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MŐSSBAUER AND MAGNETIC INVESTIGATIONS ON OPC BLENDED WITH SILICAFUME

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Abstract

The Mössbauer spectra of optimum amount of (20%) silica fume blended cement paste using CO(Rh) Source have been interpreted for its hydration kinetics using two waters namely DW and EW. The obtained results were correlated with the setting time, compressive strength and magnetic data measurement using Kappa bridge. This is preferred as its offers some resistance to sulphate attack observed from their studies.

Key Words: Silicafume; Mossbauer Spectroscopy; Magnetic susceptibility; Compressive strength and setting time.

Introduction

Cement, is a composite material cum binder. During hydration, the byproducts determine strength, durability etc. Concentration on the effects of Ca^{2+}, OH^{-}, SO_4^{2-} on cement hydration is enormous (1-4). The studies on iron-ion dissolution, its oxidation, replacement of Al^{3+}, Si^{4+}, iron during hydration are limited and hence the present investigation using Mössbauer and magnetic methods. Silica fume as admixture using addition method is preferred.

Materials and Methods

Commercial OPC and 20 micron Elkem microsilica of known composition is used (Table 1). Distilled water and sugar factory effluent water after water analysis (Table 2) were used for hydration.

20% SF by addition as admixture and 0.4 (water / cement) w/c ratio was found optimum after a pilot study and were preferred.

20% SF homogenously mixed OPC (using 1250 rpm vibrator) is hydrated and dehydrated at 1, 3, 6, 7 hours, 4 day – 1 week & 12 weeks. These samples were prepared for magnetic and Mössbauer studies using standard procedures[5,6].

Kappa-Bridge-KLY-4B magnetometer available at Indian Institute of Geomagnetism, Mumbai was used for magnetic susceptibility measurement. Constant acceleration Mössbauer spectrameter (Wissel MDU 1200) with 25 m Ci^{57} Co(Rh) Mössbauer source at Nuclear Physics Department, University of Madras, Chennai was made use of to record Mössbauer spectra. The data wereevaluated using least square fitting of computer fit fed to a superposition of Lorentizian shaped lines [7].

Table.1 Oxide composition (wt.%) of OPC and Silica fume.

Constituents	OPC	Silica fume
CaO	62.94	0.34
SiO_2	21.47	91.00
Al_2O_3	5.40	1.21
Fe_2O_3	3.27	3.37
SO_3	2.81	0.31
MgO	2.65	1.18
Na_2O	0.44	0.46
K_2O	0.25	1.24
Loss on Ignition (LOI)	0.77	0.89

Results and Discussion

Mőssbauer spectra of anhydrous cement, silica fume and OPC+20% SF admixtured cement, samples at

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different time intervals treated with effluent water are presented in fig 1-2.

The results of present investigation show that the isomer shift lies between 0.14 – 0.28 mms^{-1} and the quadrupole splitting lies between 1.56 – 1.93 mms^{-1} which coincides well with other reported values [1-4].

Table. 2. Contents (μg/g) of the different waters

Content	Distilled water (DW)	Effluent water (EW)
Colour	Colour less	Light Brown
Odour	Nil	Nil
Total Dissolved Solids	45	1520
Total Hardness	4	170
Chlorine	-	102
Sodium	-	299
Magnesium	1	2.7
Calcium	-	47.37
Potassium	-	17.2
Iron	-	0.91
Sulphar	-	10.7
Flouride	-	0.2
Electrical conduction (μ S)	10	670
p^H	6.9	7.1

In the spectra of anhydrous samples (Fig.1(a-c)), iron atoms occupy distorted tetrahedral (site A) and octahedral sites (site B). On de-convelution, the spectra contain a doublet, the outer being tetrahedral and the inner being cctahedral sites (Fig. 1a-b) [3]. The intensity of sixlet in fig (1b) indicates the presence of iron in anhydrous cement and /or in SF. In the 20% SF admixture though the shapes were similar, the higher intensity indicates higher number of iron – ions. The pure silica spectra represents less intensities of magnetic hyperfine structures than the both anhydrous OPC and OPC + 20% SF.

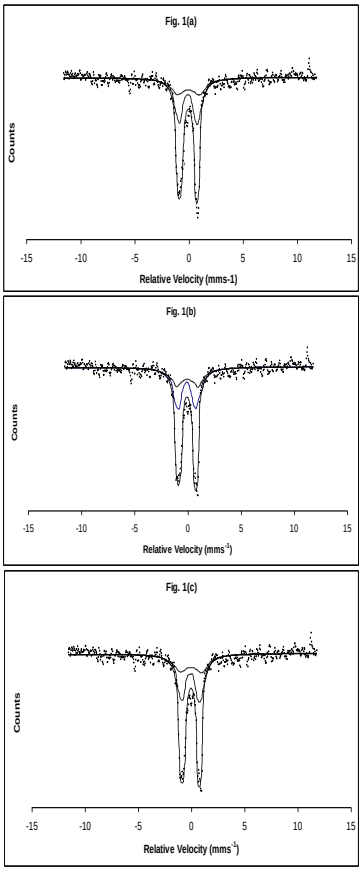


Fig. 1. Mőssbauer Spectra of (a) Anhydrous OPC and (b) Anhydrous Silica fume (c) Anhydrous OPC + 20% Silica fume

In the Fig. 1 (abc) both Fe distorted sites of both samples show an increases in intensities which may be attributed to the association of Fe_2O_3 in SF and OPC.

Mössbauer spectra of ordinary Portland cement hydrated with EW in a W/C of 0.4's is shown in fig (2a-c). In 1 hour spectra both Fe- ion (A and B) have higher intensities. These sites have an isomer shift δ = 0.24 mms^{-1} and quadrupole splitting, ΔE_Q = 1.74 mms^{-1} respectively.

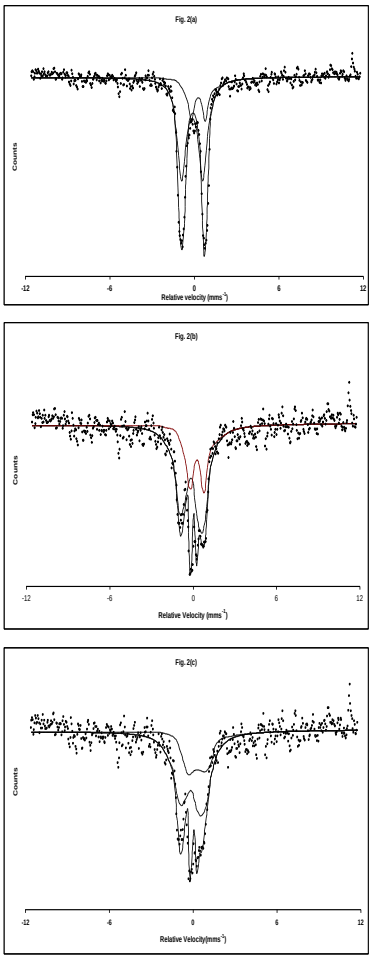


Fig. 2. Mossbauer Spectra of OPC treated with EW (a) 6 hours, (b) 4 weeks and (c) 12 weeks.

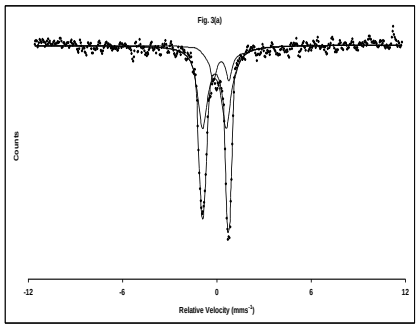
In fig. 2a as hydration time increases (i.e., 6 hours) the hyperfine structure of both sites and intensity become almost equal indicating the formation of hydration by-product like ettringite. When water is added with cement, at first the C_3A phase starts hydrating with sulphate to produce ettringite (AF_t) [8] as given below.

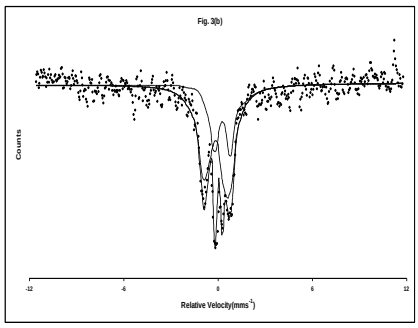
$$C_3A+3C\bar{S}H_2+26H \longrightarrow C_6AS_3H_{32} \quad \text{(Etrringite, } AF_t\text{)} \qquad \ldots\ldots\ldots\ldots (1)$$

The decrease in intensity of Fe^{3+} (T_d) represents probably their replacement by Al^{3+} available in C_3A and C_4AF phases of cement, in every Fe substituted ettringite formation. This is a spinal based structure with disordered cation vacancies, which is not basically change during topotactic transformations. The difficulty of Al_2O_3 nucleaction in this system is directly responsible for unwanted porous microstructure [9]. Hence strength of the cement system is decreased. Magnetic susceptibility study also substantiates this view [10,11,12]. The formation of ettringite at that time is defined by the following equation and causes initial setting.

$$3C_4AF + 12C\hat{S}.H_2 + mH \longrightarrow A\,C_3\,(A_{0.75}\,F_{0.25}).C\hat{S}.H_{31} + 2FH_3 \ldots\ldots (2)$$

According to crystallographic concept, the ferric oxide (Fe_2O_3) is not so simple, and hence nucleation efficiency of Fe_2O_3 acts as a seeding agent and is higher than Al_2O_3 [13]. This can be attributed to the higher oxide particle number concentration afforded by insitu formation of Fe_2O_3 upshoting higher nucleation frequency and matrix interfacial contact.





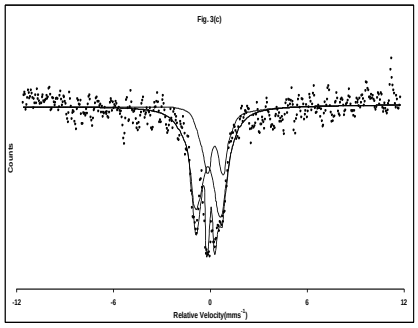
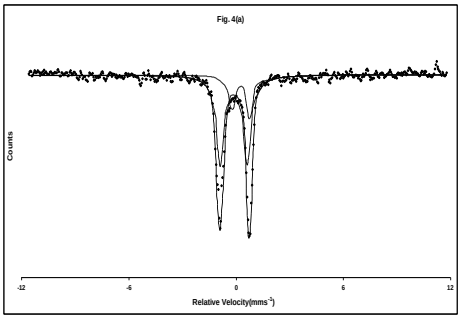
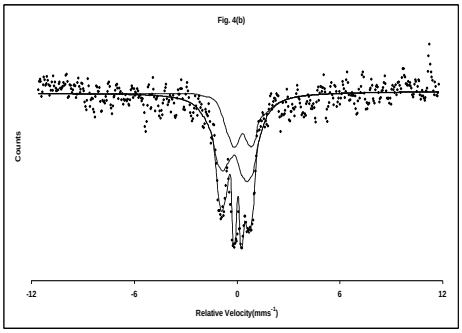


Fig. 3. Mőssbauer Spectra of OPC + 20% Silica fume treated with EW (a) 6 hours, (b) 4 weeks and (c) 12 weeks.

As time matures the intensity of A site is increased whereas the intensity of B site has started diminishing (Fig 2(b,c)). In all the spectra, the magnetic hyperfine sixlet appeared with higher quadrupole splitting (ΔE_Q =1.76 mms^{-1}) showing that the octahedral Fe have asymmetric electron environment. The presence of Fe^{2+} could have been flown out due to oxidizing atmosphere, hence a higher value of isomer shift [11]. Due to replacement/decreasing concentration of Fe^{3+} there is every possibility of transformation to Fe^{2+} forming an inverse spinal structure [14]. Due to this strength of the cement matrix increases as evidenced. This can also be inferred from the magnetic susceptibility study.





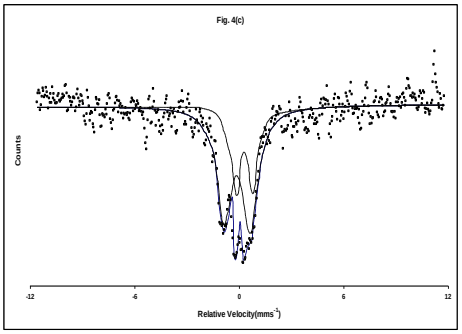


Fig. 4. Mossbauer Spectra of OPC + 20% Silica fume treated with DW (a) 6 hours, (b) 4 weeks and (c) 12 weeks.

According to Mackenzie [11] under reducing conditions, all these spectra show a pair of Fe^{3+} doublets

characteristic of ferrite phases and a pair of Fe^{2+} doublets suggesting fourfold coordination in distinctly different sites. Consideration of the possible ferrous sites in the aluminate and alumino ferrite systems suggests the ferrous ions might replace Al in the aluminate.

From Fig. 2(abc) it is observed that magnetic hyperfine structure of quadrupole splitting has decreased and started vanishing upon time [4,11,12] suggesting the conversion of ettringite to iron-substituted mono sulphoaluminate (AF_m).

The decrease in Fe^{3+} concentration due to Fe^{2+} transformation and increase in percentage of Fe^{3+} (T)/ $\sum$ Fe^{3+} ratio is observed for pure and SF admixture system which is an identification of increase in compressive strength [1].

In Mössbauer Spectra of 20% silica fume admixtured cement pastes (Fig 3(a-c)), the site A intensities are decreased with corresponding increase in site B intensities. These intensities are comparatively higher than that for EW controlled pastes, at a particular time. The Fe^{3+} (T)/ $\sum$ Fe^{3+} ratio has increased around 2 units (Table 3) and hence higher strengths of 20% SF than the control paste (Table 3).

In the spectra of DW water treated with 20% SF admixtured pastes (Fig. 4(a-c)) also, a trend of 20% SF+OPC(EW) was observed. But the intensity variation of both A and B sites are in the order EW>DW. This trend is due to accelerating ions present in EW which is observed only upto 1 week of hydration (Fig not shown).

After 1 week (4^{th} and 12^{th} weeks), the intensity of hyperfine structure starts disappearing, at a slower rate than both control and silica fume admixtured matrix treated with EW. The intensity of site B is higher compared to that of EW treated pastes indicating higher rate of conversion of Fe^{3+} to Fe^{2+} in DW treated pastes which tends to increase the strength and hence compressive strength of the cement matrix in the order EW<DW.

Magnetic susceptibility of EW control, EW blended and DW blended pastes by 20% silica fume addition is given in a non-linear scale (Fig.5,6).

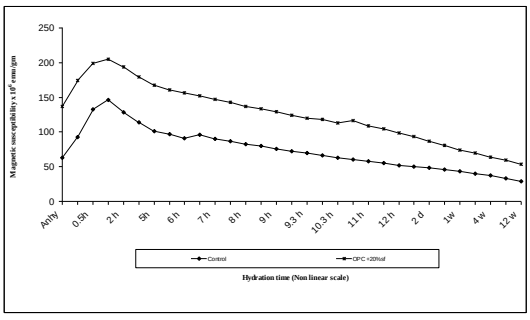


Fig. 5 A Plot between Magnetic Susceptibility Vs Hydration time of DW Treated OPC and 20% of Silica Fume Admiuxured OPC Paste

The magnetic susceptibility value increases from immediate to the maximum value during first two and half hour and then decrease and reaches a minimum, again slightly increases and starts decreasing slowly. This trend is similar for various composition of SF but the attainment of the maximum and minimum both in intensity and time differ.

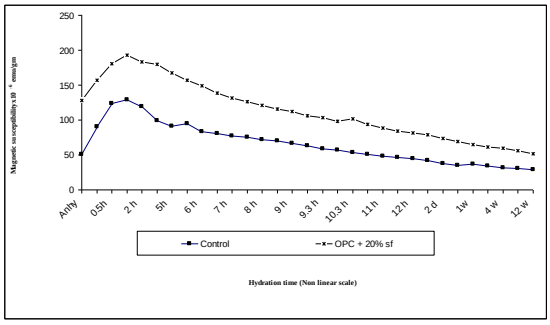


Fig. 6 A Plot between Magnetic Susceptibility Vs Hydration time of EW Treated OPC and 20% Silica Fume Admiuxured OPC Paste

As soon as cement is in contact with water, C_3A and C_3S start reacting producing ettringite and C-S-H [1]. When the blend is in contact with water the reaction increases the number of Fe^{3+} ions by replacing Al^{3+} ions which is similar in character to Mössbauer spectral data (Table 3).

Hydration Time	Fe^{3+} (T)/ $\sum$ Fe^{3+}			Compressive Strength (MPa)		
	Control	DSF 20%	ESF 20%	Control	DSF 20%	ESF 20%
6h	29	32	40	-	-	-
4w	56	59	60	58.81	78.64	75.93
12w	68	71	74	75.29	95.27	92.15

Table 3. Impact of Fe3+ on compressive strength of 20% Silica fume admixured cement paste

The trend is in the order of EW>EW blend>DW blend. This may be due to higher amount of accelerating ions in EW and due to iron-ion present in the silica fume. The slope indicates the rate of reaction. The maximum is the point where saturation attains for the replacement of Al^{3+} by Fe^{3+}. After attaining a maximum, susceptibility value starts decreasing due to conversion of Fe^{3+} to Fe^{2+}, whose rate is in the order of EW>EW blend>DW blend. This transformation is well evidenced through Mössbauer spectroscopy (Fig. 1-4). The first minimum coincides well with the final setting time of the paste by Vicat's test. This represents the solubility limit [10,11,15] of Fe^{2+} hence a tapering is seen in all the two figures (Fig.5,6).

Proceeding from the first minimum the Fe^{2+} are replaced by Ca^{2+} producing more ettringite. The secondary maximum corresponds to the conversion of

AF_t to AF_m. Area of the curve under second maxima represents the unreacted component. By the combined effect dissolution of Fe^{2+} and conversion of Fe^{3+} to Fe^{2+}, the bulk paste behaves as ferromagnetic and obtained an inverse spinal structure [14]. Mössbauer spectral data well pictures the same. As time passes, the susceptibility value decreases in all cases, and reaches a value less than that of anhydrous cement as a result of gradually increasing amount of hydrated compounds.

Conclusion

The magnetic and Mössbauer studies acts as a fine tool to interpret the kinetic reaction. The replacement of Fe^{3+} by Fe^{2+} is well evidenced by Mössbauer spectra and supported by magnetic data. The conversion of Fe^{3+} to Al^{3+} is well seen by the two studies. The setting time can be observed using magnetic data coincides with observed vicats results. The change in Ca^{2+} is well understood using magnetic data.

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