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UTILIZATION OF STAINLESS-STEEL SLAG BY CEMENT HARDENING

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ABSTRACT

The utilization of wastes as construction material is one of the most desirable strategies to solve environmental problems caused by the generation of wastes. There are only a few researches that have discussed the utilization of slag derived from stainless-steel industry. Stainless-steel slag, which is simply disposed of, is one kind of electric furnace slags which exhibit the expansion phenomenon associated with water absorption.

The objective of this study is to illustrate the effective utilization of stainless-steel slag as ground materials by solidification. Strength and durability characteristics of stainless-steel slag hardened by stabilizers were investigated experimentally. It has been shown that the Carbonated-Aluminate Salts can be used effectively in stabilizing this slag. The addition of kaolin clay as a pre-mixed admixture to raw materials improves the hardening effect considerably and the durability of materials, and the durability characteristic of stabilized mixtures depends on the curing condition, especially drying method. It is recommended that the hardened stainless-steel slag examined in this study can be applied as road (subbase course) materials.

Key words: cement, road base, soil stabilization, unconfined compression test, wastes (IGC: D10/K6)

INTRODUCTION

A wide variety of wastes are presently generated in large quantities in Japan. About half of the industrial wastes are reused due to recent developments in waste management technology, but the present situation, which is reflected by the increase of the waste generation, the lack of proper disposal area, and the latest conscious-raising of "Environment Preservation", necessitates further strengthening of waste utilization technology. The waste

utilization in construction works can be one of the most effective strategies because we need large quantities of materials for embankment and road construction. Recent researches have shown that some types of industrial wastes, e.g. coal ash and steel slag etc., can be used positively as embankment or concrete materials (Gidley et al., 1984; Mehta, 1989; Kamon et al., 1991). The generation of slags from the metallurgical industry, for example, has reached 40 million tons per year, and more than 85% of them are reused as road material,

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cement material, fertilizer, pottery material, and soil stabilizer.

Slags can be classified as blast furnace slag, converter furnace slag and electric furnace slag. The blast furnace slag and the converter furnace slag are produced through the process in which iron is made of iron ore, and the electric furnace slag is generated from the steel making process using scrap iron as main raw material. While the production of the blast furnace slag and the converter furnace slag has decreased in recent years, however, the generation of the electric furnace slag is still on the rise. The characteristics of the electric furnace slags vary due to the method of production, e.g., some types of steel are made in the electric furnace, e.g. carbon steel, stainless steel, nickel steel, etc. The trouble with this material is that the electric furnace slags have the efflorescence and expansion characteristics like the converter furnace slags. So most of this production (2.5 million tons per year) is disposed of in reclamation areas.

The electric furnace slags are classified into two categories, namely oxidizing and reducing slags due to the production process of slags. Oxidizing slag is produced in the process to eliminate the porosity and the impervious composition in molten steel by oxidizing. The reducing slag is produced in the process to eliminate oxygen in molten steel and adjust the steel composition. It has been clarified that the oxidizing slags have similar expansion characteristics as those of the converter slags. Slags expand by the volume increase associated with the hydration of free lime, and slags with the expansion characteristics eliminated by aging can be utilized as construction materials (Kuwayama et al., 1992). The reducing slags form the hydration products of calcium silicate hydrate (CaO·SiO2·H2O; CSII) and hydrated gehlenite (CaO·Al₂O₃·SiO₂·H₂O; CASH) in long term, so they not only exhibit the hydraulic properties but continue the volume increase (Kuwayama et al., 1992). The reducing slags are mostly disposed of, because the properties, such as hardening and expansion, have not been quantified.

It is our main objective to illustrate the effective utilization of stainless-steel slag (S-slag) stabilized by using Carbonated-Aluminate Salts (one kind of cement-based stabilizers; CAS). S-slag used in this study is a kind of the reducing electric furnace slags derived from Austenitic Stainless-Steel Plants, and mostly disposed of. Authors have shown the potential utilization of S-slag as additive of soil stabilizer; the contribution of S-slag to the strength development for dredged sludge (Kamon et al., 1989, 1990). In this study, to use a larger amount of wastes as main material, we discuss the potential utilization of the stabilized S-slag as road materials through the experimental works on strength or durability.

EXPERIMENTAL PROCEDURE

1) Materials

Two types of S-slags used in this study are derived from different Austenitic Stainless-Steel Plants. The physical properties and the chemical compositions of the materials are given in Table 1. The S-slags are composed of fine-grained particles equivalent to the size of silt grains, and have a lower specific surface area (2025 cm²/g and 2225 cm²/g) than blast furnace iron slag (4000-4800 cm²/g). The particle density (3.10 g/cm³ and 3.19 g/cm³) is within the limits of the general reducing electric furnace slags (2.80-3.25).

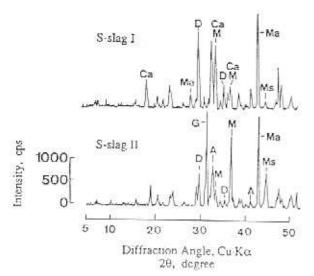
The chemical composition of S-slag varies, but it mainly consists of oxides such as

Table 1. Physical properties and chemical compositions of materials used

		S-slag I	S-slag II
Particle density p.	(g/cm ¹)	3.10	3.19
Grain size distribution	(%)	0.0000000	
Sand fraction	20080	0.0	0.0
Silt fraction		92.6	91.8
Clay fraction		7.4	8.2
Blaine specific surface area	(cm^2/g)	2025	2225
Optimum moisture content	(%)	-	30.5
Maximum dry density	(g/cm3)		1.72
Chemical compositions	(%)		
SiOz		22.4	19.4
Al ₂ O ₃		9.8	11.4
CaO		45.6	30.2
Fe ₂ O ₃		1.1	6.7
MgO		14.2	12.3
SO ₃		0.2	0.8

calcium oxide (CaO), silicon oxide (SiO2), and aluminum oxide (Al2O3), causing materials to possess latent hydraulic properties. chemical compositions of both slags are similar and are close to the average in composition of general electric furnace reducing slags except for the CaO content. The CaO content of the general reducing slags ranges from 30% to 50%. S-slag I and S-slag II used in this study are considered to represent the reducing slag with rich and poor CaO content respectively. This difference in composition may be due to the collecting spots and the raw materials. Regarding the efflorescence of slags, the volume change when free-lime is hydrated to Ca(OH)2 or the expansion for the formation of CSH (calcium silicate hydrate) and (hydrated gehlenite), have been reported as the causes (Kuwayama et al., 1992; Narita et al., 1978). CaO content can influence the formation of Ca(OH)2, CSH, and CASH, so it is expected that these two materials have different hydraulic or efflorescence properties.

Fig. 1 shows X-ray diffraction patterns of S-slags used. It has been reported that the main minerals of the general reducing electric furnace slags are dicalcium silicate (2CaO·SiO₂), magnesium silicate (2MgO·SiO₂), calcium aluminate (12CaO·7Al₂O₃), etc. (Kuwayama et al., 1992). Both slags used in this study exhibit peaks of merwinite (Ca₃Mg(SiO₄)₂), diop-



M:Merwinite, D:Diopside, Ma:MgO-Al₂O₃, Ms: β -2MgO-SiO₂, Ca:12CaO-7Al₂O₃, A:Alite, and G:Gehlenite.

Fig. 1. X-ray diffraction patterns of S-slags

side (CaMg(SiO₃)₂), magnesium aluminum oxide (MgO·Al₂O₃) and magnesium silicate (β-2MgO·SiO₂). While S-slag I contains calcium aluminate (12CaO·7Al₂O₃), S-slag II shows the existence of alite (3CaO·SiO₂) and gehlenite (2CaO·Al₂O₃·SiO₂), which are cement minerals.

Two types of S-slags were used in this study, namely, the raw material as obtained from the factory and the S-slag finer than 0.425 mm. It is mainly larger than $5 \mu m$. Therefore, kaolinite was used to arrange the grain size distribution of slags, and its particle size is finer than $5 \mu m$. Kaolinite used in this study has silt fraction of 15.8%, clay fraction of 84.2%, liquid limit of 84.7% and plastic limit of 35.1%.

As the admixture, Carbonated-Aluminate Salts (CAS) are used, which are cement-based stabilizers containing lime, sulfate aluminate and sodium carbonate. It has been previously shown that CAS are effective as hardening materials for soft clays or waste materials (Kamon et al., 1989; Tomohisa, 1989; Nontananandh, 1990). The effects of the CAS materials are as follows:

- formation of ettringite and other reaction products and the crystallization of excess pore water in the soils;
- (2) activation of the pozzolanic reaction in long term;
- (3) control of the pH value of the hardened mixtures; and
- (4) activation of hydration through accelerating dissolution from soil/waste materials.

The composition of CAS used in this study is Ordinary Portland Cement: Ca(OH)₂: Al₂(SO₄)₃:Na₂CO₃=50:30:15:5 (dry weight basis).

2) Specimen Preparation and Experiments

Mixing and preparation of specimens were performed in accordance with the Practice for Making and Curing Noncompacted Stabilized Soil Specimens (JSF T 821-1990). The cylindrical molds of 5 cm in diameter and 10 cm in length filled with the fresh mixtures (after mixing with 51 soil mixer for 5 minutes), were vibrated for the removal of air bubbles. The

Items	Curing conditions		
Hems	Drying	Wetting	
Normal curing	sealed, 20±2°C, 80% RH		
(Drying and wetting test)			
(1) Oven curing	electric furnace, 110 ± 3°C		
(2) Drying(oven)-wetting	electric furnace, 110±3°C	water, 20°C.	
	48 hours/cycle	24 hours/cycle	
(3) 40°C curing	electric furnace, 40 ± 3°C		
(4) Drying(40°C)-wetting	electric furnace, 40±3°C	water, 20°C.	
AND THE STREET S	48 hours/cycle	24 hours/cycle	
(5) Drying(vacuum)-wetting	vacuum vessel, 20 ± 2°C,	water, 20°C.	
INVITATION CONTRACTOR	48 hours/cycle	24 hours/cycle	
(1) 2.5% Na ₂ SO ₄ solution		2.5% Na ₁ SO ₄ ,	
		continuous souking, 20°C	
(2) 5% Na ₂ SO ₄ solution		5% Na ₂ SO ₄ ,	
		continuous soaking, 20°C	
(3) 5% MgSO ₄ solution		5% MgSO4,	
1		continuous soaking, 20°C	

Table 2. Experimental conditions for durability test

sealed specimens were cured in a constant-temperature room (20°C, 80% relative humidity). Beside the curing condition which is termed as 'Normal curing', the following curing processes were performed for the durability test, using specimens of three kinds of mix proportions which can gain strength in 1-day in excess of 10 kgf/cm² (0.98 MPa) without yielding a loss in strength, after the specimens were cured in the constant-temperature room for 6 days and, thereafter, cured in water for 1 day. The following steps were taken in curing the samples (Table 2):

(Drying and wetting test)

- (1) cured in an electric furnace at 110°C, called 'Oven curing'
- (2) dried in an electric furnace at 110°C for 48 hours/cycle and stored in water for 24 hours/cycle, called 'Drying(oven)-wetting';
- (3) cured in an electric furnace at 40°C, called '40°C curing'
- (4) dried in an electric furnace at 40°C for 48 hours/cycle and stored in water for 24 hours/cycle, called 'Drying(40°C)-wetting';
- (5) dried in vacuum desiccators for 48 hours/cycle and stored in water for 24 hours/ cycle, called 'Drying(vacuum)-wetting'; (Soaking test)

Samples were stored in following solutions: 2.5% Na₂SO₄, 5% Na₂SO₄, and 5% MgSO₄.

The temperatures of all the water and solutions were maintained constant at 20°C. Unconfined compression test (strain rate 1%/min) and X-ray diffraction analysis (XRD) were carried out after the curing period. On the durability under drying and wetting cycles, the standard test method is not established in Japan and it has been reported that the durability of stabilized mixtures might be overestimated if they are dried at high temperatures (40-70°C), because these temperatures accelerate the hardening reaction (Kamon et al., 1990). In this study, the vacuum drying method, in which drying was performed with evacuation by means of a suction pump (-750 mmHg) at a temperature of 20°C, was newly adopted to evaluate the durability in early stages while keeping the temperature constant.

RESULTS AND DISCUSSIONS

1) Strength Characteristics of Stabilized Sslag

Table 3 shows the compressive strengths of some S-slag mixtures. The mix proportions of the mixtures shown in Table 3 were determined so that the fresh mixtures are workable enough to remove air bubbles from them by vibration and the bleeding does not occur.

Table 3 reveals that the CAS gives a higher

Table 3.	Strengths	of stabilized	S-slag	mixtures
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	T-1	Materials and Mixing Conditions		Compressive strength (kPa)				
Symbol	Type of Stabilizer	Type of S-slag	Stabilizer Content (%)	water/solid (% by wt.)	1 day	3 days	7 days	28 days
MIX-1	Cement (OPC)	Slag I	3	50	468	778	757	501
MIX-2		Slag I	6	50	549	733	574	432
MIX-3	CAS Hardening Material	Raw Slag 1	3	45	1088	1041	956	
MIX-4		Raw Slag 1	3	50	2021	1337	1037	913
MIX-5		Raw Slag I	6	45	1290	1136	1089	*
MIX-6		Raw Slag I	6	50	1555	1332	1402	1321
MIX-7		Raw Slag 1	9	50	1339	1739	1845	2418
MIX-8		Slag 1	9	50	1987	1178	•	*
MIX-9		Slag 1:K=95:5	9	50	1638	1859	1957	1859
MIX-10		Slag 1:K=95:5	12	50	2263	2709	2631	2479
MIX-II	CAS Hardening Material	Slag II	3	35	392	601	1359	4218
MIX-12		Slag II	6	35	1675	2604	4868	8765
MIX-13		Slag 11:K=95:5	3	35	316	568	1725	3125
MIX-14		Slag II:K=95:5	6	3.5	1591	3541	3855	4005

(Note) 'K' stands for kaolinite clay, 'Raw Slag' for the untreated S-slag, and 'Slag' for S-slag finer than 425 μm. **' stands for no data because of the failure of specimens.

hardening effect than ordinary portland cement. For S-slag I, a marked gain in early strength is observed for mixtures having particle sizes smaller than 0.425 mm. This indicates that the strength development is affected by the particle size and chemical compositions of the metalloid pellets which remained in the Sslag. For many of the mix proportions shown in Table 3, the decrease in strength is observed, which is considered to be due to the efflorescence phenomena. The mixtures without kaolinite clay cured for 3 days had approximately 40% lower strength than the mixtures cured for I day (Fig. 2). However if the mixtures are proportioned with some kaolinite (5% addition in this study), the strength of Sslag mixture can be maintained. Similar results were found in a study on the stabilization of incinerated pulp ash, which indicates that the addition of kaolinite realizes the effective stabilization due to the decrease in porosity and the acceleration in the formation of CSH (Kamon et al., 1991). As for the subbase purpose, it is recommended that the mixtures gain 14-day strength of more than 12 kgf/cm2

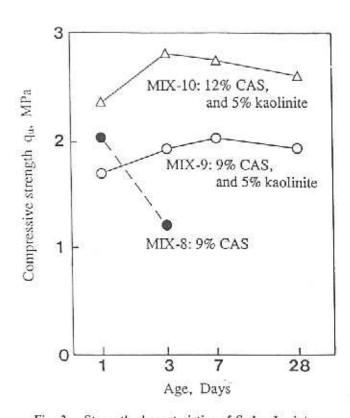


Fig. 2. Strength characteristics of S-slag I mixtures

(1.18 MPa), without yielding a loss in strength. Hence, it is considered that S-slag I

mixture blended with CAS and kaolinite can be used as subbase course materials.

For S-slag II, the strength improves considerably with the increasing curing time when the mixtures were stabilized with CAS, and the addition of 6% CAS realizes a higher strength than 1 MPa cured for 1-day, while the mixtures with 3% CAS achieve a lower strength of only 500 kPa. In contrast with Sslag I, the addition of kaolinite in Slag II mixtures was considered ineffective because this impaired the strength with a prolonged curing time. In Fig. 3, the mixtures with kaolinite, a marked trend of reduction in strength was noted after approximately 7days. Considering for the subbase purpose, the mix proportion of CAS is more important than the addition of kaolinite, and S-slag with 6% CAS has a potential use.

Fig. 4 shows the X-ray diffraction patterns of stabilized S-slag. The samples stabilized by ordinary portland cement exhibit the formation of CSH hydrate. Both S-slags treated by CAS have remarkable peaks of CASH as well

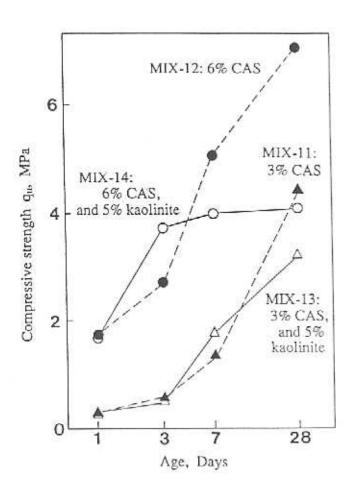


Fig. 3. Strength characteristics of S-slag II mixtures

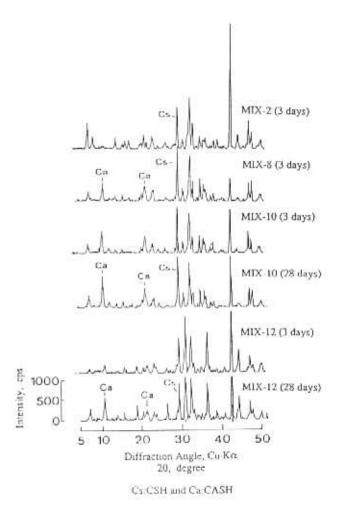


Fig. 4. X-ray diffraction patterns of S-slag mixtures

as CSH, and X-ray intensities of these hydrates also increase for the mixtures which exhibit an increase in strength with a prolonged curing time. The formations of CASH or CSH are very important as considering the efflorescence characteristics of S-slags, but in stabilizing S-slag CASH and CSH contribute to the strength development. It must be considered that the strength decrease of many mixtures of S-slag I is not due to the formation of CASH but other reaction CSH OF mechanisms.

Drying-Wetting Durability of Stabilized S-slag

The confirmation of water removal by some drying conditions is important to evaluate these curing methods proposed in this study. Fig. 5 shows the weight change ratios of specimens under drying and wetting conditions, which indicates the water removal and adsorption. Water removal ratios by 40°C dry-

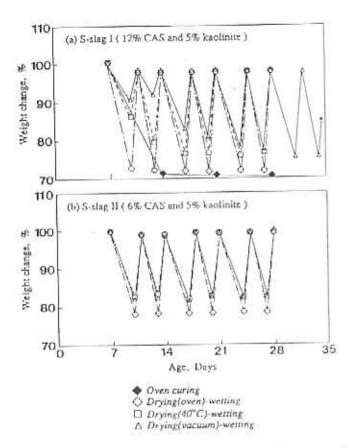


Fig. 5. Weight change of S-slag mixtures under repeated cycles of drying/wetting

ing method in 40°C curing or Drying (40°C)wetting are about 70% of the removal by 110°C drying in Oven curing or Drying(oven)wetting. The drying method with the temperature of 110°C is unlikely in in situ environment, and it is known that the soils nearby the surface of the earth are often heated to 40°C. In Fig. 5, the water removal ratio at early cycles by Drying(vacuum)-wetting is comparatively low, because the number of samples in a vacuum desiccator affects the water removal. When the number of specimens in the desiccator is between 4-6, the dehydration ratio by vacuum drying is about 70%, which is approximately the same as that of 40°C drying methods. So it is clarified that the newly adopted vacuum drying method realizes the same water removal as in 40°C condition without raising the temperature. Volume changes of S-slag mixtures under the dryingwetting condition, as shown in Fig. 6, illustrates the effects of the drying method and kaolinite additive. For the Drying(vacuum)wetting and Drying(40°C)-wetting, shrinkage

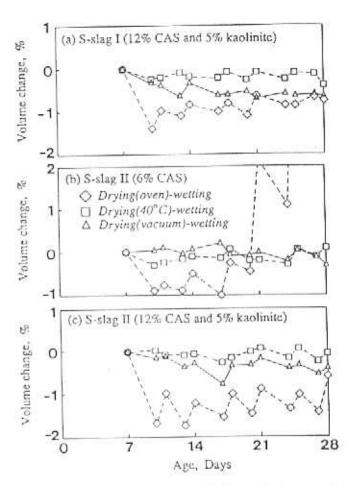


Fig. 6. Volume changes of S-slag mixtures under repeated cycles of drying/wetting

and swelling in each drying or wetting cycles are minute, and drying shrinkage ratios are less than 1% for all the cycles. For Drying(oven)-wetting, irreversible shrinkage occurred in the first drying, and afterwards a general tendency to swell was observed. Especially for S-slag II without kaolinite, a marked crack propagated and led to eventual failure.

Fig. 7 illustrates the changes in strength with respect to the curing period and curing Compressive strength conditions. specimens for 40°C curing is as high as 10 MPa. This unusual increase in strength is the result of the tightness raised due to drying and the hardening reaction accelerated due to high temperature. Drying(40°C)-wetting and Drying(vacuum)-wetting resemble in the water removal ability and drying shrinkage characteristics, but differ obviously in strength characteristics from each other. In the case of drymixtures S-slag ing(40°C)-wetting, the

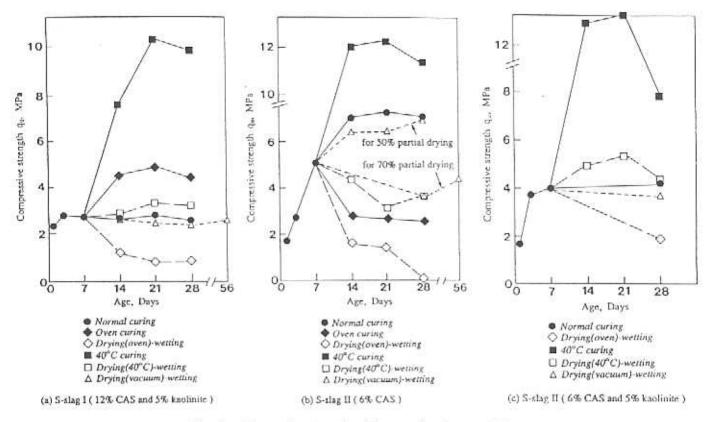


Fig. 7. Change in strength with several curing conditions

without kaolinite have half the strength as that of Normal curing after 28 days (6 cycles), while the mixtures with kaolinite clay show high strength when compared with normal-curing. In the case of drying(vacuum)-wetting, the strength of the mixtures with or without kaolinite shows a reduction in strength by 10-20% and 50% respectively, when compared with Normal curing. As the 40°C-drying is nearly equal to the vacuum-drying in drying shrinkage, it is considered that the strength development for drying(40°C)-wetting is due to the acceleration of the stabilization reaction with a high temperature. The strengths of stabilized S-slag I with kaolinite and S-slag II without kaolinite, obtained from Oven curing, are respectively twice and a half as high as those for Normal curing (Fig. 7(a) and (b)). Sslag mixtures with kaolinite obtained from Drying(oven)-wetting do not show any remarkable expansion and/or failure, and maintain the strength of about 1 MPa. So, the durability of mixtures shows more dependence on the existence of clay minerals and curing conditions than the type of S-slag and the mixing water content. It is inferred that the S- slags with CAS materials and kaolinite clays can potentially be used as subbase course materials.

Fig. 8 shows the X-ray diffraction patterns of S-slag mixtures under several curing conditions. As stated above, CSH and CASH are considered to be main reaction hydrates which contribute to the strength development. While the peaks of CSH are unchangeable for the curing conditions, those of CASH are owing to drying and wetting cycles. CASH was not observed in the specimen for 40°C-curing and Oven curing. For drying(40°C)-wetting, CASH appeared again when the sample was rewetted, but consequently, the reduction in CASH was observed compared with Normal curing. For Drying(oven)-wetting, CASH did not reappear when the specimens were rewetted. These phenomena can be the signs of dehydration and re-hydration of the water of crystallization. For drying(vacuum)-wetting, CASH which seems to be sensitive to dryingwetting decreases, but the addition of kaolinite restrains the decline in CASH. In consideration of the stability of hydrate compounds which play the role of strength

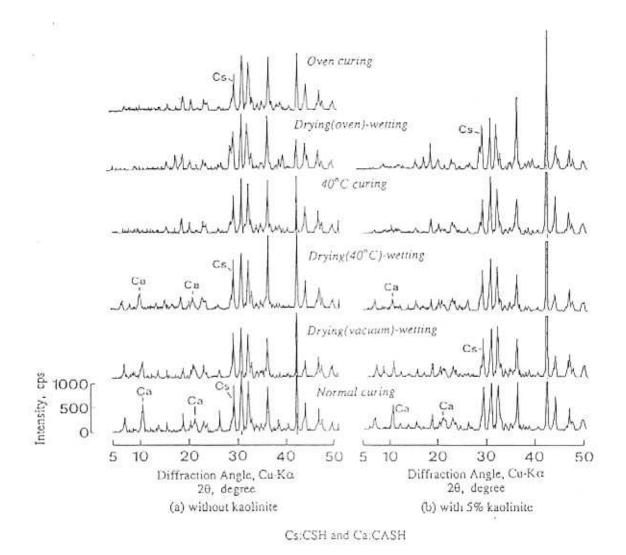


Fig. 8. X-ray diffraction patterns of S-slag II mixtures with various curing conditions at 28-day curing

development, kaolinite leads to the improvement in durability.

3) Soaking Durability of Stabilized S-slag

The assessment of the durability for sulfate attack is of great importance if these materials are to be used as ground materials. Fig. 9 shows the strength characteristics of the specimens cured in the long period by Normal curing and in 2.5% Na₂SO₄ solution. The strength deterioration of both S-slag mixtures does not appear in the long term. S-slag cured in Na₂SO₄ solution has a much higher strength than the slag cured by Normal curing. X-ray diffraction patterns exhibit the formation of ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) in these specimens as shown in Fig. 10. On concrete and concrete-like materials, it is general-

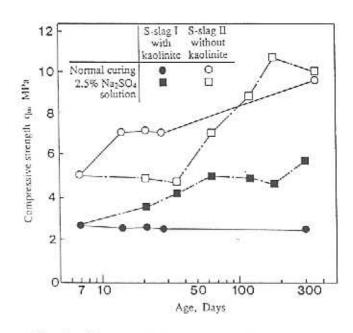
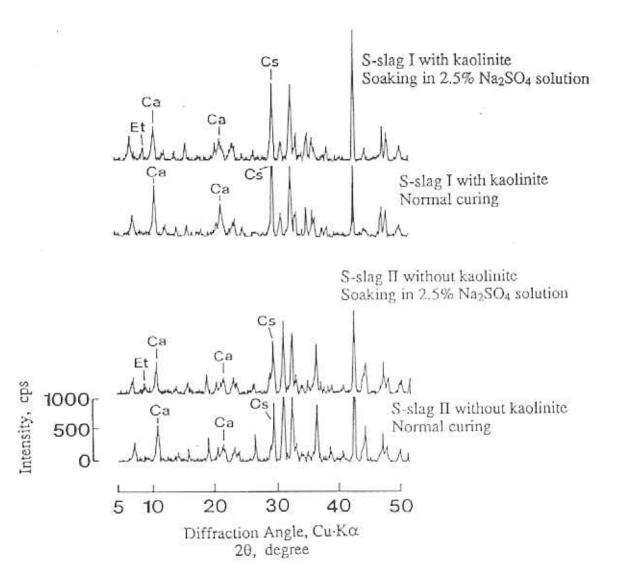


Fig. 9. The strength-time curves of S-slag mixtures



Et:Ettringite, Cs:CSH, and Ca:CASH

Fig. 10. X-ray diffraction patterns of S-slag mixtures with soaking conditions

ly said that the formation and subsequent expansion of the hydrated ettringite causes the deteriorative expansion of mixtures, for some concentrations of some kinds of sulfate solutions. These deteriorative phenomena are due to types and concentration of sulfate, chemical and physical properties of stabilized materials, the characteristics of the mixtures, and the curing term. The experimental condition in this study does not lead to a decrease in strength. The change in weight over time for specimens stored in sulfate solutions and in water is presented in Fig. 11. The specimens stored in 2.5% sulfate solutions show only a slight change in weight over time and remain in an excellent condition after a soaking

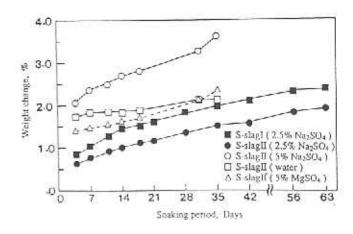


Fig. 11. Weight changes of S-slag mixtures with souking conditions

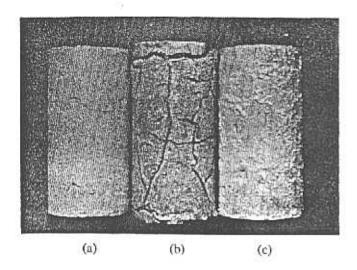


Photo 1. Five-month-aged stabilized S-slag II stored in: (a) water, (b) 5% Na₂SO₄ solution, and (c) 5% MgSO₄ solution

period of one month. It is evident that the specimens stored in an extremely high concentration of sulfate solution undergo marked changes in total moist weight and exhibit a sign of deteriorative expansion. The specimens in 5% MgSO₄ show poor crystallization of sulfate on the surface and those in 5% Na₂SO₄ were badly cracked, whereas those stored in water remain in a good state as shown in Photo 1. One must be aware that the resistance to sulfate attack on stabilized S-slag depends on the curing condition.

CONCLUSIONS

Strength and durability characteristics of stabilized stainless-steel slag, which is an electric furnace reducing slag and has expansive characteristics, were tested to establish their potential use as ground materials.

Stainless-steel slags used in this study are typical electric reducing slags in view of the physical properties and the chemical composition. The main minerals constituting S-slag are merwinite (Ca₃Mg(SiO₄)₂), diopside (CaMg(SiO₃)₂), magnesium aluminum oxide (MgO·Al₂O₃) and magnesium silicate (β-2MgO·SiO₂).

The use of Carbonated-Aluminate Salts (CAS) accelerates the formation of CSH and CASH. It is considered that these hydrates

contribute to the strength development of Sslag mixtures, and the strength deterioration due to the expansion of S-slags does not occur.

With the addition of kaolinite the specimens show improvement in durability. It has been confirmed that the supplement of fine grain materials to S-slag brings about denser mixtures.

The durability of stabilized mixtures depends on the properties of materials and the curing conditions. The drying condition with the temperature raised can accelerate the hardening reaction of stabilized S-slags. The vacuum drying method proposed in this study is effective to assess the drying-wetting durability of cement stabilized mixtures because it realizes sufficient dehydration of specimens sufficiently keeping the temperature constant normal.

It is concluded that S-slag has a potential use as subbase course materials if it is treated by means of CAS and kaolinite.

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