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Magnetic susceptibility study on metakaolin admixtured cement paste

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ABSTRACT

The present works gossip the upshot of metakaolin on the properties of Portland cement through magnetic susceptibility study. Cement pastes containing 0%, 10%, 20% and 30% metakaolin in substitution for cement and in a Water/Cement (W/C) ratio of 0.4 have been prepared. The magnetic susceptibility at different hydration ages has been determined by Faraday Curie balance method and this has been related to changes in setting time and compressive strength measurement. The results illustrate to facilitate the magnetic susceptibility increases with increasing metakaolin content in the cement.   © 2010 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Cement is a powdered material which develops strong adhesive qualities when mixed with water. During hydration of cement, various phase transformations occur. As hydration progresses the magnetic constituents of Portland cement and/or the reaction products acquire magnetic properties due to their dipole alignment with the external field and there is every possibility of change in susceptibility. Susceptibility (χ) measurement was used to detect the solubility limit of iron in different forms in C_3A[1]. Beata Goluchowska[2] reported that the magnetic susceptibility of cement dust depends on the iron content in raw materials, additives and fuels introduced into the kiln in which the clinker is backed. According to David et al.[3] clay minerals have higher amount of iron oxides and hence enhanced the susceptibility values. The magnetic susceptibility is an vital physical property and it is another way to analysis the cementitious materials.

Now a days, there is an increasing use of pozzolanic materials such as metakaolin in Portland cement. It offers cost reduction, energy savings, superior quality and also one way to reduce greenhouse gases and global warming. Metakaolin is produced by thermal activation of kaolinite clay in the temperature range of 650-850°C, is an established pozzolanic component[4]. The hydration mechanism of cement and metakaolin admixtured cement using DTA, XRD, FTIR, SEM, NMR and Dielectric measurements was explained by number of authors[5-9]. But, to our knowledge, no magnetic susceptibility studies have been reported so far on hydration of cement admixtured with metakaolin at different hydration periods. Many methods are available for measuring magnetic susceptibility but Faraday-Curie balance is a very sensitive and versatile method to measure small susceptibility.

Cement nomenclature

$C = CaO$; $S = SiO_2$; $H = H_2O$; $C_3S = 3CaO.SiO_2$; $C_2S = 2CaO.SiO_2$; $C_3A = 3CaO.Al_2O_3$; $C_4AF = 4CaO. Al_2O_3.Fe_2O_3$; $CH = Ca(OH)_2$.

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Variations

In the present study, the authors present magnetic susceptibility studies on cement and metakaolin admixtured cement pastes at different hydrated time intervals using a Faraday-Curie balance available in the Material Science Laboratory, Department of Physics, Annamalai University, Tamil Nadu, India.

MATERIALS AND METHODS

Metakaolin (MK) was received from M/S.20 Microns Limited, Vadodara, India and Ordinary Portland cement (OPC) is a commercial one. Both samples were subjected to the chemical analysis using standard procedures and are given in TABLE 1.

Sample preparation

In this exploration, OPC and metakaolin admixtured cement paste was prepared by mixing double distilled water in water to cement ratio (W/C) of 0.4. Metakaolin was replaced with three different weight percentages (10%, 20% and 30%) with respect to cement. The samples were thoroughly mixed with water using a glass rod for two minutes and then allowed to hydrate in air-tight plastic containers. The hydration was stopped at different time intervals viz., immediate, every 30 minutes for 10 hours after mixing and then 1 day, 2 days, 4 days, 1 week, 2 weeks, 4 weeks by using acetone. To remove water content the hydrated samples were oven-dried at 105°C for 1 hour[10]. The dried samples were powdered using agate mortar and used for magnetic susceptibility measurements. The samples hydrated for more than 1 day were cured properly.

Setting time test

Initial and Final setting times of OPC and 10%, 20%, 30% Metakaolin admixtured cement paste for a W/C of 0.4 was measured using a Vicat's apparatus using the standard procedure[11] and revealed in TABLE 2.

Compressive strength test

Compressive strength of cement and MK admixtured pastes (TABLE 2) were determined using Compression Testing Machine (Techno-Science Trading Corporation, New Delhi, India) setup available in the Department of Structural Engineering, Annamalai University, India and using standard procedure[11].

EXPERIMENTAL

Figure 1 shows the Faraday-Curie balance along with Heyding's type pole pieces[12]. It consists of a light aluminium beam (AB) of length 25cm suspended by means of a fine copper wire and its upper end is soldered to a torsion head (T). The sample holder is connected to the lower end of the glass tube (G) suspended from the left end of aluminium beam. A small mirror (m) is attached at the center of the beam. A circular scale (S) graduated in degree is provided at the upper end of the glass tube facilitate the rotation of the sample from 0° to 360°. The right end of the arm carries a damping vane (V) made of aluminium and is dipped in a dash-pot of light viscous oil. This arrangement effectively damps out all spurious vibration. Above the aluminium beam there is a balancing coil (C) comprising of 500 turns of copper wire wound over a hollow rectangular frame. The powerful horse shoe shaped permanent magnet (MM) produce a strong radial field enclosing the coil 'C'. The coil moving in the radial field constitutes a galvanometer. By passing a suitable current through the coil using potential divider arrangement, the deflection can be nullified. A digital millivoltmeter measures the current flowing in the balancing coil and directly displays the value in terms of voltage[13].

Calibration

Curie balance has to be calibrated for various samples of known susceptibility value. The sample in powder form is filled in sample holder and is suspended in the predetermined region where magnetic force is uniform and maximum in the non uniform field. When the magnetic field is switched on, the sample experiences a magnetic force. This produces a deflection of the beam and the deflection is noted by mirror (m) and the lamp and scale arrangement. The force exerted on the sample is counter-balanced passing a suitable current, by adjusting the resistance in the potential divider arrangement and hence the voltage required to compensate the magnetic force on the sample is noted. The sample is rotated in steps of 20° and at each position the procedure is repeated and finally the average annulling voltage Vs is calculated. The experiment is repeated for empty sample holder to determine its annulling voltage V_O. The difference in voltage (V_S-V_O) is a measure of annulling voltage for the sample. A calibration graph (Figure 2) is drawn between the known

TABLE 1 : Chemical composition of portland cement and metakaolin (mass %)

Samples	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	SO$_3$	MnO	Loss on ignition	Insoluble residue
Portland cement	63.32	21.70	5.40	3.40	2.09	2.10	0.12	0.79	1.08
Metakaolin	0.50	68.54	23.55	0.58	0.60	1.03	0.02	3.98	1.20

TABLE 2 : Setting time and compressive strength of metakaolin admixtured cement

Samples	Setting time (h:min)		Compressive strength (MPa)		
	initial	final	1 day	1 week	4 weeks
MK0%	5.05	6.50	10.4	32.6	47.7
MK10%	4.45	6.25	18.4	41.2	55.3
MK20%	3.25	5.40	21.4	52.4	69.3
MK30%	2.30	4.40	27.4	57.4	74.2

susceptibility value of different samples (K$_2$Cr$_2$O$_7$, NiSO$_4$, CaSO$_4$.7H$_2$O, FeSO$_4$.7H$_2$O, MnSO$_4$, Gd$_2$O$_3$, Fe(OH)$_3$, HOCl$_3$, Er$_2$O$_3$) and the corresponding annulling voltage per unit mass.

The magnetic susceptibility at different time intervals of hydrated cement is obtained from the calibration graph, using the annulling voltage. The sensitivity of the instrument is ± 0.001. All the measurements were taken at $28 \pm 2°C$.

RESULTS AND DISCUSSION

The observed susceptibility values for anhydrous cement and metakaolin are 51.05×10^{-6} emu/gm and 123.02×10^{-6} emu/gm respectively. This value $\chi > 0$ indicates the cement and metakaolin samples are paramagnetic[14,15]. The positive paramagnetic susceptibility of the anhydrous cement may be considered as a resultant of the contribution from all the impurity ions and especially Fe$_2$O$_3$ contained in C$_3$A and C$_4$AF phases[16]. Graphs are drawn between the obtained susceptibility values and different hydrated time intervals for cement and metakaolin admixtured cement paste (Figure 3 and 4) in a non-uniform scale.

For hydrated cement paste (Figure 3), the χ values are found to increase from immediate and reach a maximum value during the first 2 hours. On contact of cement with water due to initial dissolution, hydroxyl (OH$^-$) and calcium (Ca^{2+}) ions concentration increases and the first reaction product ettringite (AF$_t$) formed with layer of hydrous alumina from the reactions between C$_3$A, C$_4$AF and gypsum[17]. Initially, the cement materials are easily dispersed with water and hence a strong reactive capacity causes an amorphous iron-rich phases

appears to form simultaneously with the AF$_t$ phase and hence χ values increases up to 2 hours. Moreover, according to Mohamed Ahmed et al.[1] the Fe$_2$O$_3$ has a tendency to dissociate and liberate Fe ion in the form of Fe^{2+} and Fe^{3+}. This tendency may increase near the solubility limit of Fe in C$_3$A. Initially, the active substitution of Fe^{3+} for Al^{3+} in C$_3$A lattices causes a steep increase in χ values. This replacement was confirmed by Majumdar[18], Moore[19] and Schlaudt and Roy[20].

After attaining a maximum, susceptibility values begin to decrease gradually with time and reach a minimum at a particular time interval. Because the reaction of C$_3$A, C$_4$AF with gypsum is slightly retarded by hydrous alumina, the formation of hydration products is less paramagnetic than reactants. The fall of susceptibility values can be attributed to continuous decrease of highly magnetic anhydrous cement phase composition and simultaneous formation of various hydrates. i.e. products which incorporate water in their structure. The formation of hydration products which incorporate water as chemically bound water, not only lower the magnetic susceptibility to some extent but also maintains the susceptibility at relatively lower but still positive values. As time advances C$_3$A contain more Fe^{2+} than Fe^{3+} and Fe^{2+} substitutes Ca^{2+} in C$_3$A lattices[1]. This partial reduction of Fe^{2+} and Fe^{3+} leading to decreases the χ values after the first maximum. The time taken for this paramagnetic susceptibility value reaching a minimum coincides well with the starting of final setting time of that particular sample measured using Vicat's apparatus (TABLE 2). After reaching a first minimum the χ values increase slightly and then decrease forming second maximum. This is due to a sudden increase in the reactivity of unreacted C$_3$A. At the starting of final set, the rapid conversion of AF$_t$ into AF$_m$ takes place and increase the iron content[21].

After the second maximum, the susceptibility values decreases gradually with hydration time. This due to the formation of hydration products such as calcium silicate hydrate gel (C-S-H), Ca(OH)$_2$ and hence the cement paste becomes condensed and thickens[14]. The C-S-H gel is one of the major strength rendering components of the hydrated cement and hence in-
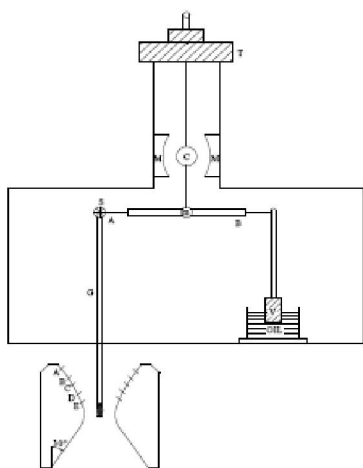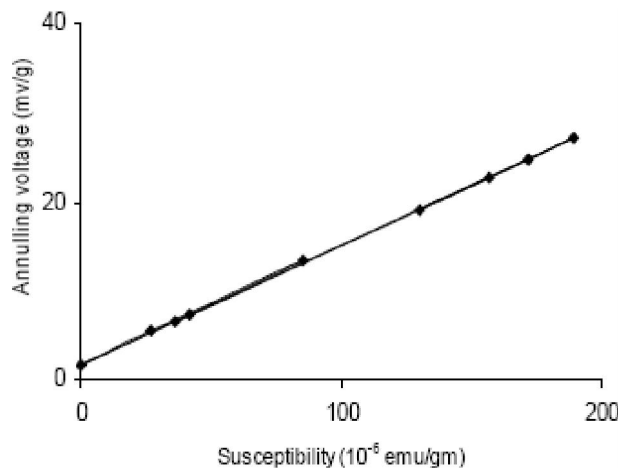
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Figure 1 : Faraday curie balance
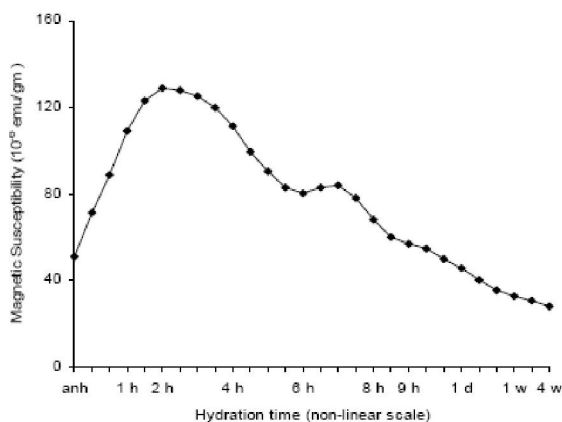

Figure 2 : Calibration graph

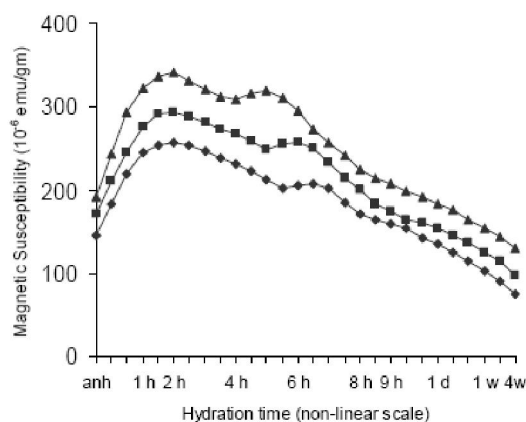**Figure 3 : Magnetic susceptibility *vs.* different hydration time intervals of cement paste**

Figure 4 : Magnetic susceptibility *vs.* different hydration time intervals of metakaolin admixtured cement paste
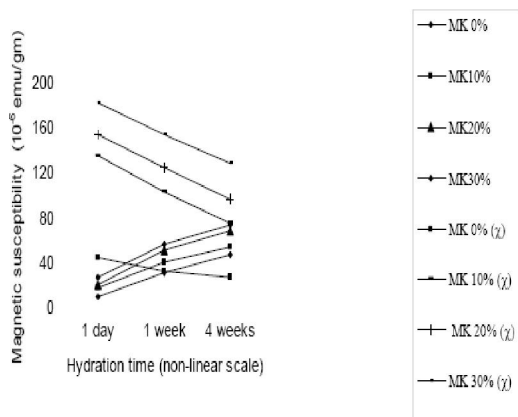

Figure 5 : Relationship of MK replacement in cement vs. magnetic susceptibility and Compressive strength

Figure 6 : Variation of magnetic susceptibility *vs* various % of MK for anhydrous, 2 hours, first minimum and 4 weeks

creases the strength of cement with decreasing the magnetic susceptibility.

From the graph (Figure 4), it is observed that MK admixtured cement also follows the same fashion as that of ordinary Portland cement. It is evidenced that as the replacement of MK% increases, the χ values also
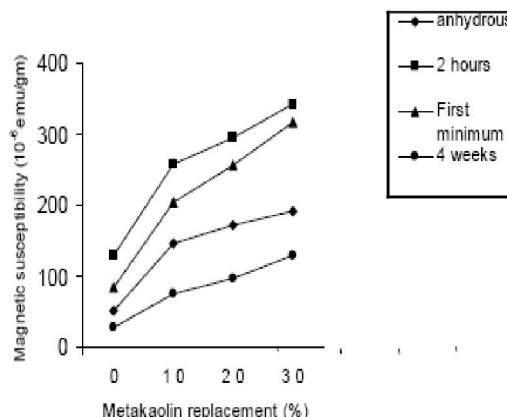
increases. There is a clear trend observed that both the first minimum and starting of final setting time is shortened as the replacement of MK% is increased. This is due to the presence of silicon and aluminium oxides in MK which accelerates the reaction of the cement. This increases the formation rate of AF_t in the early hydra-

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tion period and hence shortens the setting time[22]. The increase and decrease of χ values from immediate to first minimum are faster when compared to Portland cement. This result corroborates with Helene Lecoanet et al.[23] and state that quickly setting cement has high susceptibility value.

MK reacts with calcium hydroxide produced in the hydration of Portland cement. As a consequence extra calcium silicate hydrate (C-S-H) gel is produced and it increases the strength of the cement but it decreases the magnetic susceptibility values after second maximum.

The figure 5 shows summarized results of compressive strength and magnetic susceptibility at 1 day, 1 week and 4 weeks of cement and MK admixtured cement. The graphs clearly demonstrate that the systematic increase in compressive strength and decrease in magnetic susceptibility values are due to high pozzolanic activity of metakaolin. Figure 6 shows the variation of magnetic susceptibility of MK admixtured cement at different curing periods. From the graph, as percentage replacement level of MK increases, the magnetic susceptibility values also increases when compared to anhydrous and at 4 weeks χ values lies less than anhydrous cement.

CONCLUSIONS

The results can be summarized as follows,

1 On hydration, before setting time, the produced amorphous iron-rich phase associated with AF_t in the admixtured cement paste increases and hence high magnetic susceptibility values. After setting time, the production of cement gel particles condense and thicken and hence low susceptibility with high compressive strength.

2 For all samples the first minimum coincides with starting of final setting time.

3 After 1 day, the compressive strength of the cement increases with decreasing magnetic susceptibility with increase in % replacement of MK.

4 The magnetic susceptibility study is a corroboration of the well known accelerating effect of MK in the hydration of the Portland cement.

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