

# Long term durability and environmental safety of various kinds of coal ash mixed material

## Durabilité à long terme et sécurité environnementale de divers types de matériaux mélangés à base de cendres de charbon

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**ABSTRACT:** In 2017, more than 12.7 million tons of coal fly ash was generated in Japan, among which were 9.1 million tons generated by the electric power industry and 3.6 million tons by general industry. The generation of coal fly ash is unlikely to decrease. Approximately 70% of coal fly ash is used as a raw material for cement and a little less than 15% is used in civil engineering works. Coal fly ash mixed material is prepared by mixing with cement, water, and soil. It is considered environmentally friendly. The mix can be adjusted by various strengths and water permeability characteristics. This study focuses on the slurry type coal ash mixed material (hereinafter referred to as slurry material) and plastic type coal ash mixed material (hereinafter referred to as plastic material), under long curing conditions (air, water and seawater curing) in various environments. This paper reports the effect of long term durability on the strength and environmental safety of coal ash mixed materials.

**RÉSUMÉ:** En 2017, plus de 12,7 millions de tonnes de cendres volantes de charbon ont été générées au Japon, dont 9,1 millions de tonnes générées par le secteur de l'énergie électrique et 3,6 millions de tonnes par l'industrie générale. % des cendres volantes de charbon sont utilisées comme matière première pour le ciment et un peu moins de 15% dans les travaux de génie civil. Mélange de cendres volantes à base de charbon, mélangé avec du ciment, de l'eau et du sol, considéré comme respectueux de l'environnement et pouvant être ajusté à différentes résistances et caractéristiques de perméabilité à l'eau. Cette étude porte sur le matériau mélangé de cendres de charbon de type lisier, dans des conditions de durcissement prolongé (durcissement à l'air, à l'eau et à l'eau de mer) dans différents environnements. Ce document décrit l'effet de la durabilité à long terme. de matériaux mélangés de cendre de charbon.

**Keywords:** coal fly ash; coal ash mixed material; durability; unconfined compression strength; leaching properties; needle penetration strength

## 1 INTRODUCTION

In Japan, after the Great East Japan Earthquake occurred in 2011, the amount of coal ash generation has been increased due to the increase of the operation of thermal power plants. In recent years, coal ash has been effectively used mainly as a coal ash mixed material mainly in the port areas, but application development accompanying the increase in generation amount is an urgent issue. Examples of types of coal ash mixed materials include slurry materials, plastic materials, crushed materials of solidified materials, granulated materials of solidified materials, etc., and actual results of utilization in construction are also reported. Coal fly ash mixed material is prepared by mixing the ash with cement, water, and soil. The mix can be adjusted to give a variety in strengths and water permeability characteristics, and it is considered environmentally friendly. The Japan Coal Energy Center (JCOAL) published the ‘Effective use of coal fly ash mixed material in port construction’ in 2011 and the ‘Effective use guidelines of coal fly ash mixed material (Reconstruction Materials Edition)’ in 2014. The latter addressed effective utilization of coal fly ash mixed material in the reconstruction projects of the 2011 Great East Japan Earthquake affected area. Finally, JOAL published ‘Effective use guidelines of coal fly ash mixed material (High Standard Road Embankment Edition)’ in 2015. The guidelines are an easy-to-understand assessment of safety and quality control for application in reconstruction projects, disaster preventions, green spaces, high ground relocation works, and other projects.

However, data of the long-term mechanical properties, durability, environmental issues to evaluate the safety of coal ash mixed material is limited and cross-evaluation of each material is an important issue. Therefore, this paper focuses on slurry materials and plastic materials, and reports the results of investigation of long term mechanical properties, durability and

environmental safety under curing conditions simulating various environments.

## 2 TESTING PROCEDURE

### 2.1 Material and testing condition

In this study, as shown in Figure 1, we have

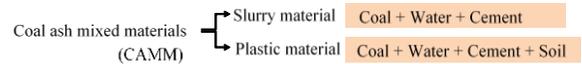


Figure. 1 Coal ash mixed materials

Table 1. Physical properties of materials

Materials	Coal ash	Kaolin clay (soil)
Ps (g/cm <sup>3</sup> )	2.347	2.731
W <sub>o</sub> (%)	0	0
W <sub>L</sub> (%)	N.P.	51.7
W <sub>P</sub> (%)	N.P.	34.3
F <sub>c</sub> (%)	99.7	100.0

Table 2. Chemical properties (Fly ash)

Chemical composition	Coal ash
SiO <sub>2</sub> (%)	58.2
CaO(%)	7.9
Al <sub>2</sub> O <sub>3</sub> (%)	20
FeO(%)	5.0
MgO(%)	1.7
Na <sub>2</sub> O(%)	0.5
K <sub>2</sub> O(%)	1.9

studied two types of coal ash which are mixed material slurry material and plastic material. The slurry material was prepared by mixing cement and a large amount of water with coal ash.

Plastic material was prepared by mixing cement, water and kaolin clay into coal ash. Table 1 shows the physical properties of coal ash (JIS ash) and kaolin clay used for plastic material, and Table 2 shows the chemical composition of coal ash. The mechanical properties of the samples are

evaluated using uniaxial compression test (JIS A 1216) and needle penetration test (JIS S 3008).

### 2.2 Production method of slurry material

Table 3 shows mixing conditions of specimens.

The amount of cement per 1 m<sup>3</sup> of the slurry material was fixed at 50, 75, 100 kg / m<sup>3</sup> so that

Table3. Mixing condition of slurry material

Cement C(kg/m <sup>3</sup> )	Coal ash (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	Pe (t/m <sup>3</sup> )	Flow (mm)
50 (5.1%)	985	564	1.599	222
75 (7.7%)	975	560	1.610	219
100 (10.4%)	960	558	1.618	212

the target strength at curing 28 days was about 28 to 300 to 1,000 kN / m<sup>2</sup>. The flow value of slurry material was 220 ± 20 mm. The preparation of the slurry specimen was poured into a mold of PVC (diameter 5 cm, height 10 cm). After that, the upper part of the specimen was shaped after 24 hours and demolished from the mold the next day. The specimens were wrapped in a lap and cured in a thermostatic chamber.

### 2.3 Production method of plastic material

Table4 shows mixing conditions of specimens. For the slurry material, the cement addition rate was set to 3 types (C = 3, 5, 7%) so that the target strength at curing 28 days was about  $qu_{28} = 300$  to 1,000 kN / m<sup>2</sup>. The water content ratio of the kaolin clay used in the experiment was adjusted to 2.5 times the liquid limit. In addition, cement and coal ash are added to the wet mass of the

Table4. Mixing condition of plastic material

Cement C(%)	Coal ash(%)	Soil	Setting water content(%)
3	100	Kaolin clay	2.5 W <sub>L</sub> (129.3%)
5			
7			

※W<sub>L</sub> = 51.7

kaolin clay at a predetermined ratio. For preparation of specimens of plastic materials, treated mixed soil was divided into about 3 layers in a PVC mold and air bubbles were removed for each layer (JGS 0813). After preparation of the specimen, prescribed curing was carried out by the same method as curing the slurry material.

### 2.4 Curing method

The specimens were cured for 7 days after preparation of specimens. After that, the specimen were cured in air, water immersion and seawater immersion to simulate the natural environment. For water immersion curing, it is assumed that the coal ash mixed material is applied below the groundwater. In addition, seawater curing is assumed to be effective use of materials for port facilities. In air curing, the specimen was cured in a thermostatic chamber (20±3°C) after being wrapped with with lap.

For water immersion curing, specimens were immersed in distilled water. Sea water curing was used seawater after suspended matter removed by pressurized filtration. Here, the solvent of distilled water and sea water did not take into consideration the solid / liquid ratio, the volume ratio, etc., and filled the inside of the tank so that the upper part of the sample was sufficiently submerged. We also exchange solvent once a month. Table 5 shows the curing test period of

Table5. Curing condition and terms

Condition	Type	Curing days
Air	Slurry	0, 7, 28, 56, 91, 182, 365
Water Seawater	Plastic	0, 7, 28, 56, 91, 182, 365

each material.

## 2.5 Evaluation method of deterioration of slurry material

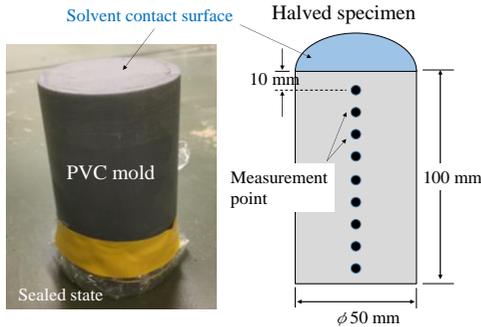


Figure 2. Measurement position of needle pen-

In order to observe the condition of deterioration, water and seawater immersion exposure curing was performed in a state in which only the upper surface was opened using a specimen that was cured for 7 days. The solvents are the same as those used in 2.4. The needle penetration test was performed at a pitch of 10 mm from the upper end face of the specimen using the specimen which was divided in half in order to reveal the strength change from the upper end face of the specimen in the depth direction (as shown in Figure 2.)

## 2.6 Curing method

Coal ash mixed materials are not subject to abrasion or dust scattering of materials due to the use in the environments such as roadbed materials and backing materials.

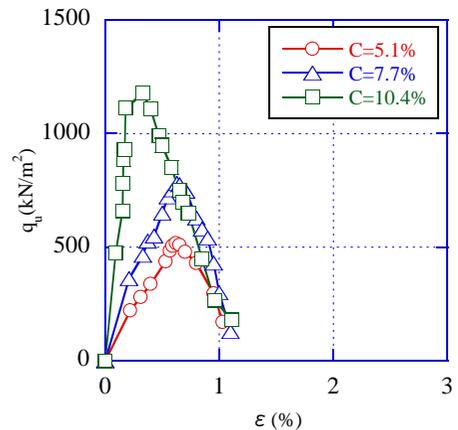
Therefore, in this report, the leaching test (JIS K 0058-1) based on the use appearance was used. For the experiment, a test piece after the uniaxial compression test was used. F (fluorine), B (boron), Pb (lead), Cr (VI) (hexavalent chromium), and Ca (calcium) were taken as measurement items of elution amount.

For analysis of F (fluorine), ion chromatography was used. ICP plasma emission spectrometer was used for B (boron), Pb (lead) and Ca (calcium), and a spectrophotometer was used for Cr (VI) (hexavalent chromium).

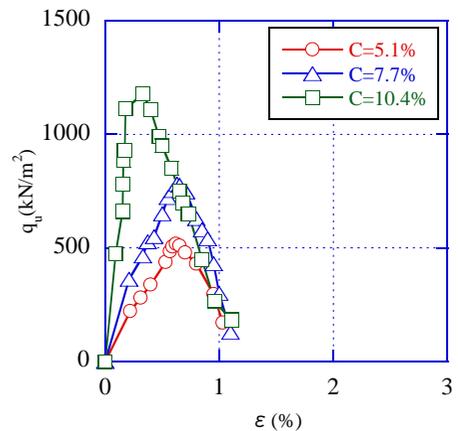
## 3 RESULTS AND DISCUSSIONS

### 3.1 Mechanical properties of coal ash mixed material

The results of unconfined compression test of slurry material and plastic material on initial curing 28 days are shown in Figure 3. Unconfined compression strengths of the two materials are increasing with increasing cement addition rate. The plastic material shows a tough type of failure mode as compared with the slurry material.



(a) Slurry material



(a) Slurry material

Figure 3. Results of Unconfining Compression Test (Curing time, 28days)

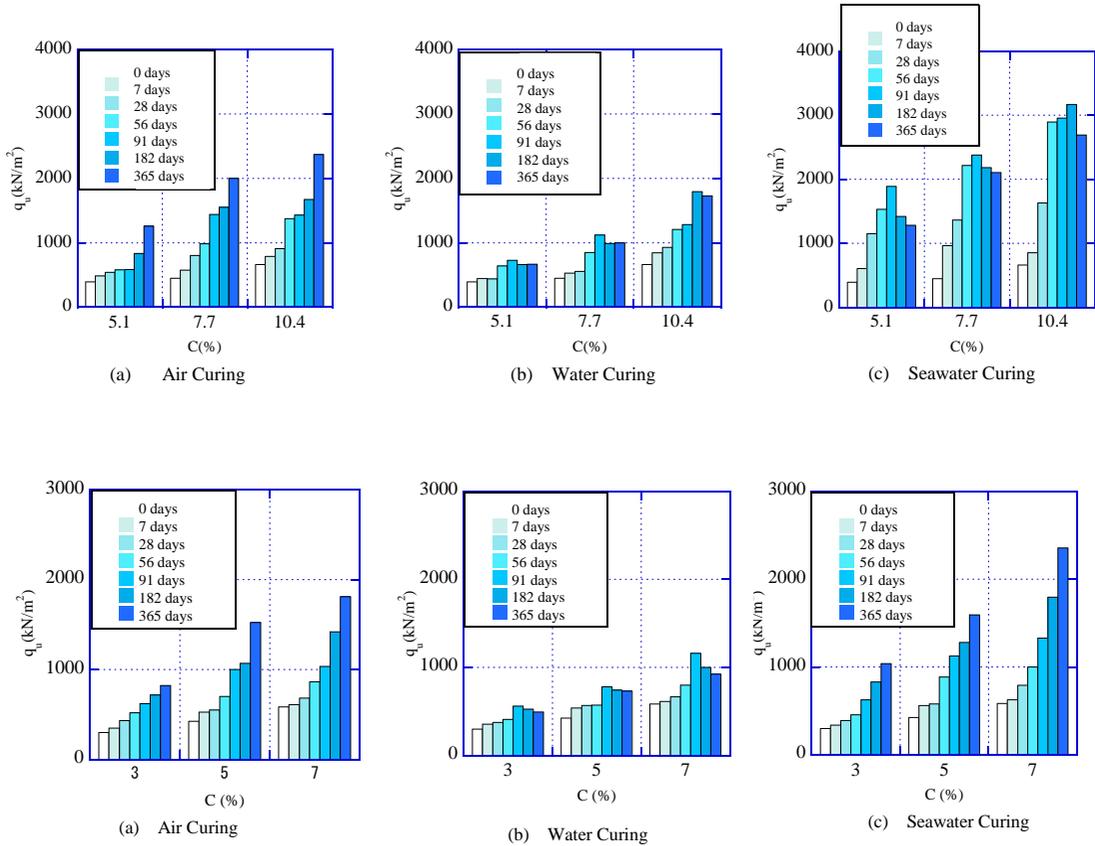


Figure 4. The correlation of UCS ( $q_u$ ) and cement content ( $C$ ) on exposure tests

### 3.2 Long term durability of coal ash mixed material

Figures 4 show the long-term durability test (365 days) results of slurry materials and plastic materials under each curing condition. The unconfined compression strength of the slurry material and the plastic material increased with the cement addition rate and the number of curing days in each curing condition. Particularly in the three curing conditions performed this time, strength development was remarkably observed under seawater curing conditions. Comparing the unconfined compression strength of the same

curing days in seawater and air curing, it can be seen that there is a strength difference of about 1.4-2.3 times in the slurry material. On the other hand, the unconfined compression strength of seawater and air curing in plastic material differ by about 1.3 times. Moreover, it can also be seen that the strength development of water immersion curing is small in both slurry material and plastic material. This behavior of strength development is subjected to alkali activator latent hydraulic by blast furnace slag by sea water (pH = 8.53), which is why that curing and pozzolanic reaction occurred. On the other hand, in water and seawater curing of the slurry material after 365 days of curing, the strength of slurry material decreases under all cement addition rate

conditions. Generally, it is known that when calcium hydroxide leaches, it becomes porous and accelerates deterioration (Terashi M., et al., 1983). It is considered that elution of calcium in the specimen is the cause of the strength decrease.

more calcium than water immersion curing and it is thought that the strength of slurry material was decreased by porosifying the inside of the specimen. Therefore, it is suggested that the countermeasure of reduce strength of this

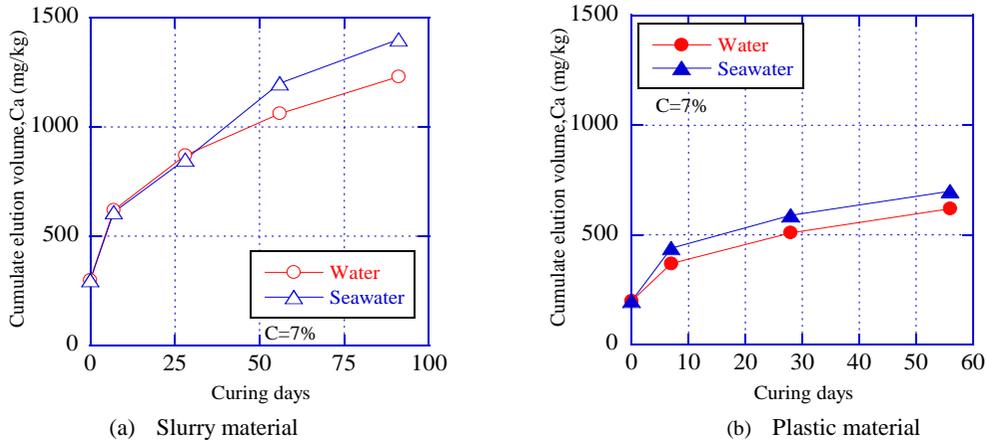
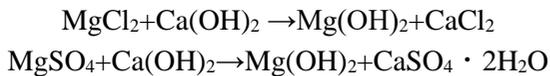


Figure 5. The correlation curing days and the cumulative calcium elution amount (C=7%)

Figures 5 (a),(b) show the relationship between the number of curing days and the cumulative calcium elution amount in slurry and plastic materials with a cement addition rate of 7%. In both materials, it is found that calcium elution amount is larger in seawater curing than in water curing.

It is reported that the cement treated soil contacts with seawater shows the following reaction formula (Hara et al., 2013).



This reaction formula shows that calcium hydroxide ( $\text{Ca(OH)}_2$ ) elutes in the form of calcium chloride ( $\text{CaCl}_2$ ) or calcium sulfate ( $\text{CaSO}_4$ ) as the formation of brucite is generated. Since the seawater used in the experiment contains a lot of  $\text{Mg}^{2+}$ , it is conceivable that the above reaction occurs by immersing the specimen in seawater. This elution phenomenon in this sea water curing is a factor which elutes

material is necessary when seawater and groundwater are used in direct contact with coal ash mixed material.

### 3.3 Understanding the depth of degradation due to difference in exposure condition

Since the unconfined compressive strength decreased with the increase in exposure curing in the water immersion/seawater immersion exposure test, the strength deterioration mechanism was evaluated using the needle penetration test. Figure 6 shows the relationship between penetration resistance and unconfined compressive strength. Since the correlation was found between the penetration resistance and the unconfined compressive strength, the compressive strength converted from the result of the needle penetration test is used for the subsequent of the results. Figure 7 shows the relationship between the distance from the contact surface and the converted unconfined compressive strength. When comparing the converted unconfined compressive strength at each depth obtained from the needle penetration test with

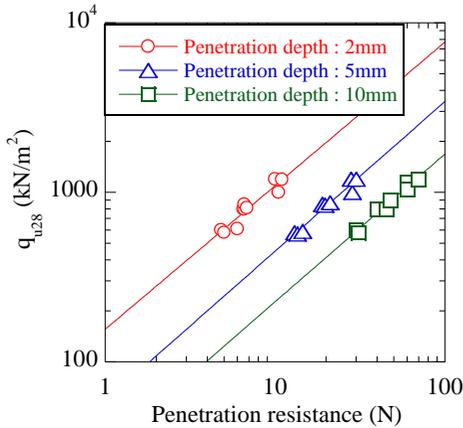


Figure 6. Relationships between penetration resistance and unconfined compressive strength

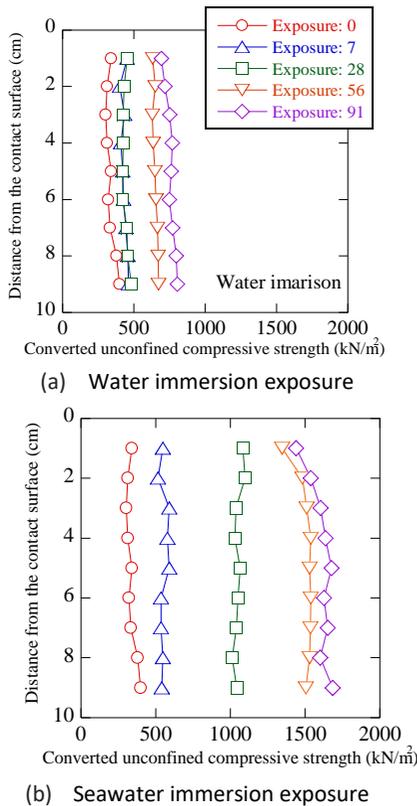


Figure 7. Relationship between the distance from the contact surface and the converted unconfined compressive strength.

the various exposure results shown in Figure 5, it can be seen that the compressive strength at the same number of days has the same strength. Under the water immersion exposure condition, the converted unconfined compressive strength was low up to 2 cm deep from the solvent contact surface at 91 days of exposure. Also under the seawater exposure of 56 days, the converted unconfined compressive strength decreased from the solvent contacting surface to 2 cm deep.

Similarly, at exposure days of 91 days, the converted unconfined compressive strength decreased to 4 cm deep from the solvent contact surface.

From these results, it was revealed that the deterioration proceeds from the contact surface with the solvent and spreads deeper into the specimen as the number of exposure days increases. As described above, calcium eluted from the surface of the specimen, it is considered that the sample became porous and caused the strength to decrease.

Based on the above results, the reason why the strength reduction occurred after 91 days in the exposure test shown in Figure 5 is considered to be that the surface deterioration advanced to the deep portion and the strength decreased as confirmed by the needle penetration test.

### 3.4 Leaching properties

In this study, the leaching test (JIS K 0058-1) based on the use appearance was used. For the experiment, a test piece after the unconfined compression test was used. The results of the leaching test of the slurry and plastic material are shown in Table 6 and Table 7, respectively. It is understood that F (fluorine), Pb (lead), Cr (VI) (hexavalent chromium) is not more than the lower limit of quantitation in any condition regardless of the material difference in the slurry material and the plastic material. For B (boron), the amount of elution also increased with increasing number of curing days, but it was below the soil environmental standard value. For each coal ash mixed material used for the experiment, it was shown that there is no problem

concerning environmental safety during the test period. amount of elution from the coal ash mixed material was below the soil environmental

Table 6. Leaching test results of Slurry materials

Curing days	JSV	0	7			28			56			91			182		
Type	-	-	A	W	S	A	W	S	A	W	S	A	W	S	A	W	S
pH	-	11.1	11.4	11.2	10.1	10.9	11.1	9.4	11.2	10.9	9.9	11.2	10.9	9.9	11.2	10.9	9.9
Cr(VI)(mg/l)	0.05mg/l	N.D.															
B(mg/l)	1mg/l	0.05	0.02	0.02	0.05	0.02	0.04	0.08	0.02	0.05	0.14	0.03	0.09	-	0.07	-	-
F(mg/l)	0.8mg/l	N.D.															
Pb(mg/l)	0.01mg/l	N.D.															

A: Air curing, W: Water curing, S: Seawater curing

Table 7. Leaching test results of Plastic materials

Curing days	JSV	0	7			28			56		
Type	-	-	A	W	S	A	W	S	A	W	S
pH	-	10.6	10.6	10.4	9.5	10.9	10.2	9.6	10.6	9.4	9.0
Cr(VI)(mg/l)	0.05mg/l	N.D.									
B(mg/l)	1mg/l	0.07	0.06	0.07	0.12	0.08	0.08	0.09	0.09	0.09	0.08
F(mg/l)	0.8mg/l	N.D.									
Pb(mg/l)	0.01mg/l	N.D.									

## 4 CONCLUSIONS

1) In the coal ash mixed material, the strength increases as the cement addition rate increases and the number of curing day increases. In addition, the plastic material shows a tough fracture mode as compared with the slurry material.

2) Coal ash mixed material can be expected to increase in strength when seawater is used as a solvent regardless of material difference. However, in water slurry or seawater exposure in slurry materials, strength decreases after 1 year as Ca leaches out.

3) Progress of deterioration of the coal ash mixed material proceeds from the surface of the specimen toward the deep part. In addition, the progress of the deterioration is faster better of seawater exposure.

When utilizing a slurry-type coal ash mixed material, construction of the case, such as direct contact with water or seawater, it is necessary to pay attention in terms of long-term durability.

4) Regarding the environmental safety of the coal ash mixed material, it has been found that the

standard value of Japan under any condition, regardless of the material type.

## 5 REFERENCES

- JCOAL (Japan Coal Energy Center) 2016. Coal fly ash survey report (fiscal 2016 result in Japanese).
- JCOAL, Effective use of coal fly ash mixed material in port construction, 2011 (in Japanese).
- JCOAL, Effective use guidelines of coal fly ash mixed material (Reconstruction Materials Edition)', 2014 (in Japanese).
- JCOAL, 'Effective use guidelines of coal fly ash mixed material (High Standard Road Embankment Edition)' 2015 (in Japanese).
- Terashi M., et al., Fundamental Properties Lime and Cement Treated Soils 3rd report), *Report of the Port and Harbor Research Institute*, Vol.22, No.1, pp.69-97, 1983 (in Japanese).
- Hara et al., Deterioration Mechanism of Cement-Treated Soil under Sea Water, *Journal of JSCE C*, Vol.69, No.4, pp469-479, 2013 (in Japanese)