Quantitative Study of Hydration of PPC-FA Based using Powder X-Ray Diffraction

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Abstract— *Pozzolana is the most commonly used mineral in cement industry. Pozzolana doesn't possess cementitious property on its own but derives its strength by reacting in the presence of moisture with calcium hydroxide formed as a result of hydration. The pozzolanic reaction is slow and required high pH and calcium ion content. This paper deals with study the PPC-FA based cement conforming to IS 1489 Part 1:2015. The LSM, AR, SR, Degree of sulphurization, Burnability Index, Burnability Factor and Percentage Liquid is obtained for the cement using X-Ray diffraction analysis. The hydration of the cement is also studied for 1 day,3 days,7 days,14 days,21 days,28 days and 56 days of curing. The samples for initial setting and final setting of cement obtained as per IS 4031 Part 5:1988 were also analysed for X-Ray diffraction analysis. The paper presents a procedure for sample preparation, X-Ray analysis of cement and cement slurries, identification of phases in cement, identification of silicate hydrates, AFm and AFt phases, percentage variation of these phases and rate of change. The changes in the phases occurring are checked by performing physical tests on cement and cement mortar cubes.*

Keywords— pH, LSM, AR, SR, AFm, Aft, X-Ray diffraction.

I. INTRODUCTION

The most commonly used mineral mixture cement industry is pozzolans. The pozzolans are defined as the siliceous and aluminous materials which by themselves possess very little or no cementitious property but in finely divided form in the presence of moisture, they react chemically with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. Chemically speaking, the pozzolanic reaction occurs between calcium hydroxide (CH) also known as portlandite and silicic acid (H_4SiO_4 or $Si(OH)_4$), their crystal structure details are given in Table 1.

$$Ca(OH)_2 + H_4SiO4 \rightarrow CaH_2SiO_4.2H_2O$$

Many pozzolans also contain Aluminate $Al(OH)^-_4$,that will react with calcium hydroxide and water to form hydrates such as C_4AH_{13},C_3H_6 or hydrogarnet or in combination of silica forming stratlingite (C_2ASH_6) given in Table1.In the presence of anionic group such as sulphates, carbonates or chlorides, Afm phases and Aft phases or ettringite phases can form. The process is a long term process, sufficient amount of free calcium ion and pH of 12 and above is necessary for the solubility silicon and calcium ions and to support pozzolanic reaction.The pozzolans are classified into natural and man-made. Natural pozzolans include trass, certain pumicites and perlite which are generally of volcanic origin. The man made pozzolans include flyash, blast furnace slag and silica flume. Flyash is the most frequently used man-made pozzolan in concrete. The name flyash came from being finely divided residue that results from the combustion of ground or powdered coal.

1.1 Cement Minerals

Alite (C_3S-tricalcium Silicate) it forms the major part in cement composition about 50%.Alite has polymorphs belonging to three different families viz. Triclinic (T_1,T_2,T_3) , Monoclinic (M_1,M_2,M_3) and Rhombohedral (R) depending upon the temperature . Alite hydrated rapidly and hardens the cement slurry and provides high initial (1-3 days) and final mechanical strengths . Monoclinic (M_3) alite is similar to the mineral named Hatrurite.Belite (C_2S-dicalcium silicate) exhibits three to four polymorphs and it reacts with water and forms hydrated dicalciumsilicate . It hydrates slowly and is responsible for the strength of cement after 7 days and is responsible for providing ultimate strength of the cement. Larnite is the naturally occurring mineral similar to belite. Aluminate (C_3A-tricalcium aluminate) is the least abundant phase in a Portland cement. This phases reacts the fastest with water exothermally releasing maximum heat about 207 cal/g. If not controlled, it on immediate hydration with water is responsible for flash set and thereby making the cement paste unworkable. So, retarder such as gypsum is used.C_3A can incorporate Na^+ by substitution of Ca^{2+} ion in an otherwise vacant site, thus giving solid solutions ofgeneral formula $Na_{2x}Ca_{3-x}Al_2O_3$.Its crystal structure is cubic(x=0) but monoclinic(x=0.4375) and orthorhombic(x=0.75) aluminate also exist.

Ferrite (C_4AF-tetracalcium-aluminoferrite) phase is very similar to aluminate phase with orthorhombic crystal structure. Like Aluminates this phase is formed from the melt during cooling. At clinkering temp it facilitates the formation of silicates by increasing the ion mobility. At ordinary pressures in the absence of oxide components other than CaO , AI_2O_3 and Fe_2CO_3,

the ferrite phase can be prepared with any composition in the solid solution series $Ca_2(Al_xFe_{1-x})_2O_5$,Where $0<x<0.7$. The mineral similar in composition to ferrite is called Brownmillerite. Other minor phases present in cement include oxides such as Na_2O, K_2O, SO_3, MgO, loss on ignition,insoluble residueetc. These oxides are not present in cement in their pure form but exist in combined forms . The minerals resembling these combined phases include aphthitalite, langbeinite , arcanite, thenardite, periclase, syngenite(responsible for lumps formation in storedcement) ,calcite, anhydrite and lime (free lime).

1.2 Hydrated Products

C-S-H gel (calcium silicate hydrate) is not only the most abundant about 50% of the hydration product but is also responsible for the most of the engineering properties of the cement. Generally two different types of C-S-H gel structures has been observed found in researches done by Viehland *et al*[1], Slegers *et al* [2],Jenning *et al* [3] and other chemists. These two forms are in close resemblance with 1.4nm tobermorite and Jennite. A gelatinous calcium silicate hydrate, called plombierite, occurs in nature. Calcium Hydroxide (CH) is also know by mineral name portlandite. It forms form C3S and to a lesser extent form C2S. It occupies around 15-20% of the volume of the hydrated cement paste. It forms as a crystal with wide range of shapes and sizes depending upon the space available for growth.AFm are shorthand for a family of hydrated calcium aluminate phases structurally related to hydrocalumite and occurring mainly in hydrated cement paste. A representative formula is $[Ca_2(Al,Fe)(OH)_6] \cdot X \cdot xH_2O$ where X equals an exchangeable singly charged (e.g. chloride) or half of a doubly charged anion (e.g. sulfate, carbonate and aluminosilicate) . Some Fe(III) may also substitute for aluminium. The term 'mono' relates to the single formula unit of CaX_2 in another way of writing the formula, viz. $C_3(A,F).CaX_2.yH_2O$ [or $C_4(A,F)X_2.yH2O$], where $y = 2 (x + 3)$. Many different anions can serve as X, of which the most important for Portland cement hydration are OH^-, SO_4^{2-} and CO_3^{2-}. The AFm phases consists of hydroy–Afm ,hemi-carboaluminates, mono-carbo aluminate , mono-sulpho aluminate, stratlingite, vertumnite, kuzelite and Friedel's salt found in cement concrete exposed to chlorine. AFt (Al_2O_3-Fe_2O_3-tri) phases have the general constitutional formula $[Ca_3(Al, Fe)(OH)_6 \cdot 12H_2O]2 \cdot X_3 \cdot xH_2O$, where x is, normally at least, $\leq$2and X represents one formula unit of a doubly charged, or, with reservations, two formula units of a singly charged anion. The term Aft refers to the three units of CX in an alternative way of writing the formula, $C3(A, F). 3CX.yH_2O$ [or $C_6 (A,F)X_3.yH_2O]$, where $y = x+30$. The most important Aft phase is ettringite, $[Ca_3Al(OH)_6.12H_2O]2-(SO_4)3-2H_2O$ or $C_3A \cdot 3CaSO_4 \cdot 32H_2O$; a phase of or near this composition is formed during the early hydration of most Portland cement. Ettringite is trigonal, with a=1.123nm, c = 2150nm, Z = 2, D_x=1775kgm^{-3}; the space group is P31c.

II. LITERATURE REVIEW

Tomislav Matusinovic et al[4] paper deals with the environmental degradation of the concrete infrastructure.Concrete from a hydro-electric power plant's pipeline 30 years old was characterised with X-ray diffraction (XRD), and thermogravimetric analysis (TGA/DTA). The study highlights the capabilities of the methods for the analysis of concrete towards the determination of hardened cement paste degradation. XRD results showed small quantity of ettringite, calcium carbo-aluminate hydrate and Friedel's salt, and a complete leach of portlandite, while TGA results indicated small quantities of hydrates. Samples taken from flawless inside of concrete layer showed expected quantities of hydrates for the concrete.

F.Guirado et al[5] paper present the quantitative Rietveld analyses of twenty samples of CAC from four different manufacturers over the world, one synthetic mixture and a NIST standard were performed using synchrotron radiation. As compared with conventional XRD, synchrotron powder diffraction permitted to find new minor phases, improve the characterization of solid solutions of iron rich CAC phases and reduce preferential orientation and micro absorption effects

Jumate Elena et al[6] paper presents a study performed on type I Portland cement with respect to the cement hydration processes performed at various time intervals. The methods used concern X-ray diffraction and electronic microscopy applied to define materials and to understand the changes occurring in mineral compounds (alite, belite, celite and brownmillerite) during their modification into hydrated mineral compounds (tobermorite, portlandite and ettringite).

T. Matschei, B. Lothenbach and F.P. Glasser et al [7] studied the solubility and stability of AFm phases in Portland cement. The paper also gives an idea of the thermodynamic stability of the mono sulphate phases and the amount of substitution. The paper helped my research immensely in choosing the AFm phases for the study of hydration of ordinary Portland cement.

III. EXPERIMENTAL PROGRAM

3.1 X-Ray Diffraction

The X-Ray diffraction analysis was done with Bruker's D8 Advance diffractometer. The CuKα radiation of wavelength 1.5418740 Å,theta range of 10-90 degrees, 25kV voltage and Bragg-Brentano arrangement was employed in the study. The phase quantification was done using Match software with maximum of 20 entries.

3.2 Sample Preparation

About 10 g of cement was taken out of the bag, sieved using 75 microns IS sieve, the amount passing were oven dried at 55℃ for 10 minutes to remove any absorbed moisture. The cement is then enclosed and sent to the laboratory for XRD testing. 3 samples of the cement were analysed. ASTM C1365-06[8] was also referred. For the hardened cement slurries, the cement cubes were made by adding water required for standard consistence calculated as per IS:4031 Part 4-1988[9], placing in a mould, unmoulded after 24 hours and placing it in the curing tank. The cubes are then taken out of curing tank at their respective ages of curing, surface water was removed by sun drying for about 15 minutes, and then the samples were crushed to smaller bits using ball mill. Samples obtained for ball mill were further crushed and sieved using 75 micron IS sieve. The fine particles passing through 75 micron sieve were further grounded using a mortar and pestle. The ground samples are then enclosed and sent to lab for testing.

The samples for initial and final setting times as per IS 4031,Part 5-1988[10] were prepared in a slightly different manner. The samples were plastic and thus had to be oven dried at 110℃ for 15 mins. Rest of the procedure is same only ball mill is not required in this case. The figure below shows an enclosed sample prior to testing. The sampling for compressive test on cement mortar was done as per IS:3535-1986. Phase selected for analysis of cement and hydrated cement pastes are given in Table 1 below. The table also gives the mineral names of the phases. The phase given in the table is chosen carefully and fully represents the various types of cement compounds formed.

TABLE 1
PHASES SELECTED FOR ANALYSIS

PHASE TYPE	PHASE	MINERAL NAME	CHEMICAL FORMULAE	CRYSTAL STRUCTURE
MAJOR CEMENT PHASES	ALITE	Hatrurite(M3)	$3(CaO).SiO_2$	Monoclinic
		T1-C3s	$3(CaO).SiO_2$	Triclinic
	BELITE	B-C2S/LARNITE	$2(CaO).SiO_2$	Monoclinic
		ϒ-C2S/Calcio Olivine	$2(CaO).SiO_2$	Orthorhombic
	ALUMINATE	Cubic-Aluminate	$3(CaO).Al_2O_3$	Cubic
		Orthorhombic-A	$Al_{5.175}Ca_{8.393}Fe_{0.45}Na0_{.875}O_{18}Si_{0.375}$	Orthorhombic
		Monoclinic-B	$Al_6Ca_{8.25}Na_{1.5}O_{18}$	Monoclinic
	FERRITE	Brownmillerite-A	$Al_{0.909}Ca_2Fe_{1.091}O_5$	Orthorhombic
		Brownmillerite-B	$Al_{1.346}Ca_2Fe_{0.654}O_5$	Orthorhombic
		Brownmillerite-C	$AlCa_2FeO_5$	Orthorhombic
MINOR CEMENT PHASES	APHTHITALITE		$K_3NaO_8S_2$	Trigonal
	LANGBEINITE		$Ca_2K_2O_{12}S_3$	Cubic
	THENARDITE		Na_2O_4S	Orthorhombic
	ARCANITE		K_2O_4S	Orthorhombic
	GYPSUM		$CaSO_4.2H_2O$	Monoclinic
	LIME		CaO	Cubic
	ANHYDRITE		$CaSO_4$	Orthorhombic
	PREICLASE		MgO	Cubic
	CALCITE		$CaCO_3$	Trigonal
	SYNGENITE		$CaH_2K_2O_9S_2$	Monoclinic
HYDRATED PRODUCTS	C-S-H GEL	Tobermorite	$Ca_2H_3O_{11}Si_3$	Trigonal
		Jennite	$Ca_9H_{22}O_{32}Si_6$	Triclinic
		Plombeirite	$Ca_{2.5}H_{11}O_{12.5}Si_3$	Monoclinic
	AFt	Ettringite	$Al_2Ca_6H_{64}O5_0S_3$	Trigonal
		Thaumasite	$CH_{30}Ca_3O_{25}SSi$	Hexagonal
	CH	Portlandite	CaH_2O_2	Trigonal
	Afm	Hemi Carbo Aluminate	$C_{0.25}AlCa_2O_{9.5}$	Trigonal
		Mono Carbo Aluminate	$CH_{22}Al_2Ca_4O_{20}$	Triclinic
		Stratlingite	$Al_{2.11}Ca2H_{18}O_{16.25}Si_{1.11}$	Trigonal
		Vertumnite	$Al_{2.126}Ca2H_{22}O_{15.72}Si1.434$	Hexagonal

3.3 Phase Analysis of PPC-FA Based and PPC-FA Based Paste

The raw xrd patterns are obtained from the D8 advance spectrometer and these raw data is analysed using the Match Software. The software gives output in terms of mass percentages of the selected phases. The results obtained from the software are represented up to two decimal places. The minor phases were also identified and the results are presented in Table 2. The oxide composition of the cement was found out calculated based on the chemical formulae of the selected phases. The chemical requirements for PPC-FA based cement are given in IS 1489-Part 1:2015[11]. Cement parameters like Lime Saturation Factor (LSF), Alumina Ratio (AR), Silica Ratio (SR), Alkali content expressed as Na_2O equivalent, SO_3 content were obtained. The values of these parameters are given in Table 3.In addition to the above parameters Percentage liquid, Burnability Index and Burnability Factor is obtained. The LSF controls the ratio of alite to belite in the clinker.

A clinker with a higher LSF will have a higher proportion of alite to belite than will a clinker with a low LSF. This determines the potential relative proportions of aluminate and ferrite phases in the clinker. In ordinary Portland cement clinker, the AR is usually between 1 and 4. A high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite. SR is typically between 2.0 and 3.0. The degree of sulphurization for a cement as the ratio between $C3A_{cubic}/C3A_{orthorhombic}$.The degree of sulphurization depends on the percentage of alkali percent in the cement. The water consumption is greater by orthorhombic C3A and thus its rate of hydration is high.

The phase composition of hydrated cement paste was done for initial setting, final setting,1 day,3 days,7 days,14 days,21 days,28 days and 56 days of curing. The initial and final setting time of the cement was found out to be 55 minutes and 235 minutes obtained as per IS 4031-Part 5-1988.The composition in percentage by mass is given in Table 3 with varying ages of curing .The raw XRD data of samples taken at various ages of curing were analysed using Match software .

The gamma-belite is similar to olivine group which does not participate in hydration and are mostly absent in cement. For the purpose of study, it is included as one of the phases similarly monoclinic and orthorhombic aluminate are rare in cement. The background radiation for different output, diffraction peaks and unidentified peak area is also given below

IV. RESULTS AND DISCUSSIONS

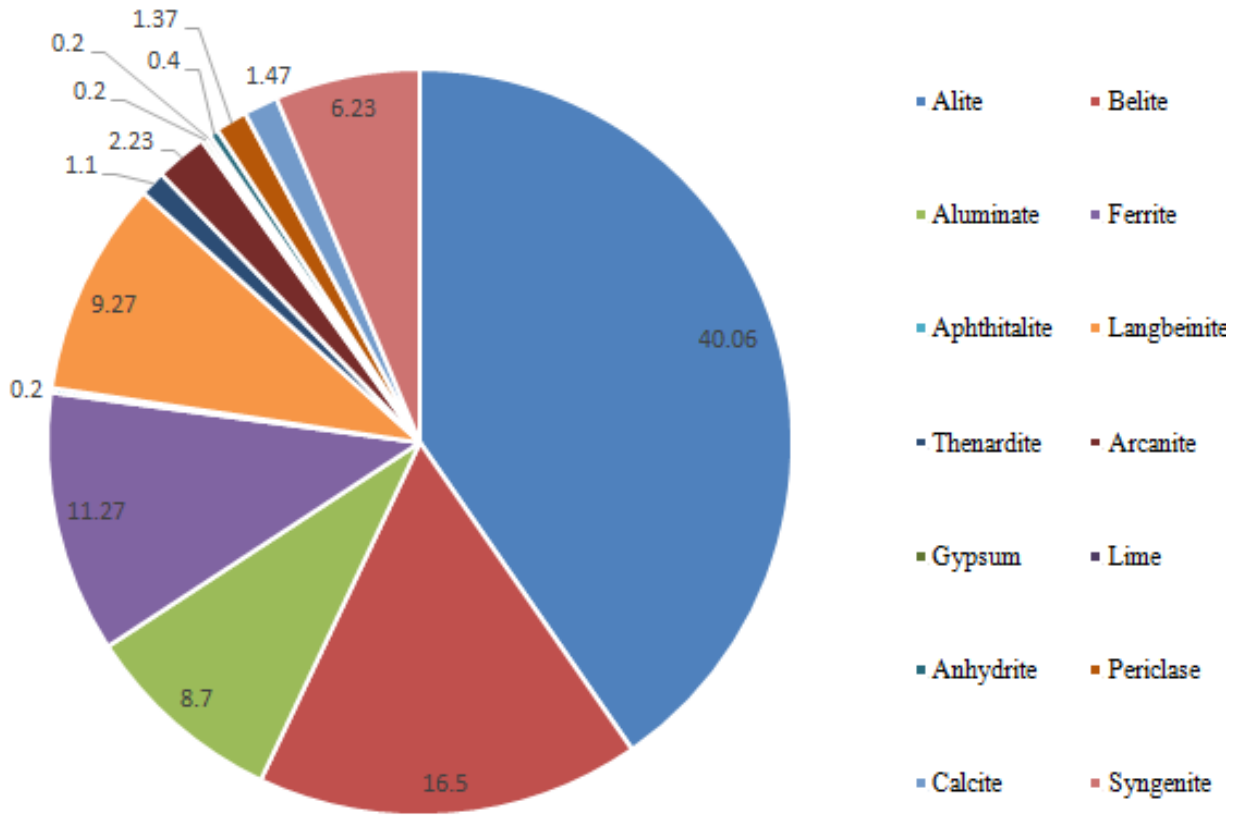

FIGURE 1- PHASE COMPOSITION OF CEMENT

TABLE 2
PHASE COMPOSITION OF CEMENT ALONG WITH CEMENT PARAMETERS

PHASES	PERCENTAGE BY MASS	CEMENT PARAMETERS	VALUES	CODAL PROVISION
Alite(M_3+T_1)	40.06	**Lime Saturation Factor(LSM)**	1.1	
Belite(β+γ)	16.5			
Aluminate (cubic+ortho+mono)	8.7	**Alumina Ratio(AR)**	2.48	
Ferrite	11.27	**Silica Ratio(SR)**	3.08	
Aphthitalite	0.2	**Magnesia**	1.37	6
Langbeinite	9.27	**SO3**	8.89	3
Thenardite	1.1	**Alkali Content**	4.38	
Arcanite	2.23	**Percent Liquid**	28.59	
Gypsum	0.2			
Lime	0.2	**Burnability Index**	2.25	
Anhydrite	0.4			
Periclase	1.37	**Burnability Factor**	14.63	
Calcite	1.47	**Degree of Sulphurization**	0.622	
Syngenite	6.23			

NOTE:

- M3 stands for monoclinic alite and T1 stands for triclinic alite.
- β-C2S stands is also called as larnite and γ-C2S is similar to olivine group and it doesn't participate in hydration and is rarely present in cement.
- Cubic aluminate is similar to Cyclohexa-aluminate, ortho is shorthand for orthorhombic aluminate and mono stands for monoclinic aluminate.

Both monoclinic as well as orthorhombic forms are Na^+ doped aluminates.

The *Lime Saturation Factor* (LSM) was found out to be 1.1. The LSM limits are not given in IS:1489, Part 1 , 2015.*The Alumina Ratio* (AR) is 4.8,*Silica Ratio* (SR) 3.08, *Magnesia* is 1.37 which is with the limiting value 6 as per standards, SO_3 is 8.89 which much greater than that mentioned in the code and the alkali content is 4.38.

TABLE 3
OXIDE COMPOSITION OF CEMENT

OXIDES	MASS PERCENT
CaO	60.036
SiO_2	15.552
Al_2O_3	3.604
Fe_2O_3	1.45
Na_2O	0.739
K_2O	5.529
SO_3	8.892
MgO	1.37
H_2O	1.379

The mass percent of M3 alite is39.2 while for T1alite it is 0.83. The β-C2S is 8.83% and γ-C2S is 7.67%. The mass percent of cubic aluminate is 1.2, ortho-aluminate is 1.93 and mono-aluminate is 7.67.The degree of sulphurization which is the ratio between cubic-C3A to orthorhombic-C3A is 0.622.The smaller the ratio more is the water consumption by aluminates.

TABLE 4
PHASE DATAS IN MASS PERCENTAGE WITH AGE OF CURING

PHASES	*MINERAL NAME*	*AGE OF CURING (HOURS)*									
		0[1]	*0.916*[2]	*3.916*[3]	*24*	*72*	*168*	*336*	*504*	*672*	*1344*
Alite	M_3-Alite/ Hatrurite	39.2	7.2	7.33	9.5	7.87	3.17	5.27	2.93	3.7	1.3
	T_1-Alite	0.83	18.2	10.03	5.23	6.73	5.1	5.63	9.9	9.53	6.67
Belite	β-C_2S o/Larnite	8.83	1.3	1.87	1.83	0.13	5.33	3.83	3.8	0.17	0.87
	γ-C_2S /Olivine	7.67	2.07	5.43	1.63	3.47	5.5	0.9	2.53	3.1	3.63
Aluminate	*Cubic-a*	1.2	0	0	0	1.4	1.2	0.27	0	0.33	0.33
	Ortho-b	1.93	13.83	8.97	17.6	7.43	7.63	8.07	7.47	10.4	7.33
	Mono-c	5.57	0	0	0	0	0	0	0	0	3
Ferrite	Brownmillerite	11.3	5.07	6.03	5.77	6.57	7.23	6.23	5.97	5.33	3.8
C-S-H GEL	Tobermorite	0	6.33	4.57	5.8	9.57	8.3	9.5	5.8	7.97	8.03
	Jennite	0	19.2	23.03	21.7	21.9	19.53	24.4	21.9	18.8	24.43
	Plombeirite	0	5.17	8.57	5.57	10.7	8.37	9.77	10.2	9.03	4.7
Aft	Ettringite	0	6.57	5.5	6.73	7.73	6.33	4.87	6.93	5.93	8.13
	Thaumasite	0	0.23	0.4	0.3	0.37	0.37	0.33	0.3	0.33	4
CH	Portlandite	0	0.23	0.23	2.3	0.43	3.97	5.13	6.9	6.13	3.77
Afm	Hemicarbo-Aluminate	0	0.17	0.13	0.2	0.2	0.2	0.3	0.2	0.23	1.23
	MonoCarbo-aluminate	0	2.7	2.77	3	3.57	3.67	4.13	3.27	4.43	2.5
	Stratlingite	0	5.07	3.8	5.8	3.93	9.03	2.27	7.63	6.83	8.07
	Vertumnite	0	6.63	11.33	7.13	7.47	5.1	8.7	3.7	7.8	9.23
Diffraction Peak		98.083	96.33	96.333	96.3	96.3	96.11	96.12	94.8	95.1	96.035
Background Radiation		1.917	3.67	3.667	3.67	3.66	3.887	3.88	5.17	4.85	3.965
Unidentified Peak Area		20.823	13.54	29.923	13.4	30.1	31.22	30.59	28.5	30.2	31.005
Note:1.Composition of cement,2.Composition for initial set,3.Composition of Final set											

The Jennite phase has maximum percentage by mass in the C-S-H group, the ettringitic is the dominant phase in Aft group and the Stantlingitic and Vertumnite phases comprised almost 85% of the Afm phase for most of the ages of curing.

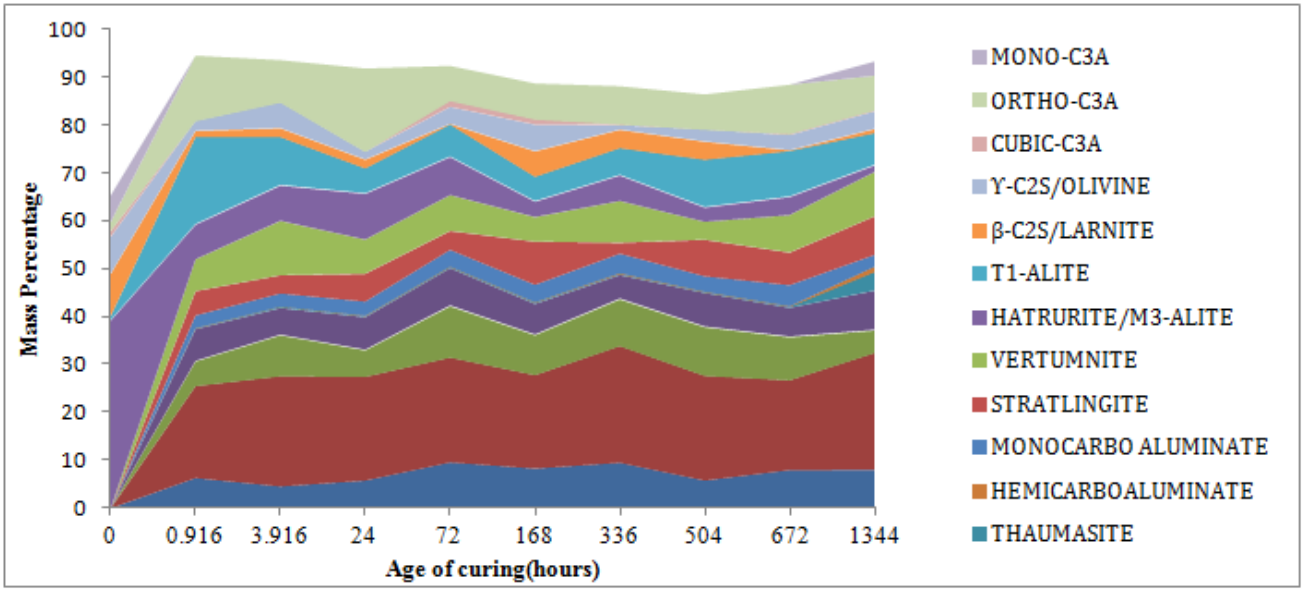

FIGURE 2- VARIATION OF PHASES WITH AGE OF CURING

The maximum value of C-S-H was obtained on 14 days of curing about 13.67% (Tobermorite = 8.03 %, Jennite =24.43% and Plombierite = 47%) by mass. The maximum value of Aft is 12.13 % (Ettringite = 8.13 % and Thaumasite = 4%) by mass on 56 days of curing. Calcium Hydroxide CH is maximum on 21 days of curing which is 6.9 % by mass and Afm phase was maximum on 56 days of curing and its value is 21.03% (Hemicarbo aluminate = 1.23 % , Monocarbo aluminate =2.5 %, Stratlingite = 8.07 % and Vertumnite =9.28%) by mass.

TABLE 5
HYDRATION INDEX VARIATION WITH INTERVALS OF 7 DAYS.

HI (Hydration Index)	1st 7 days	2nd 7 days	3rd 7 days	4th 7 days
C-S-H	0.215	0.044	-0.035	-0.013
Aft	0.04	-0.009	0.012	-0.006
CH	0.024	0.007	0.011	-0.005
Afm	0.107	-0.015	-0.004	0.027
Hydrated Products	0.386	0.027	-0.016	0.003

The *Hydration Index* (HI) is a parameter used in tis paper to define the rate of increase of phase percentages divided by the duration of 168 hours or 7 days. The HI has units *% by mass/hr* .HI also denotes the slope of curve drawn between mass percent of phases with age of curing at 168 hours of intervals. This parameter gives the slope of plot between mass percentages of phases with age of curing in hours. The Hydration Index(HI) is the most for 1st 7 days which is around 0.386 and the second most is during the 2nd 7 days of 0,027 .In the 3rd 7 days the HI is -0.016 which can be attributed due to fall in HI of C-S-H by -0.035 and fall in HI of Afm by –0.004.During the 4th 7 days, there is a marginal increase of 0.003 in the HI of the hydration products. This is due to decrease in HI of C-S-H by -0.013,Aft by -0.006,CH by -0.005 and increase of HI by Afm by 0.027.

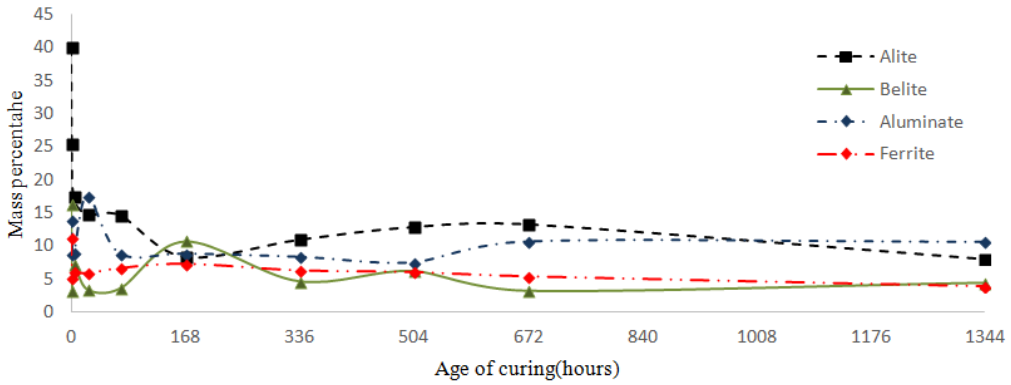

FIGURE 3-VARIARTION OF MAJOR PHASES WITH AGE OF CURING

The Figure 3 shows the variation of four major phases with the age of curing as the hydration progresses. The curves for Alite, Belite and Aluminate shows a zig-zag pattern which the Ferrite phase shows a very little variation minimum being -0.26 and maximum being -6.2 during initial setting.

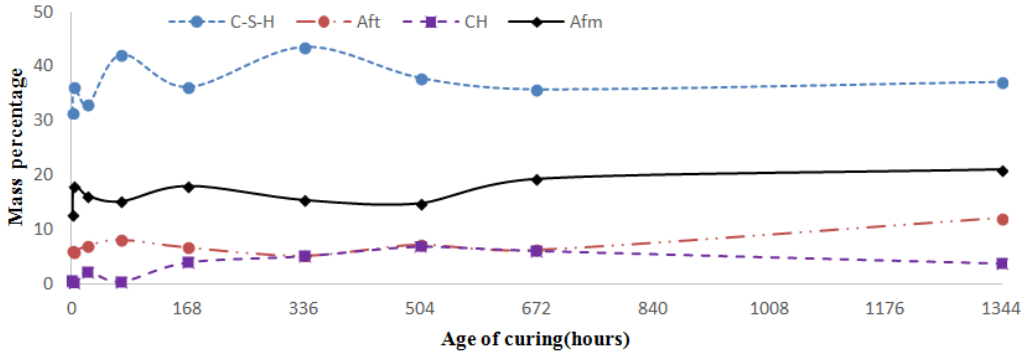

FIGURE 4- VARIATION OF HYDRATED PRODUCTS WITH AGE OF CURING

In the Figure 4, the hydration products vary rather randomly with age of curing. The most of the calcium hydroxide in lost by leaching of the sample when in water. The C-S-H gel at the end of 56 days of curing comprises of 37% of the products while there has been a jump in Aft percentage during this phase of 5.87 which is nearly its double. Afm value saw a marginal rise of 1.27 but its composition in quite high as compared to Aft. After 21 days of hydration the plot of Afm and Aft is more like a mirror image upto 56 days of curing with Afm increasing at a HI 0.027 while Aft decreasing an HI of -0.006 from 21days to 28 days.

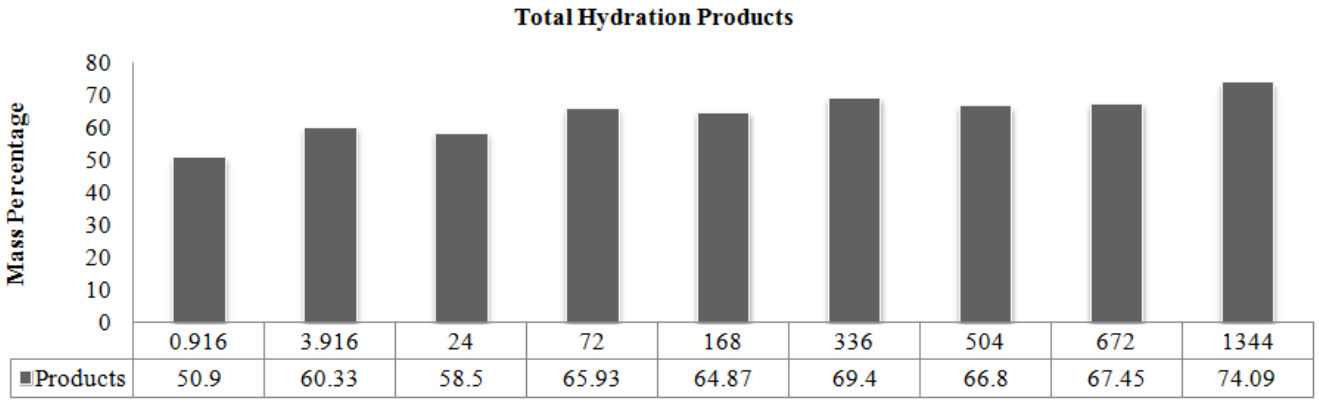

FIGURE 5- TOTAL HYDRATION PRODUCTS FORMED WITH AGE OF CURING

There is a decrease in hydration products on day 1 by 3.033% (C-S-H=-8.65%↓,Afm=-10.54% ↓, Aft = 19.15%↑ and CH=900% ↑),on day 7 by 1.608% (C-S-H=-14.28%↓,Aft=-17.28% ↓,CH = 823.26 % ↑ and Afm = 18.66% ↑) and on day 21 by -3.746%(C-S-H =-13.28%↓, Aft=39.04%↑, CH= 34.5%↑ and Afm= -3.9%↓).

The variation of the total mass percent of hydration products in given in Figure 5 .The most of the products are formed during initial setting as this is the phase of maximum heat release. The percentage increase in hydration products form initial set to final set which is about 18.527%.

The percentages are obtained taking products formed during the initial set as reference. The 2nd most and 3rd most increase was observed during period of 1 day to 3 days of 12.701 and 9.844% during 28 to 56 days. At the end of 56 days of curing the total amount of hydration products formed is 74.09% which comprises of 37.16% C-S-H , 12.13% Aft , 5.77% CH and 21.03% Aft. At the time of initial setting the total amount of hydration products were 50.9%.

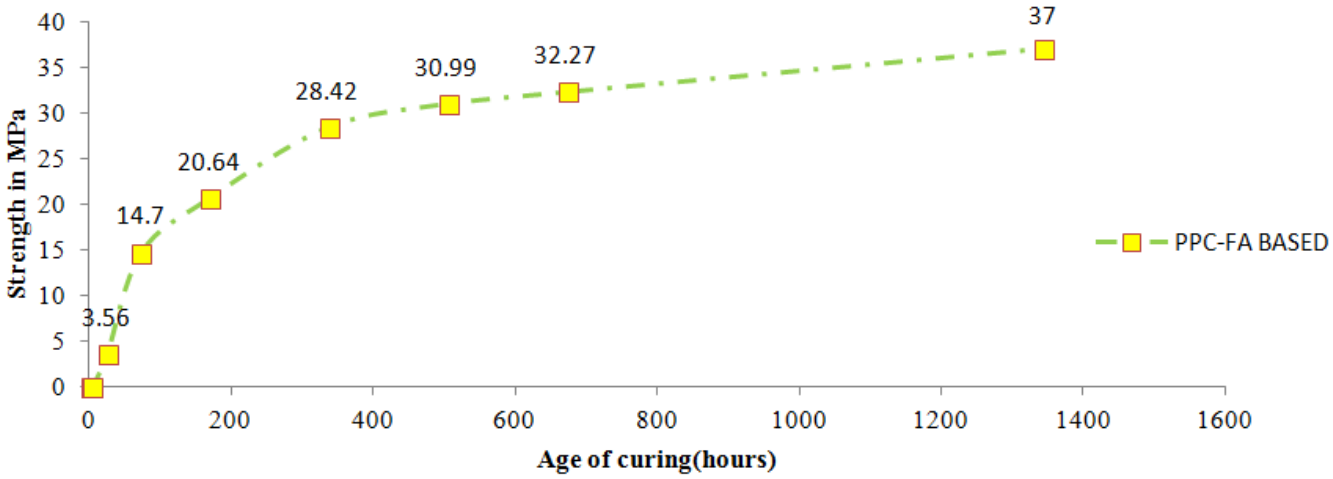

FIGURE 6- STRENGTH INCREASE FOR PPC-FA BASED

A parameter called *Strength Index* (SI) was used which gives the rate of increase in strength of the cement during the period of 168 hours or 7 days. Thus, the strength index is calculated by considering the compressive strengths obtained during the course of 1-7 days, 7-14 days, 14-21 days and 21-28 days dividing by 168 hrs. The unit being *MPa/hr*. The SI for the 1st 7 days is 0.123, 2nd 7 days is 0.022, 3rd 7 days is 0.015 and for the 4th 7 days is 0.01756.

TABLE 5
SI VARIATION WITH INTERVALS IN 168 HRS.

SI (Strength Index,MPa/hr)	1st 7 days	2nd 7 days	3rd 7 days	4th 7 days
PPC-FA Paste	0.1228	0.0463	0.0153	0.0076

The maximum increase in strength was obtained during the period 1 day to 3 days of about 312.92% followed by 40.41% during the period 3 days to 7 days and 37.39% during 7 days to 14 days.

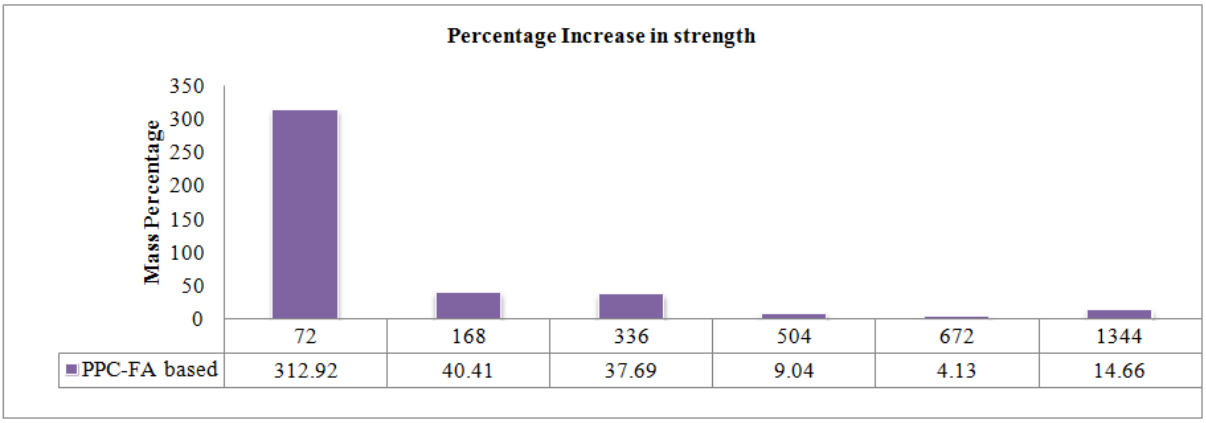

FIGURE 7- PERCENTAGE INCREASE IN STRENGTH WITH AGE OF CURING

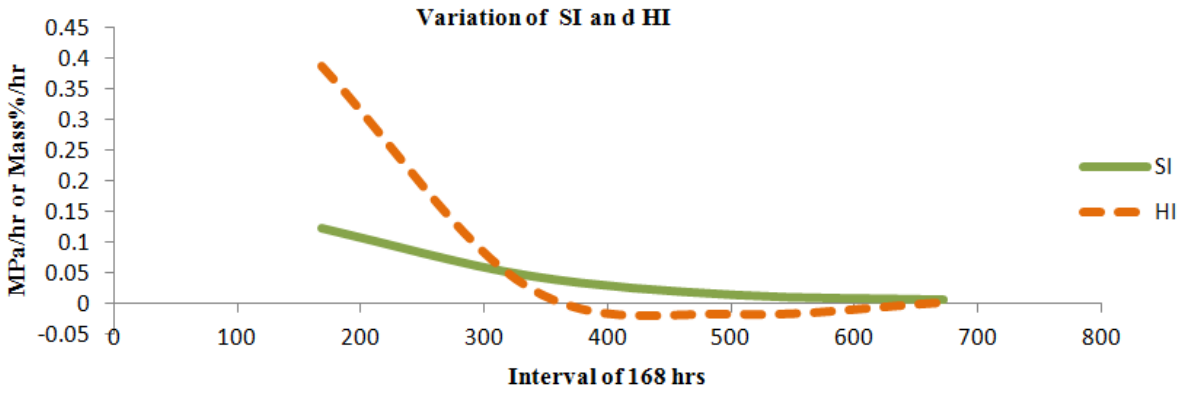

FIGURE 8- COMPARISON BETWEEN SI AND HI FOR PPC- FA BASED.

The unhydrated products percentages include, Alite=7.97% , Belite = 4.5% , Aluminate = 10.66% (the cubic aluminate is around 0.33% which the orthorhombic aluminate is 7.33% and monoclinic aluminate is 3%).The Figure: shows the plot between values for HI and SI with the interval of 168 hrs. The curves meet somewhere in between 7 and 14 days.

V. CONCLUSION

The *Lime Saturation Factor* (LSM) was found out to be 1.1. *The Alumina Ratio* (AR) is 4.8, *Silica Ratio* (SR) 3.08, *Magnesia* is 1.37 which is with the limiting value 6 as per standards, SO_3 is 8.89 which much greater than that mentioned in the code and the alkali content is 4.38. The degree of sulphurization is about 0.62 at MgO content of 1.37.

The HI is the most for 1st 7 days which is around 0.386 and the second most is during the 2nd 7 days. In the 3rd 7 days the HI is -0.16 which can be attributed due to fall in HI of C-S-H by -0.035 and fall in HI of Afm by –0.004. During the 4th 7 days, there is a marginal increase of 0.003 in the HI of the hydration products. This is due to decrease in HI of C-S-H by -0.013,Aft by -0.006,CH by -0.005 and increase of HI by Afm by 0.027.

There is a decrease in hydration products on day 1 by 3.033%, on day 7 by 1.608% and on day 21 by -3.746%. The most of the products are formed during initial setting as this is the phase of maximum heat release. The percentage increase in hydration products form initial set to final set which is about 18.527%.

There is increase in compressive strength of the cement with age of curing. The chage being drastic during the initial stages which smoothes with passage of time. The maximum increase in strength was obtained during the period 1 day to 3 days of about 312.92% followed by 40.41% during the period 3 days to 7 days and 37.39% during 7 days to 14 days. The SI for the 1^{st} 7 days is 0.123, 2^{nd} 7 days is 0.022, 3^{rd} 7 days is 0.015 and for the 4^{th} 7 days is 0.01756.

At the end of 56 days of curing the total amount of hydration products formed is 74.09%.At the time of initial setting the total amount of hydration products was 50.9%.The unhydrated products percentages include, Alite =7.97% , Belite = 4.5% , Aluminate = 10.66% (the cubic aluminate is around 0.33% which the orthorhombic aluminate is 7.33% and monoclinic aluminate is 3%).

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