

Sorption Characteristics of Fly Ash for Use as Additive in Backfill Material

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뒷채움재 첨가제로서 석탄비회의 수작특성

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Abstract

Fly ash and bentonite samples were selected and characteristics of them were investigated. Fly ash was found to be similar to bentonite in particle size distribution but quite different in microstructure. The most special aspect of fly ash was high alkalinity of its solution. Distribution coefficients of Cs and Co on the samples were measured to survey the effects of mixing. Fly ash showed higher distribution coefficient of Co than that of Cs. Through various experiments, factors affecting the distribution coefficients of Co and Cs on mixture of bentonite and fly ash were identified. Comparison of the distribution coefficients of Cs on fly ash and bentonite mixture with those on sand and bentonite mixture suggests that fly ash would be useful as an efficient additive of backfill material if pertinent mixing ratio was chosen.

요 약

국내의 석탄화력발전소에서 발생하는 석탄비회와 국내산 벤토나이트 중에서 시료를 선정하였으며 특성분석을 수행하였다. 석탄비회는 입도분포에 있어서 벤토나이트와 유사하였으나 미세구조는 매우 다르게 나타났다. 석탄비회의 가장 큰 특징은 물과 섞었을 때에 나타나는 높은 알칼리성이었다. 석탄비회와 벤토나이트를 섞었을 때 나타나는 Cs와 Co의 분배계수의 특성을 조사하기 위한 실험을 수행하였다. 실험결과, 석탄비회의 경우, Co의 분배계수가 Cs보다 높게 나타났다. 여러종류의 실험을 통하여 벤토나이트와 석탄비회 혼합물의 Co와 Cs에 대한 분배계수에 영향을 미치는 요인을 확인하였다. 또한, 벤토나이트와 석탄비회 혼합물의 Cs에 대한 분배계수와 벤토나이트와 모래 혼합물의 동일핵종에 대한 분배계수 비교를 통하여 벤토나이트와 석탄비회를 적절한 혼합비율로 섞는다면 석탄비회가 효과적인 첨가제로 유용함을 보였다.

1. Introduction

Coal ash, arising from coal combustion power plants, is generally categorized into fly ash and bottom ash, depending on the locations where it is collected. Coal, depending on its type, contains 15 to 45 percent of its weight as coal ash. Fly ash, forming 75 to 90 percent of coal ash, is collected at electrical precipitator and of which the particle diameter is mostly smaller than 0.1mm [1].

At present the amount of coal ash arising annually from coal combustion power plants in Korea reaches about 2 million metric tons and, according to government's long-term electricity supply plan, is expected to be about 5.5 million metric tons by the middle of the first decade of the 21st century [2].

Utilization of fly ash in Korea is limited to the field of ready-mixed concrete, cement additives, and brick manufacturing, which requires only about 15 percent of annual amount. Rest of it is buried in the ground, causing the difficulties in securing plant sites. On the other hand, there are countries that have developed and used the methods and technical criteria to utilize fly ash in massive amount mostly in the field of civil engineering such as runway construction, light weight structural material manufacturing, and farm field construction [3]. A few researchers in Korea are investigating applicability of fly ash to areas such as additive in fertilizer, high strength and light weight concrete, and fill material [4, 5].

Radioactive waste repository requires backfill or buffer (backfill hereafter) to keep the waste components contained in waste volume isolated as long as possible to ensure public health. When backfilling, massive amount of backfill material is required. In the studies of high-level radioactive waste repository design, bentonite has been paid much attention as a candidate backfill material for its low permeability, high swelling capacity, high cation exchange capacity, etc. Bentonite, however, has been found to have poor mechanical properties such as bearing capacity and thermal diffusivity. Moreover,

the cost of bentonite was reported to form 30 to 40 percent of the total construction and operation cost of repository [6]. To improve the mechanical properties of bentonite as a backfill material, the possibility of mixing it with other materials has been investigated [6, 7, 8]. Thus, the economics of the backfill material will also be enhanced. The materials considered to be mixed with bentonite were sand and crushed rock. Should the repository be defined to be also a nuclear facility, quality control or quality assurance over bentonite-sand or bentonite-crushed rock may become a bottle neck during the construction and operation of the repository due to the random characteristics of sand and crushed rock. As substitutes for sand and crushed rock, loam and fly ash have been investigated [9, 10]. Loam may have the same problem as described above whereas fly ash, as it is generated through more or less a process under controlled environment, may not.

The purpose of this work was three fold: (a) to observe the characteristics of fly ash related to backfill performance; (b) to survey the effects of adding fly ash to bentonite on the distribution coefficients, K_d , of important radionuclides; and (c) to compare the sorbabilities of bentonite-sand and bentonite-fly ash mixtures. Several experiments were conducted according to the purpose, varying the mixing ratio of bentonite, sand, and fly ash.

2. Experimental

〈Sample Selection〉

The fly ash used in this work was obtained from Bo-Ryung coal combustion plant where imported bituminous coal is used. The fly ash of bituminous coal is reported to have rougher surface than that of anthracite coal [11], which would lead to larger surface area. Pozzolanic effect caused by forming compounds of silica (SiO_2) or alumina (Al_2O_3) with lime (CaO) is reported to be more remarkable for the fly ash of bituminous coal [12]. At Bo-Ryung site,

ash classifier and storage silo are equipped so that high class fly ash can be obtained continuously.

The bentonite used in this work was named as Dong-Hae A after a local bentonite producing company that recommended raw samples of good property. Dong-Hae A is produced at a mine Yun-Il 33. Dong-Hae A was reported to be a calcium bentonite with low permeability, relatively high swelling capacity, and high sorbability[13].

〈Sample Characterization〉

Experiments were conducted to characterize and compare the characteristics of fly ash and bentonite. Items of experiments are as follows:

1. Chemical composition was investigated for their oxide forms.
2. pH of sample suspension was measured following Electrometric Method[14] of which the procedure is to mix 30g of crushed and sieved sample with 75ml of distilled water and allow to stand overnight and measure with electric pH meter. And another set of experiments was performed to observe the time when pH of sample suspension with different sample-to-solution ratio reaches equilibrium. In this work, instead of using distilled water, synthetic ground water of which the pH was controlled to about 6 was employed to give the same condition as in the distribution coefficient measurement.
3. Water content was measured by weighing samples before and after drying at $105 \pm 5^\circ\text{C}$ for 24 hours.
4. Particle size distribution was determined by Coulter Counter with 0.5g of sample dispersed in low concentration NaCl solution.
5. Microstructures of samples were studied by scanning electron microscopy (SEM).
6. Permeability of fly ash was measured by Falling Head Method[14].

〈Distribution Coefficient Measurement〉

Radionuclides of Cs-137 and Co-60 dissolved in

0.1N HCl were diluted and used in this study. Cs-137 has been reported to be one of the major fission products that pose great potential hazard to man for several hundred years after disposal of high-level waste[15] and Co-60, although having relatively a short half-life, is a major corrosion product contained in intermediate-level waste from nuclear power plants.

A well known batch method[16] was slightly modified and employed to determine the distribution coefficients of Cs-137 and Co-60 on the fly ash and bentonite samples. Radionuclide-spiked solution was prepared by adding appropriate amount of radionuclide in 0.1N HCl to synthetic ground water(see Table 1.) which was made following the method introduced in a published report[17].

Concentrations of the spiked solutions were made to be very low for the experimental conditions to meet the concept of the distribution coefficient. This experiment was carried out at room conditions and the time given to contact the sample with the solution was 7 days which had been found to be enough to reach equilibrium[13].

Table 1. Chemical Composition of Synthetic G/W

Chemical component	Concentration (mol/ℓ)	Reagent
Na	3.6×10^{-4}	NaHCO ₃
K	9.0×10^{-5}	KOH, KNO ₃ , KF
Mg	1.6×10^{-4}	MgSO ₄ , MgCl ₂
Ca	3.2×10^{-4}	Ca(OH) ₂
Cl	1.4×10^{-4}	MgCl ₂
SO ₄	9.0×10^{-5}	MgSO ₄
NO ₃	1.0×10^{-5}	KNO ₃
F	1.0×10^{-5}	KF
pH	7.0 ± 0.5	

3. Results and Discussion

〈Sample Characterization〉

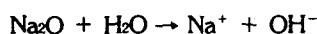
Chemical compositions of the fly ash and Dong-

Hae A bentonite are listed in Table 2. Both the fly ash and the bentonite are composed chiefly of silica, alumina, ferric oxide, and lime, and also contain small quantities of magnesia, potassium oxide, and sodium oxide. The amount of lime, being considered as a major component for pozzolanic effect of fly ash [12], existing in both the samples did show little difference.

Table 2. Chemical Composition of Fly Ash and Dong Hae-A Bentonite

Oxide Analysis	unit	Fly Ash	Dong Hae-A Bentonite
SiO ₂	%	62.0	64.5
Al ₂ O ₃	%	21.5	14.6
Fe ₂ O ₃	%	6.56	5.67
CaO	%	2.43	2.35
MgO	%	0.71	2.57
K ₂ O	%	1.09	0.76
Na ₂ O	%	0.94	1.73

Measured pH values of sample suspensions were 9.80 to 9.90 and 9.04 to 9.14 for fly ash and bentonite, respectively. This difference of pH can be explained in part by the results of other studies [10] that some components of fly ash dissolve in water, leading to increase of pH, as follows:



In order to answer the question of pH difference between fly ash and bentonite, it is necessary to assume that the lime and the sodium oxide contained in bentonite are not as reactive as those in fly ash.

The time required to reach pH equilibrium was found to be about three days, regardless of the amount of fly ash-to-solution ratio, as shown in Fig. 1. Hong et al. [5] performed similar experiments on fly ash with distilled water and sea water and

reported that pH rapidly increased within three hours and then decreased to reach equilibrium in a day in the case of distilled water and that in sea water pH increased rapidly within two hours and slowly reached equilibrium. And they also reported that the decrease of pH in the case of distilled water was due to precipitates formed by contact of CO₂ in the air and sample suspension and that slow change of pH in the case of sea water was due to the existence of buffer materials in sea water. In our experiment, the first measurement was made 24 hours after fixing the sample suspensions and the solution was synthetic ground water which contained many types of buffer materials like in sea water.

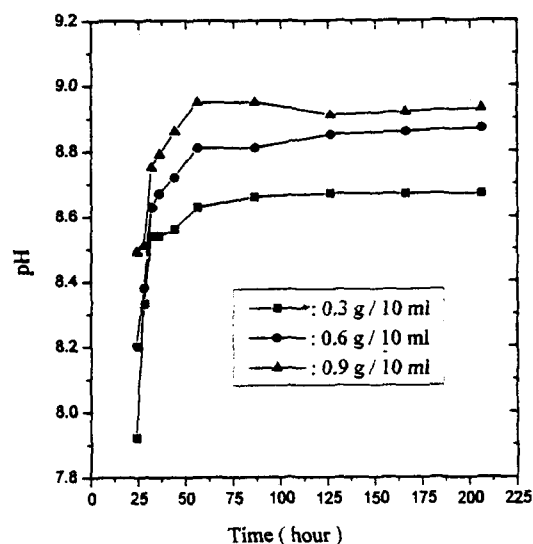


Fig. 1. pH of Fly Ash v.s. Time

Water content of fly ash, as had been expected, was negligibly low due to its shape to be explained below. Dong-Hae A bentonite was reported to have water content of $12.56 \pm 0.01\%$ [13].

Figures 2 and 3 show particle size distributions of fly ash and Dong-Hae A bentonite, respectively. Big particles like silt were removed from Dong-Hae A sample during the measurement. The portion of the

particles of Dong-Hae A bentonite smaller than $22.84\text{ }\mu\text{m}$ was 50.3% and that of fly ash was 50.7%. From the figures it can be said that Dong-Hae A bentonite is composed of more numbers of finer particles than fly ash.

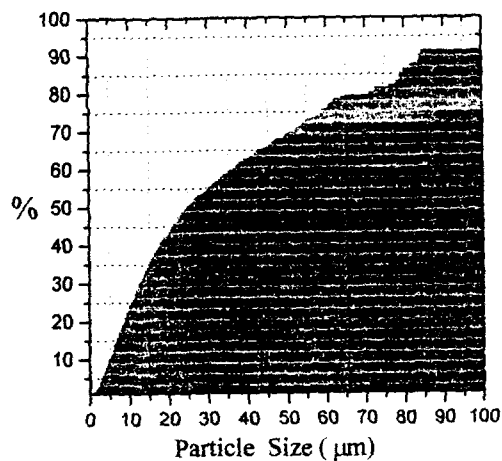


Fig. 2. Particle Size Distribution of Fly Ash

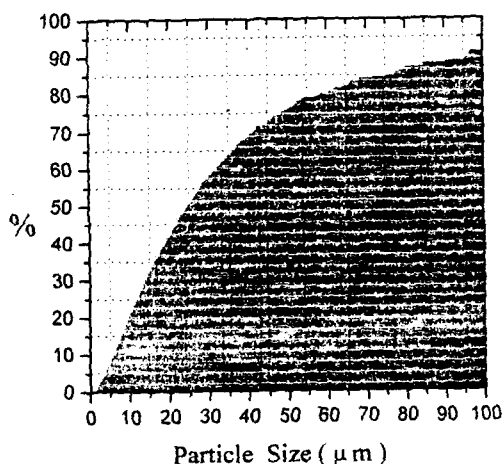


Fig. 3. Particle Size Distribution of Dong-Hae A Bentonite

Pictures taken by SEM (Fig. 4 and 5) show distinctive difference between bentonite and fly ash.

Dong-Hae A bentonite, as has been reported, has a layered shape while fly ash shows spherical one. One thing special to fly ash is that the inside of the particle is hollow, which results in smaller particle density than those materials consisting of the same components.

Permeability of fly ash measured by Falling Head method was determined to be 3.6×10^{-8} cm/sec which agrees with other values reported [18].

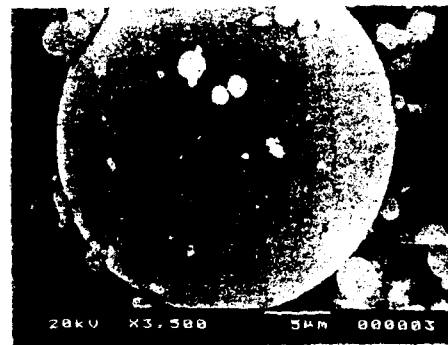


Fig. 4. Shape of Fly Ash by Scanning Electron Microscopy

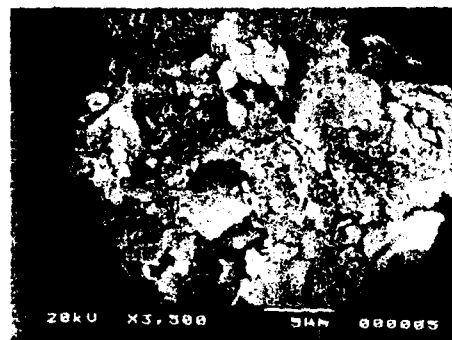


Fig. 5. Shape of Dong-Hae A Bentonite by Scanning Electron Microscopy

〈Distribution Coefficient Measurement〉

Before running experiments on distribution coefficient measurement of mixed samples, single sample measurements were carried out for sand and fly ash.

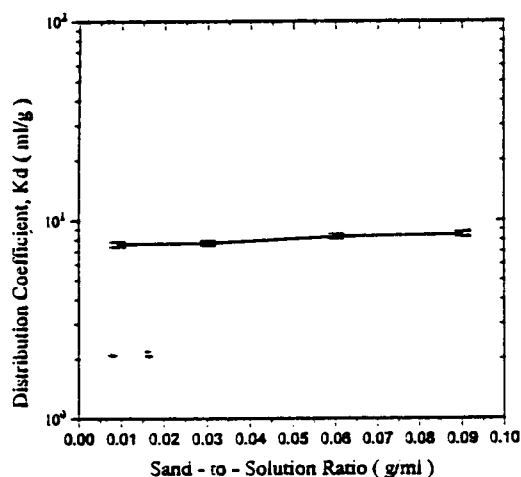


Fig. 6. Distribution Coefficient of Cs on Sand

Figure 6 shows the distribution coefficient of Cs-137 on sand. Amount of spiked solution was kept constant to be 10ml while the mass of sand was changed. Distribution coefficients in this figure agrees well with other ones reported [19], and sample-to-solution ratio does not seem to affect distribution coefficient. The specific surface area is so small that distribution coefficients of other cations like Co may be expected to be very low.

Distribution coefficients of Co-60 and Cs-137 on fly ash are shown in Figure 7. In this experiment, the amount of fly ash was changed as was done in the sand case while the amount of solution was fixed. Comparing Figure 6 with this result, it is shown that fly ash has almost an order of magnitude larger distribution coefficient of Cs-137. Specific surface areas of fly ash and sand are reported to be smaller than $1\text{m}^2/\text{g}$ and about $4\text{m}^2/\text{g}$, respectively [9, 20]. Considering that specific surface area is one of the major factors affecting distribution coefficient, the comparison as above may imply that the surface morphology of fly ash was changed to increase the surface area during the measurement due to the dissolution of some constituent or formation of calcium silicate hydrate or calcium aluminate hydrate [5], or that the change of solution chemistry following the dissolution

of soluble compounds of fly ash affected the distribution coefficients. Co-60 showed a lot larger distribution coefficient than Cs-137 on fly ash. Co-60 at high pH values of fly ash suspension solution was reported to show high distribution coefficient due to likely formation of cobalt hydroxide as precipitate [10]. There were dependences of distribution coefficient on sample-to-solution ratio. As the sample-to-solution ratio increases, the distribution coefficient of Co increases while that of Cs decreases. This can be explained as follows: (a) as the fly ash-to-solution ratio increases, pH of the solution increases due to the dissolution of some constituents as explained above, and cobalt ions have more chances to form hydroxides to precipitate; (b) dissolution of fly ash increases concentrations of cations like Ca and Na, competing with Cs in sorption sites.

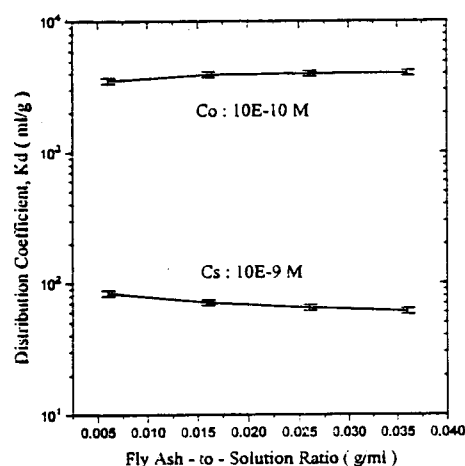


Fig. 7. Distribution Coefficient of Co and Cs on Fly Ash

Distribution coefficients of Cs and Co on fly ash and Dong-Hae A bentonite mixture were determined while varying the mix ratio to survey effects of mixing and the results are shown in Figure 8. The distribution coefficient of Co increased slightly as fly ash content increased and that of Cs decreased drastically. Comparing the results with those in Figure 7,

the distribution coefficients of Co behaved in a similar fashion. Addition of bentonite in the case of Figure 8 gave rise to higher distribution coefficient of Co by the factor of two to three than in the case of fly ash only. This effect shows that bentonite itself has a large distribution coefficient of Co, which was reported by Choi[13]. However, increasing the portion of bentonite decreased the distribution coefficient of Co, which means that the distribution coefficient of Co is also affected by the amount of reactive material to form precipitates, i.e., fly ash. The distribution coefficient of Cs decreased as fly ash portion increased. Factors affecting the distribution coefficient of Cs on fly ash and bentonite mixture may be summarized as follows:

1. Effect of pH increase; Addition of fly ash increases the pH of solution and leads to a decrease of H^+ ion concentration relative to OH^- ion. Decrease of H^+ ion in the solution means the decrease of strong competing ion of Cs for sorption sites. Thus, the sorption of Cs increases.
2. Specific surface area; As fly ash has very small specific surface area, smaller than $1m^2/g$, compared with that of Dong-Hae A bentonite, $613.34m^2/g$ [13], the increase of fly ash portion in the mixture leads to the decrease of specific surface area, which results in the decrease of distribution coefficient of Cs.
3. pH dependent charge; It was reported that the increase of pH of montmorillonite suspension changes positively charged oxide surfaces of montmorillonite to negatively charged ones[21]. Increase of negatively charged surfaces gives rise to more sorption sites for cations.
4. Concentration of competing ions; Dissolution of fly ash constituents, such as lime and sodium oxide, increases the concentration of cations competing with Cs for sorption sites, which results in the decrease of distribution coefficient of Cs.

The four factors as described above may affect distribution of Cs on fly ash and bentonite mixture in a

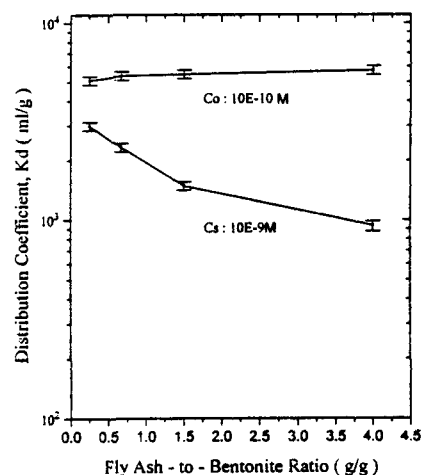


Fig. 8. Distribution Coefficient of Co and Cs on Fly Ash and Bentonite Mixtures

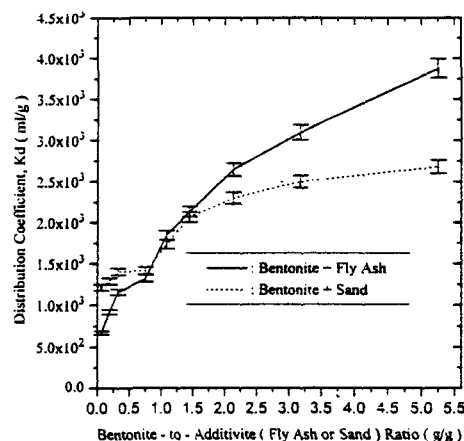


Fig. 9. Comparison of Cs-Distribution Coefficient on Two Different Mixtures

combined manner so that the result as shown in Figure 8 indicates that as fly ash portion increases the second and fourth factors and override the first and third factors.

In figure 9, two different cases were compared: fly ash-bentonite mixture with sand-bentonite mixture. In both the cases, increase of bentonite portion increases the distribution coefficient of Cs. But the

slopes of the curves are different. Recalling that the distribution coefficient of Cs on sand is negligibly small, the increase of Cs distribution is thought to be due only to the increase of bentonite sorption sites. This figure shows a possibility that mixing appropriate fly ash with bentonite may be better than sand-bentonite mixture in retarding the movement of some radionuclides.

4. Conclusions

Although the fly ash employed in this work was found to be composed of similar constituents to those of Dong-Hae A bentonite, it showed quite different physical and chemical characteristics from those of bentonite. Things peculiar to fly ash are that its shape is spherical and inside of the particle is hollow and that it shows high alkalinity when dissolved.

Relation between distribution coefficients of Cs and Co and fly ash-to-solution ratio comes out with rather reversed tendencies, which tells that fly ash is very effective in sorbing Co. Distribution coefficient measurement of Cs and Co on fly ash and bentonite mixture showed the reversed tendency in a more outstanding way, implying that addition of fly ash may be effective in sorbing Co but, in the case of Cs, the amount of fly ash to be added should be controlled to level off the effect.

Comparison of the distribution coefficients of Cs and Co between fly ash-bentonite mixture and sand-bentonite mixture showed that fly ash, if mixed with bentonite to meet performance criteria, may play a better role in retarding the movement of some radionuclides.

The work presented in this paper was done on short-term basis. To be applicable as a backfill additive, long-term based experiments on fly ash are required.

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