- Technical Paper -

CHEMICAL CHARACTERIZATION OF SEWAGE SLUDGE ASH AND SLAG

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ABSTRACT

This research deals with sewage sludge incineration ash and molten slag. The great difference from other material lies in the high contents of phosphorus especially in the former. Calcium is adsorbed in saturated calcium solution due to the phosphorous composition. There may be cases of portions less stable being corrosively dissolved and releasing silica and phosphorus, but the degrees of these are low, rather the elution of aluminum is characteristic. The points to be paid attention when using these ash or slag are calcium adsorption related to setting time or durability.

Keywords: sewage sludge, ash, slag, chemical character, phosphorus, calcium, iron, color

1. INTRODUCTION

Sewers play a great role in preservation of our living and environments. However, there is huge amount of pollutants removed from the drainage system, i.e. an enormous quantity of sludge is generated. In Japan it was about 79 million tons in 2006, constituting approximately 20% of total industrial wastes. This amount will increase with future increases in sewer construction, thus treatment and disposal programs for the building of a Material Circulation Society will be importance. The state of sewage sludge treatment and disposal in fiscal 2007 is summarized in Fig. 1 [1]. While landfill disposal had declined since 1995, use as a construction material such as by transforming into a resource for cement has continued to increase and has become the leading method of effective utilization. The final states of sewage sludge treatment, also in 2007, are shown in Fig. 2, with material stabilized by heat treatment into the form of incineration ash or molten slag comprising approximately 73% for ease of material recycling[1].

In 2001, “Manual for Utilization of Sewage Sludge as Material of Construction” was compiled by the Japan Sewage Works Association[2], and the standard of ”Melt-solidified slag aggregate for concrete derived from municipal solid waste and sewage sludge” was established in 2006 as JIS A 5031[3]. This is featured by the inclusion of elution properties of harmful components in addition to general physical properties and chemical compositions. It is stipulated that elution tests be performed on the acidic side of pH with water and dilute hydrochloric acid, while chemical tests other than ASR tests had not been carried out on the pH alkaline side.

Meanwhile, Ozaki et al.(2004)[4], aiming for recovery of phosphorus component from sewage sludge, especially from incineration ash often forms difficultly, water-soluble compounds with calcium and other in incineration ash, technologies such as for phosphorus is eluted from sewage sludge incineration ash under specific pH alkaline conditions to raise concern that there will be concern about expansion due to matter such as quicklime remaining. Aquino et al (2010)[5] referred to the cracking inhibition effect of concrete consisting of molten slag and point out the necessity for explanation of its chemical mechanism.

Thus, it was decided that characterization of sewage sludge incineration ash and molten slag under pH alkaline conditions before hardening the cement past, would be done in this paper to gain a grasp of the degrees of influence differences in chemical constitution would have.

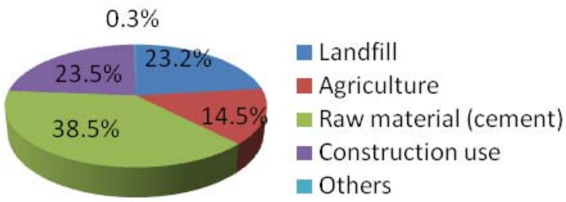

Fig.1 Sewage sludge utilization of each sector in Japan (Ds-ton: 2007)

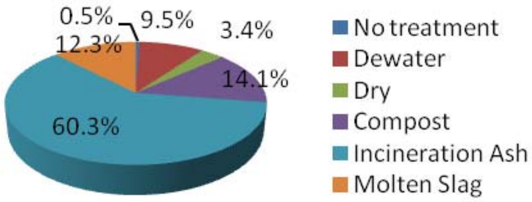

Fig.2 Sewage sludge final disposal in Japan (2007)

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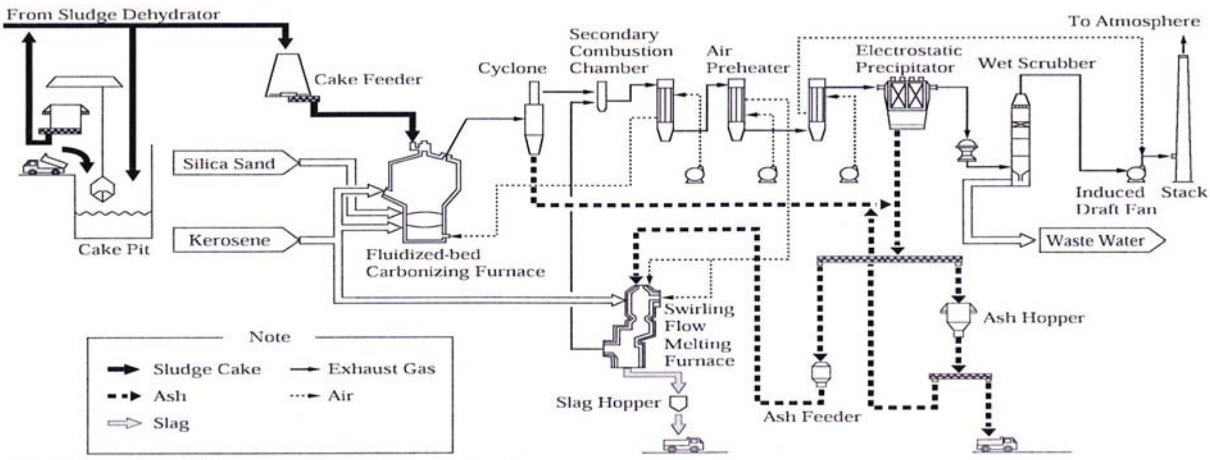


Fig.3 Schematic diagram of sewage sludge molten slag system in Konan plant (Shiga)

2. TEST PROGRAMS

2.1 Materials

Chemical evaluations were made of sewage sludge incineration ash and molten slag produced in the last 15 years at 48 facilities in Japan. Sewage sludge incineration ash consisted of 35 varieties of high polymers (flocculant used) type, 8 varieties of inorganic (flocculant used) type, and 20 varieties of slag (see Fig. 3), with comparison materials 2 varieties of coal fly ash, 1 of finely powder blast furnace slag, and 2 varieties of natural aggregates from Japan. They are showed in Photo 1.

2.2 Testing method

Samples were crashed to pulverized and, in addition to the method of Tanosaki et al(1997)[6], quicklime component and insoluble residue were measured. As described by Ozaki et al(1997)[7], the features of the slag are low crystalline phase content and high glassy phase content. Mineral crystal content differs depending on the cooling and after-treatment processes. However, it had been difficult to determine the characteristics of the glassy phase itself by X-ray diffraction or optical means. In such a circumstance, Tanosaki et al(2007)[8] focused on the insoluble residue contents of municipal wastes incineration ash and molten slag, classifying glassy matter into TypeI and II, and thus these insoluble residues were included also as objects of evaluation. Calcium consumption in slaked lime-saturated solution was tested in the manner of the pozzolanic reaction test in EN196-5 along with component elution tests and measurements of setting times.

Table 1 Methods of evaluation

Chemical Compositions	JIS M 8815 (1989)
Free calcium	JCA No. 1
Insoluble content	JIS R 5204 (2002)
pH (25% slurry)	JIS Z 8802 (1993)
Reactions in saturated calcium	EN 196-5 (2001)
Mortar test	JIS R 5201 (1997)
Carbonation test	Tanosaki et al (1997)
Caustic soda solution test	JTL No. 19

Sewage sludge incineration ash is red in color and has been used coloring material for tile, brick, and other items .The hues of Munsell color systems of individual samples are measured by dry and wet conditions. The methods of evaluation are summarized on Table 1.

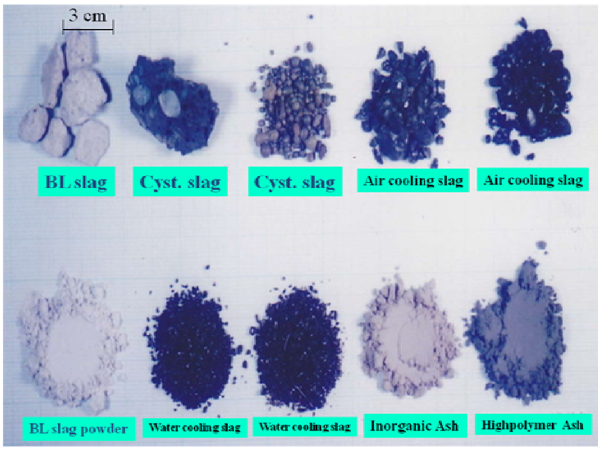


Photo 1 Ash and slag samples

2.3 Evaluations results and discussion

A part of the evaluation results is given on Table 2 and the ranges of scatter in qualities are shown on Table 3. Although detailed descriptions are not provided since the focus is on chemical properties in this paper, the quantities of CaO and Fe_2O_3 have relation to specific gravities, while specific surface of incineration ash will influence absorption characteristic, the maximum of specific surfaces of samples listed on Table 2 was 5.6m^2/g and it was judged that there had been little effect on physical adsorption. It can be ascertained from Table 3 that a great feature of sewage sludge incineration ash or molten slag, differing from coal fly ash and blast furnace slag, is that phosphorus is contained in large quantity. Differences in components by lot are large, the causes of which, by element, are:

A: Those thought to depend on geology of the drainage basin: Si, Al, Fe, Na, K, Ca, Mg, etc.
B: Components accompanying removal of sewage pollutants: P, (C, N).Heavy metals, etc.
C: Additive during water treatment and melting: Fe, Ca, Cl, etc.

Table 2 Part of the evaluation results (wt%)

Sample	Abbr.	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	CaO	SO_3	P_2O_5	TiO_5	Cl	FreeCa	Insol	pH
Sewage ash 1 (high polymer)	SA1	41.4	21.8	7.0	1.0	1.1	2.6	11.7	0.1	11.8	1.0	0.0	12.8	12.8	7.7
Sewage ash 4 (Inorganic)	SA4	10.9	6.0	23.5	0.3	0.4	2.9	36.5	4.3	8.1	0.3	1.8	0.0	11.3	12.4
Sewage slag F (water cooling)	SSF	19.7	17.3	22.0	0.7	0.9	1.6	17.8	2.0	15.9	1.3	0.0	0.0	4.0	7.5
Sewage slag T (Air cooling)	SST	40.4	18.4	9.0	1.1	1.4	2.6	9.6	0.0	11.2	1.1	0.0	0.3	55.7	10.9
Sewage slag A (Air cooling)	SSA	16.4	32.8	2.8	0.4	1.2	1.5	17.1	0.0	25.9	0.4	0.0	0.0	15.5	8.1
Sewage slag E (Air cooling)	SSE	34.9	8.9	11.4	0.1	0.8	1.1	33.4	0.2	7.5	0.2	0.1	0.0	1.1	8.2
Sewage slag E (Crystalized)	SE2	31.0	14.0	5.4	0.6	1.7	1.9	31.2	0.1	10.6	1.1	0.0	0.0	17.9	8.8
Coal fly ash I	CF1	49.6	26.4	5.7	1.7	1.6	2.1	10.3	0.4	0.0	1.1	0.0	0.0	64.4	11.8
Coal fly ash T	CFT	58.7	30.9	4.7	0.2	0.4	0.6	1.4	0.3	0.4	1.8	0.0	0.0	93.1	7.4
Blastfurnace Slag	BFS	34.9	14.8	0.2	0.2	0.3	6.4	41.5	0.8	0.0	0.5	0.0	0.0	0.6	11.0
Sandstone (Osaka)	SST	58.6	18.6	6.5	2.1	3.5	3.5	5.7	0.2	0.0	0.7	0.0	0.0	84.1	7.1
Limestone (Shiga)	LST	0.5	0.2	0.1	0.0	0.0	0.4	55.9	0.0	0.1	0.0	0.0	0.0	0.4	8.9

Table 3 Part of the evaluation results (wt%)

Sample	Lot	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	CaO	SO_3	P_2O_5	TiO_5	Cl	FreeCa	Insol	pH
SA1	35	22.2~64.5	2.9~9.7	1.7~36.3	0.3~1.2	0.0~1.5	0.9~3.8	24.3~52.5	0.0~5.8	9.3~30.3	0.3~1.8	0.4~8.3	0.6~19.1	11.1~12.9	11.1~12.9
SA4	8	9.6~48.3	15.9~20.5	6.7~26.3	0.3~1.7	0.0~1.2	0.3~2.7	3.3~22.6	0.0~2.8	7.0~29.1	0.3~3.8	0.1~2.7	0.0~0.3	10.1~22.9	6.1~8.9
SSF	5	9.2~45.5	10.9~28.6	1.7~26.3	0.1~2.2	0.0~2.5	0.2~0.8	3.3~38.4	0.0~0.8	9.0~33.8	0.3~2.8	0.0~1.3	0.0~0.1	42.1~65.6	7.1~9.5
SST	12	22.1~45.3	9.9~29.7	1.8~26.9	0.1~2.2	0.0~2.4	0.2~0.7	6.3~33.8	0.0~1.0	10~34.3	0.3~2.8	0.0~1.2	0.0~0.9	11.1~75.9	7.5~9.3
SSE	3	32.2~41.5	9.8~19.5	4.7~9.8	0.0~1.2	0.0~1.5	1.4~2.8	26.4~42.2	0.0~0.8	7.0~14.3	0.3~1.8	0.0~0.3	0.0~0.1	12.8~67.9	8.1~9.3
CF1	144	45.1~72.2	17.7~38.9	2.7~12.3	0.1~3.2	0.2~1.5	0.3~1.4	0.0~14.3	0.3~3.9	0.0~0.8	0.3~2.8	0.0~0.2	0.0~0.6	62.2~95.9	1.9~13.0
BFS	12	32.1~36.4	12.4~19.7	0.2~1.2	0.3~0.8	0.0~0.5	5.4~6.8	40.1~44.4	0.3~2.8	0.0~0.2	0.0~0.8	0.0~0.3	0.0~0.3	0.4~3.3	8.1~9.9
SST	88	42.1~71.3	9.9~29.7	0.7~16.3	0.3~7.2	0.0~5.5	0.4~0.8	0.3~12.4	0.0~1.8	0.0~4.3	0.3~2.8	0.0~1.3	0.0~0.1	12.1~95.9	4.1~10.3
LST	54	0.0~15.4	0.0~4.6	0.0~2.9	0.0~0.5	0.0~0.3	0.0~18.0	34.2~56.9	0.0~0.6	0.0~0.4	0.0~2.4	0.0~0.4	0.0~0.1	0.0~25.4	8.0~9.9

It is learned that fluctuations occur by season and by year even though at the same disposal plant. Although stipulated that it is important to know the upper and lower limits of these fluctuations, the degrees of importance by item had not been pointed out in the past.

Free lime (Free Ca) and chlorite (ClO_2) were identified as components most affecting structural concrete and will require special attention in case of inorganic incineration ash. Added to this there is elution of heavy metals also, but discussion of this will be omitted here since there are many reports concerning the matter, while the focus of this report is on major inorganic component quantities.

Examples of reactions in saturated calcium solutions are given on Table 4, where the characteristics of sewage sludge incineration ash and molten slag in comparison with fly ash, blast furnace slag and natural aggregates were:

A: Calcium component was adsorbed in large quantity

B: There was hardly any elution of Silica component, while Alumina and others were eluted

C: Elution of Phosphorus component was recognized in part of air-cooled slag.

The influence of these chemical composition is on concrete properties is hard to predict (see Fig.4). One of the first recycled materials to be used at the concrete industry was the blastfurnace slag, this material itself has slightly variations even from different facilities. The Coal fly ash was used after the blastfurnace slag, and it shows slightly more variation than the blastfurnace slag. However, the molten Sewage ash and slag was used after the 2 previous and it has more even more chemical variations. The chemical reactions of the Sewage materials themselves are still unpredicted and these characteristics affect the performance in concrete. Possibly, the ordinary oxides that affect the concrete from the natural aggregates are also affecting from the Sewage ashes and slags.

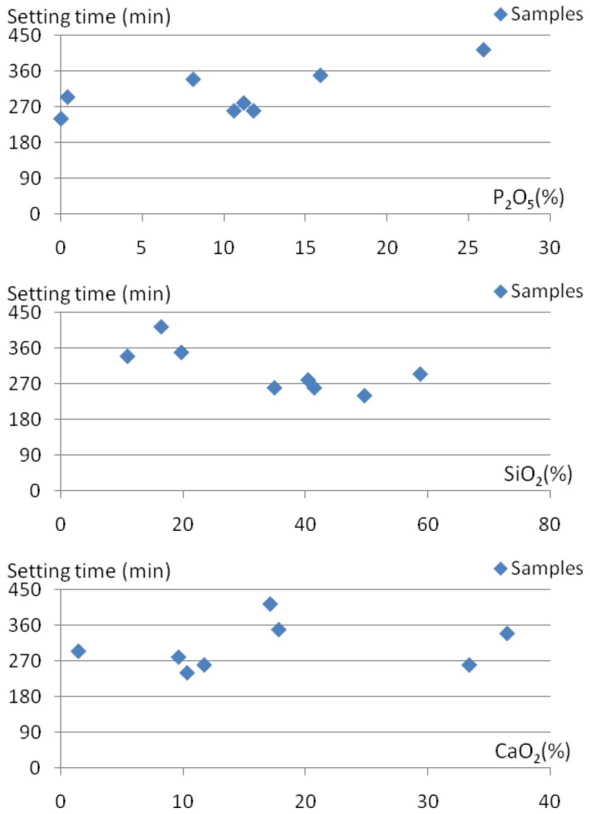


Fig.4 Relation of some oxides and setting time

As Ozaki et al.(2004)[4] have indicated, it could be anticipated that stabilization is achieved through formation of phosphoric acid minerals such as SiP_2O_7, and $Al(PO)_4$, substantiating the fact that content of phosphorus is extremely important. However Ozaki et al.(2004) had considered though sequential extraction tests that the states of existence were all as residue, and no further information could be obtained.

Tanosaki et al.(2007)[8] indicated that, in municipal waste incineration ash and molten slag or coal fly ashes glassy matter such as showed in Fig. 5, calculated from chemical components, classification as Type I and II could be done depending on non-dissolved residue quantity and the rough yardstick of active glass Type II being dominant is $CaO+MgO+Na_2O+K_2O>28\%$, also Tanosaki et al.(2009)[9] indicated that the case of IGCC (Integrated coal gasification combined cycle) slag's case. Glass I has low flux compositions, and Glass II has high flux compositions which are making the basis character of the slag. Using for civil engineering work. Pozzolanic reactions are important with hydration materials, but long time is necessary to get the result of pozzolanic reactions.

Table 4 Examples of reactions in saturated calcium liquid (mg/little)

Sample	Ca Adp	Fe Elu	Al Elu	Si Elu	P Elu
SA1	120	<0.1	10	2.6	<0.1
SA4	710	<0.1	92	<0.1	<0.1
SSF	790	<0.1	94	<0.1	<0.1
SST	850	<0.1	2	<0.1	1.5
SSA	860	<0.1	<0.1	<0.1	<0.1
SSE	810	<0.1	<0.1	<0.1	<0.1
SE2	670	<0.1	<0.1	<0.1	<0.1
CF1	180	<0.1	2.2	4.2	<0.1
CF T	90	<0.1	0.5	3.2	<0.1
SST	50	<0.1	0	0	<0.1

In the case of sewage sludge incineration ash I and molten slag T (Water cooled type) on Table 2, even with around $CaO+MgO+Na_2O+K_2O<20\%$, there are samples with insoluble residue 13% or less and it may be considered that this cannot be explained merely by the analysis method predicated simply on an alumino-silicate framework.

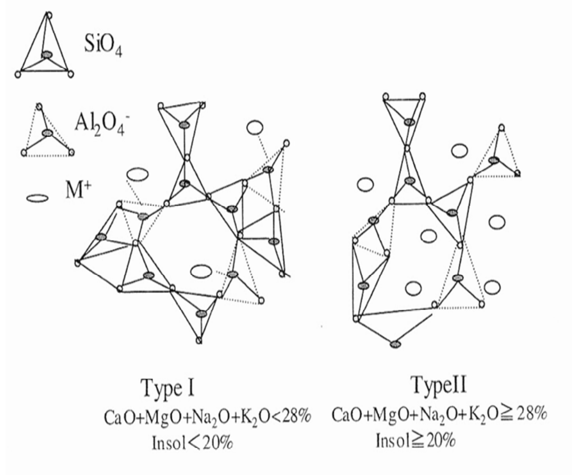


Fig.5 Ideal structure of Glass Type I and II

Table 5 Results of evaluation of mortars

Sample	Setting time		Mortar test		Carbonation
	Start	End	28 d.	91 d.	Depth in mm
SA1	2H05M	4H20M	92	99	1.4
SA4	4H05M	5H40M	60	67	2.9
SSF	4H55M	5H50M	85	88	2.7
SST	2H55M	4H40M	82	84	2.9
SSA	5H05M	6H55M	71	72	2.5
SSE	2H05M	4H20M	77	88	2.6
CF1	2H45M	4H00M	81	94	1.5
CFT	3H20M	4H55M	71	87	1.9
OPC	2H35M	3H55M	100	100	0.3

The results of evaluations of mortar using sewage sludge incineration ash or molten slag's powder as cement "additives" equivalently to fly ash and blast furnace slag are given on Table 5. In case of 25%

displacement of cement, except for inorganic incineration ash, setting times were greatly returned, and carbonation of the hardened objects had progressed. This is thought to have been the influence of the quantity of calcium adsorption given on Table 4. As Koyanagi et al.(1998)[10] have indicated, it is thought elution of phosphorus sufficient to affect cement hydration will not be seen if pH is under 13.

According to Yamamoto(2011)[11] , “In pozzolanic reaction of fly ash, alkaline component(Na^+,K^+,Ca^{2+}) eluted from cement particles contact the surfaces of fly ash particles and cause dissolution reactions of amorphous phases”. Even though Silica frameworks were not main, in order to ascertain what effects were caused by Sodium ions in early stages, the leaching method of Environment Ministry Notification No.19 was adapted and measurements were made of component elution quantities when immersed in 1 mol/little of caustic soda solution in place of 1mol/little of hydrochloric acid, the results of which are given on Table 6. The tests were conducted varying L/S (Liquid-Powder) ratios.

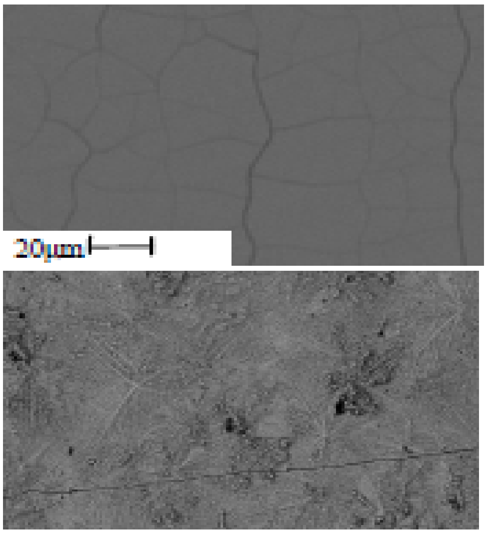
Table 6 Results of caustic Na(OH) solution test(mg/little)

Sample	L/S	Ca Elu	Fe Elu	Al Elu	Si Elu	P Elu
SST	300	8.0	0.6	90.0	3.1	90.0
	30	11.0	1.7	190.0	8.8	160.0
	3	15.0	2.8	280.0	12.0	220.0
SSA	300	13.0	0.1	50.0	1.0	60.0
	30	76.0	0.5	77.0	6.5	130.0
	3	99.0	1.2	159.0	9.1	180.0
CF1	300	0.0	0.0	0.0	0.1	0.0
	30	1.3	0.0	0.3	1.2	0.0
	3	12.0	0.0	2.2	16.0	0.0
SST	300	0.2	0.0	0.2	0.2	0.0
	30	2.0	0.2	2.9	3.1	0.0
	3	16.3	2.3	28.3	35.5	0.0

According to Table 6, whereas elution quantities of the individual components become 1/10 as L/S ratio rise tenfold in the cases of the fly ash and crushed natural crushed aggregate powder evaluated, it is more than 1/10 with sewage slag to show that components are excessively supplied from the interior. The SEM surface image of slag T after immersion is shown in Photo 2 and it can be observed that selective corrosion has occurred.

In JIS A 5031 shows the leaching test of harmful material by JIS K 0058 as acid extractable contents in human stomach conditions but too show as ASR test as JIS A 1145 etc with using caustic soda solutions so this is accordance to each conditions.

In colorimetry, the Munsell color system is a color space that specifies colors based on three color dimensions: hue, value (lightness), and chroma (color purity). It was created by Professor Albert H. Munsell. Each horizontal circle Munsell divided into five principal hues: **R**ed, **Y**ellow, **G**reen, **B**lue, and **P**urple, along with 5 intermediate hues halfway between adjacent principal hues. Each of these 10 steps is then broken into 10 sub-steps, so that 100 hues are given integer values. Two colors of equal value and chroma, on opposite sides of a hue circle, are complementary colors, and mix additively to the neutral gray of the same value. The diagram below shows 40 evenly-spaced Munsell hues, with complements vertically aligned. It is defined in JIS Z 8721[12], as shown in Photo 2.



Before

After

Photo 2 SEM image of Sewage slag 1

Distributions of the hues of Munsell color systems of individual samples are shown in Fig. 7. Sewage sludge incineration ash are R (red) to Y (yellow), differing greatly from cement and blast furnace slag which are G(green) to Y(yellow) and would be very conspicuous when mixed in.

The relation between the point represented by the FeO value obtained by wet analysis and hue is shown in Fig. 8. It may be seen that, as FeO quantity increases (as Fe_2O_3 quantity decreases) there is trend for transition toward the R(red) side. In case of inorganic incineration ash of CaO value quantity 20% and over, perhaps due to atomic CaO→FeO displacement in the chemical structure, the degree of this shift to the R(red) side is weakened. Hardly any precipitation of metallic iron could be seen by either X-ray diffraction or optical means. Crushed and pulverized slag product differed greatly in hue depending on size to pose a problem requiring further study.

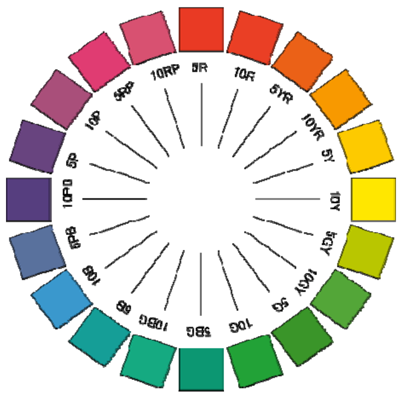


Fig.6 Graduation of Hue circle

3. CONCLUSIONS

Free lime (Free Ca) and chlorite (ClO_2-) were identified as components most affecting structural concrete and will require special attention in case of inorganic incineration ash or molten slag of sewage sludge. Added to this there is elution of heavy metals also, but discussion of this will be omitted here since there are many reports concerning the matter, while the focus on inorganic component quantities.

(1) The great difference of sewage sludge incineration ash and molten slag from other additives and aggregates lies in the high content of phosphorus in the former.

(2) Such phosphorus exists in incineration ash and molten slag as phosphate minerals and amorphous Matter. It may be predicted that their structures differ greatly from aluminum-silicates of fly ash or blast furnace slag.

(3) Red coloration nature shows a tendency for decrease with increase in quantity of Fe_2O_3.

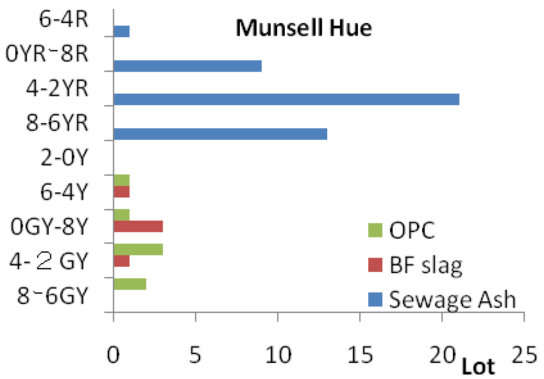


Fig.7 Munsell Hues analysis of each sample

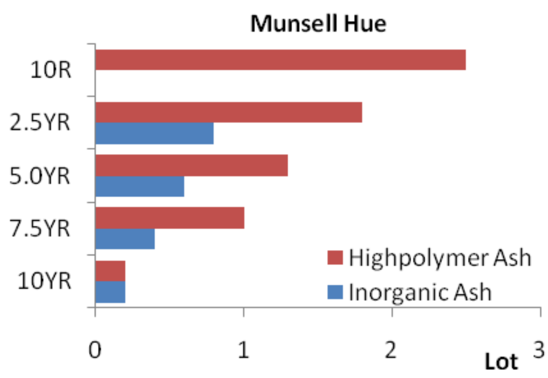


Fig.8 Relationship between FeO content and Hues

(4) Calcium is absorbed in saturated calcium solution due to the phosphorous composition. On the other hand, there may be cause of portions less stable being corrosively dissolved and releasing silica and phosphorus, but the degrees of those are low in the reason of not vandalized the crystal framwork, rather the elution of aluminum is characteristics.

(5) When used as an admixture for cement displacement is done, setting time retardation occurs substantially and carbonation increases in degree, there are probably due to scarcity of calcium.

(6) The point to be paid attention when using sewage sludge incineration ash or molten slag are calcium absorption and aluminum extraction rather than phosphorus elution.

ACKNOWLEDGEMENT

The authors acknowledge the supports of Taiheiyo Cement Corp. and Shiga prefecture, in making this research.

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