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Characterization of ecocement pastes and mortars produced from incinerated ashes

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Abstract

In this study, the microstructure and the hydration characteristics of the pastes using ecocement, which is a new type of hydraulic cement, produced with incinerator ashes, limestone and clay was investigated. In addition, the beneficial effect of granulated blast-furnace slag on this new type of cement was also investigated in comparison to ordinary portland cement (OPC). Several tests including AC impedance spectroscopy, mercury intrusion porosimetry, X-ray diffraction (XRD) analysis and differential scanning calorimetry (DSC) were used for the study. The results of the various tests were discussed in a complementary manner; in particular, the results of the AC impedance were discussed in conjunction with that of the mercury intrusion porosimetry in order to gain insight into the interpretation of impedance spectrum plots in a physical manner. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ecocement; Granulated blast-furnace slag; Microstructure; AC impedance; Mercury porosimetry

1. Introduction

Ecocement is a type of hydraulic cement produced from the incinerator ashes. The New Energy and Industrial Technology Development Organization (NEDO) of Japan developed the technology for its manufacture [1]. This new cement is designed to use municipal waste incinerator ashes in amounts up to 50% of the raw materials. The manufacturing process of ecocement [2] is almost the same as ordinary portland cement (OPC). The first type of ecocement produced is designed to take advantage of chlorides in the incinerator ashes to make rapid-hardening cement. During the sintering process, chloride combines with calcium aluminate to form calcium chloroaluminate ($C_{11}A_7{\cdot}CaCl_2$) in place of tri-calcium aluminate (C_3A) [2]. The performance of this type of ecocement is similar to the rapid hardening cement, which develops that performance because of $C_{11}A_7{\cdot}CaF_2$. This type of ecocement, however, contains relatively large amounts of chlorides. Table 1 shows the chemical compositions of ecocement in comparison to OPC, while Fig. 1 shows the X-ray diffraction (XRD) pattern of ecocement. As seen in the table, the essential difference between ecocement and OPC is that the former contains more sulfate, aluminate and chloride than the latter. Ecocement contains 20% of $C_{11}A_7{\cdot}CaCl_2$ in place of C_3A. The other components, C_3S, C_2S, C_4AF are also present in OPC. The XRD pattern of ecocement shows its resemblance to OPC. In the hydration of ecocement, the $C_{11}A_7{\cdot}CaCl_2$ reacts with water to form ettringite and small amount of Friedel's salt [2]. The C_3S and C_2S react to form calcium-silicate hydrates (C-S-H) in a similar manner to OPC. The hydration of the aluminate phase in ecocement is expected to favour the formation of ettringite and Friedel's salt as opposed to monosulfo-aluminate. This reaction is expected to bind some of the chloride present in ecocement, however, free chloride would remain in the pore solution to cause corrosion of steel reinforcement when applied in reinforced concrete structures. In this study, the beneficial effect of blending ground granulated blast-furnace slag with ecocement is investigated,

Table 1
Chemical compositions of ecocement, OPC and slag used for the study

Cement type	Ig. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl
ECO	0.5	15.7	10.4	2.2	59	1.7	8.1	0.6	0	0.6
OPC	1.6	21.7	5.3	2.9	63.7	1.2	2.1	0.33	0.54	0
SLAG	1.6	32.2	13.3	0.7	42.3	6.5	2.0	–	–	–

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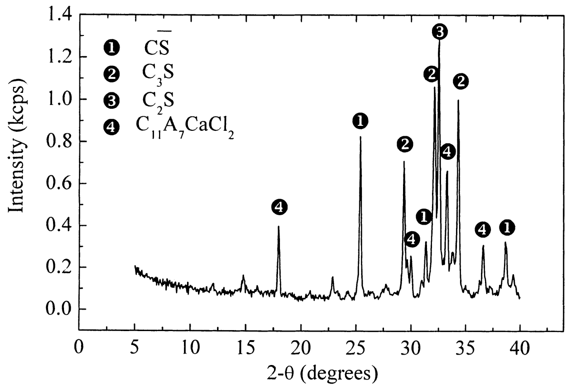

Fig. 1. XRD pattern of ecocement.

in particular, microstructure improvement and chloride binding ability of the slag [3]. XRD, differential scanning calorimetry (DSC) and AC impedance measurements were used to characterize the microstructure and also to determine the hydration products of ecocement or ecocement–slag pastes in comparison to OPC pastes.

2. Experimental

2.1. Materials

The materials used for the experiment are ecocement, OPC, ground granulated blast-furnace slag and standard sand.

2.2. Mortar mixture proportions

Ecocement and OPC were used to prepare cement pastes with water to cement ratios of 0.45 and 0.55. Slag replacement percentages of 30%, 50% and 70% were also used to prepare cement pastes with similar water to binder ratios. Mortar specimens with cement/sand ratio of 1:2 were also prepared at the same water to cement ratios and slag replacement ratios as the cement pastes.

Cylindrical mortar and paste specimens of 50 mm in diameter and 100 mm in height were produced with both types of cement. Both the mortar and paste specimens were then cured in a saturated calcium hydroxide solution. The cement paste specimens were used for the AC impedance measurements while the mortar specimens were used for the compressive strength measurements. In the AC impedance measurements, cylindrical specimens of the pastes with dimensions 50 mm in diameter and 50 mm in length were placed between two parallel copper plate electrodes, in effect, forming a geometrical capacitance. An AC signal of amplitude 10 mV was applied to the electrodes and scanned over a frequency range of 5 mHz to 100 kHz and the data acquired by means of a computer. Measurements were taken at 1 day, 7 days, 91 days and 1 year of curing in saturated calcium hydroxide solution. Measurements of all specimens were taken in the saturated condition. The MIP test was also conducted on the 28-day and 2-year cured specimens while XRD, SEM and DSC were conducted on 7-day, 28-day, 91-day and 2-year cured specimens. Compressive strength and electrical resistivity of the mortar specimens were measured at 7, 28 and 91 days of curing in the saturated calcium hydroxide solution.

3. Results and discussion

3.1. Pore size distributions

Fig. 2 shows the pore size distributions of OPC and ecocement pastes, respectively. The figure shows that in

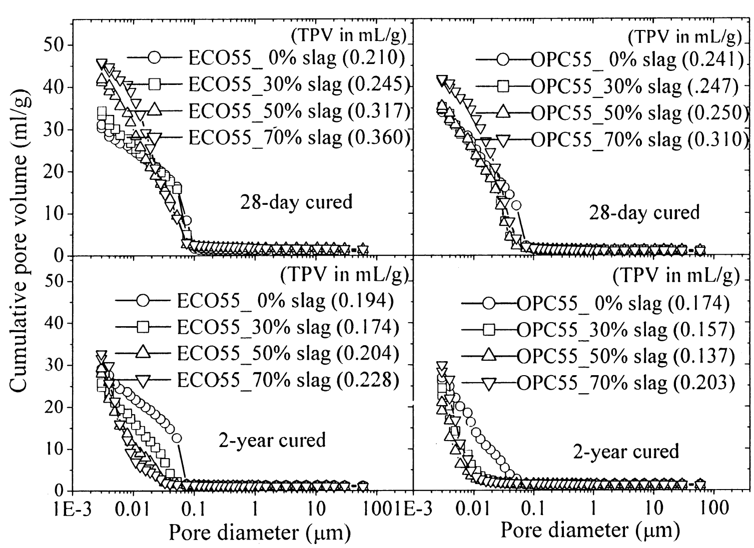

Fig. 2. Cumulative pore volumes of ecocement–slag and OPC–slag pastes at the curing periods of 28 days and 2 years.

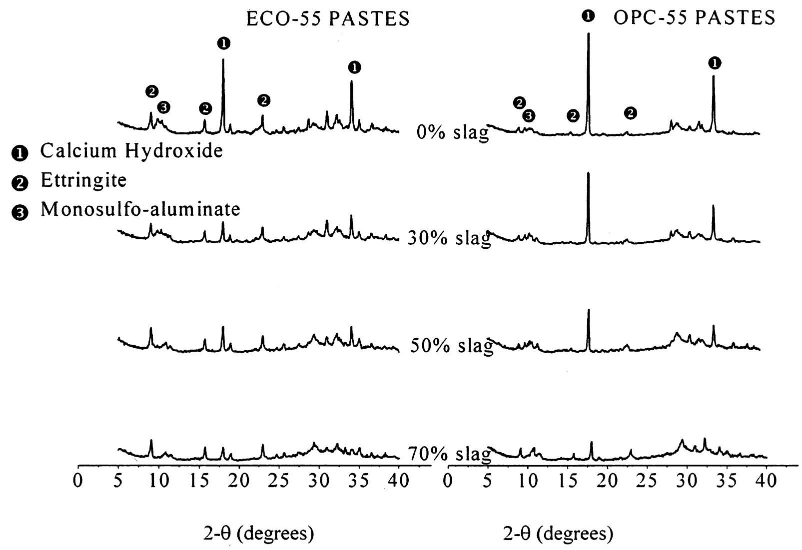

Fig. 3. XRD diagrams of ecocement–slag and OPC–slag pastes at the curing period of 28 days.

both cements, slag replacement results in a pore refinement, the coarse pores in the control specimen being replaced by fine pores in the slag-blended specimens especially at late age of hydration. The total pore volume, however, increases with slag replacement ratio. It is also seen that, at the curing age of 28 days, there is slight difference between the pore size distributions of OPC and ecocement pastes, however at the curing period of 2 years, the pore size distribution of ecocement pastes is significantly coarser than the corresponding OPC specimens. Comparison of the 28-day and 2-year pore size distribution curves indicate that the pore diameter at which the cumulative pore volume shows a sudden transition, decreases from 0.1 to 0.03 μm in the ecocement–slag specimens and from 0.04 to 0.01 μm in the case of the OPC–slag specimens.

The beneficial effect of slag with respect to pore refinement at advanced ages of hydration is clearly manifested in both OPC and ecocement specimens as shown in the figure. In both cases, the pore diameter at which there is a sudden transition in pore volume is smaller in the OPC specimens in comparison to corresponding ecocement specimens.

3.2. Hydrated products and microstructure

Fig. 3 shows the powder XRD patterns while Fig. 4 shows the DSC results of ecocement–slag and OPC–slag pastes. Fig. 3 depicts that there are more peaks in the XRD diagrams of the pastes of ecocement–slag than that of OPC–slag.

The analysis of the XRD diagrams indicates the presence of the following hydration products in both ecocement and OPC pastes: calcium hydroxide, ettringite and monosulfo-aluminate hydrate. The presence of Friedel's salt in ecocement pastes was not resolved by the XRD analysis, however, the DSC analysis indicates its presence as a weak peak around 300°C. In addition, the presence of C-S-H gel in both ecocement and OPC pastes were resolved by the DSC analysis, but not in the XRD analysis because of its low crystallinity. Both the XRD and DSC results indicate that the amount of calcium hydroxide formed in the OPC pastes are more than that in corresponding ecocement pastes. In both cases, the amount of calcium hydroxide decreases with the slag replacement ratio. Fig. 4 also shows that the quantity of ettringite formed in ecocement paste, which is equivalent to the area under the endothermic peak at about 115°C, is more than in OPC paste. In fact, the peaks of ettringite are clearly seen in the XRD curves of ecocement pastes but almost absent in that of OPC. This is to be expected since ecocement contains more aluminate and sulfate phases that favour the formation of ettringite.

3.3. AC impedance spectrum

Fig. 5 shows the impedance plane plots while Fig. 6 shows the bulk arc diameter (Rp) vs. curing period of both

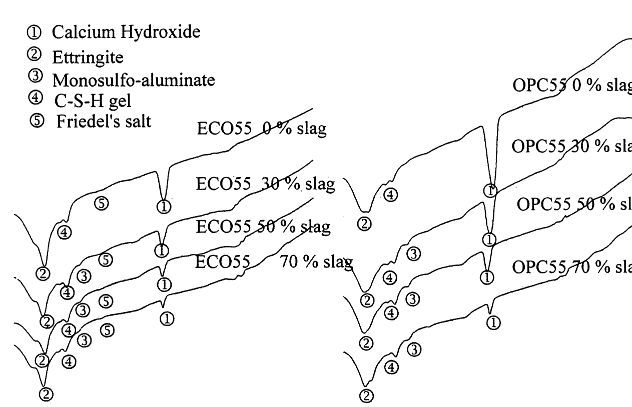

Fig. 4. DSC curves of ecocement–slag and OPC–slag pastes at the curing periods of 28 days.

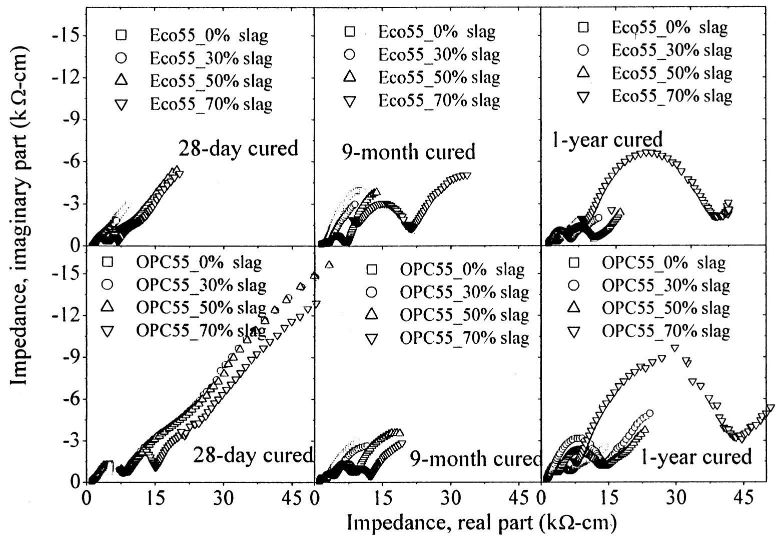

Fig. 5. Impedance spectrums plot for ecocement–slag and OPC–slag pastes at various periods.

ecocement–slag and OPC–slag pastes. The equipment used for the measurement has a frequency range from 1 mHz to 100 kHz and as such, the bulk arc, which appears in the megahertz range in young pastes, was not observed during the early ages of curing. However, at 9 months and above of curing, the bulk arc was observed within the measured frequency range. The figure shows that the diameter of the bulk arc of both ecocement–slag and OPC–slag pastes increases with curing age and slag replacement ratio. In cement systems, the bulk arc diameter, Rp, has an inverse relationship with the product of the porosity, the mean pore size and also the ionic concentration in the pore solution [4,5]. Large porosity, large pore size and increasing ionic concentration result in a bulk arc with a very small diameter. That is, for pastes with similar ionic concentrations, small diameter bulk arc is an indication of high porosity while a large diameter bulk arc indicates low porosity. As shown in Fig. 6, the diameter of the bulk arc of both cement pastes increases with curing age. This result is in agreement with the basic property of cement systems that microstructure improves with curing age.

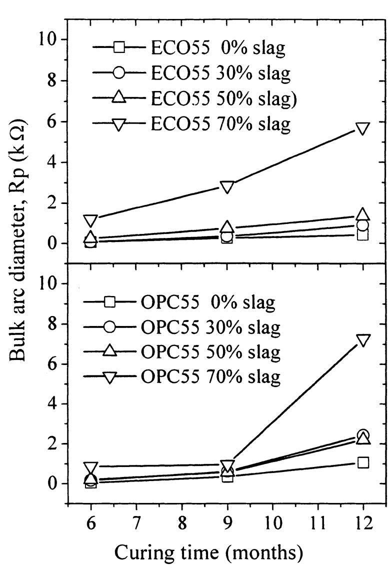

Fig. 6. Bulk arc diameter vs.curing period for ecocement–slag and OPC–slag pastes.

The results of the AC impedance measurements are in agreement with that of the MIP. The nondestructive nature of the AC impedance measurement, makes it the most suitable method for microstructure characterization of cement systems in comparison to the MIP test, however, the main difficulty is the lack of an effective method for quantitative analysis of the results. A lot of work has been done in this regard by many researchers employing equivalent circuit models [6–8] and computer simulation methods [9,10], however, an acceptable method that could be standardized has not yet emerged.

3.4. Compressive strength

Fig. 7 shows the compressive strengths of ecocement and OPC mortars. The graphs show that for the control specimens, the rate of strength development during the initial 28 days was faster in the ecocement mortar than the OPC mortar. However, at 91 days of curing, the compressive strength of the OPC mortar was higher than that of the ecocement mortar. For the slag-blended mortars, the compressive strength of the ecocement specimens are lower than that of the control specimen while that of OPC are higher than that of the control specimen. In addition, in all the slag-blended mortars, the OPC specimens were higher in compressive strength than the corresponding ecocement specimens. The possible explanation may be partly due to the fact that, in a hydrating ecocement, the amount of calcium hydroxide available for a pozzolanic reaction with the slag is lower in comparison to OPC. In addition, the rate of the

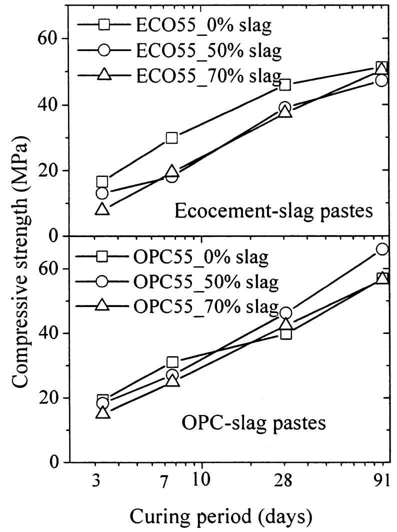

Fig. 7. Compressive strength vs. curing period for ecocement–slag and OPC–slag mortars.

pozzolanic reaction may be slower in comparison to OPC–slag system. Thus, the extent of beneficial effect, when ecocement is blended with slag, is less compared to OPC.

3.5. Relation between compressive strength and electrical resistivity

Fig. 8 shows the relationship between the compressive strength and the electrical resistivity of both ecocement–slag and OPC–slag mortars. The figure indicates a positive correlation between the compressive strength and electrical resistivity in both cements [4]. The coefficient of regression is above 0.9 in all cases. The percentage of slag replacement affects the parameters of the relation, which is in the form $Y = A + BX$ (Y = compressive strength in MPa; X = electrical

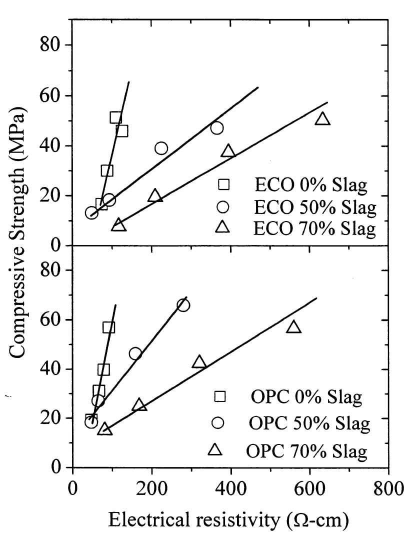

Fig. 8. Compressive strength vs. electrical resistivity for ecocement–slag and OPC–slag mortars.

Table 2
Parameters of the empirical relationship between compressive strength and electrical resistivity of ecocement–slag and OPC–slag pastes

	A			B		
Slag	0%	50%	70%	0%	50%	70%
Ecocement	− 26.1	8.86	1.21	0.62	0.11	0.08
OPC	− 21.73	12.31	10.26	0.83	0.20	0.09

resistivity in Ω cm). Parameters A and B for corresponding ecocement–slag and OPC–slag mortars are, however, comparable, as shown in Table 2. This result cautions that while in general, compressive strength is proportional to electrical resistivity, the rate of change of compressive strength with electrical resistivity (parameter B) depends on the chemistry of the constituents in a particular mix. Thus, while the addition of slag to cement results in a significant increase in electrical resistivity, the compressive strength does not necessarily increase in a corresponding manner as indicated in Fig. 7. The same could also be inferred about the increase in the bulk arc diameter with slag replacement ratio as shown in the impedance plane plots in Fig. 5.

In this case, while the diameter of the bulk arc increases with slag replacement ratio, the ionic concentration of the pore solution decreases with slag replacement ratio and since it is the product of these two quantities that has an inverse relation with porosity, it is difficult to make any inference from the results of the impedance spectrums alone.

4. Conclusions

The following conclusions could be drawn from the study:

1. Ecocement is comparable to OPC in its hydration characteristics.
2. The compressive strength of ecocement–slag mortars is less than corresponding OPC mortars but meets the strength requirement specified by many standards organizations.
3. Blending ecocement with ground granulated blast-furnace slag improves the microstructure of the resulting mortar in a similar manner to OPC.
   (i) The higher the slag replacement ratio, the better the improvement.
   (ii) The extent of microstructure improvement in ecocement–slag paste is less than that of corresponding OPC pastes.
4. AC impedance method is useful for characterizing the microstructure of the cement pastes.

It should be mentioned that, presently, another type of ecocement with characteristics very close to OPC has been manufactured. In the production of this second type of ecocement, chlorides vaporize in the sintering process, mostly by combining with alkalis; thus, chloride ion content is reduced to below 0.1%. Similar studies on this cement are ongoing.

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