Available online at www.jpsscientificpublications.com
Volume – 1; Issue - 4; Year – 2015; Page: 290– 297

Indo – Asian Journal of Multidisciplinary Research (IAJMR)
ISSN: 2454-1370

A MÖSSBAUER STUDY ON BLENDED TERNARY CEMENT PASTE

R. Nithya[1*] and S. Barathan[2]

[1]*Department of Physics, Chendu College of Engineering and Technology, Zamin Endathur, Madurantakam, Kancheepuram - 603 311, Tamil Nadu, India.*

[2]*Professor and Head, Department of Physics, Annamalai University, Annamalai Nagar - 608 002, Tamil Nadu, India.*

Abstract

Pastes containing High Alumina Cement (HAC), Ordinary Portland Cement (OPC) and Silica fume (SF) blends are recorded for different hydration time intervals. The environmental iron-ion in this blend for certain selected samples is identified with the measurements from quadrapole splitting, Isomer splitting using Mossbauer spectra. The recorded spectra were compared with the observed mechanical measurements of these blends. The hydration kinetics is well explained through these results. It is evidenced that 10%SF addition is optimum for this blend.

Key words: HAC, OPC, SF and Mössbauer.

1. Introduction

The reliability of Mössbauer spectroscopic data acts in supplying information about the nature of bonding, site symmetry, oxidation state of Fe atom. This has made it an important tool for the study of iron phase in cement and admixtured cements. Ferrous and Ferric ion are known to exist in multi layered silicate minerals (Saveria Monosi *et al*., 1996). The exact lattice position of the iron ions, however it is difficult to determine. The Mössbauer effect provides an excellent spectroscopic method for studying the iron ion environment in layered silicate minerals. The isomer shift obtained from the Mössbauer spectrum, indicates the valence state of iron in the mineral. The magnitude of the quadrupole splitting reflects the local surroundings of iron ions (Charles Fentiman, 1985 and Dong Jianmiao and Long Shizong, 2005).

The exact position of iron ions can be easily determined in the two sheet phyllosilicates which have limited cation sites available (ElSokkary *et al*., 2004). The structural position of iron in the more complexed layer silicate minerals can be ascertained by comparison of isomer shift and quadrupole splitting values to those from iron and is known as octahedral and tetrahedral coordination.

Any cement matrix contains aluminium and iron. During hydration these metal ions undergo variations. The variations can be well studied with spectroscopic, XRD, thermal and Mössbauer studies (Antiohos *et al*., 2007; Faucon *et al*., 1997). However, the reaction and position of the iron-ion cannot be estimated clearly with other methods except Mössbauer, since the aluminium and iron reaction overlaps. Hence, this Mössbauer is considered to be a fingerprint characterization technique.

2. Experimental Methods

The Mössbauer measurements has been carried out with a conventional constant acceleration spectrometer (M/s. WISSEL, Germany) equipped with a room temperature Rh

*Corresponding author: **R. Nithya**
E-mail: nivelan_15@yahoo.com
Received: 03.07.2015; *Revised*: 30.07.2015;
Accepted: 29.08.2015.

© 2015 Published by JPS Scientific Publications Ltd. All rights reserved

matrix ^{57}Co source. This facility is available at UGC consoritium, Calcutta is made use of. The instrument was standardized with iron as medium. All the measurements were taken at 28±2°C. The sample preparation suggested by Wagner, 2004; Wertheim, 1964 is followed. The software supplied along with instrument is made use of for recording Mössbauer spectra.

3. Results and Discussion

Mössbauer spectra of HAC, OPC, Silica fume samples are displayed in Fig - 1 (a-c).

The recorded Mössbauer spectrum of anhydrous HAC at (28±2°C) is shown in fig. 1. It contains two humps with quadrupole splitting of 2.43 and Isomer shift of 0.22. The values matches well with the reported values are Harchand *et al*. (1984) and Übelhack and Whitmann *et al*. (1976).

Since the spectra represents, coupling forces of the entire system it has been deconvoluted and studied. On deconvolution, it contains two doublets the outer being tetrahedral and inner being octahedral. The central hump/doublets in the spectrum represent the ferrite available in the system.

The calculated isomer shift value and quadrupole splitting value (Table - 1) agrees well with other reporters Harchand *et al*. (1984). In the present study, the value lies between 0.14 -0.27 mms^{-1} and the quadrupole splitting lies between 1.51 - 1.80 mms^{-1} suggesting octahedral (O_d) (say A-site) and tetrahedral sites (T_d) (say B-site) (Hassaan and Eissa, 1986).

Harchand *et al*. (1984) is of the opinion that ferric oxide in HAC mainly occurs in C_2F_{1-x} A_x($0.3\leq \times\leq 0.7$) and can be distributed in CA and $C_{12}A_7$ phases. However, qualitatively the number of Fe sites should be similar to sites in the spectra of other cements with $C_2F_{1-x}A_x$ as an iron containing phase [Fig. 1 (a-c)].

The envelop of HAC spectrum recorded at 28±2°C closely resemble the spectrum of CF reported by Mackenzie (1980) and $C_2F_{1-x}A_x$ series recorded by Harchand *et al*. (1984). This suggests the author to believe that there co-exist two phases CF and CA. Fe and Al are distributed in CA and CF phases respectively. A close scrutiny of the fig - 2 suggests that the iron occurs in CA, $C_2F_{1-x}A_x$ and other phases. Comparing with the compound in pure state one can ascertain the first two sites to CF, 3rd and 4th one to $C_2F_{1-x}A_x$ and CA phases (Fiona *et al*., 2001: Goñi and Guerrero, 2003). Also it is evident that the distribution of Fe in the six sites of CA and its presence in small quantity in the phase likely to broaden the Lorentzian lines (Hassan, 2001; Hassan and Eissa, 1986).

According to Young $C_2F_{1-x}A_x$ phase is a slow hydrating phase and hence a complete hydration cannot be expected in the 4th week. When the HAC sample is hydrated in GW, a close scrutiny of the 3rd site reveals that the intensity goes on decreasing with time (Gordana Stefanović *et al*., 2007). This is attributed to the fact that the $C_2F_{1-x}A_x$ phase is almost anhydrated and its contribution is negligible whereas the hydrated phase appears to contribute to the second site whose value are very close to these. The hydration behaviour and production of more and more product is well evidenced with the intensity I_2 which is in increasing trend. The values found suggest that the site assigned to parameter δ_1 and ΔE_1 in dry HAC continues to support the first site whereas δ_1 and ΔE_1 offer its contribution to the 2nd site.

On the moment the water reacts with HAC, a continuous change in the values of quadrupole splitting and Isomer shift are observed. This increase in value, the product $C_2F_{1-x}A_x$ and Fe^{3+} values with time suggests the ongoing reaction and development of strength.

Mössbauer spectra of OPC hydrated with GW at a W/C = 0.4 are shown in fig – 3 (a-c). In fig - 3(a),1week spectra, the intensity of Fe ion in both A and B sites have higher intensities with an isomer shift δ = 0.15 mms^{-1} and quadrupole splitting ΔE_Q = 1.63 mms^{-1}.

© 2015 Published by JPS Scientific Publications Ltd. All rights reserved

Table - 1: Mössbauer parameter for ternary and hydrated HAC Samples treated with GW and TW

S. No.	Hydration time	Mössbauer Parameter			
		GW		TW	
		Isomer Shift	Quadrupole Shift	Isomer Shift	Quadrupole Shift
1.	1w	0.24	0.23	1.87	1.80
2.	4w	0.26	0.25	1.82	1.80
3.	12w	0.27	0.27	1.82	1.81

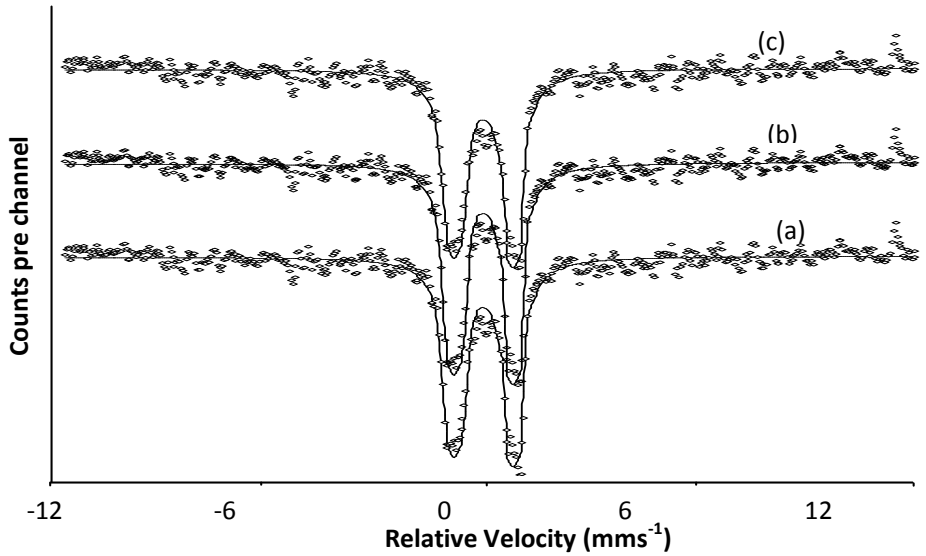

Fig.1 Mössbauer spectra of (a) Anhydrous OPC (b) Anhydrous HAC and (c) Anhydrous Silica Fume (SF)

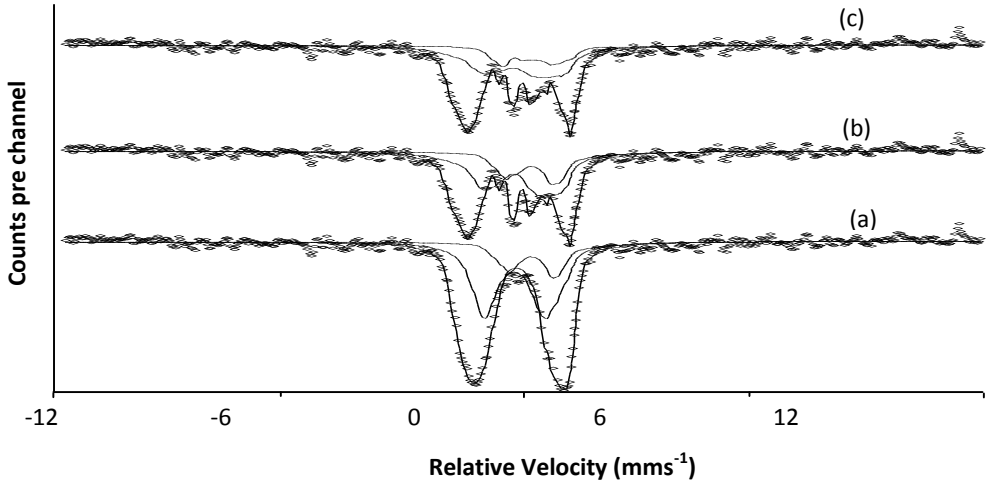

Fig.2. Mössbauer spectra of hydrated HAC treated with GW (a) 1 week (b) 4 week (c) 12 week

© 2015 Published by JPS Scientific Publications Ltd. All rights reserved

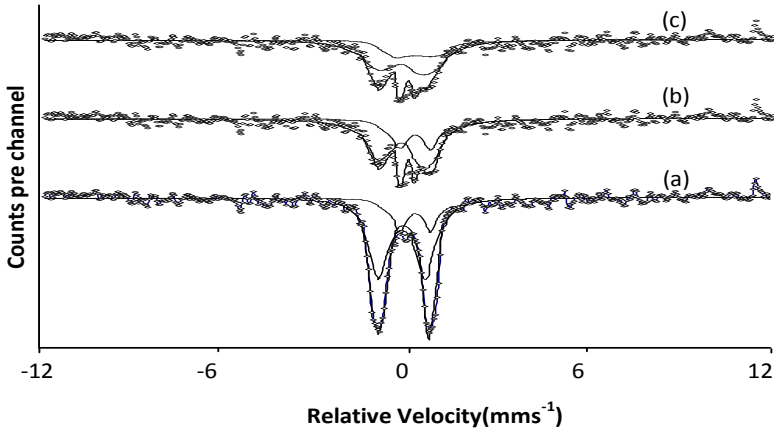

Fig.3. Mössbauer spectra of hydrated OPC treated with GW (a) 1 week (b) 4 week (c) 12 week

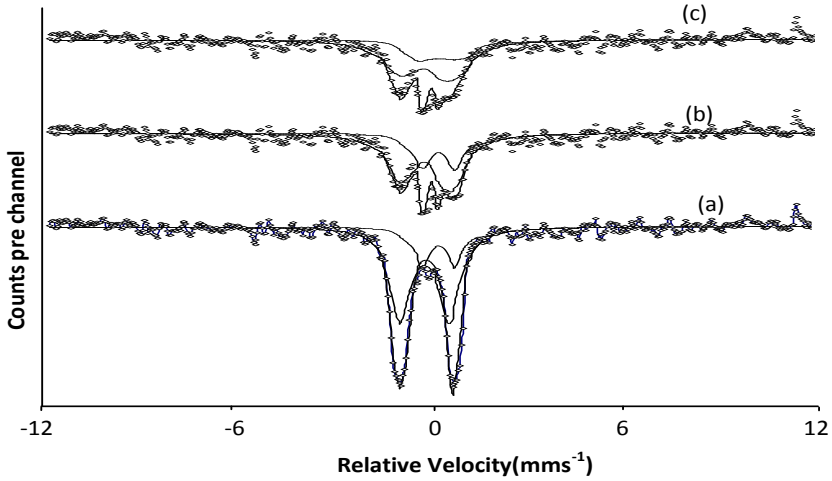

Fig. 4 Mössbauer spectra of 80%HAC+10%OPC+10%SF treated with GW (a) 1 week, (b) 4 week, (c) 12 week

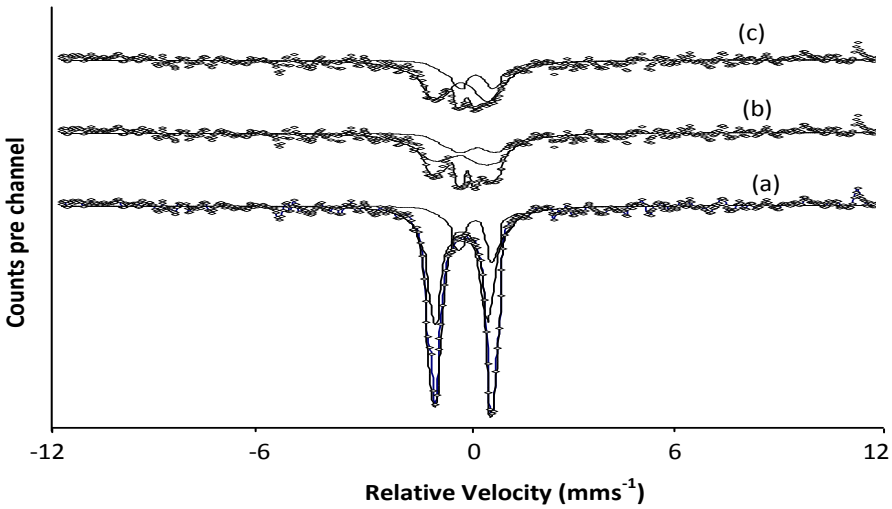

Fig. 5. Mössbauer spectra of 80%HAC+10%OPC +10% SF treated with TW (a) 1 week, (b) 4 week, (c) 12 week

© 2015 Published by JPS Scientific Publications Ltd. All rights reserved

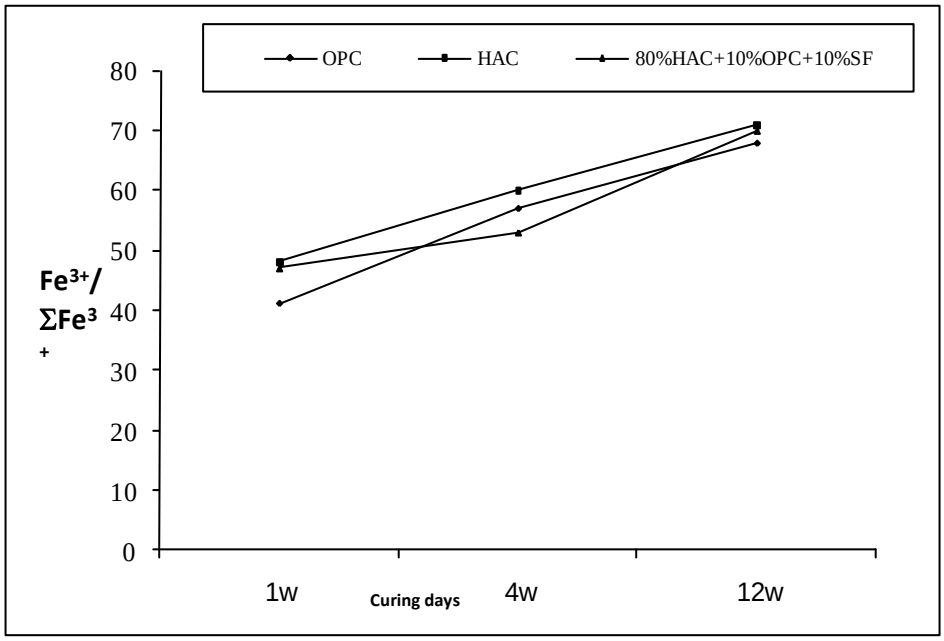

Fig.6 Plot between the $Fe^{3+}/\Sigma Fe^{3+}$ and curing days

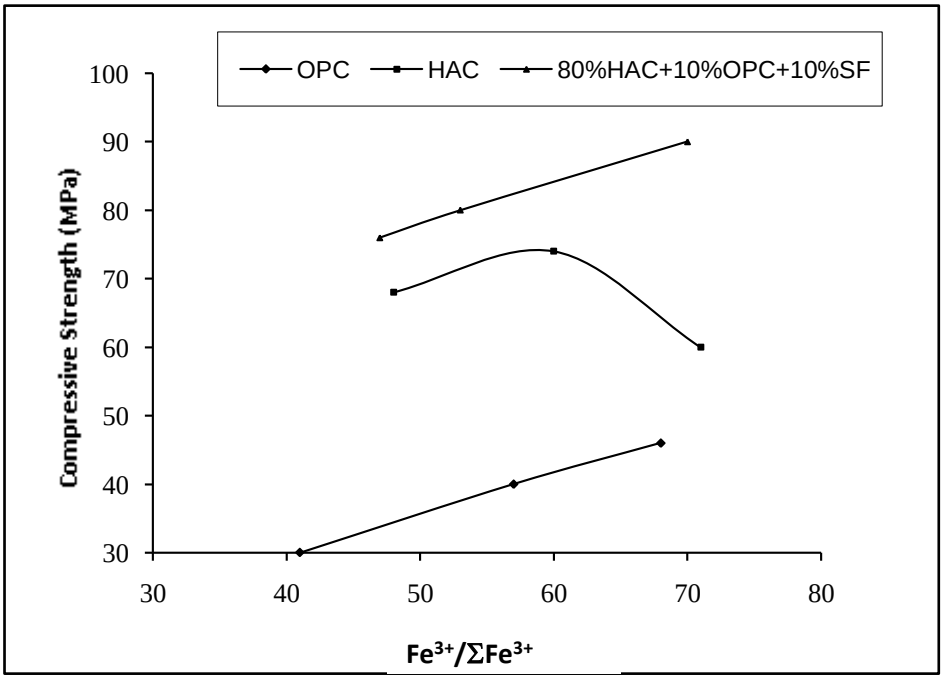

Fig.7. Plot between the $Fe^{3+}/\Sigma Fe^{3+}$ and compressive strength of hydrated OPC, HAC, 80%HAC+10%OPC+10%SF

© 2015 Published by JPS Scientific Publications Ltd. All rights reserved

As hydration time increases [Fig. 3(b)], the hyperfine structures of both sites intensity become almost equal. This is an indication of 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) as given below (Hassaan and Eissa, 1986).

$$C_3A+3C\bar{S}H_2+26H \longrightarrow C_6A\bar{S}_3H_{32} \quad \ldots (1)$$

A further decrease in intensity of $Fe^{3+}(T_d)$ represents probably their replacement of Al^{3+} by Fe^{3+} available in C_3A and C_4AF phases of cement, in every Fe substituted ettringite formation. The formation of ettringite causing setting (IST) at that time is defined by the following equation (Barathan *et al*., 2009; Vili Lilkov *et al*., 2013; 2012).

$$3C_4AF+12C\bar{S}H_2+mH\longrightarrow AC_3(A_{0.75}F_{0.25})C.\bar{S}H_{31}+2FH_3 \quad \ldots (2)$$

As time matures the intensity of A-site is increased whereas the intensity of B-site has started diminishing. In all the spectra, the magnetic hyperfine sexlets appear with higher quadrupole splitting implying that octahedral Fe have asymmetric electron environment. The presence of Fe^{2+} could be flown out due to oxidizing atmosphere; hence a higher rate of isomer shift is observed Mackenzie (1980). Due to replacement, a decrease in concentration of Fe^{3+} is plausible and there is every possibility of transformation to Fe^{2+} forming a spinal structure and preferably an inverse spinal structure. Due to this strength of the cement matrix increases.

According to Mackenzie (1980), under reducing condition all these spectra are observed with a pair of Fe^{3+} doublets suggesting fourfold coordination in distinctly different sites. Consideration of ferrous sites in the aluminates and alumino ferrite systems suggests that the ferrous ions might have replaced Al.

From fig. 3(a-c), it is observed that quadrupole splitting decreases as time passes and started vanishing. This suggests that the ettringite is being converted to iron substituted monosulphoaluminate (AF_m).

The Mössbauer spectra of the hydrated 80 % HAC + 10 % OPC + 10 % SF are shown in fig. 4 (a-c). This spectra contains two doublets representing the Fe^{3+} ion in two paramagnetic sites (i) octahedral site with larger quadrupole splitting (ii) tetrahedral site with smaller quadrupole splitting, probably the ferrite phase is having a smaller intensity (Megaw,1934; Midgley and Ryder, 1977; Mohamed Heikal, 2006). In general, this represents a combination of blended sample containing rich aluminate, rich aluminoferrite, calcite and rich silicate. These values are in good agreement with the values reported by Eissa *et al*. (1982) and Harchand *et al*. (1984). When the sample was hydrated with increasing time of hydration it was observed that the peak due to Fe^{3+}(T) increases whereas Fe^{3+}(O) decreases.

At 1st week [Fig. 4(a-c)] of hydration Fe^{2+} state disappears due to $3Fe^{2+}\longrightarrow 2Fe^{3+}+Fe$ maintaining percentage of iron to be a constant. When the time of hydration increases Fe^{3+} intensity increases suggesting higher strength (Eissa *et al*., 1982).

As percentage of SF increases, the concentration of Si^{2+} increases. At the same time the amount of HAC decreases, reducing the amount of aluminates. A reduction in quadrupole splitting suggests the substitution of Fe^{3+} by Al^{3+} according to Lubos Baca *et al*. (2001) and Kula *et al*. (1980). Naturally, the rest of the irons are in paramagnetic phase in Fe^{3+} valence state. During hydration, Al replacing some of the Fe ions at the distorted octahedral site. This distribution further distorts the octahedral leading to an increase in quadrupole splitting at both the sites (Robertschoen and Charles Roberson, 1970).

When percentage of SF increases further the process is taking place with a delayed time probably due to the pozzolanic reactions, evidenced through iron sites (Sung Gyu Lyu *et al*., 1999; Turanli *et al*., 2005).

© 2015 Published by JPS Scientific Publications Ltd. All rights reserved

The above conjuncture is suppose to be in harmony for a combination of 80 % HAC + 10 % OPC + 10 % SF where the conversion of Fe^{3+} to Fe^{2+} and replacement of Fe^{3+} by Al^{3+} as well as $Ca^{2+}$to occur making the combination more compact increasing its strength. This is true in the 4th week of hydration Hassaan *et al*. (2000).

Also the addition of SF found to decrease the relative intensity of the inner doublet of the spectrum and in turn increase as Si content increases. This behaviour is an indication to a new doublet with larger quadrupole splitting and intensity is maximum according to Hassaan *et al*. (2004). In our study this holds good for 10 % addition of SF.

In the case of TW Fig - 5(a-c), a delayed transformation of Fe^{3+} and the conversion of Fe^{3+} to Fe^{2+} and delayed transfer of Fe^{2+}/Al^{2+} is evidenced suggesting a delayed reaction (Rettel, 1993; Noethig - Laslo and Brecevic, 1998).

Computing the ratio $Fe^{3+}/\Sigma Fe^{3+}$ it is observed (Fig.6) that the value increase showing a higher strength.

A plot of time (V_s) $Fe^{3+}/\Sigma Fe^{3+}$ and compressive strength (V_s) $Fe^{3+}/\Sigma Fe^{3+}$ is drawn with the available data (Fig.7). It shows higher strength value for 80%HAC+10%OPC+10%SF.

4. Conclusion

- As percentage of SF increases, the stratlingite amount increases. This is true for Ground Water paste only. This stratlingite is responsible for strength.
- As percentage of SF increases the strength decreases when gauged Tannery Water upto 4th week of hydration.
- At 4th week, the carbonate polymorph will be in the order for GW paste aragonite > Calcite > Vaterite and for TW paste Vaterite > Calcite > aragonite
- In the initial period of hydration the amount of bayerite is higher and gibbsite is higher at later period of hydration. This is true for both water the gauged paste in a 5% and 10%SF addition. When the SF percentage is 15 and 20%, the reverse is true.
- Due to addition of Tannery Water no structural changes an evidenced and phases are same as that of GW paste.
- The conversion of Fe^{3+} to Fe^{2+} and replacement of Fe^{3+} by Al^{3+} making the combination more compact increasing its strength. This is true for both water.

5. References

1) Antiohos, S. K., V. G. Papadakis, E. Chaniotakis and S. Tsimas. 2007. *Cem. Concr. Res*., 30: 437 - 445.
2) Barathan, S., P. Veluchamy, D. Govindarajan, N. Anandhan and K. Raghu. 2009. *Rec. Res. Sci.Tech.*,1(3): 142 -146.
3) Charles Fentiman, H. 1985. *Cem. Concr. Res.,* 15: 622 - 630.
4) Dong Jianmiao and Long Shizong. 2005. *Journal of Wuhan University of Technology*, 20(2): 77 - 79.
5) Eissa, N. A., M. Y. Hassaan, S. H. Salah, H. A. Sallam and S. A. Abo-El-Enein. 1982. *Qatar Univ., Sci. Bull.,* 2(1): 59 - 65.
6) El Sokkary, T.M., H. H. Assal, A. M. Kandeel. 2004. *Ceramics International,* 30: 133 -138.
7) Faucon, P., P. Le Besup, F. Adenot, N. Genand - Riondet, Jacquinot and J. Virlet. 1997. *Cem. Res.*, 9(35): 99 - 104.
8) Fiona, C., L. Meldrum, T. Stephan and Hyde. 2001. *J. Crys. Grow.*, 231(4): 544 - 558.
9) Goni, G and A. Guerrero. 2003. *Cem. Concr. Res.*,33: 21-26.
10) Gordana Stefanović, Zivko Sekuli, Ljubica Ćojba and Vladimir Jovanovic. 2007. *Ceramics-Silikaty*,51(3): 160 - 167.
11) Harchand, K. S., R. Kumar, K. Chandra and Vishwamittar. 1984. *Cem. Concr. Res.,* 14: 170 - 176.
12) Hassaan, M. Y and N. A. Eissa. 1986. *Scientific and Cultural Organization,* 32 -51.

© 2015 Published by JPS Scientific Publications Ltd. All rights reserved

13) Hassaan, M. Y. 2001. *Mater. Lett.,* 50: 172 - 178.
14) Hassaan, M. Y., F. M. Ebrahim and S. H. Salah. 2004. *Hyp. Interact.,* 156/157: 459 - 464.
15) Hassaan, M. Y., M. M. El-Desoky and Y. M. Abouzeid. 2000. *Mat. Sci. Engg. A,* 276: 147 - 151.
16) Kula, T. M., M. D. Meiser and R. E. Tressler. 1980. *Cem.Concr. Res.,* 10: 491 - 497.
17) Lubos Baca, Jozef Lipka, Ignac Toth, Ladislav Pach. 2001. *Ceramics Silikáty,* 45(1): 9-14.
18) Mackenzie, K. J. D. 1980. *J. Mater. Sci.,* 15(11): 2795 - 2802.
19) Megaw, H. D. 1934. *Z. Kristallogr,* 87: 185 - 204.
20) Midgley, H. G and J. F. Ryder. 1977. *Cem. Concr. Res.,* 7: 669 - 672.
21) Mohamed Heikal. 2006. *Ceramics Silikaty,* 50(3): 167 - 177.
22) Noethig-Laslo, L.J and L. Brecevic. 1998. *J. Chem. Soc.,* 94: 2005 - 2009.
23) Rettel, A., R. Seydel and W. Gessner. 1993. *Cem. Concr. Res.,* 23: 1056 - 1064.
24) Robertschoen, M and E. Charles Roberson. 1970. *The American Mineralogist,* 55: 1 - 60.
25) Saveria Monosi, Roberto Troli, Luigi Coppola and Mario Collepardi. 1996. *Materials and Structures*, 29.
26) Sung Gyu Lyu, Sangdae Park and Gil Soo Sur. 1999. *Korean J. Chem. Eng.,* 16(4): 538 - 542.
27) Turanli, L., B. Uzal and F. Bektas. 2005. *Cem. Concr. Res.,* 35: 1106 - 1111.
28) Ubelhack, H. J and F. H. Whitmann. 1976. *Journal de Physique*, 12(37): 273 – 276.
29) Vili Lilkov, Ognyan Petrov, Yana Tzvetanova and Plamen Savov. 2012. *Const. and Build. Mats.*, 29: 33 – 41.
30) Vili Lilkov, Ognyan Petrov, Yana Tzvetanova, Plamen Savov and Milen Kadiyski. 2013. *J. of Spect.*, 9.
31) Wagner, F.E and U. Wagner. 2004. *Hyp. Inter.,* 154: 35 - 82.
32) Wertheim, G.K. 1964. Mössbauer effect: Principles and Applications: Academic Press, New York.

© 2015 Published by JPS Scientific Publications Ltd. All rights reserved