Journal of Ceramic Processing Research. Vol. 20, No. 1, pp. 35~40 (2019)

JOURNAL OF
Ceramic
Processing Research

Quantitative evaluation of free CaO in electric furnace slag considering temperature and aging periods

Hee Seob Lim[a], Han Seung Lee[b], Keun-Hyeok Yang[c] and Seung Jun Kwon[a,*]
[a]*Department of Civil Engineering, Hannam University, 70 Hannam-ro, Daedeok-gu, Daejeon 34430, Korea*
[b]*Department of Architecture Engineering, Hanyang University-ERICA, Ansan 15588, Korea*
[c]*Department of Plant Architectural Engineering, Kyonggi University, Suwon, South Korea*

Electric arc furnace slag is reported to contain considerable amount of free CaO which may cause volume swelling so that its application to construction material is very limitedly performed. Free CaO still remains in the slag with unreacted condition. Electric arc furnace slag can be classified into EOS (electric arc furnace oxidizing slag) and ERS (electric arc furnace reduction slag), and they have different chemical compositions and free CaO content. In the present work, free CaO in EOS and ERS are quantitatively evaluated through ethylene glycol method considering solution temperature, measuring period, aging period on site, air-exposure conditions, and ERS replacement ratio. EOS shows a reasonable level of CaO, basicity (CaO/SiO_2), and free CaO content that can be used for construction materials, however ERS exceeds the critical level of usage. In the work comprehensive property evaluation of EOS and ERS is performed for utilization of electric arc furnace slag to construction materials, and the results are discussed.

Key words: Electric arc furnace slag, free CaO, Electric arc furnace oxidizing slag(EOS), Electric arc furnace reduction slag(ERS), Ethylene glycol.

Introduction

The by-products from steel production industry has increased for decades but much of them are used with low added-value such as reclamation or embankment [1, 2]. Several slag types which contain considerable SiO_2 and lime are produced in the refining process of steel production [3]. GGBFS (ground granulated blast furnace slag) has been used for construction industry with many engineering merits such as pore condensation and excellent resistant to acid [4, 5], however the rests are limitedly applied and still studied for construction material [6, 7]. Electric arc furnace slag has such similar chemical components as GGBFS that many researches have been performed for its application to construction and building industry [8-10].

Electric arc furnace slag is produced from iron-scrap refining during the steel production process and has considerable amount of FeO, SiO_2, and CaO which can be reused for engineering and construction works [11]. Electric arc furnace slag can be classified into two types; One is EOS (electric arc furnace oxidizing slag) and ERS (electric arc furnace reduction slag) with different refining process. While after oxidation of impurities in steel, EOS is produced, ERS is produced after arranging components, de-oxidation, and removing acid. Electric arc furnace slag has been reported to contain unstable components like free CaO [12]. Free CaO still exists with unreacted form in the electric arc furnace slag. The composition of electric arc furnace slag varies with the type of furnace, desired grade of steel purity, and furnace operation conditions. During steel manufacturing process, melt pure steel move downwards and the by-product (slag) moves upwards with free CaO [13]. Free CaO is generated in all steel slag during the cooling process and remains in the slag as unreacted. In order to reduce free CaO content, aging process is usually adopted, which means natural exposure to open space. Free CaO in the cooled crushed electric arc furnace slag is reacted with air and then it forms $Ca(OH)_2$ which can be stable without expansion. The crushed slag usually stucks about 3.0m in the aging yard and the exposure period can be reduced through accelerating the reaction between H_2O and free CaO or CO_2 and free CaO. The aging needs at least 3 months but it increases for high content of free CaO. In South Korea, the related guide lines [14] suggest over 3 months of aging period for 100 mm size of slag and over 1 month under 100mm at least. They also require enough stack height (3~8 m) and well ventilated condition. Aging process always requires long exposure period and open space, so that additional cost is burdened to both users and manufacturers [15].

The typical problem of free CaO in concrete is volume swelling. Free CaO reacts with H_2O in mixed water and forms $Ca(OH)_2$. In the process, volume

*Corresponding author:
Tel : +82-629-8020
Fax: +82-42-629-8366
E-mail: jjuni98@hannam.ac.kr

Table 1. Quality standard of EOS (KS F 2527, JIS A 5011-4).

Chemical composition (%)	EOS
CaO	Not more than 40.0
MgO	Not more than 10.0
FeO	Not more than 50.0
CaO/SiO_2 (Basicity)	Not more than 2.0

fractile of $Ca(OH)_2$ is greater than CaO and it causes cracking in the cement matrix [16-18]. Several researches have been focused on utilization of EOS as construction materials since it has little content of free CaO and volume expansion [19, 20]. For the utilization of EOS, International Standards for aggregate of concrete have been already proposed in South Korea and Japan and their summary is listed in Table 1. The chemical components of CaO, MgO, FeO, and CaO/SiO_2 (so called Basicity) are provided and 40% of the maximum allowable content of CaO is suggested.

The physical and chemical components of ERS are much different from those of EOS. After aging process, much of ERS are transformed to $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$ ($C_{11}A_7CaF_2$), $2CaO{\cdot}SiO_2$ (C_2S), $3CaO{\cdot}Al_2O_3$ (C_3A), and considerable amount of free CaO. Previously explained, ERS with cement clinker components has been studied for substitution of OPC (ordinary Portland cement) but the residual free CaO causes volume expansion, which hinders active application to construction material [21].

It is very important to control and evaluate the content of free CaO but the studies on quantitative evaluation of free CaO in ERS has been conducted very limitedly. OPC and GGBFS usually has about 0.5 ~ 1.5% and 0.3 ~ 0.5% of free CaO, respectively. More content over 2% of free CaO in OPC may have serious effect on the concrete such as strength reduction, durability degradation, and unavoidable concrete expansion. As 65 ~ 70% of concrete volume is occupied with aggregate, concrete can be adversely affected by performance degradation of aggregates with abundant content of free CaO. EOS with little free CaO can be utilized for construction material, however EOS is mixed with ERS during aging process, so that entire slag aggregates are only used for reclamation and embankment, which should have been used more valuably.

In the present work, the chemical and physical properties are studied in EOS and ERS from South Korea, and quantitative evaluation of free CaO is performed with ethylene glycol. Free CaO amount is evaluated considering exposure location, aging period, and production region.

Experimental Program

Outline of the work

Two representative companies are selected for EOS and ERS property evaluation. The samples are obtained after aging for 1 hr from electric arc furnace. The test procedures and contents are listed in Table 2.

Table 2. Test contents for EOS and ERS.

Experiment contents	Experimental details
(1) Physical and Chemical property evaluation for EOS and ERS	- Physical (density and absorption ratio) - Chemical (XRF evaluation)
(2) Temperature and duration time of Ethylene glycol titration	- Temperature effect on Ethylene glycol titration (60 °C and 80 °C) - Duration effect on Ethylene glycol titration (20 min., 30 min., and 40 min.)
(3) Production company characterization for EOS and ERS	- Site condition of aging - Aging period
(4) Free CaO evaluation in mixed EOS with different level of ERS ratio	- Free CaO and Basicity measurement in mixed EOS with ERS

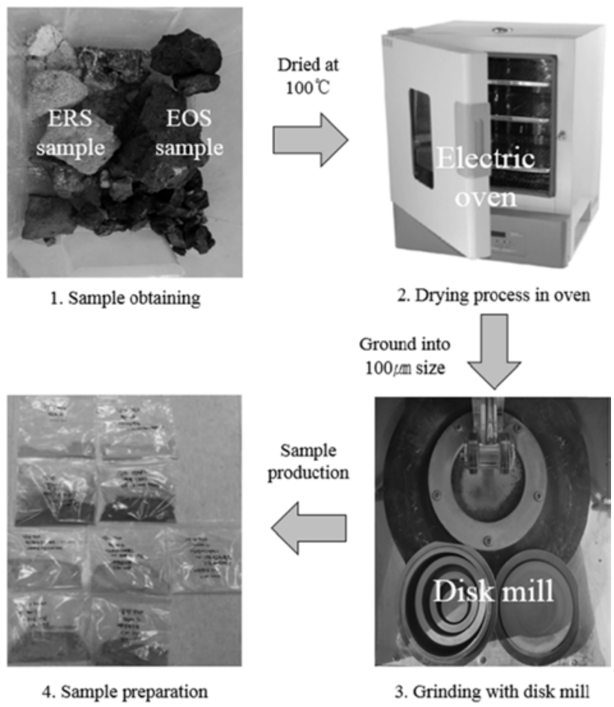

Fig. 1. Sample preparation process.

Sample preparation for EOS and ERS

Referred to KS F 2501 (standard test method for sampling aggregates) and KS F 2553 (standard practice for reducing samples of aggregate to testing size), EOS and ERS samples are obtained, and the process of sample preparation is shown in Fig. 1. The samples are dried at 100 °C for 1 hr for dried condition of surface and ground into 100μm size through disk mill. The samples are kept hermetically before Ethylene glycol evaluation.

Ethylene glycol method [22]

Table 3. Physical properties of EOS and ERS.

Company	A		B	
Slag type	EOS	ERS	EOS	ERS
Density (ton/m^3)	3.02	1.16	3.70	1.24
Water absorption (%)	2.00	1.65	1.30	1.64

Table 4. Chemical properties of EOS.

Content (%)	A		B	
	IN	OUT	IN	OUT
MgO	4.31	4.28	3.38	3.01
Al_2O_3	11.38	10.37	11.90	12.10
SiO_2	20.17	21.90	15.54	13.39
SO_3	0.28	0.21	0.24	0.18
CaO	27.74	20.72	26.06	26.07
MnO	5.92	8.22	6.02	5.96
Fe_2O_3	30.20	34.30	36.86	39.29
CaO/SiO_2 (Basicity)	1.38	0.95	1.68	1.95

Table 5. Chemical properties of ERS.

Content (%)	A		B	
	IN	OUT	IN	OUT
MgO	2.80	2.97	4.96	6.60
Al_2O_3	17.01	16.02	12.73	13.12
SiO_2	19.14	19.03	17.26	19.43
SO_3	0.75	0.51	1.39	1.32
CaO	59.07	60.10	53.09	48.51
MnO	0.14	0.14	1.48	1.61
Fe_2O_3	0.54	0.59	8.45	8.84
Etc.	0.55	0.64	0.64	0.57
CaO/SiO_2 (Basicity)	3.09	3.16	3.08	2.50

Etc.: K_2O, P_2O_3, Na_2O.

A 1 g sample is placed along with 50 mL of ethylene glycol in a 100 mL conical flask, which is placed in a water bath maintained at 60~80 °C for 20~40 min. It is important that the sample does not come in contact with moisture before extraction. Each treated sample is filtered using two layers of No. 5B filter bed through a Buchner funnel, and is washed thrice with 30 mL of ethylene glycol. The filtrate is then collected in an induction conical flask and titrated with N/10-HCl standard solution with 2 to 3 drops of Brome-cresol green solution added as the indicator. The terminal point is set when an N/10-HCl standard solution turns from blue to green. Using the amount of N/10-HCl standard solution consumed, the amount of free CaO can be calculated. Free CaO content can be measured as in Eq.(1).

$$FreeCaO = \frac{ml\ Hcl \times normlity\ of\ CaO}{10 \times sampleweight} \times 28 \quad (1)$$

Test Results and Discussion

Physical and chemical property evaluation for EOS and ERS

The physical properties evaluated for EOS and ERS from different companies are listed in Table 3, which shows that the density of EOS and ERS is within 3.02 ~ 3.70 ton/m^3 and 1.16 ~ 1.24 ton/m^3, respectively.

Through XRF (X-ray fluorescence) analysis, chemical properties of EOS and ERS are evaluated, and summarized in Table 4 and Table 5, respectively. In the Tables, "IN" means the sample obtained in 1.0 m inside from the stack and "OUT" mean samples from the surface exposed to air. The differences of density with the production companies are thought to be the amount of Fe_2O_3 in EOS. In the result of Basicity (CaO/SiO_2), all the results show satisfactory level below 2.0 suggested by KS and JIS standard.

As shown in Table 5 for ERS, the differences of chemical composition from companies are greater than those in EOS, but the trend with location shows consistency with little variation of components. It is noticeable that all the results of basicity are not satisfactory for KS and JIS standard (below 2.0).

Free CaO evaluation with Ethylene glycol

It is reported that the measurement result with ethylene glycol varies with temperature and duration period for free CaO content in cement [23]. In the work, 2 levels of solution temperature (60 °C and 80 °C) and 3 levels of duration period (20 min, 30 min, and 40 min.) are considered for free CaO measurement.

The results are shown in Fig. 2 for changing temperature and duration period. Free CaO increases linearly with measuring period regardless of temperature. In 60 °C condition, free CaO content increases from 0.17% for 20 min. to 0.25% for 40 min while it increases from 0.25% to 0.32% at 80 °C, where the result in 60 °C of temperature for 40 min. of duration period shows similar level in 80 °C of temperature for 20 min. With increasing temperature, the duration period can be shortened but measurement precision is affected. In the lower temperature (60 °C), linear increasing content with high determination coefficient ($R^2 = 0.9995$) is observed, but it decreases to 0.8691 in the higher temperature (80 °C) since the crystalized CaO is partially dissolved in the higher temperature. The test at higher temperature can obtain the larger free CaO, however the precision with duration period may decrease due to addition dissolved free CaO.

The results of ERS are plotted in Fig. 3 where the measured free CaO linearly increases with duration period as in EOS. In the lower temperature (60 °C), 1.05% is measured for 20 min and it increases to 1.19% for 40 min, while it increases to 1.30% in the higher temperature of 80 °C. In the lower temperature

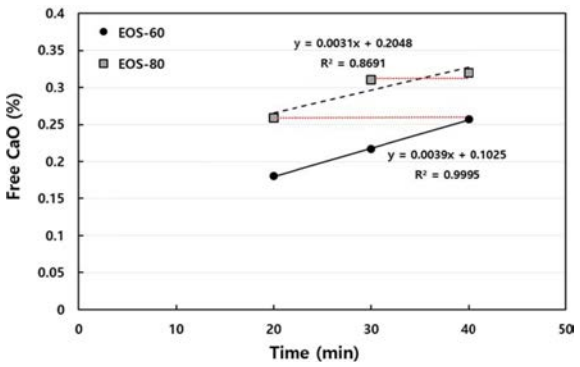

Fig. 2. Free CaO content of EOS with temperature and time.

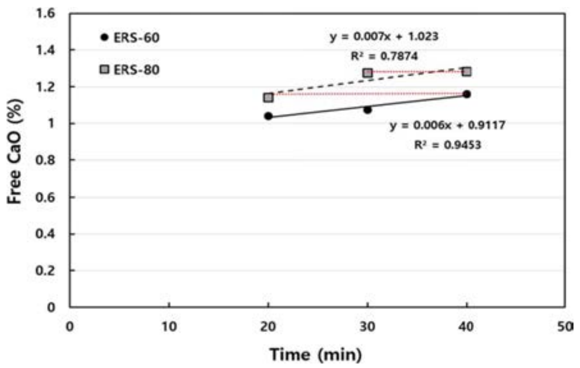

Fig. 3. Free CaO content of ERS with temperature and time.

Table 6. Free CaO with different site location.

Type	free CaO (%)			
	A company		B company	
	IN	OUT	IN	OUT
EOS	0.224	0.098	0.439	0.192
ERS	0.860	0.631	1.762	0.907

condition of 60 ℃, higher determination coefficient (0.9453) is observed, which is consistent with the results of EOS.

Free CaO measurement with site location and aging period

Free CaO content in EOS and ERS are measured considering exposure conditions-IN (1.0 m inside) and OUT (direct exposure to air). The results are listed in Table 6.

In EOS, small content of CaO is measured which shows 0.098 ~ 0.439% of content range, however relatively large content range (0.631 ~ 1.762%) is measured in ERS. The samples of OUT show much reduced contents with 26.6 ~ 48.5% of reduction ratio. The slag aggregate in outer location is exposed to abundant CO_2 and moisture, so that free CaO turns into chemically stable components.

It is interesting that not only site location but also grading of size affects the content of free CaO. The

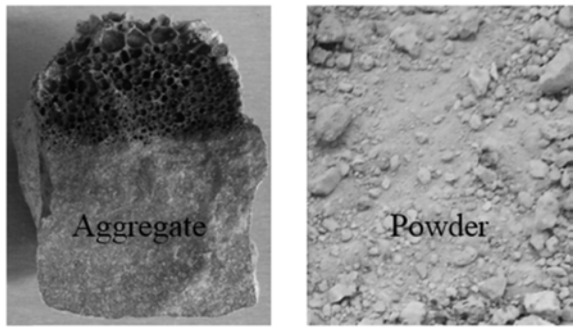

Fig. 4. Type of ERS.

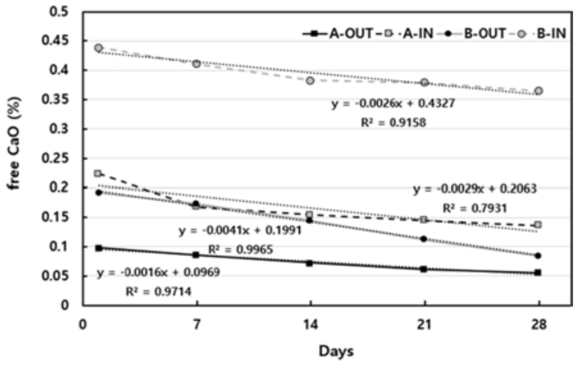

Fig. 5. Decreasing free CaO with aging in EOS.

Table 7. Free CaO with size and types of ERS.

Type		free CaO (%)	
		A	B
ERS	Powder	0.86	1.75
	Porous	0.69	1.25
	Solid	0.62	0.88

photos for ERS aggregate and powder are shown in Fig. 4. ERS is produced from electric arc in the form of relatively homogeneous powder and aggregate which has porous and solid parts at random, so that they have different chemical compositions and sizes.

Table 7 shows the free CaO content with the particle size of ERS. ERS powder shows similar level of free CaO as IN condition of ERS, and ERS solid part contains similar level as OUT condition of ERS. Solid part is relatively located in internal area of ERS stacks but shows high free CaO content. With aging stage, ERS slowly turns to powder type due to reaction of CaO, however cool water is usually sprayed for removing dust and rapid cooling. ERS exposed to water turns to water-granulated slag partially, which yields crystallization of ERS with reaction of water [24, 25].

Fig. 5 shows the results of free CaO in EOS with aging period, which shows linearly decreasing free CaO with increasing aging period. Free CaO content in EOS is less than 0.5% regardless of exposure location and production region. The reduction ratio is shown in

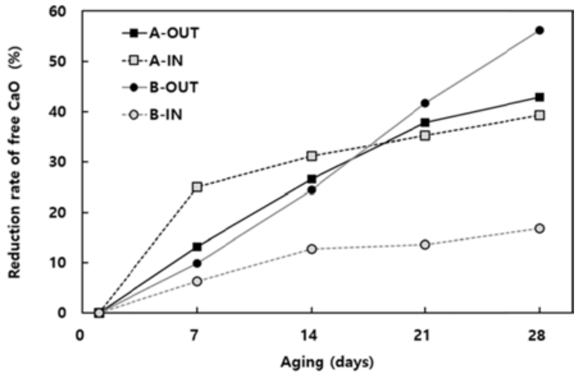

Fig. 6. Reduction ratio and content of free CaO in EOS.

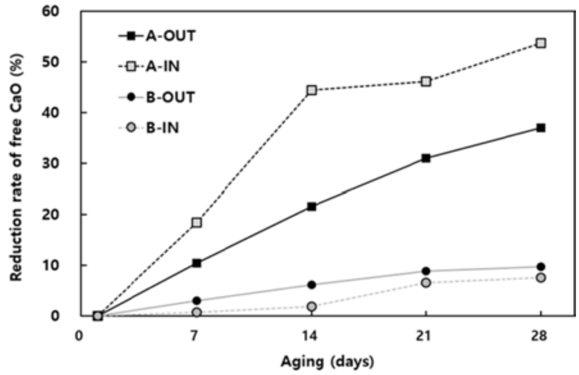

Fig. 8. Reduction ratio and content of free CaO in ERS.

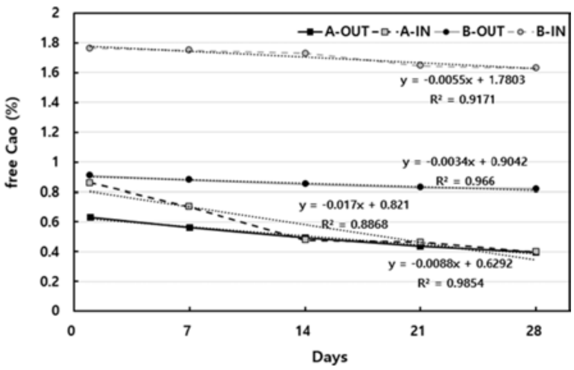

Fig. 7. Decreasing free CaO with aging in ERS.

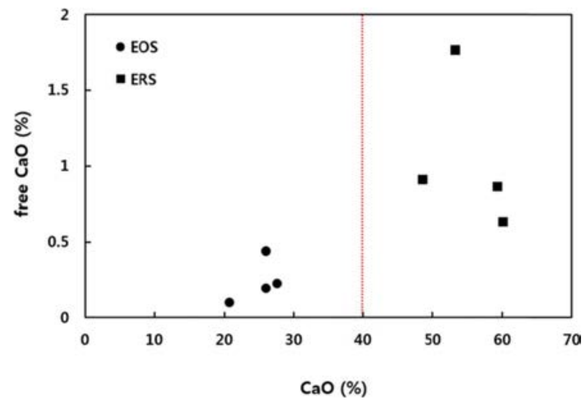

Fig. 9. Results of CaO(%) - free CaO(%) analysis of EOS and ERS.

Fig. 6. EOS in OUT condition has more free CaO which leads more clear reduction with aging.

Fig. 7 shows the changing free CaO in ERS with aging period. ERS which has abundant free CaO shows a big reduction with aging period and has big variations with production companies and site location with aging period. Free CaO in A company with 0.631% and 0.860% of initial free CaO decreases to 0.397% after 28 days aging. In B company, 0.907% and 1.762% of free CaO decreases to 0.818% and 1.628%, respectively. The reduction ratio of free CaO is shown in Fig. 8. In the results of A company, clear reduction of free CaO is observed with aging period but relatively small reduction is monitored in B company.

The crystallization velocity of free lime in steel slag is relatively slow compared with that of CaO. Free CaO is an amorphous material so that it may not change into crystallization significantly despite of extended aging period. Free CaO in ERS has different crystallization characteristics and depending on the influence of temperature during cooling. The reason for slow aging effect of ERS in B company is thought to be the difference of cooling temperature in the production region.

Free CaO and Basicity measurement in mixed EOS with ERS

In the section, EOS is partially replaced with ERS, and free CaO and basicity are measured. The results are listed in Table 8. In the Table, EOS9:ERS1 and EOS8:EOS2 mean the weight replacement ratio of ERS 10% and ERS 20%, respectively.

Table 8. Basicity and free CaO measurement in mixed EOS and ERS.

Sample	CaO/SiO_2	Free CaO
EOS	1.68	0.491
ERS	3.08	1.738
EOS9:ERS1	2.08	0.560
EOS8:ERS2	2.36	0.700

Free CaO in EOS shows 0.491% and it increases to 0.560 (10% replacement of ERS) and 0.70 (20% replacement of ERS) when mixed with ERS. Basicity of ERS is about 3.08 and it decreases to 2.08 and 2.36 in the same replacement conditions. The EOS mixed with ERS is evaluated to be unsatisfactory for KS and JIS Standard.

The ratios of free CaO to CaO in EOS and ERS are evaluated and the results are plotted in Fig.9. EOS shows reasonable results for CaO below 40% and free CaO below 0.5% in all the cases, however ERS shows CaO over 40% and free CaO over 0.5% with 1.8% of maximum content.

Conclusions

In the present work, the effects of temperature and aging period on free CaO measurement are evaluated with ethylene glycol method. The conclusions on quantitative evaluation of free CaO in electric arc furnace slag considering temperature and aging periods are as follows.

1. Through ethylene glycol method, free CaO in ERS which is a major parameter causing volume swelling is evaluated over 1.0%. In the condition of 60 ºC free CaO linearly increases with duration period with high determination coefficient (0.995). In the condition of 80 ºC, the linearity between free CaO and duration period decreases due to dissociation of crystalized CaO.

2. In the powder type of ERS, free CaO content is within the level of 0.86 ~ 1.75%. With extension of aging period, a clear reduction of free CaO content is evaluated. For 4 weeks of aging, ERS inside stack shows more reduction in free CaO due to abundant free CaO content but EOS shows more reduction in outside condition. For free CaO reduction, exposure condition is important for effective aging. Free CaO is an amorphous material and its crystallization characteristics are affected by temperature when it is cooled.

3. Basicity (CaO/SiO_2) and CaO in EOS show good level below 2.0 and 40.0%, respectively. They are all acceptable to the related Standards like KS and JIS, but the mixed EOS with 10 ~ 20% replaced with ERS shows unsatisfactory to the critical level. EOS application to construction material is expected with separating ERS form mixed slag aggregates.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (No.2015R1A5A 1037548)

References

1. N. Faraone, G. Tonello, E. Furlani, S. Maschio, Chemosphere 77 (2009) 1152-1156.
2. H. Qasrawi, F. Shalabi, I. Asi, (2009) Use of low CaO unprocessed steel slag in concrete as fine aggregate. Constr. Build. Mater. 23, 1118-1125.
3. I. Arribas, A. Santamaria, E. Ruiz, V. Ortega-Lopez, J.M. Manso, Constr. Build. Mater. 90 (2015) 68-79.
4. H.W. Song, S.J. Kwon, Cem. Concr. Res. 39 (2009) 814-824.
5. S.W. Yoo, S.J. Kwon, Constr. Buil. Mater. 115 (2016) 247-255.
6. T. Sturm, R. Milacic, S. Murko, M. Vahcic, A. Mladenovic, J.S. Suput, J. Scancar, J. Hazad. Mater. 166 (2009) 277-283.
7. S.L. Correia, F.L. Souza, G. Dienstmann, A.M. Segadaes, Waste Manage. 29 (2009) 2886-2891.
8. W.T. Kuo, C.Y. Shu, Constr. Build. Mater. 50 (2014) 463-470.
9. W.T. Kuo, C.Y. Shu, Constr. Build. Mater. 94 (2015) 488-493.
10. H. Motz, J. Geiseler, Waste. Manage. 21 (2001) 285-293.
11. G. Salihoglu, V. Pinarli, J. Hazad. Mater. 153 (2008) 1110-1116.
12. G. Wang, Constr. Build. Mater. 24 (2010) 1961-1966.
13. A. Rastovčan-Mioč, T. Sofilic, B. Mioč, “MATRIB 2009”, (Croatian Society for Materials and Tribology, Vela Luka Island, Croatia, 2009) p. 436-444.
14. Ministy of environment of Korea No. 2014-193, Recycling guideline of company emitting steel slag and coal ash.
15. H.S. Lee, H.S. Lim, M.A. Ismail, Constr. Build. Mater. 131 (2017) 676-681.
16. A.S. Brand, J.R. Roesler, Cem. Concr. Compos. 60 (2015) 1-9.
17. G. Wang, Y. Wang, Z. Gao, J. Hazad. Mater. 184 (2010) 555-560.
18. G. Adegoloye, A.L. Beaucour, S. Ortola, A. Noumoumowe, Constr. Build. Mater. 76 (2015) 313-321.
19. F. Faleschini, M.A. Fernandez Ruiz, M.A. Zanini, K. Brunelli, C. Pellegrino, E. Hernandez Montes, Constr. Build. Mater. 101 (2015) 113-121.
20. N.H. Roslan, M. Ismail, Z.A. Majid, S. Ghoreishiamiri, B. Muhammad, B. Constr. Build. Mater. 104 (2016) 16-24.
21. Y.N. Sheen, D.H. Le, T.H. Sun, Constr. Build. Mater. 101 (2015) 268-276.
22. M.P. Javellana, I. Jawed, Cem. Concr. Res. 12 (1982) 399-403.
23. D. Chalasani, F.K. Cartlendge, H.C. Eaton, M.E. Tittlebau, M.B. Walsh, J. Hazad. Mater. 3 (1986) 167-173.
24. J.M. Kim, S.M. Choi, J.H. Kim, Journal of Korean Recycled Construction Resources Institute. 7 (2012) 70-77.
25. J.S. Choi, P.S. Jang, Y.J. Cho, Journal of the Korea Academia-Industrial Cooperation Society. 15 (2014) 6890-6897.