

Entrapment of Zinc & Lead in Clinker Produced with a Nonferrous Waste Slag

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Abstract

The chemical and mineralogical properties of waste slag of a smelting lead zinc plant, its application in cement manufacturing, entrapment of zinc and lead in clinker and its leaching behavior were studied. Laboratory clinkers were prepared with 0, 2.0 and 5.0% slag replacing siliceous and ferrous material in agreement with the composition of major raw materials. The clinker thus obtained was subjected to extensive characterization using XRF, XRD, SEM and EDAX. Phase separation technique and Scanning Electron Microscopy revealed that zinc is incorporated in both silicate and interstitial phases of clinker. EDAX analysis confirmed that zinc is entrapped in the alite and ferrite phases.

The hydraulic characteristic of clinker was also studied. Leaching behavior of hydrating phase showed that zinc is entrapped with hydrated products and up to 28 days of hydration no leaching of zinc was observed. Lead was beyond detectable level due to very low concentration in slag.

1.0 Introduction

One of the lead and zinc smelting units in the northern part of India generates about 200 tonnes of slag every day and has an accumulation of 9.0 million tonnes over several years. In order to minimize the problem of environmental pollution as well as of ground water contamination from this slag, an endeavor has been made to utilize the slag as a raw mix component in clinker making. The content of ZnO and PbO in the slag varies in the range of 4.86 – 12.36% and 0.33 to 1.33% respectively. The composition of the slag is given in Table 1.

It is well known that zinc oxide acts as a mineralizer during clinkering process and improves the burnability of raw mixes [1-2]. ZnO addition accelerates clinker formation and approximately half of the zinc is distributed in silicates with preference for alite over belite [3]. Odler and Schmidt [4] revealed that the enhanced formation of alite and C₂(AF) at the expense of belite and C₃A is due to ZnO doping. According the Hornain [5] zinc in clinker is preferably retained in ferrite followed by alite,

aluminate and belite. HFW Taylor [6] suggested that with increasing ZnO content triclinic, monoclinic and rhombohedral polymorphs of C_3S are formed. Stephen et. al. [7] have found that the heavy metals upto 1000 ppm have no measurable influence on burning process and hydration properties. They concluded that increased addition of heavy metals changes the formation of pure clinker phases. Knofel [8] has found that approximately half of the zinc is distributed in silicates with preference for alite over belite; the other half is distributed into the matrix with preference for the ferrite phase.

Waste solidification often leads to heavy metal fixation in cement paste. Felix Ziegler & co-workers [9] suggested that zinc is incorporated in the inter layer of C-S-H (I). It is reported that small amount of PbO or ZnO retards the hydration of Portland cement strongly. This effect has been attributed to the formation of an impermeable layer of products—heavy metal hydroxides or amphoteric salts produced in the reaction between the oxides & C_3S . The effect of heavy metals was studied from the point of view of their immobilization in the hardened cement matrix [10]. Many researchers have focused on the studies of the stabilization mechanism & leaching of heavy metals from different cement composite materials [11,12]. A very high degree of Pb or Zn immobilization was found as well as the formation of highly disordered C-S-H in the presence of heavy metal compounds [13].

From the previous literature it appears that the fixation of zinc and lead in the clinker particularly when non-ferrous slag is used as a corrective raw material has not been studied and reported. The present paper aims to highlight the fixation of zinc and lead in the clinker phases and possible reason of their immobility.

2.0 Experimental

2.1 Materials

For the present work the required raw materials viz. limestone and red ochre were taken from a plant. Non-ferrous slag referred as NFS, was collected from the Smelting unit.

2.2 Chemical characterization of raw materials

The limestone, red ochre and NFS were characterized using Bruker S-4 Pioneer Sequential XRF at varying X-ray generator power according to elements. The results are given in Table 1.

2.3 Mineralogical characterization of NFS

The mineralogical composition of NFS was determined using Bruker D-8 Advance diffractometer with the instrumental Bragg-Brentano Geometry

equipped with a Cu K_{α} radiation & a graphite monochromator on the diffracted beam. The X-ray diffractogram of NFS given in Fig.1 indicates

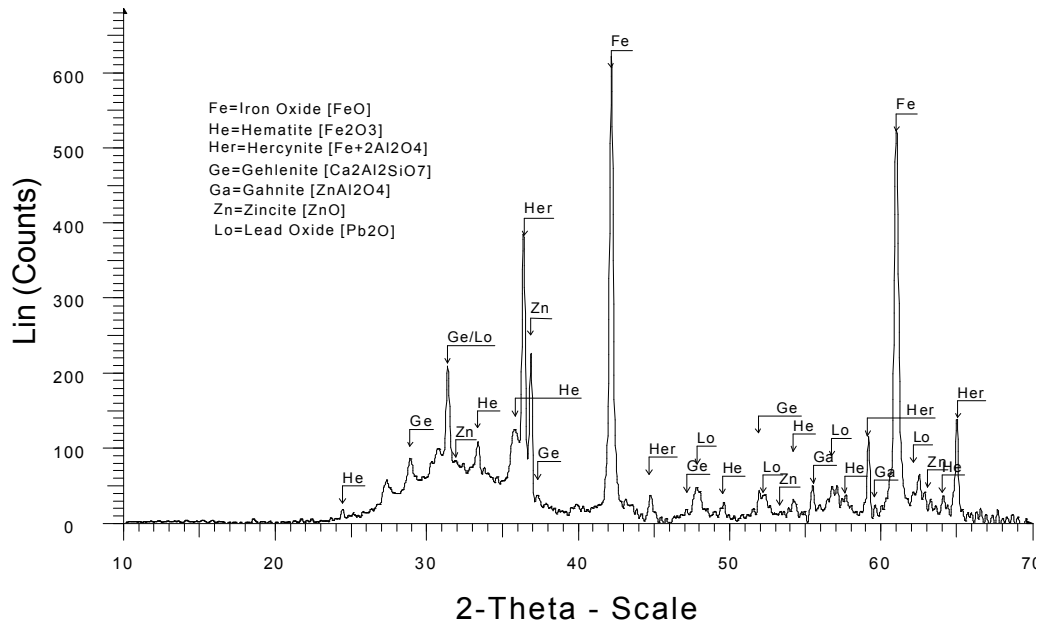


Fig. 1: XRD of Nonferrous Slag showing minerals.

the presence of predominantly amorphous material along with Hematite (Fe_2O_3), Iron Oxide (FeO), Gehlenite ($Ca_2Al_2SiO_7$), Hercynite ($FeAl_2O_4$) and Zincite (ZnO). The oxide and mineralogical compositions of slag confirmed that it is suitable as a corrective raw mix ingredient.

Table-1: Chemical Composition of Raw Materials

S no	Composition (%)	Sample Identifications					
		LS1	LS2	LS3	Red Ochre I	Red Ochre II	NFS
1	LOI	36.03	34.65	35.11	17.17	17.83	4.08
2	SiO ₂	13.99	13.30	13.44	9.86	13.28	17.46
3	Al ₂ O ₃	2.12	2.73	2.21	32.37	37.95	8.72
4	Fe ₂ O ₃	1.58	1.98	1.16	32.94	21.00	38.98
5	CaO	45.69	45.05	42.41	1.99	3.96	14.88
6	MgO	0.50	0.50	0.56	0.15	0.39	0.93
7	PbO	-	-	-	-	-	1.33
8	ZnO	-	-	-	-	-	12.36
Raw material Proportion							
1	Control	94.3	-	-	5.7	-	-
2	2% NFS	94.3	-	-	3.7	-	2
3	5% NFS	-	71.8	21.1	-	1.8	5

2.4 Preparation of laboratory clinkers

Three raw mixes were prepared with the above raw materials using 2.0% and 5.0% NFS (Table1). 1% coal ash was added in all mixes. The homogenized raw materials were mixed with distilled water thoroughly. Nodules of about 1 cm diameter were prepared and dried in an oven at $105 \pm 5^\circ C$ for 2 hrs before subjecting them to firing. The nodules were fired

in a programmable high temperature furnace at 1450°C for 30 minutes starting from ambient; the heating rate was maintained at 20°C/min. The nodules cooled in air were stored in a desiccator.

2.5 Chemical-Mineralogical Characterization of Laboratory Clinkers

The chemical analysis of the lab fired clinker samples with & without NFS were carried out using S-4 pioneer XRF. Free lime of each clinker sample was determined volumetrically in accordance to IS: 4032. The mineralogical compositions of lab fired clinkers with & without NFS were determined using D8-Advance diffractometer.

2.6 Selective Dissolution Extraction

To know the distribution of zinc and lead in silicate & non-silicate phases, selective dissolution extraction technique was adopted [6]. The solution was filtered. The residues thus obtained were analyzed by using X-ray fluorescence.

2.7 SEM – EDAX Analysis

To identify the distribution of zinc & lead in different clinker mineral phases, SEM & EDAX spot analysis of selected lab fired clinker samples were carried out using Zeiss EVO 40 SEM and Oxford EDAX. The clinker samples were mounted on the specimen stub and transferred to SEM sample chamber for microstructural examination. The samples were examined under Back Scattered Electron Diffraction (BSED) mode. All samples were precisely scanned and crystal structure of different clinker mineral phases were identified. The spot analysis was carried out on the identified phases. The scanning electron photomicrograph and EDAX spectra for compositional analysis of spots were recorded.

2.8 Hydraulic Characteristics

2.8.1 Preparation of hydrated cement sample

The clinker samples prepared with and without NFS, were ground in agate mortar with 4% mineral gypsum to produce a cement with 2.80% SO₃. The samples were mixed with distilled water in polythene bags keeping W/C ratio 0.5. The bags were sealed after removing the air to avoid carbonation and were kept in an incubator maintained at 27°C for 0.5 h, 1 h, 4 h, 8 h, 12 h, 24 h, 3 days, 7 days & 28 days. Hydration was stopped at different time intervals by using iso-propyl alcohol/ether. Every sample was dried at 105°C for one hour and then stored in a desiccator for XRD and TG-DSC analysis.

2.8.2 Characterization of hydrated products by XRD

The X-ray diffraction patterns of hydrated cement samples with and without NFS were taken using D8 Advance Powder X-ray Diffractometer using Cu K α radiation.

2.8.3 TG–DSC analysis

The TG-DSC analysis of hydrated sample for different time periods were carried out using Netzsch STA 409 PC LUXX. The samples were placed for heat treatment up to 1000°C keeping heat rate 10°C/min in an inert atmosphere. The TG and DSC curves with respect to temperature were recorded. The non-evaporable water content of hydrated samples were calculated from the weight loss in the temperature range of 100°C to 1000°C using thermo gravimetric curves.

2.8.4 Leaching Test

The cement prepared with 5% NFS clinker was mixed with water keeping water-cement ratio 1.0 and allowed to hydrate for 30 min, 1h, 4 h, 8 h, 12 h & 24 h. The liquid phase of hydrating paste was extracted at the above hydration period using vacuum pump. The liquid phase (filtrate) was subjected to estimation of zinc and lead heavy metals by Leeman inductively coupled plasma (ICP) spectrometer. The residue obtained after filtration was dried at 100°C for one hour and then placed for estimation of zinc and lead by XRF. The leaching of zinc in cement hydrated for 28 days was also determined. The sample was ground to 50 µm and water was added in excess. The mix was kept with continuous stirring for 8 hour. The mix was filtered with 40 No Whatman filter paper. The filtrate was acidified to avoid any precipitation due to carbonation and was analyzed by ICP.

3.0 Results & discussions

The free lime results of clinker prepared in laboratory with varying dosage of NFS is given in Fig. 2. The free lime in presence of NFS is lower in

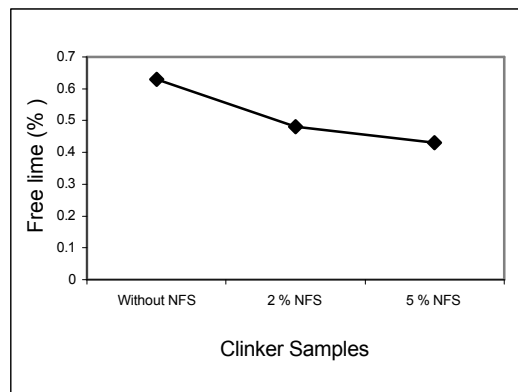


Fig.2: Variation in Free lime with varying dosage of NFS

comparison to control. The reduction in free lime is more at the higher addition of NFS. From the result it is clear that NFS accelerates the clinkering reaction.

The oxide compositions of clinkers determined using XRF are given in Table 2. The results indicate all three clinkers have almost similar oxide compositions except ZnO contents. The ZnO in clinkers with 2% and 5% NFS are found to be 0.33% and 0.78% respectively while no ZnO was detected in control clinker, which indicates that the assimilation of zinc in

Table-2: Oxide Composition of Clinker Samples

Sample Identification	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	ZnO	PbO
Control Clinker	21.16	63.92	4.54	3.85	1.31	0.00	0.00
2% NFS Clinker	21.20	64.19	3.91	3.76	1.35	0.330	0.005
5% NFS Clinker	21.14	63.64	3.47	3.87	1.41	0.779	0.007

clinker increases with the increase of NFS. The PbO contents in both clinkers were low as expected at 0.005% and 0.007%.

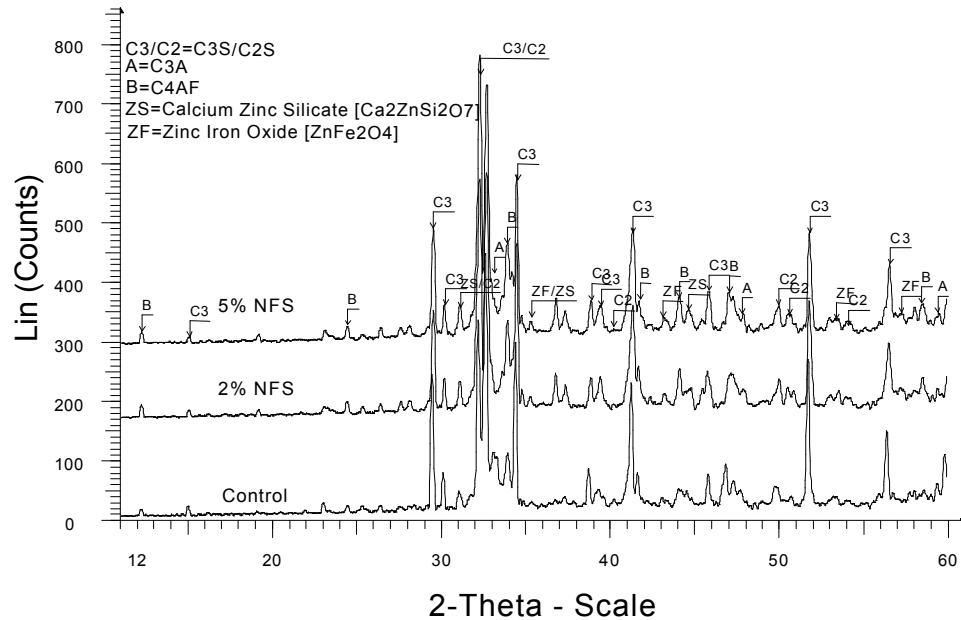


Fig.3: XRD of clinker with varying NFS

The XRD patterns of all three clinkers and the clinker mineral phase composition determined by TOPAS software, based on Rietveld refinement, are given in Fig. 3 and Table 3. The results indicate that C₃S content in clinker increases with higher dosage of NFS. The significant reduction in C₃A content was observed in presence of NFS. Apart from the normal clinker mineral phases, the XRD patterns of clinkers with NFS show zinc bearing minerals at 35.29 and 43.98 2θ values, which are identified for calcium zinc silicate and zinc iron oxide respectively. No peak was detected for Pb bearing minerals as it is below detection limit due to its low concentration in raw mix and hence in resulted clinker. The

mineralogical composition of clinker indicates the quality of clinker to be very good and is suitable for the manufacture of ordinary Portland cement.

Table - 3: Mineralogical Composition of Clinker Samples

Sample Identification	Actual phase composition (%)			
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Control clinker	55.03	25.94	7.38	11.65
2% NFS clinker	58.80	24.59	3.73	12.62
5% NFS clinker	59.32	24.49	3.60	12.53

The zinc oxide in residues of SAM and KOH-Sugar extractions of clinker, analyzed with XRF, is given in Table 4 which shows that zinc oxide is incorporated in both the silicate as well as in interstitial phases. The

Table- 4: Distribution of ZnO

Clinker	ZnO in clinker	ZnO in silicate phase	ZnO in Matrix
Control	0.00	0.00	0.00
2% NFS	0.33	0.17	0.16
5% NFS	0.78	0.44	0.34

distribution is almost half in each of the above phases. The XRD pattern of the residue after removal of interstitial phases is presented in Fig. 4.

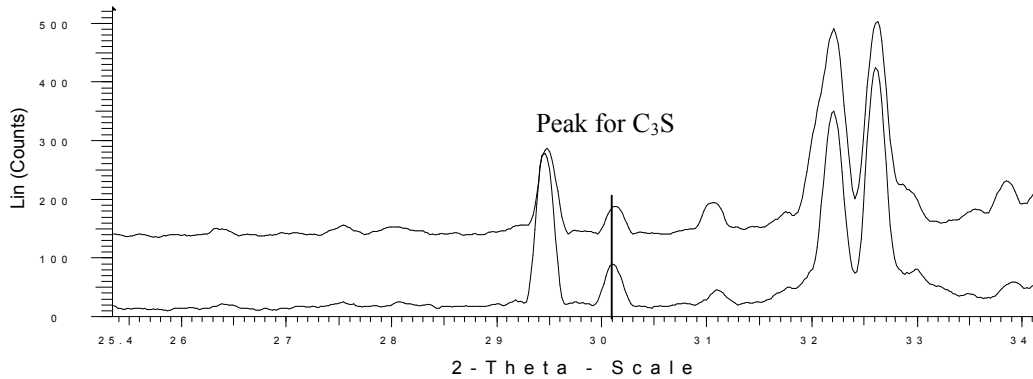


Fig.4: XRD of clinker sample after KOH-Sugar extraction showing peak shifting of C₃S

The peak appeared at 30.135 2θ value as reported for C₃S. In presence of NFS the XRD pattern at this 2θ value shows a little peak shifting. No peak shifting, however, was observed for C₃A and C₄AF. Since, no other explanation could be found to explain the minor peak shifting of C₃S, it has been presumed this may be due to zinc incorporation in the alite lattice.

The scanning electron photomicrographs showing spots for elemental analysis with and without NFS are given in Figs. 5-7. The SEMs show well development of clinker mineral phases in all clinkers. The elemental analysis of spots on particular mineral phases are given in Table 5. The zinc is found at spots 5 – 10 where NFS was used. No zinc was detected on alite and ferrite phases in control clinker. No sign of lead was found at

any spot. The SEM photograph of clinker with 5% NFS (Fig.7) shows a detectable crystal embedded in alite. The elemental spot analysis of this crystal (spot 9) contains considerable amount of zinc (Table 6). The oxide composition of spot 9 is recalculated as CaO-54.77%, SiO₂ -19.50%, Al₂O₃-1.79%, ZnO -17.14%, which comes close to the molar ratio of CaO,

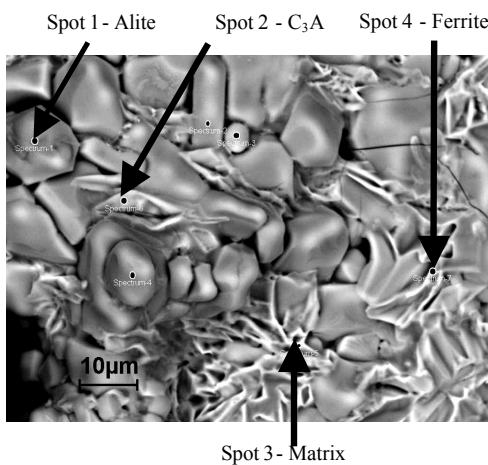


Fig.5: SEM of Control clinker with spots for EDAX analysis.

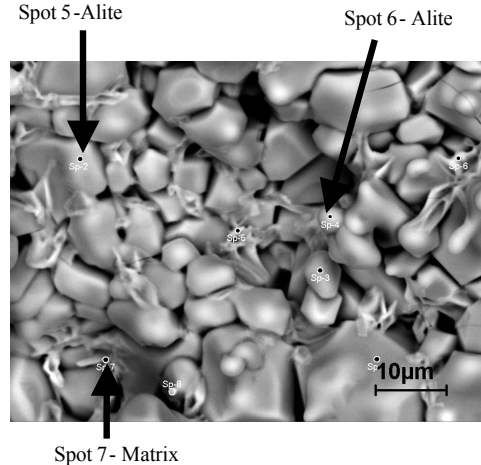


Fig.6: SEM of 2% NFS clinker with spots for EDAX analysis.

ZnO & SiO₂ of calcium zinc silicate (Ca₂ZnSi₂O₇) compound but with some excess CaO. The excess CaO may be due to presence of other minor oxides like Al₂O₃, MgO and Fe₂O₃ which are also observed in elemental

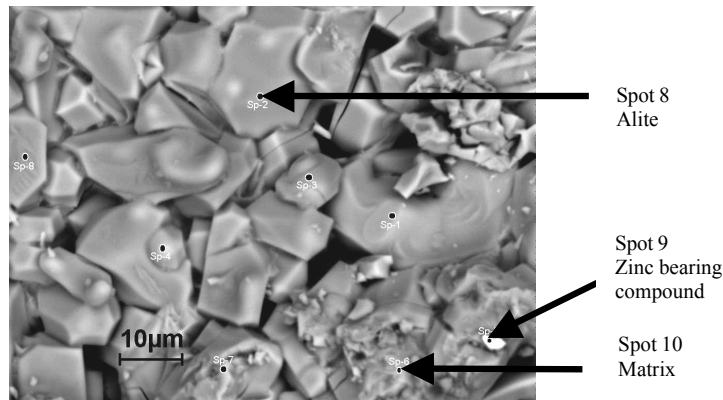


Fig.7: SEM of 5% NFS clinker with spots for EDAX analysis.

analysis. Zinc is also found with the alite (spot No. 5, 6, & 8) and in clinker matrix (spot 7 & 10) where Fe₂O₃ is in excess. The inclusion of zinc in alite may be attributed to the replacement of Ca⁺⁺ by Zn⁺⁺. The entrapment of ZnO in alite is also indicated by the XRD pattern showing some peak shifting as mentioned earlier. It may, however, be appropriate to mention here the evidences of XRD and EDAX may not be adequate to unequivocally conclude that there is presence of calcium zinc silicate compound. This appears to be most likely interpretation at this stage. The inclusion of zinc in ferrite phase may be due to entrapment of Zn in the

lattice of ferrite in the form of zinc iron oxide. Due to this reason perhaps the XRD did not show any peak shifting for C_4AF/C_3A . The SEM-EDAX analysis shows that maximum zinc is entrapped into alite and ferrite phases.

Table- 5: EDAX Analysis of Spots

Element	Percentage (Wt. %)									
	Control				2% NFS			5%NFS		
	Spot 1 Alite	Spot 2 Matrix	Spot 3 Matrix	Spot 4 C_4AF	Spot 5 Alite	Spot 6 Alite	Spot 7 Matrix	Spot 8 Alite	Spot 9 Calcium zinc silicate	Spot 10 Matrix
Ca	48.90	36.95	38.23	35.64	53.76	49.00	49.80	51.67	39.15	46.46
Si	12.77	4.38	7.41	3.47	9.74	12.79	6.39	10.77	9.16	1.20
Al	0.92	13.44	9.26	11.04	0.61	0.77	0.75	0.67	0.95	0.47
Fe	1.15	7.78	7.42	12.41	1.23	0.90	9.54	0.94	1.21	17.3
Mg	0.50	1.03	1.03	1.39	0.37	0.62	0.42	0.57	0.84	ND
Zn	ND	ND	ND	ND	0.37	0.32	1.04	0.89	13.77	5.43
Pb	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND=not detected

The XRD patterns of hydrated samples of both control and 5% NFS cement revealed the presence of ettringite peak at 9.72 d value on 30-min hydration and this peak in both the cases disappeared after 1-day

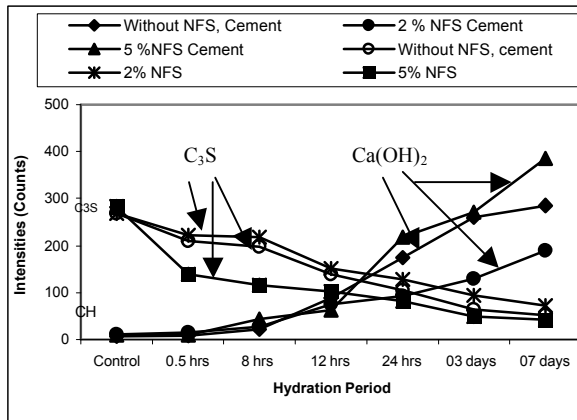


Fig.8: Variation in peak intensities for CH & C_3S in hydrated samples

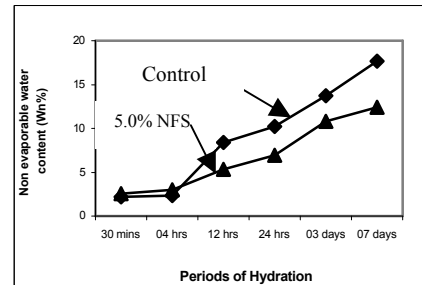


Fig.9: Non-evaporable water content in hydrated samples.

hydration. The $Ca(OH)_2$ peak at 4.918 d value is due to hydration of silicate phases mainly from alite at the early age of hydration. The peak intensity of $Ca(OH)_2$ increases with increasing hydration time. A comparative peak intensity of control and 5% NFS cement at different hydration period is given in Fig. 8. The variation of peak intensities for C_3S with respect to hydration time for control and 5% NFS samples are also given in Fig. 8.

The non-evaporable water contents of hydrated samples determined by the thermogravimetric curves considering the weight loss in the temperature range of 100 to 1000°C is given in Fig. 9. Non-evaporable water content of control samples is found higher at each hydration age. It is generally believed that the stoichiometric requirement of water in cement paste for complete hydration is 23%. Assuming theoretically the loss of 23% water as 100%, the loss of water of control cement samples and 5% NFS based cement samples at 12h, 24h, 72h and 168h (see Fig.9) were found to as given in table-6.

Table-6: Relative Degree of Hydration

Samples	Hydration Period (hours)							
	12 h		24h		72h		168h	
	Wt. loss %	Degree of Hydration (%)	Wt. loss %	Degree of Hydration (%)	Wt. loss %	Degree of Hydration (%)	Wt. loss %	Degree of Hydration (%)
Control Cement	4.27	18.56	10.25	44.56	13.73	59.70	17.70	76.96
5% NFS based Cement	2.60	11.30	6.94	30.17	10.83	47.08	12.38	53.83

The differential scanning curves (DSC) of hydrated samples with control and 5% NFS cements are given in Figs. 10(a)&10(b). The sample hydrated for 30 minutes show a characteristic peak of gypsum at ≈125°C, followed by a peak in the temperature range of 135-150°C, which is characterized for ettringite. As hydration proceeds the peaks for gypsum and ettringite gets diminished. The peaks for gypsum and ettringite have

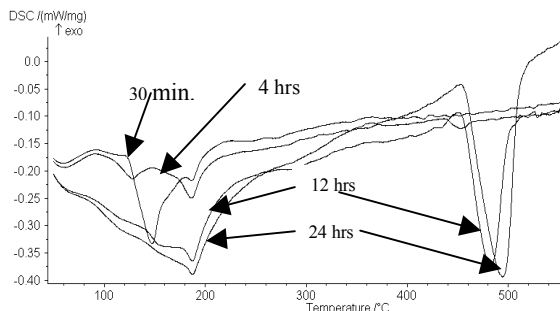


Fig.10 (a) : DSC of Control cement hydrated for different period

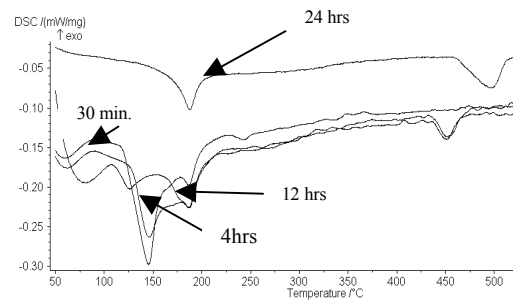


Fig.10 (b): DSC of 5% NFS cement hydrated for different period

almost disappeared at 12 h of hydration. At higher age of hydration the peak intensity for AFm in the temperature range of 160-200°C increases. The peak observed in the temperature range of 425-525°C is due to decomposition of Ca(OH)₂ formed during course of hydration of silicate phases. The peak intensity for Ca(OH)₂ increases with increasing hydration time. In presence of 5% NFS the peak intensities for ettringite, AFm and Ca(OH)₂ are always found lower in comparison to control.

The concentration of zinc oxide in residues obtained from extraction of hydrating paste at different intervals of time is given in Fig. 11. The ZnO content in hydrated samples is found to be almost constant upto 24 hours. The liquid phase received from extraction of the hydrating pastes were analyzed by ICP. The zinc and lead were not observed even in traces in ICP test which indicates that the zinc oxide does not enter into the liquid phase.

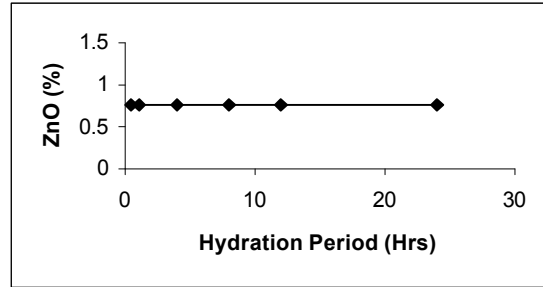


Fig.11: Zinc oxide in residue after extraction of hydrating paste.

4.0 Conclusion

The chemico-mineralogical composition of NFS are found suitable to be used as corrective raw mix component for cement manufacturing. The burnability of raw mix improves in presence of NFS due to its mineralizing effect mainly because of zinc oxide. The clinker analysis shows that in presence of NFS, zinc is incorporated in clinker and concentration of zinc increases with the increase of NFS addition. XRD and selective dissolution (SAM and KOH-Sugar) extraction results show that zinc is assimilated in both silicate and interstitial phases. SEM & EDAX analysis revealed that zinc is mostly entrapped in alite and ferrite phases. The clinker with 5% NFS examined under SEM & EDAX showed a crystal of calcium zinc silicate embedded in alite crystal.

The XRD of hydrated samples with & without NFS shows that for the clinker containing NFS the rate of hydration is substantially lower. Non-evaporable water content and DSC of hydrated sample also indicate similar results. The leaching study of hydrating cement paste of 5% NFS has confirmed that there is no mobility of zinc and lead oxides during hydration as the component is rigidly fixed in the hydrated phases of alite & ferrite.

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