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Portland cement clinker, granulated slag and by-pass cement dust composites

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Abstract

Three blends of slag cement were prepared, namely 70/30, 50/50 and 30/70 mass% of Portland cement clinker and granulated slag, respectively. Each blend was mixed with 2.5, 5.0, 7.5 and 10.0 mass% by-pass cement dust. The physical properties of cement pastes were studied, including setting times, electrical conductivity and fluidity. The results indicated that the rheological properties of Portland cement clinker were enhanced by partial replacement by granulated slag. By-pass cement dust affects the rheological properties of Portland cement clinker/granulated slag composites and depends on its amount as well as mix composition. The increase in the amount of by-pass cement dust increases the required water of normal consistency. The setting time of Portland slag cement paste was extended with the increase in slag content. The addition of 2.5 mass% by-pass cement dust to M.1 (70 mass% Portland cement clinker/30 mass% granulated slag) and M.2 (50 mass% Portland cement clinker/50 mass% granulated slag) retards the initial and final setting time, whereas it accelerates the final setting time of M.3 (30 mass% Portland cement clinker/70 mass% granulated slag). The presence of by-pass cement dust affects the location and height of the conductivity peaks. By increasing the by-pass cement dust from 2.5 to 7.5 mass%, the conductivity maximum increases. With further addition (10.0 mass%), the height of the conductivity maximum decreases.

Keywords: Fluidity; Setting time; Electrical conductivity; By-pass cement dust; Slag

1. Introduction

The utilization of by-products from various sectors of industry is a present-day concern involving the problem of energy and pollution. Cement plants generate solid waste air pollutants during the course of their operation. The by-pass cement dust is produced as a solid waste during the manufacture of Portland cement clinker by using the dry process as a result of the presence of some volatile constitutes in the kiln feed. Most by-pass cement dust have no significant value, in addition to its pollution problems. In Egypt, the raw materials contain high values of alkalis and sulphates; therefore, the accumulation by-pass is high, while the use of these by-products utilizes a product that would ordinarily be bound for the landfill. Thus, there is an environmental benefit from using by-products. The techno-economical problems that arise for the semimanufacture of raw materials, energy consumption and transportation of dust from the plant to outside, as well as the severe pollution to the surrounding atmosphere, show the necessity of utilizing by-pass dust as one of the main objectives of this investigation.

The mineralogical constituents of by-pass dust were identified in an earlier study [1]. The utilization of by-pass cement dust in blended cements was investigated [2,3]. Compressive strength, slump and initial setting time were investigated. The amounts of sulphates, volatiles, free CaO and $CaCO_3$ affected the properties of the blends. The addition of by-pass cement dust to either Portland and slag cements adversely affects the physico-mechanical properties of cement pastes [4]. The magnitude of these effects is generally proportional to the amounts of substituted dust. The amount of added cement dust must not exceed 10% of the cement content [5].

Ground granulated blast furnace slag without an activator does not react with water at room temperature. The hydraulic activity of slag depends on its chemical composi-

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tion, glass content, particle size distribution and surface morphology [6,7]. Mehta [8] reported that a coating film of aluminosilicate forms on the surface of slag grains within a few minutes of exposure to water, which inhibits further hydration. The rate of hydration is very slow, but it increases in alkaline media. Portland cement clinker or liberated lime is normally used to provide this alkalinity [9]. In the presence of lime, reaction occurs, removing the acidic film, and hydration is continued as the lime breaks the silica film on the slag grains. The hydration products usually detected in the granulated slag–lime mixtures are calcium silicate hydrates and calcium aluminate hydrates with varying compositions, in addition to hydrogarnet [9,10]. During subsequent hydration of the slag cement, there is a consumption of calcium hydroxide liberated from the hydration of Portland cement clinker and residual alkalis incorporated in the slag [11].

Extensive work has covered many aspects regarding the activation of blast furnace slag or supersulphated cements by cement dust [12,13], or waste sulphated ash [14]. Activation of slag in supersulphated cement carried out by various forms of calcium sulphate, phosphogypsum and/or fluorogypsum [9,15].

The by-pass cement dust needs high values of mixing water, therefore, the rheological properties are important for this system and give an idea on the initial hydration. The aim of the present work is to study the rheological properties, initial and final setting times and electrical conductivity to monitor the progress of the hydration of Portland cement clinker, granulated slag and by-pass cement dust composites.

2. Experimental techniques

2.1. Materials

The materials used in this investigation were Portland cement clinker, granulated slag and by-pass cement dust provided by Helwan Cement, Helwan, Egypt. The chemical composition of these raw materials is given in Table 1. Fig. 1 shows the XRD pattern of by-pass cement dust. The mix proportions are shown in Table 2. Each blend was mixed for 1 h with 2.5, 5.0, 7.5 and 10.0 mass% by-pass cement dust using a porcelain ball mill. The required water of normal consistency and setting times were determined according to ASTM specification [16,17].

Table 1
Chemical composition of starting materials (wt.%)

Oxide (%)	Portland cement clinker	Granulated slag	By-pass cement dust
SiO_2	21.26	37.30	13.37
Al_2O_3	5.53	13.50	3.36
Fe_2O_3	3.60	0.85	2.29
CaO	64.70	38.60	42.99
MgO	1.25	3.00	1.90
SO_3	0.75	–	5.10
LOI	0.52	–	15.96
Cl^-	0.0068	0.0071	7.50
Na_2O	0.4873	0.120	3.320
K_2O	0.0846	0.011	2.29
Free lime	0.75	–	2.59
Surface area (cm^2/g)	3300	3200	3700

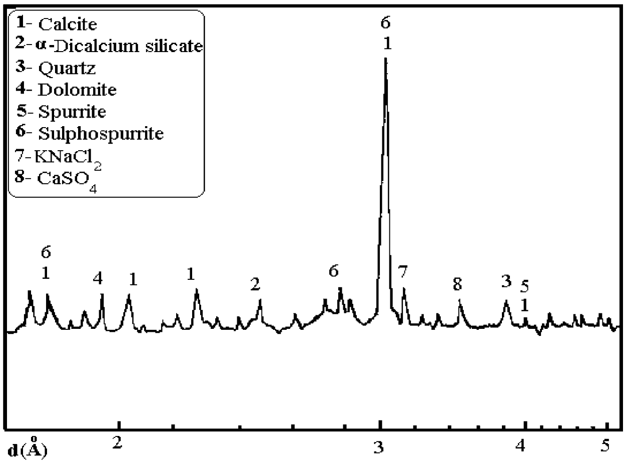

Fig. 1. XRD pattern of by-pass cement dust.

2.2. The shear stress and the torque viscosity

The shear stress (Pa) and the torque viscosity (Pa s) were determined at different shear rates (s^{-1}). The pastes were prepared by mixing exactly 50 g with constant water/cement ratio (0.35); 17 ml of the obtained paste was transported to the cell of rotating coaxial cylinder viscometer Rheotest 2.1 (manufactured by MLW Germany) (Fig. 2). A measurement cycle required 15 min at 27 °C. The measurement of the rheological properties was made after 6.5 min of mixing [18]. The mixing was done in a mechanical mixer for 3 min by agitation at about 100–120 rpm, followed by 1 min rest and another 1 min by the previous speed. Two successful cycles were done; the presentation was done only for the second cycle.

2.3. Electrical conductivity measurements

In electrical conductivity measurements, the test cell was of the coaxial cell type and included concentric inner and

Table 2
The mix proportions

	Portland cement clinker	Granulated blast furnace slag
M.1	70	30
M.2	50	50
M.3	30	30

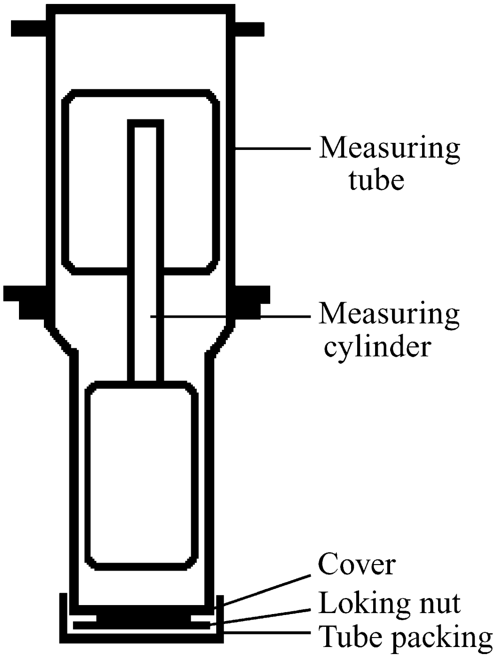

Fig. 2. Rheotest 2.1 cell.

outer electrodes mounted on an insulated base plate; the electrodes were polished before the experiment (Fig. 3). The mixing was done with the required water of normal consistency (constant workability). Measurements of electrical conductivity were begun exactly 2 min after mixing with water (0 time). The cement pastes were placed in the space between the electrodes, and then the cell was kept at 100% (RH), 27 °C during the test period from 2 min up to 24 h. The electrodes were connected with RLC meters, model SR 720, 1 V and 1000 Hz for resistance measurements.

3. Results and discussion

3.1. Rheological properties

The shear rate is one of the important variables affecting the rheological properties of fresh cement pastes. It was suggested that high shear mixing breaks down the cement agglomerates, many of which are formed prior to the addition of water. The increase in shear rate reduces the viscosity of cement slurries.

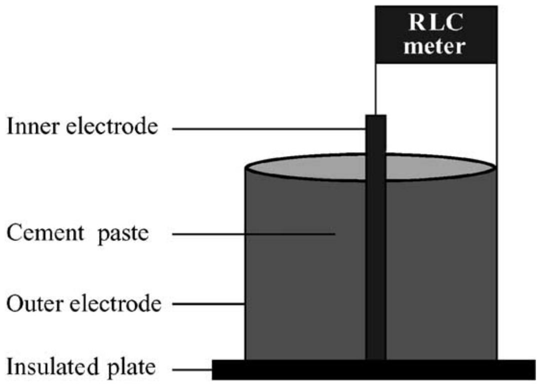

Fig. 3. Electrical conductivity cell.

Fig. 4 shows the effect of by-pass cement dust on shear stress of M.1. It is clear that the addition of by-pass cement dust up to10 mass% decreases the shear stress with the shear rate of all blends. The hydraulic properties of by-pass cement dust are less than Portland cement clinker and granulated slag. Hence, the by-pass cement dust acts as a retarder. At low shear rate (3 s^{-1}), the obtained shear stresses were 62.9, 48.6, 37.2, 25.7 and 20.0 Pa for 0.0, 2.5, 5.0, 7.5 and 10.0 mass% by-pass cement dust, respectively.

Fig. 5 shows the effect of by-pass cement dust on the torque viscosity. Torque viscosity decreases as the shear rate increases till it reaches a constant value. The torque viscosities at low shear rate (3 s^{-1}) were 20.97, 16.2, 12.4, 8.57 and 6.67 Pa s, whereas at maximum shear rate (146.8 s^{-1}), they were 1.73, 1.67, 1.57, 1.5 and 1.23 Pa s for 0.0, 2.5, 5.0, 7.5 and 10.0 mass% by-pass cement dust, respectively.

The shear stress as a function of shear rate of M.2 is shown in Fig. 6. The shear stress increases up to 2.5 mass% by-pass cement dust, this may be due to the fact that by-pass cement dust activates granulated slag to form more hydration products that increase the shear stress. The increase in the amount of by-pass cement dust from 5.0 to 10.0 mass% decreases the shear stress. The maximum shear stresses were 146.8, 248.8, 254.5, 251.7 and 160.2 at 0.0, 2.5, 5.0, 7.5 and 10.0 mass% by-pass cement dust, respectively. The torque viscosity as a function of the shear rate of M.2 is given in Fig. 7. It is clear that the torque viscosity decrea-

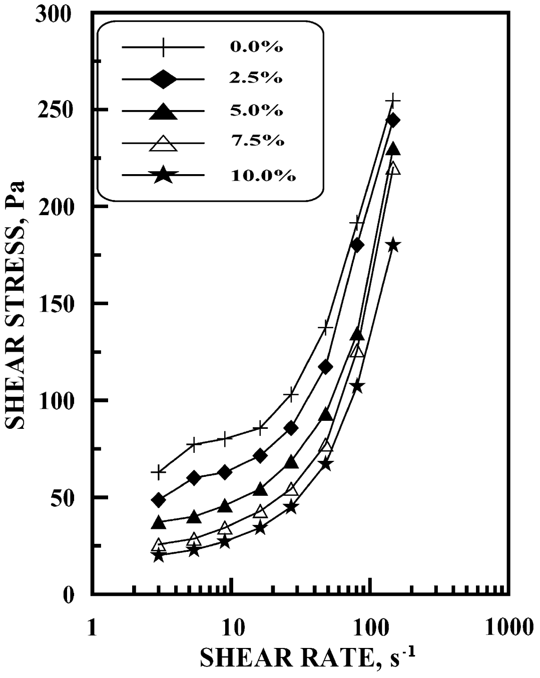

Fig. 4. Shear stress–shear rate relationship of M.1.

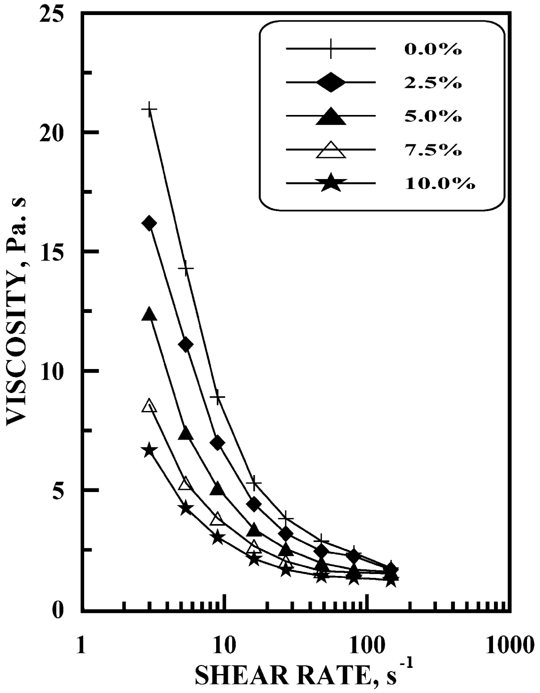

Fig. 5. Viscosity–shear rate relationship of M.1.

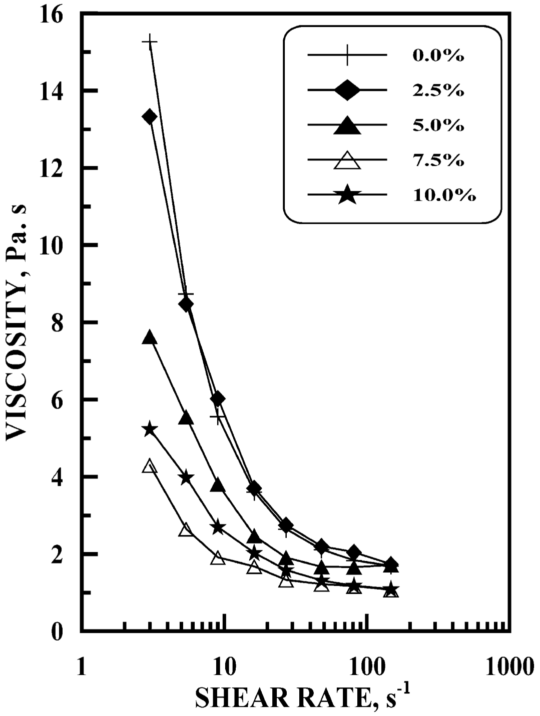

Fig. 7. Viscosity–shear rate relationship of M.2.

ses with the addition of by-pass cement dust, whereas 2.5 mass% of by-pass cement dust increases the shear stress with different shear rates (14–146.8 s^{-1}).

Fig. 8 represents the shear stress as a function of shear rate of M.3. With the addition of 2.5 mass% by-pass cement dust, the shear stress rate increases; with the increase in the amount of by-pass cement dust up to 5.0%, the shear stress decreases then increases up to 7.5–10.0 mass%. This may be due to the activation of higher content of slag (70 mass%) with by-pass cement dust. The shear stresses were 165.9, 154.4, 131.6, 128.7 and 134.4 Pa.

Fig. 9 illustrates the effect of by-pass cement dust on torque viscosity of M.3. The data show that the torque viscosity of 2.5% by-pass cement dust gives higher values

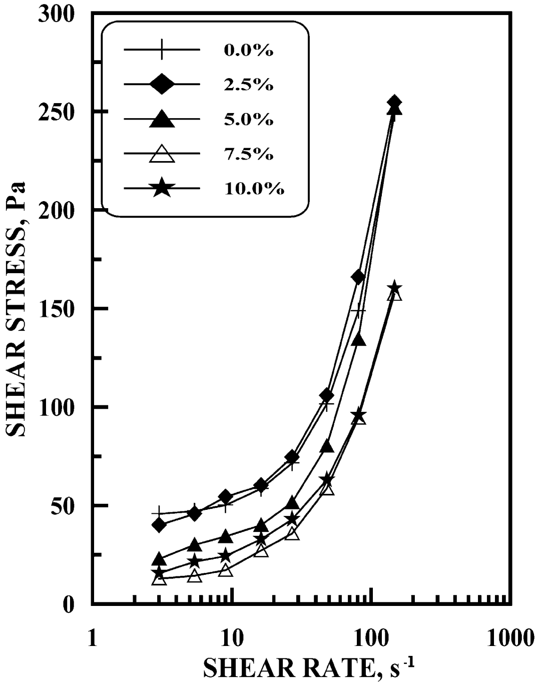

Fig. 6. Shear stress–shear rate of M.2.

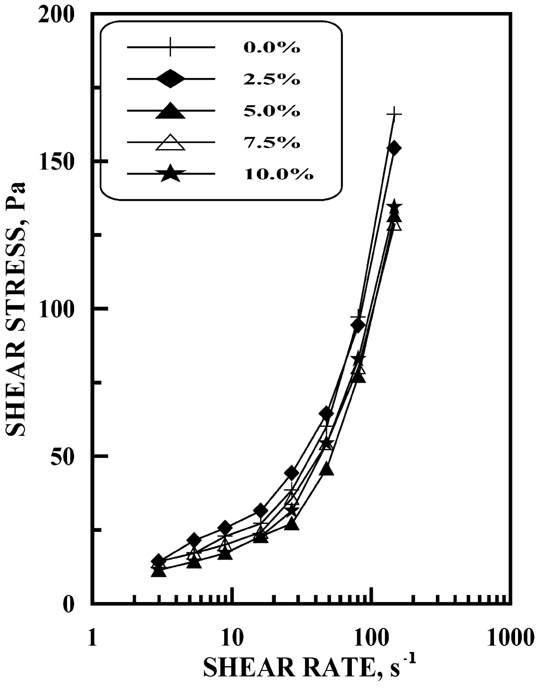

Fig. 8. Shear stress–shear rate relationship of M.3.

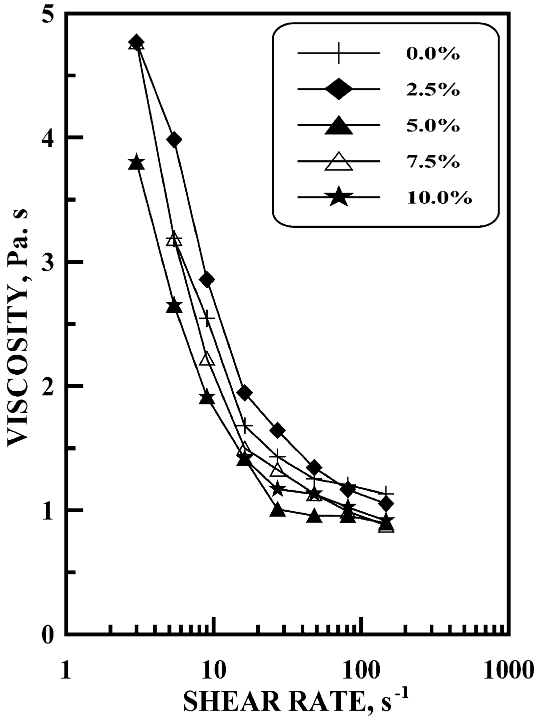

Fig. 9. Viscosity–shear rate relationship of M.3.

than the other mixes. The maximum torque viscosities were 1.13, 1.05, 0.90, 0.88 and 0.92 Pa s.

Fig. 10 shows the effect of mix composition without by-pass cement dust on the shear stress. It is clear that the shear stress decreases with Portland cement clinker due to the low hydraulic properties of granulated slag. Granulated slag can be used as a liquefying agent to reduce the shear stress; Collins and Sanjayan [19] reported that in concrete containing ground granulated blast furnace slag as a binder, the workability was improved, hence, it decreases the torque viscosity at early ages. The shear stresses at slow rate (at shear rate 27 s^{-1}) were 103.0, 71.5 and 38.6 Pa, respectively.

Fig. 11 shows the effect of by-pass cement dust on the shear stress in M.1, M.2 and M.3 at constant shear rate 27 s^{-1}. The addition of by-pass cement dust to M.1 decreases the shear stress, whereas the addition of 2.5 mass% cement dust to M.2 and M.3 increases the shear stress. Further addition of by-pass cement dust (5–10 mass%) to M.3 increases shear stress as a function of shear rate. The high content of slag is activated by the addition of 2.5 mass% by-pass cement dust due to the presence of excessive amounts of alkalis.

3.2. The required water of normal consistency and initial and final setting times

Hardening and strength development of Portland cement are the result of the hydration of both C_3S and C_3A and the formation of the C-S-H and AFt phases. Calcium sulphate acting as set regulator has to be interground with the clinker in most instances. In the presence of sufficient amounts of Ca^{2+} and SO_4^{2-} in the liquid phase, the hydration of C_3A and C_4AF in the initial preinduction period is reduced and ettringite-ferrite phase (AFt) is formed during hydration. When the gypsum is consumed and nothing remains to form ettringite, C_4AH_{13} is produced, and this reacts with ettringite already produced to form monosulphate (final set). The setting time of Portland slag cement was extended with slag content due to the low hydraulic properties of granu-

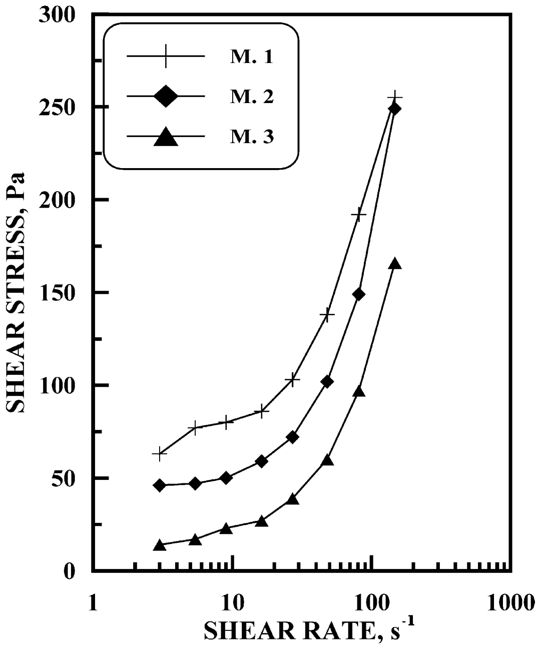

Fig. 10. Shear stress–shear rate of different mixes M.1, M.2 and M.3.

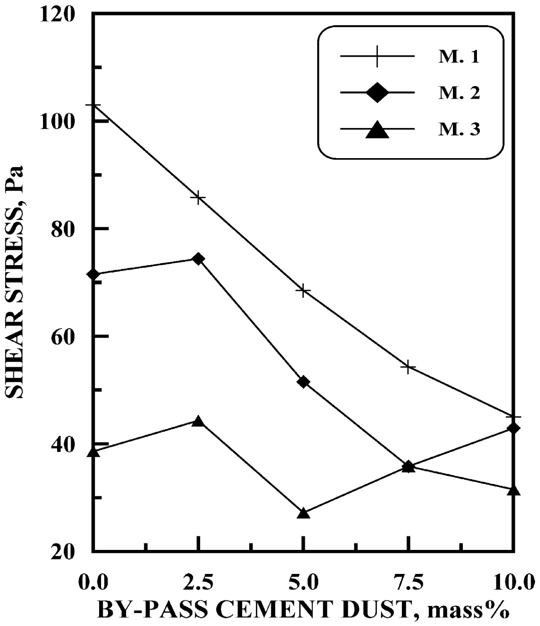

Fig. 11. Shear stress–by-pass cement dust relationship of M.1, M.2 and M.3 at constant shear rate (27 s^{-1}).

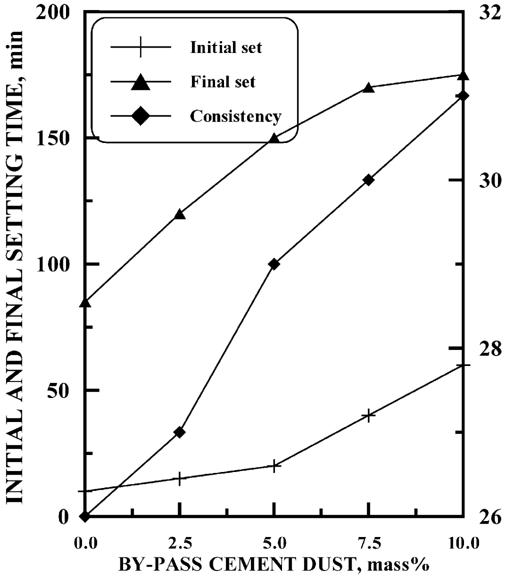

Fig. 13. Consistency and initial and final setting times of M.2.

lated slag in comparison with cement clinker. The setting process is associated with the formation of calcium sulphoaluminate hydrate. The formation of these hydrates depends on the reaction velocity of the aluminate compounds, amount of the phases, calcium sulphate retarder and calcium hydroxide. The Portland cement clinker (upon hydration) acts as a source of calcium hydroxide that gives the correct alkalinity to form ettiringite.

Figs. 12–14 show the effect of by-pass cement dust on the required water of normal consistency and initial and final setting times of M.1, M.2 and M.3, respectively. The water of consistency increases with the by-pass cement dust for all mixes. By-pass cement dust contains high amounts of alkalis and lime, which needs more water to produce standard consistency. The addition of by-pass cement dust to M.1 and M.2 retards the initial and final setting time due to the excess of mixing water. The addition of 2.5% by-pass cement dust to M.3 (70% slag) accelerates the final setting time due to the presence of some alkalis and lime in the dust. On the other hand, the other mixes M.1 and M.2 show some retardation. With the addition of 5 mass% by-pass cement dust to M.3, the initial and final setting times are extended. With the increase in the amount of by-pass cement dust from 7.5 to 10.0 mass%, the initial and final setting times are accelerated. This may be due to the increase in the amount of excess alkalis in by-pass cement dust, which act as a good activator for the hydration of granulated slag. Alkaline activation of blast furnace slag disintegrate the network structure of slag, and silicate and aluminate ions are taken into the solution [20].

3.3. Electrical conductivity

Electrical conductivity–hydration time curves for M.1, M.2 and M.3 without by-pass cement dust are shown in Fig. 15. As soon as the cement contact with water, ions such as Na^+, K^+, Ca^{2+}, OH^- and SO_4^{2-} dissolved, and these ions act as charge carriers, leading to a rapid increase in conductivity. As the concentration of these ions in the solution becomes very high, ionic association starts taking place, and as a result, the concentration of ions starts decreasing [21]. Evidently, the conductance–time curves for M.1 and M.2 blends show only one conductivity maximum followed by a sharp decrease in the conductivity value. The decrease in the conductivity values of M.1 and M.2 is mainly attributed to the formation of electrically insulating layers around the cement particles [22] and/or the decrease in the number of ions as a result of the formation of hydration products (C-S-H and ettringite). The increase in

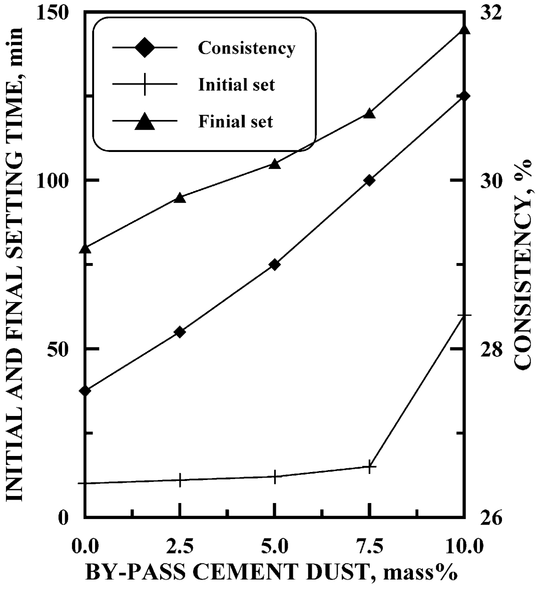

Fig. 12. Consistency and initial and final setting times of M.1.

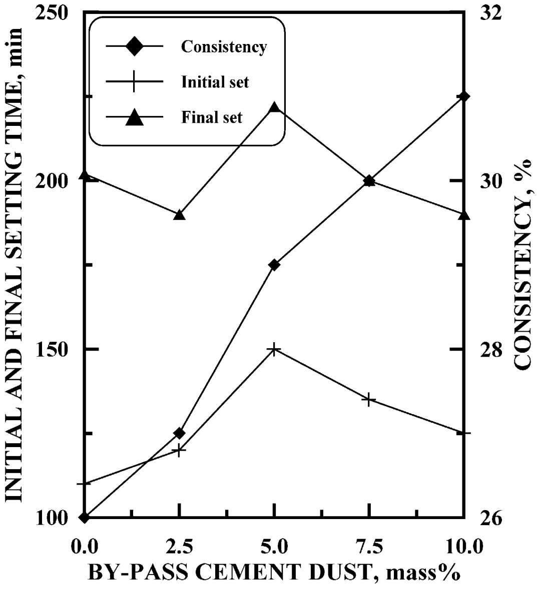

Fig. 14. Consistency and initial and final setting times of M.3.

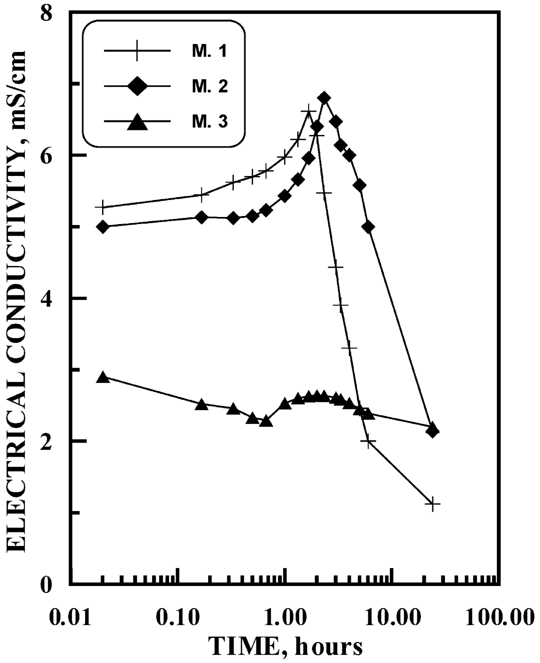

Fig. 15. Electrical conductivity of M.1, M.2 and M.3 without by-pass cement dust.

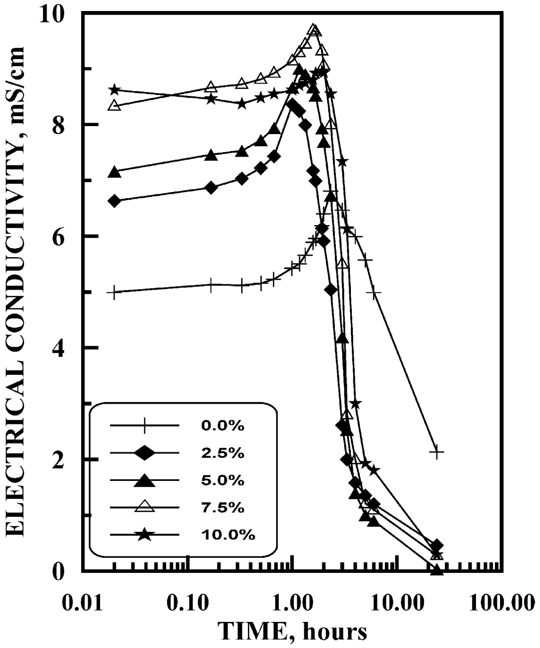

Fig. 16. Electrical conductivity of M.2 with different amounts of by-pass cement dust.

slag content instead of the amount of Portland cement clinker affected the location and intensities of the conductivity maximum. The M.3 shows a decrease in conductivity at 1 h due to the decrease in the number of ions in the liquid phase of the pastes; these ions are readily adsorbed on the surface of slag grains with the formation of hydration products. The decrease in conductivity is mainly due to the following factors: First, it is due to the decrease in the amount of Portland cement clinker (30 mass%); and the second is because a part of these ions is consumed in the activation of slag.

Fig. 16 shows the electrical conductivity of M.2 with different amounts of by-pass cement dust. Conductance increases with by-pass cement dust due to the high content of soluble alkalis, chlorides and sulphates. The presence of by-pass cement dust affects the location and height of the conductivity peaks. This effect leads to an increase in the intensity of the conductivity maximum, which is also shifted to a short time. With the increase in the amount of by-pass cement dust from 2.5 to 7.5 mass%, the conductivity maximum increases; on further addition (10.0 mass%), the height of the conductivity maximum decreases.

The variations of electrical conductivity of M.2 as a function of by-pass cement dust and curing time are shown in Fig. 17. The results show that at first contact with water (0 h), electrical conductivity increases with the addition of by-pass cement dust. At 0.5 h, electrical conductivity increases for each blend. After 3 h, electrical conductivity decreases with by-pass cement dust up to 2.5 mass% and then increases up to 10.0 mass%. After 24 h, electrical conductivity decreases with by-pass cement dust up to 10.0 mass%. The decrease in electrical conductivity is due to the increase in the number of hydration products, as well as the decrease in the number of free ions of Ca^{2+}, OH^- and SO_4^{2-}.

The addition of by-pass cement dust activates the slag hydration. The activation of slag proceeds via two steps. The first step is the preinduction period; chlorides, sulphates and alkalis of by-pass cement dust, which activate the slag

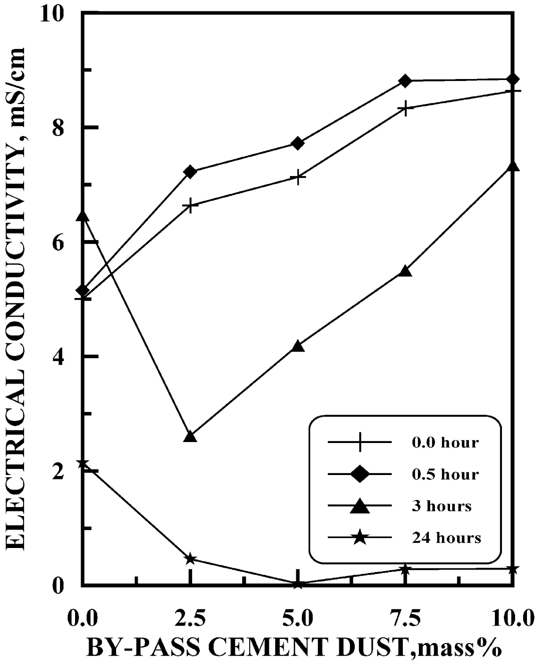

Fig. 17. Electrical conductivity versus by-pass cement dust.

[23]. As the hydration proceeds, the Portland cement clinker hydrates to accumulate more hydrated lime. This period is called the induction period. In this period, the $Ca(OH)_2$ is the main activator for the slag. As a result, more hydration products are formed. Increasing the curing time permits more accumulation of hydration products that confirm the decrease in electrical conductivity.

4. Conclusions

The following conclusions may be drawn from the above findings.

(1) The rheological properties of Portland cement clinker were enhanced (which decreases the torque viscosity) by partial replacement of ground granulated blast furnace slag. By-pass cement dust affects the rheological properties of Portland cement clinker/granulated slag composites and depends on its amount as well as mix composition.

(2) The setting time of Portland slag cement paste was extended with slag content. The addition of 2.5 mass% by-pass cement dust to M.1 and M.2 retards the initial and final setting times and accelerates the final setting time of M.3.

(3) The presence of by-pass cement dust affects the location and height of the conductivity peaks, which increases the intensity of the conductivity maximum. By increasing the by-pass cement dust from 2.5 to 7.5 mass%, the conductivity maximum increases; with further addition (10.0 mass%), the height of the conductivity maximum decreases.

References

[1] Z. Wu, Study of mineral compounds and hydration properties of kiln dusts from cement rotary kilns, ASAMCC, 1 (1980) 33.
[2] M.S.Y. Bhatty, Kiln dust blends evaluated, Rock Prod. 88 (10) (1985) 47–52.
[3] M.S.Y. Bhatty, Use of cement kiln dust in blended cements, World Cem. Technol. 5 (40) (1984) 126–134.
[4] H. El-Didamony, I.M. Helmy, A.A. Amer, Utilization of cement dust in blended cement, Pak. J. Sci. Ind. Res. 35 (7–8) (1993) 304–308.
[5] H. El-Didamony, A.A. Amer, E. Ebied, M. Heikal, Role of cement dust in some blended cements, Cemento 90 (4) (1993) 221–230.
[6] ACI Committee 266, Ground granulated blast furnace slag as a cementitious constituent in concrete, ACI Man. Concr. Pract. 266IR (1989) 1–16.
[7] H. Uchikawa, Effect of blending components on hydration and structure formation, 8th International Congress on the Chemistry of Cements, Rio de Janeiro, Brazil, vol. I, Theme III, (1986) 249–280.
[8] P.K. Mehta, 3rd International Conference on Fly Ash, Silica Fume, Natural Pozzolana in Concrete, Relim Tronheim, Norway, 1989, pp. 1–43.
[9] J. Bijen, E. Niel, Cem. Concr. Res. 11 (1981) 307.
[10] S.A.S. El-Hemaly, A.S. Taha, H. El-Didamony, Influence of slag substitution on some properties of sand–lime aerated concrete, J. Mater. Sci. 21 (1986) 1293–1296.
[11] D.M. Roy, G.M. Idron, Developments of structure and properties of blast furnace slag cements, J. Am. Concr. Inst. 79 (1982) 444–457.
[12] A.M. Amin, E. Ebied, H. El-Didamony, Activation of granulated slag with calcined cement kiln, Silic. Ind. 55 (3–4) (1995) 109–115.
[13] H. El-Didamony, A.H. Ali, A.M. Sharara, A.M. Amin, Assessment of cement dust with anhydrite as an activator for granulated slag, Silic. Ind. 62 (1–2) (1997) 31–36.
[14] S.A.S. El-Hemaly, A.F. Galal, F.H. Mosalamy, H. El-Didamony, Activation of granulated blast furnace slag by waste sulphate ash, Silic. Ind. Tom. LI (1–2) (1987) 9–12.
[15] P.C. Hewlett, Lea's Chemistry of Cement and Concrete, fourth ed., Edward Arnold, London, 1998, pp. 903–989.
[16] ASTM Standards, Standard test method for normal consistency of hydraulic cement, ASTM C187-83 (1983) 195–197.
[17] ASTM Standards, Standard test method for time of setting of hydraulic cement, Vicat Needle, ASTM Designation, C 191-82 (1983) 208–211.
[18] D.M. Roy, K. Asaga, Rheological properties of cement mixes: III. The effect of mixing procedures on viscometric properties of mixes containing superplasticizes, Cem. Concr. Res. 9 (1979) 731–739.
[19] F. Collins, J.G. Sanjayan, Effect of ultra-fine materials on workability and strength of concrete containing alkali-activated slag as the binder, Cem. Concr. Res. 29 (1999) 459–462.
[20] S.N. Ghosh, S.L. Sarkar, S. Harsh, Progress in cement and concrete: mineral admixtures in cement and concrete, in: D.M. Roy, R.I.A. Malek (Eds.), Hydration of slag cement, vol. 4, ABI Books, 1993, pp. 84–117.
[21] M. Heikal, I. Aiad, M.M. Shoaib, H. El-Didamony, Physico-chemical characteristics of some polymer cement composites, Elsevier Science, Amsterdam, The Netherlands, Mater. Chem. Phys. 71 (2001) 76– 83.
[22] S.A. Abo-El-Enein, K.Kh. Nuaimi, S.L. Marusin, S.A.S. El-Hemaly, Hydration kinetics and microstructure of ettringite, TIZ (Tonindustrie-Zeitung) 109 (1985) 116–118.
[23] A.M. Amin, E. Ebied, H. El-Didamony, Activation of granulated slag with calcined cement dust, Silic. Ind. 55 (3–4) (1995) 109–115.