IR) spectrum was composed of the near-infrared, the mid-infrared, and the far-infrared regions. Criteria for classification of clay minerals include the ratio of silica tetrahedral sheets to alumina octahedral sheets.

The IR spectra of fly ash and the product were shown in Figure 2. The IR spectrum of fly ash exhibited the broad absorption band near the wave number of 1100cm^{-1} which was attributed to Si-O-Si antisymmetric stretching vibration that indicates presence of amorphous silicate glass (Henmi, 1987a; Marel and Beutelspacher, 1976; Warren and Dudas, 1984).

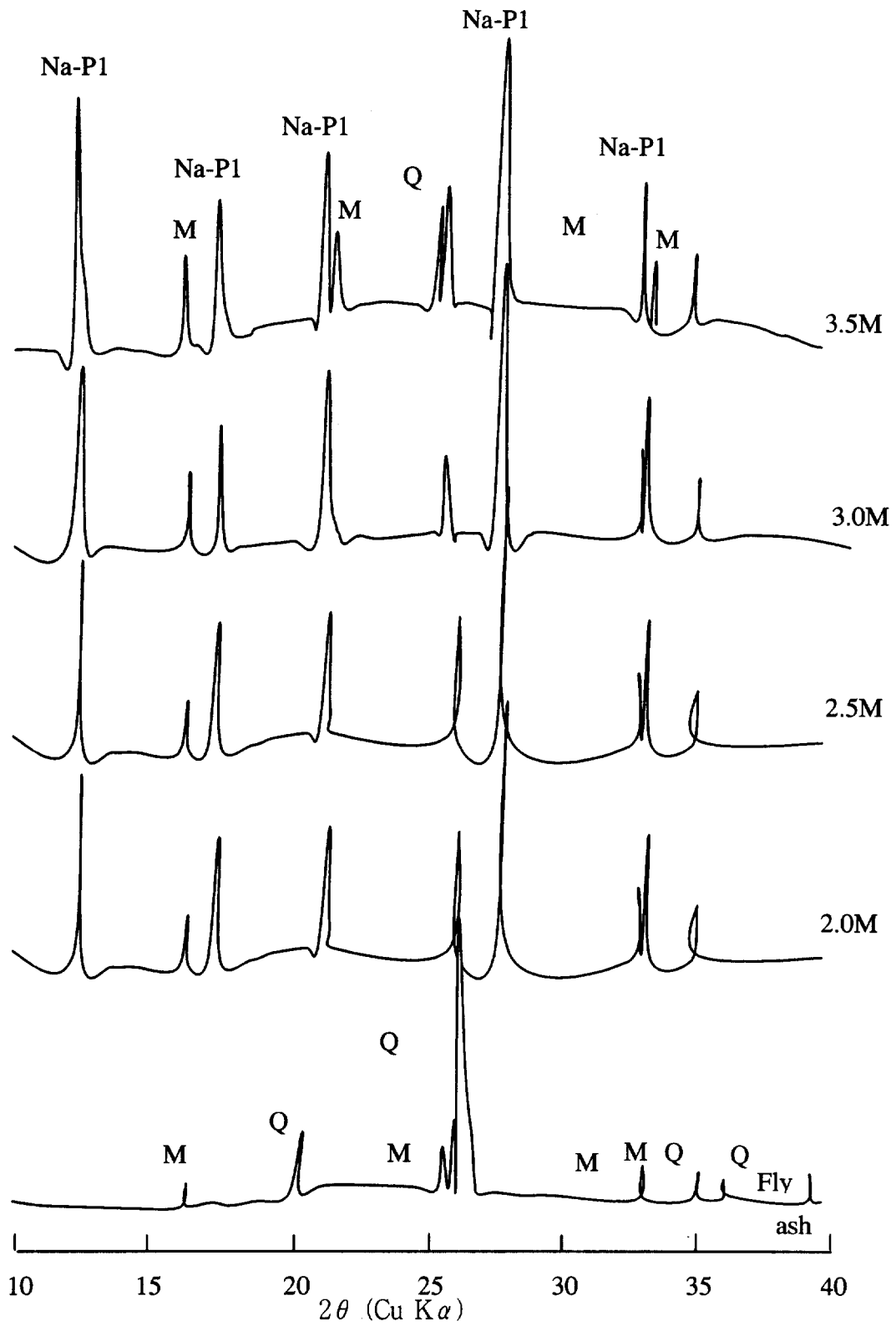


Fig. 1. X-ray diffractogram of the hydrothermal products with various NaOH solution for 72 h. M = Mullite, Q = Quartz

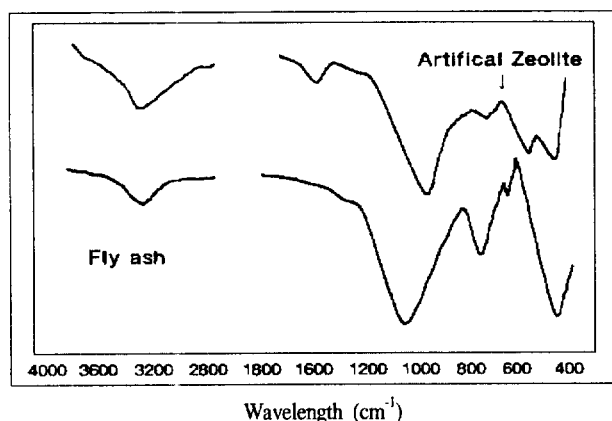


Fig. 2. Infrared spectra of bituminous fly ash and the artificial zeolite, Na-P1.

On the other hand, the IR spectrum of artificial zeolite exhibited the largest broad absorption band around 1006 cm^{-1} attributed to Si-O-Al asymmetric stretching vibration.

The band shift revealed that the Si-O-Si bonding mode became changed to Si-O-Al bonding mode during the hydrothermal treatment. Substitution of the quadrivalent Si by trivalent Al (and Fe^{3+}) giving rise to deficiencies of positive charges in the frameworks. These charges were balanced by Na^+ ions in the hydrothermal treatment and the Na^+ ions could exchange other cations such as heavy metals, ammonium ion and etc. The absorption band at 1650 cm^{-1} was corresponded to H-O-H bending vibration due to the water bound to Na-P1 (Marel and Beutelspacher, 1976). This absorption band was not found on the IR spectrum of fly ash. The absorption band at 3500 cm^{-1} was broad in bituminous fly ash and some deep broad in artificial zeolite. This band was corresponded to O-H stretch of the 1:1 group of silicates layers that the total amount of crystal-lattice water laid in the range of 13.4 to 16.2% (Tan *et al.*, 1986).

4. Scanning electron micrographs

According to Holler and Wirsching (1978), the hydrothermal alteration of glass depends on (i) temperature, (ii) chemical composition and pH of the solution, (iii) chemical composition of starting material, (iv) the existence of an open or closed system during the alteration process. In hydrothermal reaction where aqueous bases were involved, the hydroxyl could be bonded to the aluminum in preference to the silicon atoms, and the crystallization was also occurred by the copolymerization of the dissolved silicate and aluminate species. The rate of crystallization and the stability of the sodium zeolite phases were optimum in the vicinity of 100°C (Breck, 1974).

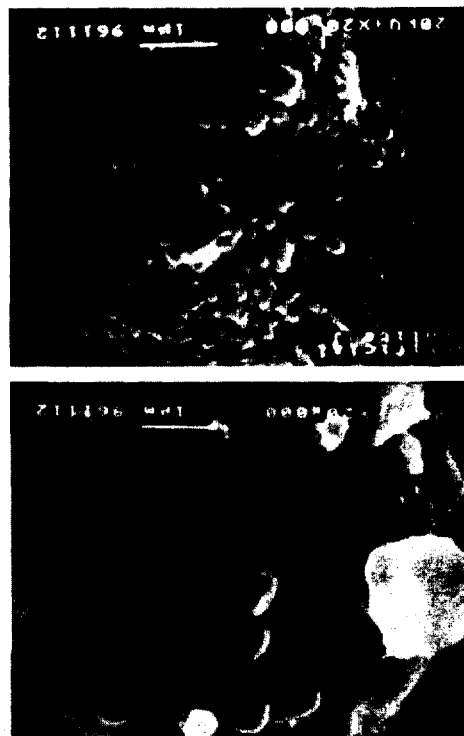


Photo 1. Scanning electron micrograph of bituminous coal fly ash(upper) and artificial zeolite(lower)

The scanning electron micrograph represented that bituminous fly ash had spherical shape without porous (Photo 1). And its surface was glassy or flecked, resulting from the melting of silicate minerals during coal combustion and the condensing of oxides, carbonates and/or sulfate during the precipitation (Adriano *et al.*, 1980; Mattigod *et al.*, 1990; Warren and Dudas, 1984).

After hydrothermal reaction with sodium hydroxide solution, large sphere structure of fly ash was transformed into three-dimensional sieve structure that aggregated to form the regular forms in their shapes. Artificial zeolite having this sieve structure could be used for conservation of agro-environment such as adsorbent of gaseous pollutants.

5. Concentration of heavy metals

Table 2 showed the concentration of heavy metals in artificial zeolite, natural zeolite and bituminous fly ash. Artificial zeolite had lower concentration of heavy metals except the zinc than natural zeolite as extracted by 0.1N HCl. And the concentration of heavy metals which was extracted from artificial zeolite by 0.1N HCl was also lower than that of bituminous coal fly ash. These might be resulted from recrystallization of bituminous ash: reduction of pH-dependent charge and increment of permanent charge by reduction of

Table 2. Concentration of heavy metals in the artificial zeolite, natural zeolite and bituminous coal fly ash as extracted by 0.1N HCl

Sample	Zn	Cu	Pb	Cd	Ni	Cr	Fe
	mg·Kg ⁻¹						
Artificial zeolite	4.7	0.2	-	0.03	0.3	0.05	0.5
Natural zeolite	3.7	0.3	0.1	0.05	1.0	1.0	17.5
Bituminous ash	3.6	1.7	0.2	0.2	2.2	2.0	26.6

active Fe, Al, organic matter and impurities (Morris *et al.*, 1976; Parker *et al.*, 1979).

Sorption of Heavy Metals in the Wastewater by the Artificial Zeolite

1. Effect of shaking time and temperature on heavy metals sorption

Molecules and atoms can stick to surfaces in two ways. In physical sorption, there is a Van Der Waales interaction between the adsorbate and the substrate. In chemical sorption, the particles stick to the surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the substrate.

In Figure 3, sorbed amount of the heavy metals were higher at 35 °C than that at 15°C. physical sorption, a long-range but weak interaction, is insufficient for the bond breaking. Therefore a physically sorbed particle vibrates in its shallow potential well, and may shake itself off the surface after short time. Since enthalpy of desorption is $K_{\text{Desorption}} = Ae^{-E_a/RT}$, A is Helmholtz function, E_a the activation energy of the reaction, R the constant ($R = kN_A$, Avogadro's constant), and T the absolute temperature, the half-life for heavy metals remaining on the surface depends upon temperature. So residence half-life in physical sorption decreased with increase temperature surrounding the surface (Atkins, 1978). Considering increment of sorption amount by higher temperature, heavy metals in the synthetic wastewater were sorbed to the artificial zeolite chemically rather than physically.

More than half of each treated heavy metal was removed by the artificial zeolite in the synthetic wastewater at two different temperatures for 20 minute shaking (Figure 1). The longer the shaking time, the more the heavy metals were sorbed by the artificial zeolite at two different temperatures. Christensen (1984) also reported that Cd sorption was occurred

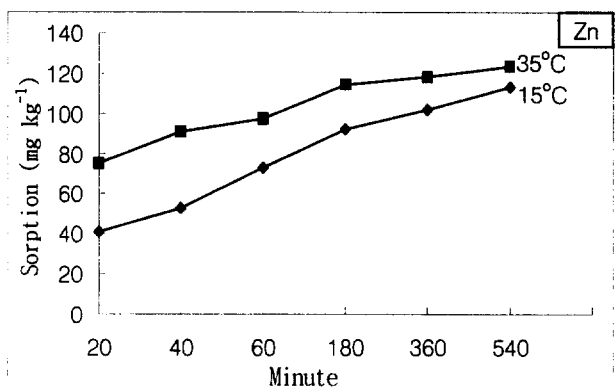
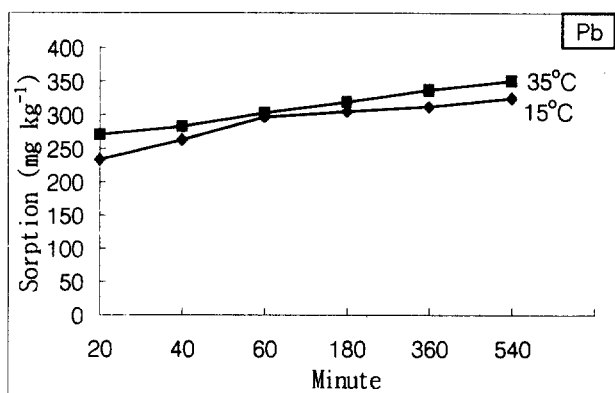
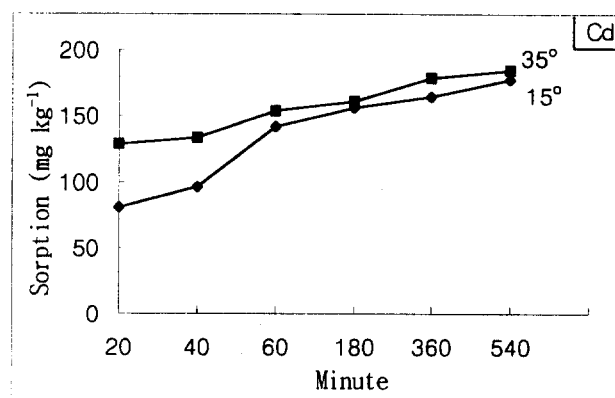
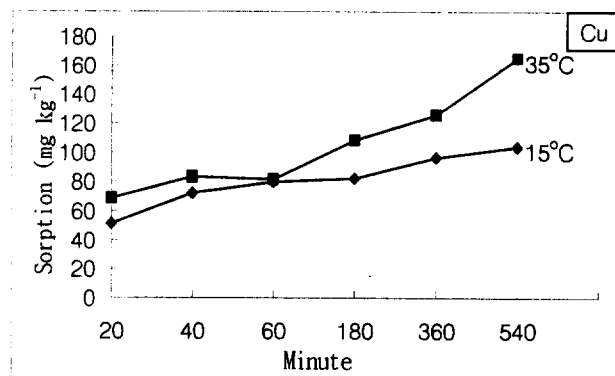


Fig. 3. Sorption of heavy metals by artificial zeolite according to the shaking time at 15°C and 35°C.

extremely rapid with 95% of the sorption within the first 10 minutes in the isotherm experiment. The enthalpy of chemical sorption is much greater than that of physical sorption. Chemical sorption can occur slowly and steadily as compared with physical sorption.

CEC of the artificial zeolite will dictate the capacity of the surface for the catalysis; The catalytic activity of a hydrated cation near a charged surface may be affected by specific interactions with various groups on the surface and by general process of polarization brought about by electric field. A chemically sorbed molecule may tear apart by the demand of the unsatisfied valence of the surface atoms and surfaces catalysis reactions by the existence of molecular fragments on the surface as a result of chemical sorption.

2. Removed amount of heavy metals by the zeolites and activated carbon

A generally accepted view is that increasing ability of metals to form hydroxy complexes increases its likelihood of specific adsorption. Brummer (1986) listed the order of heavy metals hydrolysis as $Hg > Pb > Cu \gg Zn > Co > Ni > Cd$. Kinniburgh *et al.* (1976) reported that order of metal affinities for amorphous Fe and Al hydroxides were little different from the order of hydrolysis as reported McKenzie (1980) for Mn oxides and Fe minerals such as goethite and haematite. Ross (1990) reported that Pb and Cu are retained more strongly by many soil colloids than Cd, Zn and Ni. On the while, Cd and Zn have greater cation exchange abilities on layer silicates, but the relative strength of their adsorption on soil oxide and organic fractions is less than other heavy metals.

When the artificial zeolite of 1g was treated into the synthetic wastewater of 400mL for 9 hour shaking at 35°C, 123.5 mg of Zn, 164.7 mg of Cu, 184.4 mg of Cd and 350.6 mg of Pb were removed, respectively (Figure 4). This result indicates that the produced artificial zeolite in this study could remove more 2.8 times of zinc, 3.3 times of copper, 4.7 times of cadmium and 4.8 times of lead than natural zeolite and activated carbon.

Alleviation of Heavy Metals Damage by the Artificial Zeolite in Rice Plant

1. Concentration of heavy metals in the rice

Heavy metals in the soil would be free to diffuse themselves through the liquid phase, and caused to inhibit plant growth and should be accumulated in the plant. Adsorption

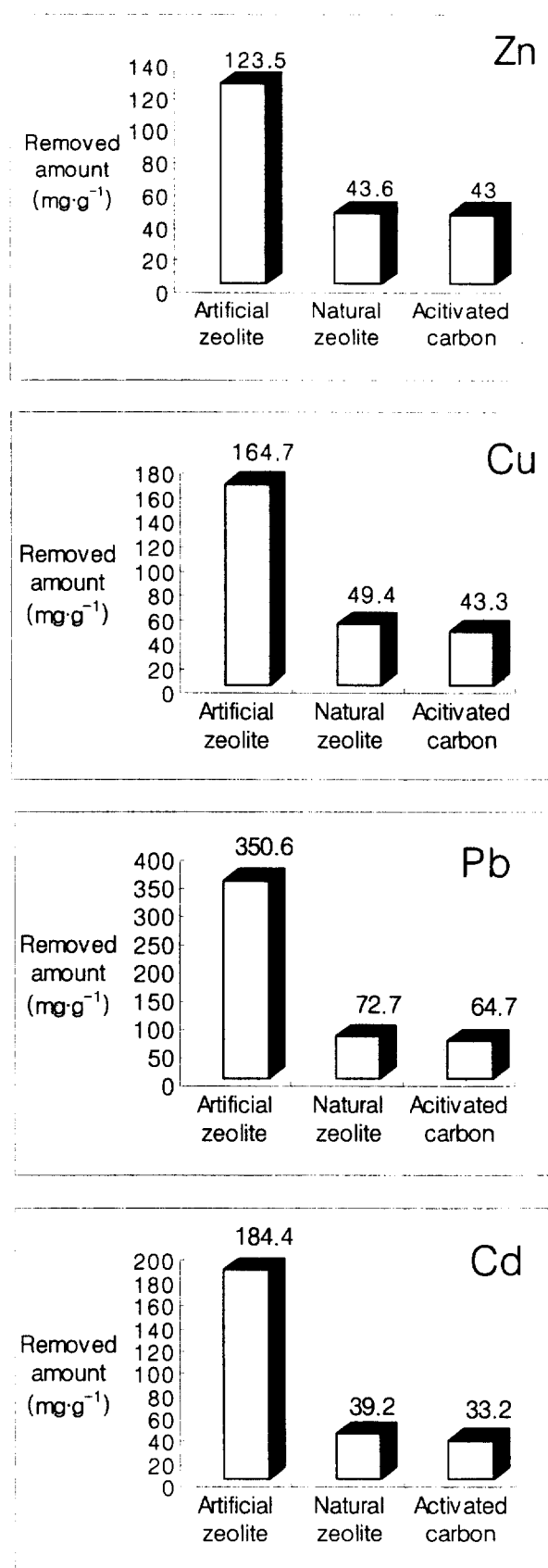


Fig. 4. Removed amount of heavy metals by artificial zeolite, natural zeolite and charcoal powder.

and ion exchange by clay minerals are of great practical significance in heavy metals uptake by plant and retention in soil. In USA, sludge application levels are based on both the heavy metal content and the cation exchange capacity (CEC) of the soil. That is the maximum cumulative Cd loading was 5.5 Kg Cd per hectare for $CEC < 5 \text{ cmol}^+ \cdot \text{kg}^{-1}$ 22 Kg Cd per hectare for $CEC > 15 \text{ cmol}^+ \cdot \text{kg}^{-1}$ (US EPA 1979).

In the brown rice, the concentration of heavy metals was decreased remarkably by application of the artificial zeolite (Figure 5). When the artificial zeolite applied at the ratio of 2000 Kg per hectare, concentration of each heavy metals in the brown rice was decreased by 46.3% in copper, 50% in cadmium, 45.4% in lead and 15.9% in zinc (Data not shown). In the copper treatment with a ratio of 150 Kg per hectare, the application of artificial zeolite of 2,000 Kg per hectare was sufficient to be down to the same concentration of copper. Additionally, when the artificial zeolite applied in the ratio of 4000 Kg per hectare, the reducing effect of the metal concentrations were greatly increased: 52.5% in copper, 75% in cadmium, 63.5% in lead and 27.3% in zinc.

Consequently, the artificial zeolite application in the ratio of 4000 Kg per hectare was sufficient to keep equivalent the concentration of copper and lead to native concentration in the brown rice even under heavy dosage of the copper and the lead. But in the case of zinc and cadmium treatment with the artificial zeolite application of 4000 Kg per hectare, concentration of zinc and cadmium in the brown rice was 1.24 times and 13.3 times higher than native concentration despite application of artificial zeolite, 4000 Kg per hectare. Korean Ministry of Environment is restricting usage of the brown rice having cadmium above $0.5 \text{ mg} \cdot \text{kg}^{-1}$ (1996). Therefore the artificial zeolite was required for more than 4000Kg per hectare to produce hygienically safe rice under heavy dosage of cadmium treatment of 150 Kg per hectare.

2. Alleviation of rice plant damage

Toxicity symptoms by the heavy metals are results of the injurious effects on the physiological processes in the plant. The physiological injury were inhibition of photosynthesis and respiration (Carlson *et al.*, 1975), water stress and wilting (Poschenrieder *et al.*, 1989), changes in cytoplasm pH and plasma membrane electrical potential having effects on the activities of metabolic enzymes (Cumming and Tomsett, 1992).

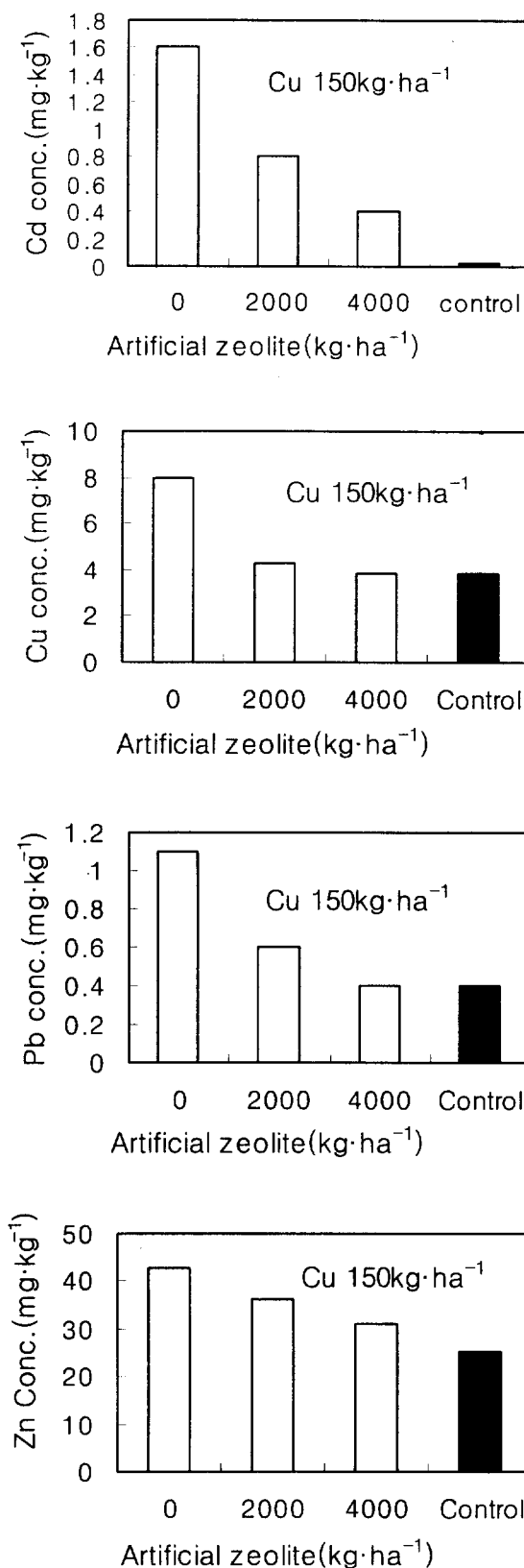


Fig. 5. Effect of artificial zeolite application on the concentration of copper, cadmium, lead, and zinc in the brown rice. (Control: Cultivation without any heavy metals and artificial zeolite)

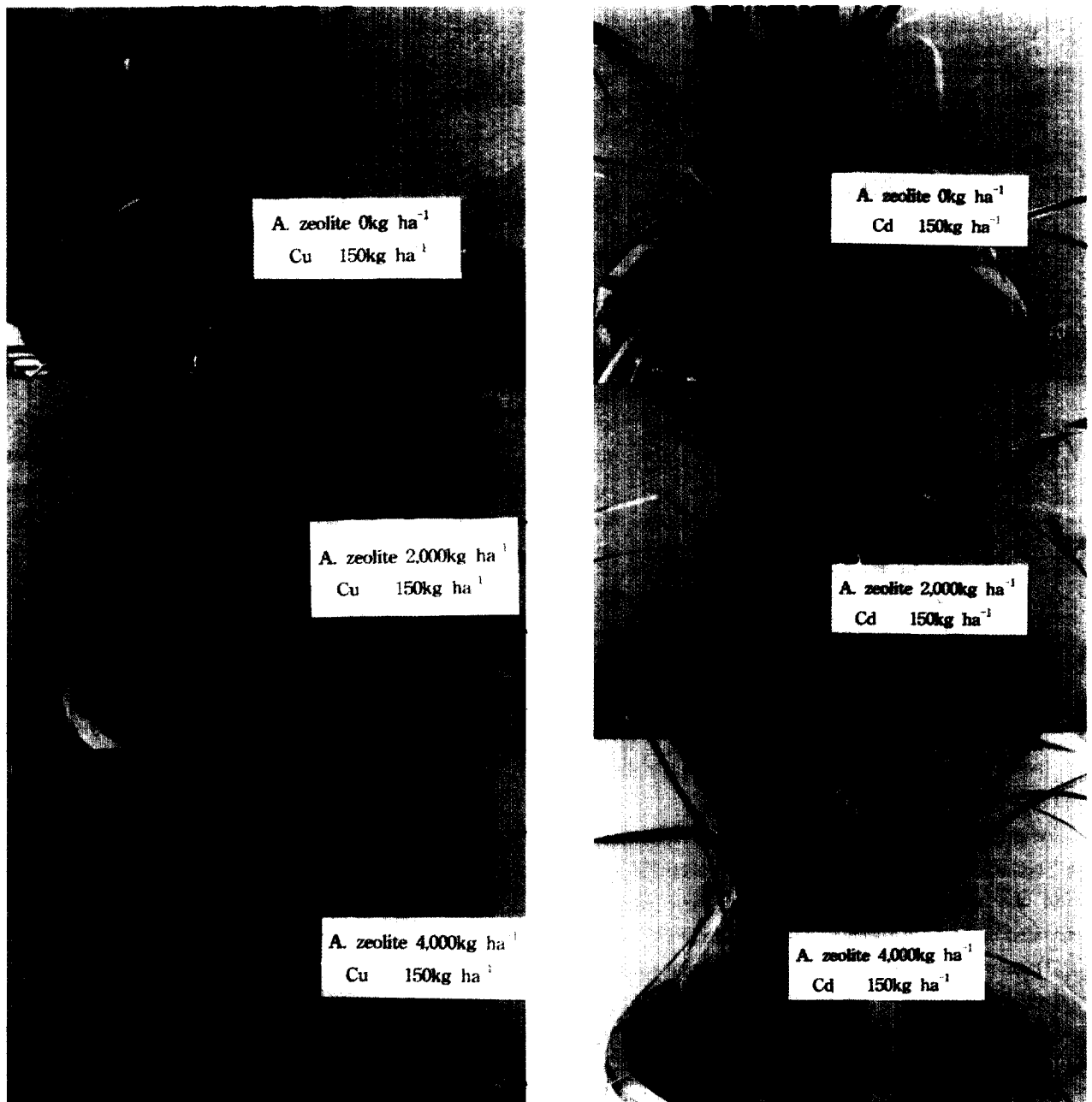


Photo 2. Effect of the artificial zeolite on the alleviation of rice plant damage caused by copper(left) and cadmium (right) treatment at panicle initiation stage.

Photo 2 shows over-all view of alleviation effect of the artificial zeolite on the growth inhibition of rice at panicle initiation stage under copper, cadmium, zinc and lead treatment. Rice plant did not grow well by treatment of heavy metals: In copper and cadmium treatment, rice leaves and leaf sheaths were withered and growth of stems were inhibited greatly. But these growth inhibitions were greatly recovered by application of the artificial zeolite. And these alleviation effects were increased by heavy application of artificial zeolite.

Morris *et al.* (1990), and Loeppert and Hallmark (1985) found that there was negative correlation between the incidence of chlorosis and the layer of silicate content of the soil.

Table 3 represents the influence of artificial zeolite and the heavy metals on the yield components and yield recovery of rice. Copper and cadmium treatment to the soil caused to inhibit greatly in culm length, number of panicles per plant, number of grains per panicle and ratio of ripened grain. In the case of the lead and the zinc treatment, the number of grains

Table 3. Alleviation ratio of the artificial zeolite on the rice growth inhibition by treated heavy metals

Treated metals (150Kg·ha ⁻¹)	Artificial zeolite (Kg·ha ⁻¹)	Culm length	Panicles /plant	Grains /panicle	Ratio of ripened grain	Yield recovery
Cu	0	75.3	58.3	62.9	80.1	18.5
	2000	77.2	79.8	95.4	83.0	43.7
	4000	77.7	90.1	92.0	89.9	59.3
Cd	0	82.7	61.3	67.4	78.1	31.4
	2000	85.6	84.0	79.6	94.8	62.0
	4000	97.6	98.1	84.3	96.4	78.0
Pb	0	106.2	102.5	92.3	99.6	94.4
	2000	106.4	98.2	94.1	99.3	96.0
	4000	107.4	100.0	96.5	99.4	100.8
Zn	0	95.2	98.2	85.9	94.0	74.6
	2000	104.6	110.4	91.1	97.8	100.6
	4000	101.1	108.6	95.1	99.9	106.7
Control ↓		63.2cm	16.3ea	57.4ea	95.7%	48.1g/pot

Yield recovery = (Treatment/Control) × 100

↓: Cultivation without any heavy metals and artificial zeolite

per panicle were reduced greatly by heavy metals. As results of these, rice yield was also decreased greatly by heavy metals.

As artificial zeolite applied at the level of 2000 and 4000Kg per hecter, these growth inhibitions were alleviated and rice yield also recovered greatly. In addition, these effects were enhanced by heavy application of artificial zeolite.

These results represent that artificial zeolite could be use for soil improver to get high yield in the adverse soil condition and to afforest the abandoned wasteland containing harmful elements too high to grow plants.

Production and Utilization of Granular Artificial Zeolite

1. Selection of superior coagulator

Removal efficiency of NH₄⁺ was the highest in portland cement and followed blast furnace slag cement, gypsum, tile cement and soil coagulator. Removal efficiency of PO₄³⁻ was also the highest in portland cement and followed gypsum, blast furnace slag cement, tile cement and soil coagulator (Table 4). These results showed that portland cement was the better coagulator having better adsorption capacity to the phosphate and the ammonium than the others.

Table 4. Concentration of NH₄⁺ and PO₄³⁻ after 4 hours shaking with swine wastewater and coagulators

Binding materials	NH ₄ ⁺	PO ₄ ³⁻
	mg·L ⁻¹	
Portland cement	1662	13.7
Tile cement	2571	58.4
Blast furnace slag cement	2238	30.7
Gypsum	2357	18.4
Soil coagulant (Newbeton)	2987	71.2
Swine wastewater	3355	149.6

2. Optimum mixing ratio of the coagulator

As blending ratio of portland cement were increased, AGZs became harder, namely, 0.4 Kg cm⁻² in 16 percent blending, 4.1 in 20 percent, 24.4 in 25 percent and 176.1 in 33 percent, respectively. On the while, when portland cement of 16% mixed to the artificial zeolite, AGZs were broken down in the shaking water with 200rpm for 5 hours. But mixed portland cement above 20% to the artificial zeolite, AGZs were kept stable in the same shaking condition.

Cation exchange capacity was related to negatively with the mixing ratio of portland cement; 151.2 cmol⁺·Kg⁻¹ in 16 percent mixing ratio, 126.8 cmol⁺·Kg⁻¹ in 20 percent, 81.4 cmol⁺·Kg⁻¹ in 25 percent and 66.5 cmol⁺·Kg⁻¹ in 33 percent. Above results means that the portland cement of 20% was required for the granulation of the powdery artificial zeolite having high CEC value.

3. Scanning electron micrograph of AGZ

Photo 3 shows the scanning electron micrograph of AGZ. There were fine micropores in the spherical artificial zeolite, and there were also macropores developed during the granulation process in the upper photo that expanded by 7500 times. This structure represents that AGZ could adsorb and adhere suspended solid and offer microbiological niche to decompose organic pollutants in addition to ion exchange.

Table 5. Influence of mixing ratio of portland cement to the artificial zeolite on hardness and cation exchange capacity

Mixing ratio of portland cement (%)	Hardness (Kg·cm ⁻²)	Cation Exchange Capacity cmol ⁺ ·Kg ⁻¹
33	176.1	66.5
25	24.4	81.4
20	4.1	126.8
16	0.4	151.2
Powdery artificial zeolite	-	299.1

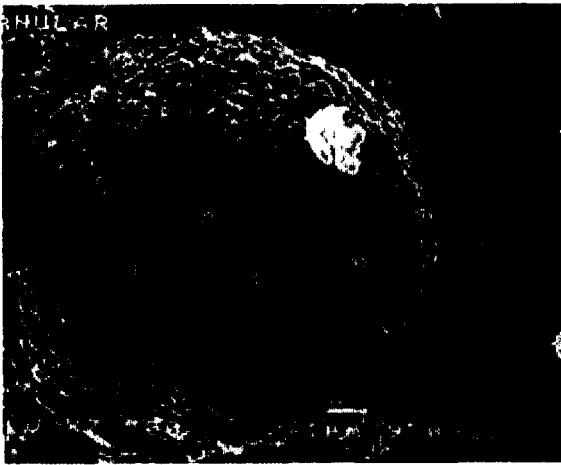


Photo 3. Scanning electron micrograph of artificial granular zeolite.

4. X-ray diffractogram

The X-ray diffractogram of powdery artificial zeolite shows that fly ash with hydroxide solution can be easily converted to the zeolite phase, Na-P1, through the hydrothermal reaction (Figure 6).

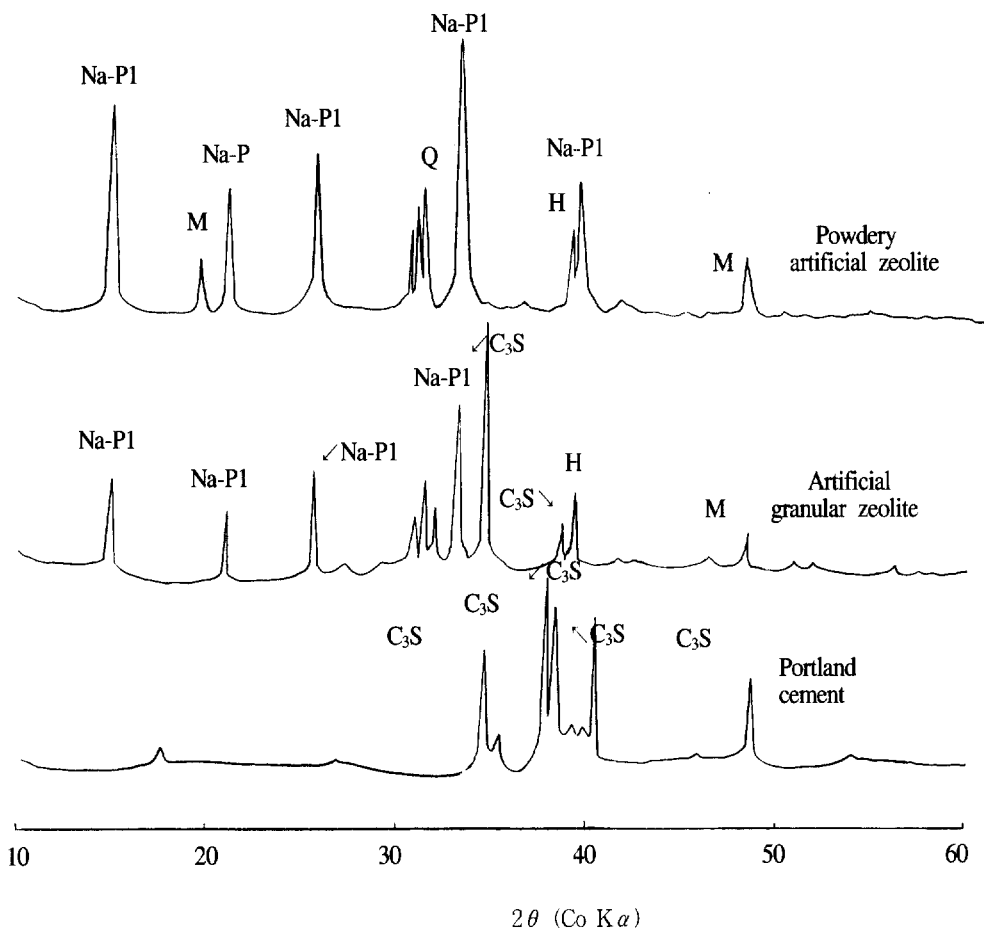


Fig. 6. X-ray powder diffraction patterns of powdery artificial zeolite, artificial granular zeolite and Portland cement. M: Mullite, H: Hematite, C_3S : $3CaO \cdot SiO_2$

As compared to peak of powdery artificial zeolite, AGZ had weak peak of Na-P1 at 14.6° , 20.8° , 25.4° and 33.4° , and no peak at 39.2° . And peak of mullite was disappeared at 17.5° , and that of quartz was also weakened at 31.2° .

On the while, AGZ had new peak of C_3S at 34.5° and 38.4° resulting from Portland cement. These results represent that Na-P1 phase was predominated in AGZ in spite of coagulation of artificial zeolite by portland cement.

5. Thermal analysis

In Figure 7, powdery artificial zeolite had a steep descent around $100^\circ C$ in thermogravimetry (TG) representing water evaporation from pore structures developed during hydrothermal reaction. In differential thermal analysis (DTA), there was a small endothermic peak below $100^\circ C$ representing heat loss by evaporation of water in macropore structure of artificial zeolite, Na-P1. There was also a deep endothermic peak around $130^\circ C$ representing presence of micropore structure of Na-P1.

On the while, AGZ had steeper endothermic curve around 100°C, and shallower endothermic curve around 130°C than that of powdery artificial zeolite. It may resulted from development of macropore structure and some clogging micropore structure by granulation (Lee *et al.*, 1998b). Barrer and Marshall (1964) reported that 90% of total water loss occurs below 450°C in the synthetic strontium zeolite and regarded it as zeolitic water.

On the other hand, there was trace exothermic peak around 860°C in powdery artificial zeolite. This result is representing the destruction of the dehydrated zeolite and the formation of a sintered amorphous phase having increased electrical conductivity (McAdie, 1970). AGZ have also deep descent in TG and steep endothermic peak below 100°C in DTA representing similar macropore structure to powdery artificial zeolite.

But there are two different points in TG and DTA pattern between powdery artificial zeolite and AGZ in Figure 7. First, there was little descent in TG and little endothermic peak around 130°C than powdery artificial zeolite. It suggested that micropores in powdery artificial zeolite were clogged by granulation with Portland cement.

Second, there was deeper decrement in TG and steeper endothermic peak in AGZ around 700°C suggesting the sintering of $\text{Ca}(\text{OH})_2$ developed during hydration of portland cement.

6. Comparison of removability of ammonium ion and phosphorous among some zeolites

Figure 8 showed simultaneous removal efficiency of ammonium ion and orthophosphate among powdery natural zeolite, powdery artificial zeolite and artificial granular zeolite in the synthetic wastewater. The synthetic wastewater contained NH_4^+ of $1545 \text{ mg}\cdot\text{L}^{-1}$ and PO_4^{3-} of $417 \text{ mg}\cdot\text{L}^{-1}$. When powdery artificial zeolite and natural zeolite shook in the synthetic wastewater in the ratio of 1: 40 for 24 hours, NH_4^+ was removed above 99% by both of powdery natural and artificial zeolite, but PO_4^{3-} was removed only 29.1% by powdery natural zeolite and 12.4% by powdery artificial zeolite. However, AGZ mixed with 33% Portland cement could remove 96.0% of NH_4^+ and 83.1% of PO_4^{3-} simultaneously.

The removability of NH_4^+ ion was inversely as the blending ratio of portland cement. But the removability of AGZ to PO_4^{3-} were in direct proportion to the blending ratio of Portland cement(Data not shown). The above results suggest that optimal mixing ratio of Portland cement to artificial zeolite could be change according to the content ratio of ammonium and phosphate. in the wastewater.

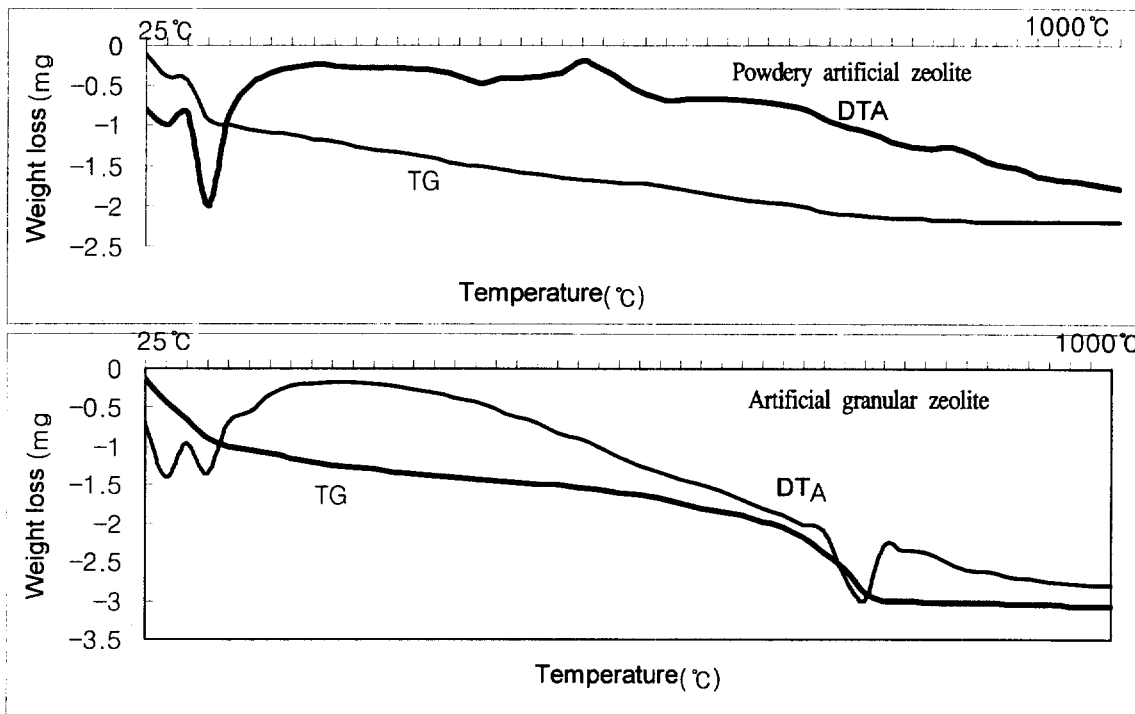


Fig. 7. Thermogravimetry (TG) and Differential Thermal Analysis (DTA) curves of powdery artificial zeolite and artificial granular zeolite.

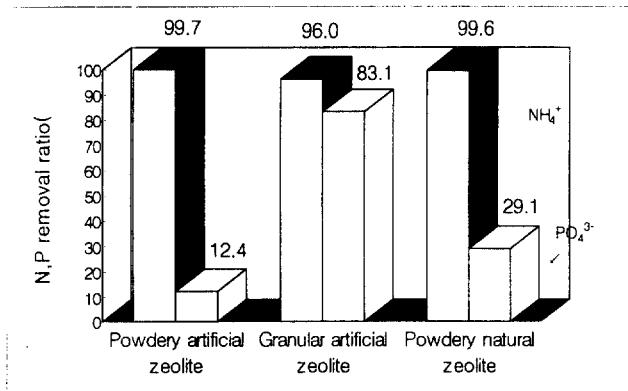


Fig. 8. Simultaneous removal of ammonium ion and orthophosphate in the wastewater after 24 hours shaking with some zeolites.

7. Purification of synthetic wastewater by AGZ

As AGZ (5g) put in synthetic wastewater (200mL) containing copper 468 mg·L⁻¹, cadmium 479 mg·L⁻¹, lead 452 mg·L⁻¹ and zinc 513 mg·L⁻¹, respectively, lead was removed 99.7%, zinc 78.9%, copper 76.1%, and cadmium 61.8% after retention for 6hours. When AGZ was treated for 12 hours, lead was removed 99.9%, copper was 91.6%, cadmium 85.0%, and zinc 83.3%. After retention for 48hours, lead, copper, cadmium were removed above 99.9%, but zinc was removed 94.2% (Table 6). Namely, the longer retention time, the more heavy metals were removed.

And removal effect of AGZ was the highest in lead and the next was copper, cadmium and zinc. In addition to this, considering CEC of AGZ having 125.1 cmol⁻·Kg⁻¹ (Lee *et al.*, 1998b) and the suggestion of Solomon (1968), Al species at broken crystal edges and Na⁺ located in the silicate layers of AGZ can act as electron accepters in surface-catalyzed polymerization of heavy metal ions.

8. Purification of mine water by AGZ

Wastewater of Deogum mine had strong acidity; pH of 2.85, and concentration of zinc, cadmium, copper and lead was too high to use for agriculture (Table 7). As AGZ treated to the

Table 6. Effect of AGZ on removal efficiency of heavy metals according to the retention time.

Retention time (hr)	Removal efficiency(%)			
	Cu	Cd	Pb	Zn
6	76.1	61.8	99.7	78.9
12	91.6	85.0	99.9	83.3
24	99.7	>99.9	>99.9	86.3
48	99.9	>99.9	>99.9	94.2
Conc. of Wastewater (W, mg·L ⁻¹)	468	479	452	513

$$\text{Removal efficiency (\%)} = (W - \text{AGZ treatment}) / W \times 100$$

mine wastewater with 1 to 50 ratio (W: V) for one day, strong acidity turned into weak, and metals such as Fe, Zn, Cu, Pb and Cd were not detected, but it was required for more 1days to remove Mn. When AGZ treated to the mine wastewater with a ratio of 1: 100 (W: V), it was required for more 3 days to remove harmful elements in the mine wastewater for the agricultural use. But AGZ treated to mine wastewater with 1: 250 (W: V), the water still had strong acidity and high concentration of harmful elements, so it could not be used for irrigation agriculture.

9. Rice seedling growth response

The major factors limiting vegetation establishment on mine tail disposal sites are (I) strong acidity, (II) high concentration of heavy metals (Pierzynski and Schwab, 1993). High level of heavy metals contamination have acute phytotoxic effects on plants, while lower but continuous concentration of atmospheric contaminants may have chronic effects on long-lived plants (Pitelka, 1988; Schulze, 1989).

Table 8 shows that alleviation effect of AGZ on the growth inhibition of rice caused by the mine wastewater. The rice seeds germinated normally and the shoots were grew normally even in the watsewater. But the roots of 10 day-seedling did not grow well with black-rot at the tip, and the seedlings were died finally. On the while, when rice seeds were immersed in the purified water by AGZ treatment with the ratio of 1 to 100 (W:V) for 4 days, seedlings were grew normally without any damage(Photo 4).

Table 7. Influence of treated ratio and retention time of AGZ on the chemical change of the mine wastewater

Treated ratio	Retention day	pH	Mn	Fe	Zn	Cu	Pb	Cd
			mg·L ⁻¹					
1: 50	1	6.64	47.0	ND	ND	ND	ND	ND
	2	7.84	ND	ND	ND	ND	ND	ND
	3	7.92	ND	ND	ND	ND	ND	ND
	4	7.91	ND	ND	ND	ND	ND	ND
1: 100	1	5.18	99.6	ND	77.1	6.6	ND	19.3
	2	5.73	72.0	ND	50.5	1.3	ND	16.0
	3	6.19	41.3	ND	16.8	ND	ND	6.7
	4	6.95	16.7	ND	1.1	ND	ND	0.5
1: 250	1	2.96	102.9	1.1	87.4	20.5	5.2	18.8
	2	3.25	89.7	ND	86.4	18.9	2.3	19.6
	3	3.86	98.7	ND	67.7	17.3	3.5	8.4
	4	4.94	88.0	ND	68.6	9.8	2.3	17.1
Inlet		2.85	118.4	21.2	94.2	21.8	5.9	21.2
Criteria for agricultural water		-	-	-	7.4	0.18	13.6	0.9

ND: Not Detected

Table 8. Effect of artificial granular zeolite on the rice seedling growth in the mine wastewater

Treatment	10day-seedling		28 day-seedling		Dry wt. (mg plant ⁻¹)
	Plant height (cm)	Root length (cm)	Plant height (cm)	Root length (cm)	
Mine wastewater	1.87	0.73	Dead	Dead	Dead
Purified wastewater ↓	1.78	3.42	7.0	7.4	11.5

↓: AGZ treatment with the ratio of 1 to 100 (W: V) for 4 days

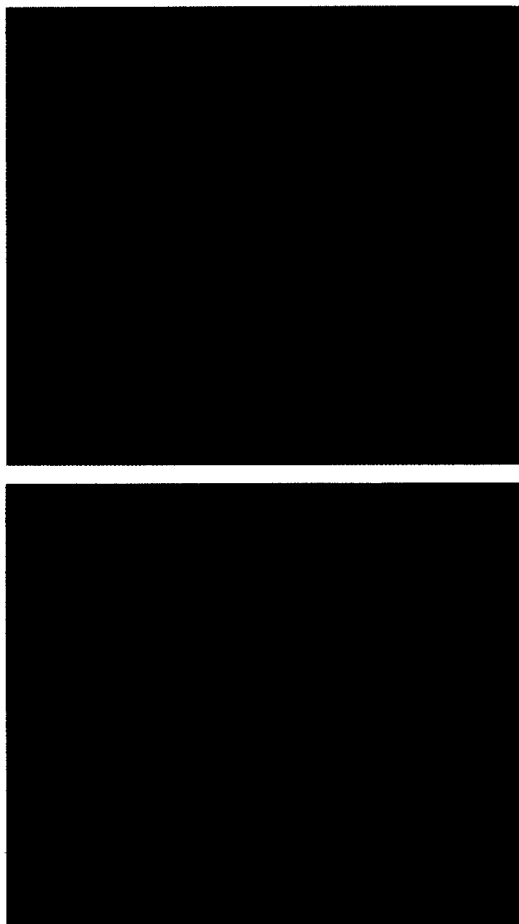


Photo 4. Effect of GAZ treatment on the alleviation of rice root growth of 10 day-seedling in the mine wastewater.

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