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Stability study and impact of the Cr (VI) reducing additives on cement performance

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Abstract

A potentially serious condition could occur when cement containing Cr (VI) comes into contact with the skin causing irritations and eczema.

The objective of the present research work is to evaluate the effectiveness of various Cr (VI) additives to Portland cement on its storage for longer periods of time. The cement samples containing various additives were stored in polythene bags and periodically their Cr (VI) levels were tested using the 1,5- diphenylcarbazide method at 540 nm on an UV-Visible spectrophotometer.

The Difference in Cr (VI) amount in freshly prepared and stored samples for different duration helped to assess the change in efficacy. The physical testing of these cement mortar samples were also carried out to understand the effect of these additives on cement quality.

The stannous sulfate ($SnSO_4$) was found to be the best additive for reducing Cr (VI) in cement and also, it was observed to be relatively stable for longest period. XRD, TG-DSC and Electron microscopic studies were further used to understand effect of $SnSO_4$ on cement when added as reducing agent for Cr (VI).

Except sodium borohydride ($NaBH_4$), no other additive investigated in this study showed adverse impact on the strength of the cement. Both $SnSO_4$ and $MnSO_4$ exhibited improvement in the compressive strengths of the cement mortars.

Key words: Cr (VI), SEM, XRD, compressive strengths, TG-DSC.

1.0 Introduction

Chromium is an unavoidable trace element present in the raw materials (Hills & Johansen, 2007; CSTEE, 2002) used in the manufacture of cement clinker. The oxidizing and alkaline burning conditions of the cement kiln form toxic hexavalent chromium Cr (VI). Hexavalent chromium is a powerful dermal irritant considered to be extremely toxic due to its high oxidation potential and ability to penetrate human tissue. It can cause skin sensitization, (Hills & Johansen, 2007; CSTEE, 2002) allergic reactions, and eczema. Chromium (VI) has high solubility in water and is released when cement is mixed with water. Thus, wet cement poses a health issue to workers who come into contact with wet cement or concrete.

In European countries the COSHH (Control of Substances Hazardous to Health**)** regulations are in place for Cr (VI) in wet cement according to which the allowed level of Cr (VI) in dry cement is upto 2 ppm. Various additives are available in the market for reducing Cr (VI). Furthermore, the European directive requires that delivery documents and cement bags be marked with information on the period of time for which the reducing agents remain potent; BCA (British Cement Association) member companies have initially declared shelf life as 61 days (BCA 2006). Present study is continuation of the authors' earlier work in Advances in Cement and Research (Vaity R. And Verma J., May 2011)

The reduction reaction that takes place when using ferrous sulphate as a chemical reducer is the following:

$$CrO_4^{2-} + 3\,Fe^{2+} + 4\,OH^- + 4\,H_2O \rightarrow Cr(OH)_3\downarrow + 3\,Fe(OH)_3\downarrow$$

However, it has been reported that the use of ferrous sulfate is not efficient because the dosage amount required for reducing Cr (VI) to Cr (III) is, at least, ten times the stoichiometric amount of ferrous sulfate (Rasmussen and Poul, 1986), to that of chromate present in the cement. The poor dosage efficiency is explained partly by the fact that ferrous sulfate readily oxidizes, from iron (II) to iron (III), during prolonged contact with air and water.

The poor storage stability decreases the efficiency of ferrous sulfate and can render it useless as a chromate reducer if not used quickly.

Many compounds viz., disulphides, polysulfides (EP 1580174, Feb 2007), catalyzed hydrazine compounds (USP 4367213, Jan 1983), hydroxyl amine and hydrazine compounds (US Patent 6872247, March 2005), sulphate dispersions (US Patent 7128782,Oct 2006) and aldehydes carboxylic acids (EP 0697380, Dec 2001) have been experimented with additives for reduction of Cr (VI).

Present work is an attempt to study sodium borohydride ($NaBH_4$), Stannous sulphate ($SnSO_4$)' (Jardine L. A. , Cornman C. R. , Gupta V. and Chun B. C.,June 19, 2007),Mangenous sulphate ($MnSO_4$) and Ethylenediaminetetraacetic acid (EDTA) as Cr (VI) reducing additives and their stability with respect to storage and time. Best reducing additive among all has been further studied for physical parameters and using TG-DSC, XRD and microscopic studies.

2.0 Materials & Methods

Sodium borohydride ($NaBH_4$), Stannous sulphate ($SnSO_4$), Mangenous sulphate ($MnSO_4$) and Ethylenediaminetetraacetic acid (EDTA) were used as reducing additives for Cr (VI) content in cement. All reagents/chemicals used were of analytical reagent grade.

2.1Incorporation of the various additives in cement

A cement specimen was prepared (referred as original cement sample) to carry out experiments with different additives. This original cement sample was having Cr (VI) equivalent to 18 ppm.

Five batches each of 5kg were prepared from the original cement sample. The additives used were sodium borohydride ($NaBH_4$), Stannous sulphate ($SnSO_4$), Mangenous sulphate ($MnSO_4$) and Ethylenediaminetetraacetic acid (EDTA). 1.0 (w/w) percent of each of the additives were blended with the cement and used for carrying out experiments. The details regarding the cement batches thus prepared are presented in Table 1.0.

2.2 Storage Stability determination of additives in cement with respect to time

The prepared samples were stored in polythene bags for further experimentation. The Cr (VI) in these samples were determined at periodic intervals to understand the efficacy of the additives with respect to time. In order to determine Cr (VI) in cement samples 1, 5-diphenyl carbazide method was used. The detailed methodology involved is described below. Cr (VI) in cement was estimated at 0, 8, 15, 30, 60 and 90 days interval.

2.3 Estimation of water soluble Cr (VI)

2.3.1 Preparation of Standard Calibration curve for estimating Cr (VI) by Colorimetric method using an UV-Visible Spectrophotometer

Varying aliquots viz., 0.5, 1.0, ….mL of 100 ppm of Cr (VI) solution were pipetted out into different 100 mL volumetric flasks. 2 mL of 6N sulphuric acid were added to each flask, followed by 2 mL of 0.25 % 1,5-diphenyl carbazide reagent(UNE-EN.196-10, 2004). The volume in each flask was made to 100 mL with de-ionized water. The absorbance of each solution was measured on Shimadzu UV-2450 spectrophotometer at 540 nm.

2.3.2 Extraction of water soluble Cr (VI) in cement samples

The samples were homogenized for uniformity and representative samples were prepared. 10 g of each cement powder was taken in a 250 mL glass beaker and 40 ml of de-ionized water were added to it carefully. The slurries were stirred using magnetic stirrer for 20 min. and then vacuum-filtered through Whatman filter paper No.1 using Buchner funnel. The filtrates were collected separately in 100 mL volumetric flasks. 2ml of 6N sulphuric acid were added to each flask, followed by 2ml of 0.25 % 1,5-diphenyl carbazide reagent. The volume in each flask was then made to the mark with de-ionized water. The absorbance of each solution was measured on Shimadzu UV-2450 spectrophotometer at 540 nm.

2.4 Evaluation of Physical parameters of cement.

2.4.1 Determination of Standard water consistency & setting time *cement samples with and without additive*

The water consistency was determined by Vicat apparatus (IS: 4031 part 4, 1988 (BIS, 1988a)). Cement samples with and without additive were tested for standard consistency.

An Initial and final setting time of cement in the presence of each of the additives at 1 % (w/w) level were determined with Vicat apparatus (IS:4031 part 5, 1988 (BIS, 1988b)). Cement samples with and without additive were tested for setting time.

2.4.2 Determination of compressive strength

Cement with various additives at 1% (w/w) level was mixed with sand in 1:3 ratio and mixed with water (IS: 4031 part 4, 1988). The mortars were placed in steel moulds to form cubes, 70.6 mm^3 in dimension. These cubes were demoulded after 1 day and stored in water at 27^0C at a relative humidity of 100%. The cubes were taken out of the water prior to testing. The compressive strength was determined at 1, 3 and 7 days as per IS: 4031 part 6, 1988.

2.5 Preparation of hydrated cement samples of with and without $SnSO_4$

Three specimen samples, 20 g each were withdrawn from bulk prepared batch of cement with $SnSO_4$, at 1% (w/w) dosage level. Similarly three specimen samples of original cement sample were also withdrawn. Each of six samples then were mixed with 7 mL of water so that the water /solid (w/s) ratio became 0.35 and was kept in a polythene tube. The air inside the tube was removed in order to avoid carbonation. The hydration reaction was allowed to continue at 28^0C and was stopped at different intervals of time (1, 3 and 7days) by adding isopropyl alcohol and diethyl ether. The hydrated samples were heated at 105^0C for 1 hr. The dried samples were stored in self-sealing polythene bags and kept in a dessicator. Three samples each from i.e cement with $SnSO_4$, at 1% (w/w) dosage level and original cement were hydrated at 1,3 and 7 days. Then the hydrated samples were employed to carry out TG-DSC, XRD and Microscopic studies.

2.5.1 Thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) studies of hydrated and original Cement Samples

TG and DSC studies of the six hydrated samples were made with a power compensated DSC NETZSCH STA 409 PC instrument in the temperature range of 30 to 1000^0C in nitrogen atmosphere at a heating rate of 10^0C/min.

2.5.2 X-ray diffraction studies

Powder X-ray diffraction (XRD) of anhydrous cement, hydrated for 1, 3 and 7days with and without $SnSO_4$ were recorded using Cu-Kα radiation at Panalytical- XpertPro.

2.5.3 Microscopic studies

A Zeol SEM was used for microscopic studies of two hydrated cement samples.

The powdered samples were mounted on stubs and then coated with gold to make it conductive in vacuum of the order of 10^{-5} torr. Scanning electron microscopy (SEM) was performed by mounting the stubs under the microscope and adjusting the desired resolution.

3.0 Results and Discussion:

3.1 Stability of additives in cement with respect to time

The results of the stability studies with respect to time on the cement batches with Cr (VI) additives are recorded in Table 2.0. The results show an increase in Cr (VI) content as the storage period increases. Cement with 1% (w/w) $NaBH_4$ and Cement with 1% (w/w) $SnSO_4$ have shown good stability upto 8 days as the Cr (VI) content is found to be zero ppm. Cr (VI) content has increased in case of Cement with 1% (w/w) $MnSO_4$ and Cement with 1% (w/w) EDTA from 0.3 ppm to 0.6 ppm and from 4.3 ppm to 10.0 ppm respectively upto 8 days.

At 15 days Cr (VI) content increased in samples of cement with 1% (w/w) $NaBH_4$, with 1% (w/w) $MnSO_4$ and with 1% (w/w) EDTA to 0.2 ppm, 1.1 ppm and 15.5 ppm respectively.

However, Cement with 1% (w/w) $SnSO_4$ showed good stability upto 15 day as the Cr (VI) content was found to be 0 ppm.

European legislation of COOSH for Cr (VI) content in cement is below 2 ppm in wet cement. Except Cement with 1% (w/w) EDTA all the three additives have shown good stability upto 15 days.

At 30 days Cr (VI) content in samples of Cement with 1% (w/w) $NaBH_4$, 1% (w/w) $SnSO_4$, 1% (w/w) $MnSO_4$ and with 1% (w/w) EDTA was found to be 1.5 ppm, 0.02 ppm, 5.2 ppm, 18 ppm, respectively i.e., $NaBH_4$ and $SnSO_4$ were potent enough in reducing Cr(VI) content upto 30 days. However, $MnSO_4$ and EDTA were found to have lost their efficacy at 30 days.

At 60 days the Cr (VI) content in the cement samples of with 1% (w/w) $NaBH_4$, Cement with 1% (w/w) $SnSO_4$, with 1% (w/w) $MnSO_4$ and with 1% (w/w) EDTA were found to be 5.2 ppm, 0.1 ppm, 18 ppm, 18 ppm, respectively. Thus the sample with 1 % (w/w) $SnSO_4$ proved to be the only sample retaining its efficacy in reducing Cr (VI).

At 90 days only Cement with 1% (w/w) $SnSO_4$ was found to be stable and retained its efficacy of reducing Cr (VI) content in cement. In the final analysis, it emerges that the additive $SnSO_4$ is the best for reduction of Cr (VI) in cement.

The data thus generated in respect to storage stability studies with respect to time have also been plotted in Fig. 1.0 and these curves are self- explanatory.

3.2 Physical properties of cement samples with and without additives

3.2.1 Standard water consistency, setting time and compressive strength of cement

Standard water consistency and setting times for various samples are indicated in Table 3.0.The results show different effects of various additives on consistency and setting time. In case of original cement sample the standard consistency was found to be 29.0 % and setting time value for IST 165 min. and for FST 225 min. In case of cement with 1% (w/w) $NaBH_4$ the standard consistency increased from 29.0 to 31.5 and thus affecting hydration adversely and leading to failure in setting time tests.

Cement with 1% (w/w) $SnSO_4$ was found to reduce the standard consistency from 29.0 % to 28.0 %, thus retarding the hydration process of cement. In case of cement with 1% (w/w) $SnSO_4$, FST crossed the limits of 600 min causing delay in final setting time. The cement with 1% (w/w) $MnSO_4$ showed reduction in the IST and FST from 165 min. to 130 min. and from 225 min. to 175 min. respectively. Cement with 1% (w/w) EDTA exhibited increase in the IST and FST from 165 min to 170 and from 225 min. to 230 min. respectively.

3.2.2 Compressive Strength studies

The compressive strength values of cement samples were affected with the use of additives for reducing Cr (VI). Please refer to Table 4.0 for the data on compressive strength of cement samples.

The compressive strength of the cement with 1 % (w/w) $NaBH_4$ was nil at 1day and 3 days, consistent with the setting time failure. However, its compressive strength at 7 days was found to be 33% of the original cement sample.

Cement sample with 1% (w/w) $SnSO_4$ exhibited good increase in the compressive strength upto 46.0 %, 39.6 % and 34.0 % respectively at 1 day, 3days and 7days in comparison to compressive strength values for the original cement.

Cement sample with 1% (w/w) $MnSO_4$ showed moderate increase in the compressive strength values which were found to be 31.7 %, 21.3 % and 10.7 % respectively at 1 day, 3days and 7days in comparison to the compressive strength values for the original cement.

However, a meagre enhancement in the compressive strength values was observed upto 2.4 %, 3.9 % and 3.0 % respectively at 1 day, 3days and 7days, in comparison to the compressive strength values for the original cement in case of cement sample with 1% (w/w) EDTA.

3.3 Studies of hydrated cement to understand any phase alteration due to addition of additive.

Cement with 1 % (w/w) dosage level of $SnSO_4$ has shown good performance with respect to Cr (VI) reduction, stability towards storage and physical properties of cement therefore, further investigation of this additive was carried out. To understand any phase alteration during hydration of cement with and without $SnSO_4$, TG-DSC, XRD and microscopic studies were performed.

3.3.1Thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) Studies

The DSC studies were performed to investigate the interaction of $SnSO_4$ with hydration products of cement.

The DSC curves of six hydrated cement samples for 1 day, 3days , 7days and unhydrated original cement have been superimposed in Fig 2.(A). Similarly the TG curves are also superimposed in Fig 2(B).

All the curves show endothermic peak at about 100 -110 ^{0}C which is due to the absorbed moisture. A very sharp endothermic peak at about 450 ^{0}C is due to dehydroxylation of the portlandite (calcium hydroxide) formed during the hydration of cement. Furthermore, the decomposition of monocarbonate phase is seen at temperature of around 720 ^{0}C.

$SnSO_4$ addition does not change the hydration products of cement. On the contrary, hydration of $SnSO_4$ is believed to take place. The difference in the amount of portlandite formation in each of the batches with and without $SnSO_4$ could be identifiable. The loss at 450 ^{0}C is clearly observed in TG and DSC curves. This fact is also ascertained by the XRD studies of original cement and cement with 1% (w/w) $SnSO_4$. Thus, $SnSO_4$ as additive for Cr (VI) reduction is not altering the cement properties adversely.

3.3.2 X-ray diffraction studies

The XRD technique is a powerful tool to determine the depletion of crystalline phases that are sufficiently crystalline to be detected by the XRD technique for cement during hydration and the formation of hydration products. The XRD Pattern of anhydrous original cement, hydrated original cement for 1 day, 3 days, 7 days and cement with 1% (w/w) $SnSO_4$ hydrated for 1 day, 3 days, 7 days were overlaid and presented in 3dimensional form in Fig 3 (A).

The XRD pattern of anhydrous cement sample gives peaks corresponding to different mineral phases present in hydrated cement. In addition to the mineral phases, the presence of calcium carbonate has also been detected.

When the hydration was allowed to occur at 1 day, the intensity of the mineral phases decreased and new diffraction lines due to formation of portlandite were observed at $2\theta = 18.0, 47.0$ and 51.0 (cf. Fig.3.(B)). It is well known fact that the calcium-silicate-hydrate (C-S-H) and ettringite formed during 1day of hydration are not crystalline in nature and were not detected in the XRD pattern. However, portlandite peak was found to be of low intensity for cement with 1% (w/w) $SnSO_4$, in comparison to that for the original cement sample. This indicates that the additive retards the hydration of cement which impacts the cement strength. Thus, increase in cement strength may be caused due to reduction in the formation of portlandite. Furthermore, no new peaks were observed in case of cement with 1% (w/w) $SnSO_4$ in comparison to that of XRD scan of original cement sample indicating no alteration in cement hydration product at this dosage level.

3.3.3 Microscopic studies

Microscopic studies were carried out only with the hydrated original cement and hydrated cement with 1 % (w/w) $SnSO_4$. Fig.4 (A) and Fig.4 (B) reveal well -hydrated products for both original cement and cement with 1 % (w/w) $SnSO_4$. Furthermore, there are no special products seen during hydration with the help of SEM studies. No microstructural changes are observed as a function of addition of $SnSO_4$ in cement for Cr (VI) reduction.

4.0 Conclusions

As a result of the present study, the following conclusions can be drawn:

(i) The $SnSO_4$ was found to be the best reducing agent at 1.0% (w/w) for reducing Cr (VI) among all the additives studied.

(ii) The $SnSO_4$ was found to be the most stable additive with respect to time and storage.

(iii) The data on setting time and compressive strength also indicate that $SnSO_4$ is the best among all the additives.

(iv) The additives viz., $MnSO_4$ and EDTA were found to possess good reducing properties at 1% (w/w) dosage level. However, stability, on storage of these additives is rather poor.

(v) The early strength of the cement is increased with the use of an additive. All cement additives studied in the present work are found to be strength enhancers except $NaBH_4$.

(vi) It has been observed that except $NaBH_4$, the Cr (VI) reducing additives are not having any adverse effect on cement's physical properties.

(vii) Each of the techniques viz., XRD, DSC-TG and SEM have revealed the presence of portlandite and C-S-H phase in original cement as well as cement with $SnSO_4$.

(viii) The compressive strength values for cement samples appear to be inversely proportional to their portlandite content. Furthermore, this conclusion is supported by the XRD, DSC-TG and SEM studies.

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Table 1.0 Batches of cement samples with/without additives

Sample	Type of additive	Amount
		w/w %
Original Cement sample	Nil	0.0
Cement with 1% (w/w) $NaBH_4$	$NaBH_4$	1.0
Cement with 1% (w/w) $SnSO_4$	$SnSO_4$	1.0
Cement with 1% (w/w) $MnSO_4$	$MnSO_4$	1.0
Cement with 1% (w/w) EDTA	EDTA	1.0

Table 2.0: Storage Stability study of Cr (VI) reducing additives

Sample Id	Concentration of Cr (VI) in ppm					
	0 day	8 days	15 days	30 days	60 days	90 days
Cement with 1% (w/w) $NaBH_4$	0	0	0.2	1.5	5.2	18
Cement with 1% (w/w) $SnSO_4$	0	0	0	0.02	0.05	0.1
Cement with 1% (w/w) $MnSO_4$	0.3	0.6	1.1	5.2	18	18
Cement with 1% (w/w) EDTA	4.3	10	15.5	18	18	18

Table 3.0 Standard water consistency and setting times

Sample	Standard water consistency: %	Setting time in min	
		Initial (IST)	Final (FST)
Original cement sample	29.0	165	225
Cement with 1% (w/w) $NaBH_4$	31.5	Failed	Failed
Cement with 1% (w/w) $SnSO_4$	28.0	420	Failed
Cement with 1% (w/w) $MnSO_4$	28.5	130	175
Cement with 1% (w/w) EDTA	30.0	170	230

Table 4.0: Compressive strength of cement samples with Cr (VI) additives

Sample Id	Cement strength (MPa)		
	1 day	3 days	7days
Original Cement sample	20.5	35.6	48.5
Cement with 1% (w/w) $NaBH_4$	--	--	16.0
Cement with 1% (w/w) $SnSO_4$	29.9	49.7	65.0
Cement with 1% (w/w) $MnSO_4$	27.0	43.2	53.7
Cement with 1% (w/w) EDTA	21.0	37.0	50.0

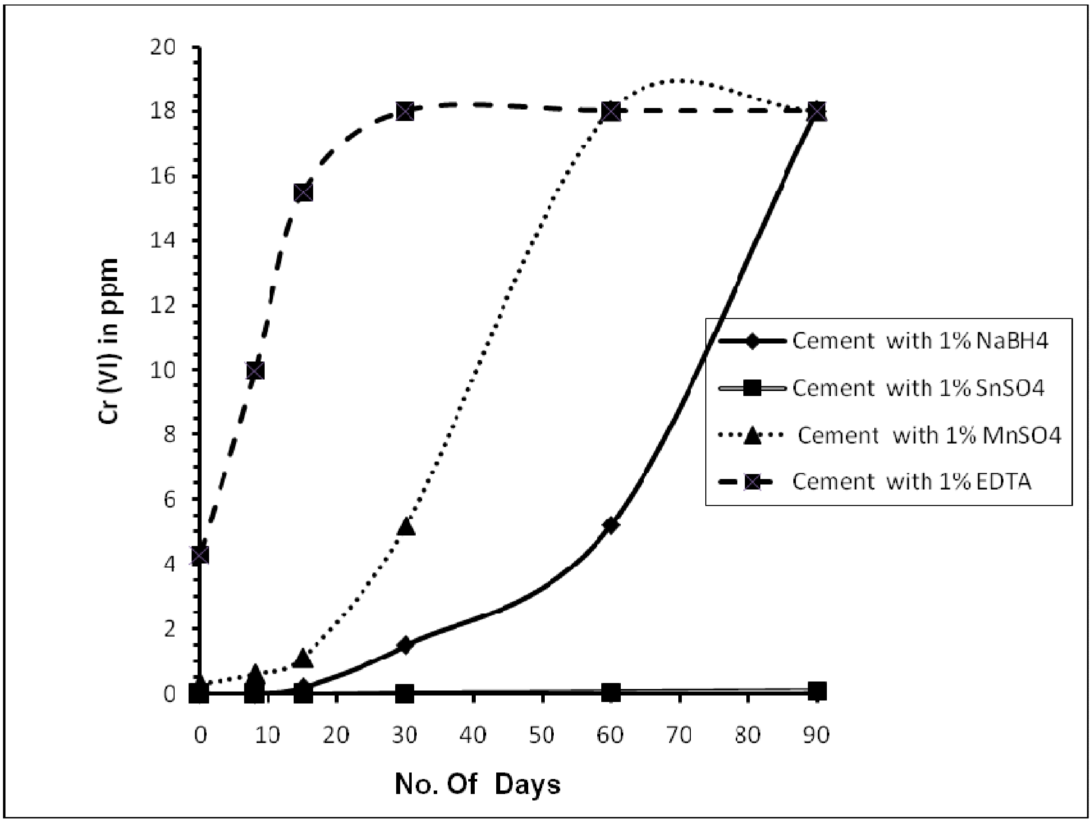

Fig 1.0 Stability study of Cr (VI) additives for 90 days

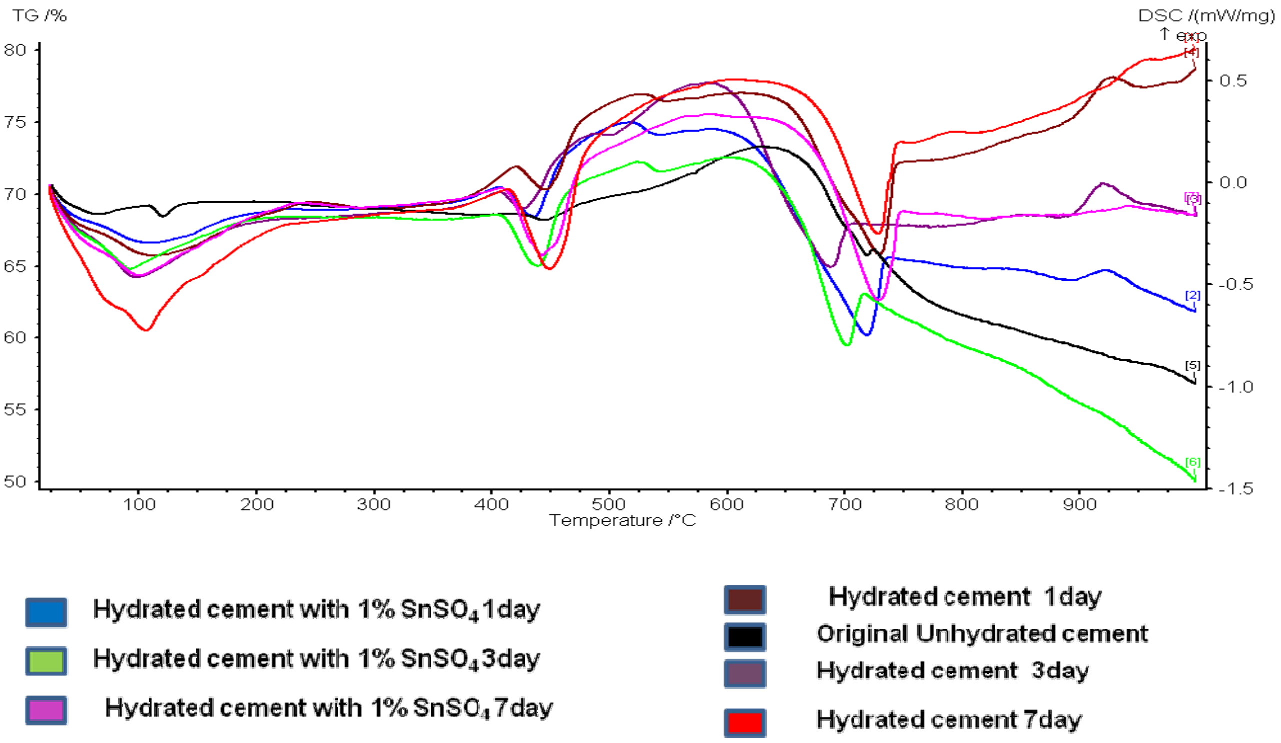

Fig. 2 (A) Effect of additive ($SnSO_4$) on Hydration of cement (DSC)

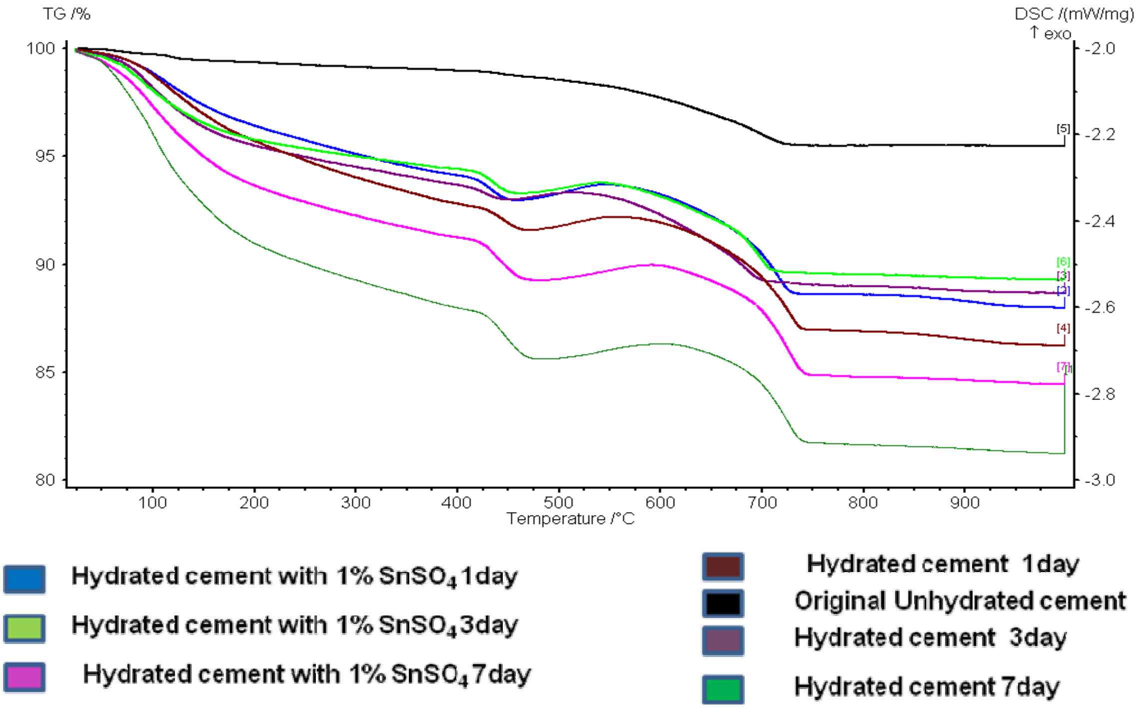

Fig. 2 (B) Effect of additive ($SnSO_4$) on Hydration of cement (TG)

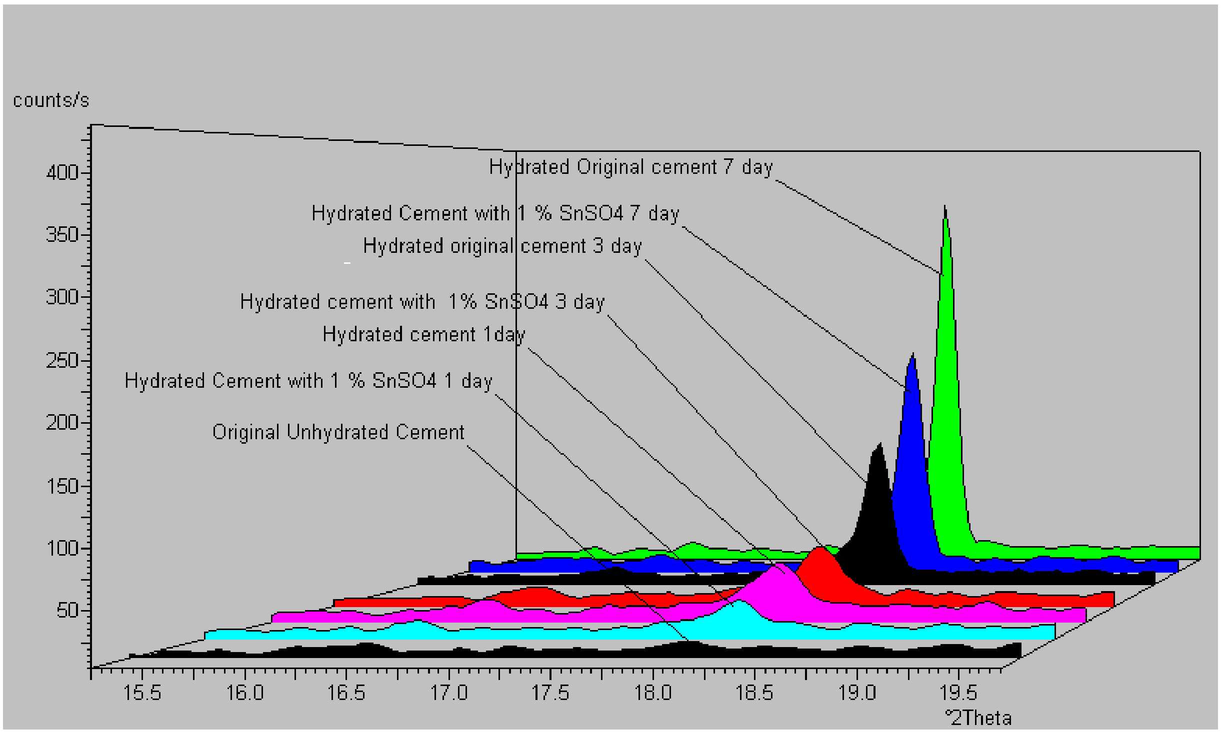

Fig. 3(A) Effect of additive ($SnSO_4$) on Hydration of cement (XRD)

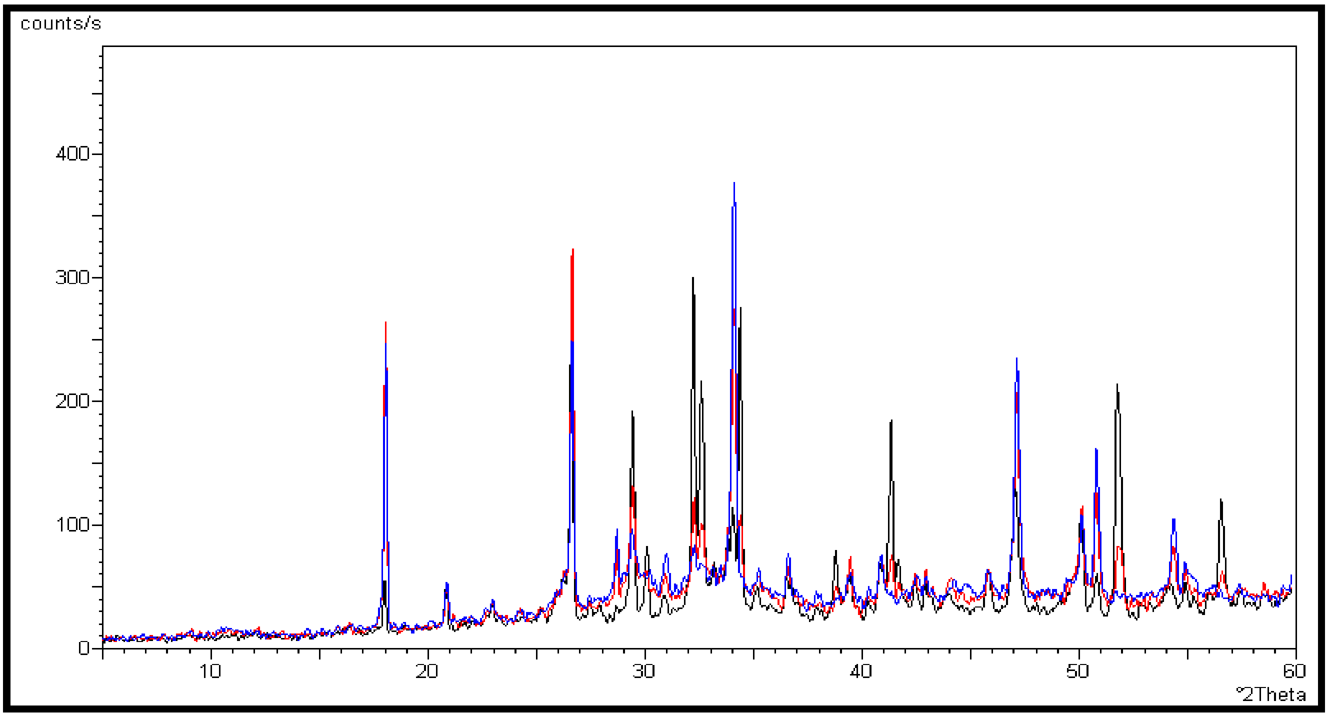

Fig. 3(B) Effect of additive ($SnSO_4$) on Hydration of cement (XRD)

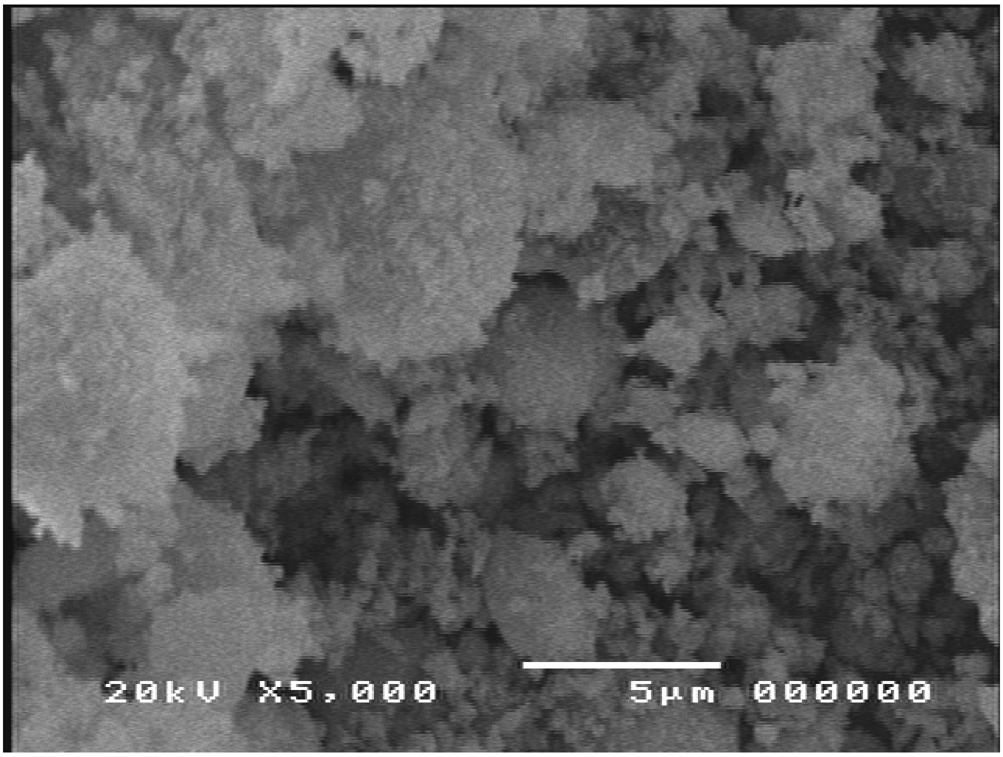

Fig 4 (A) Cement without any additive after hydration (SEM)

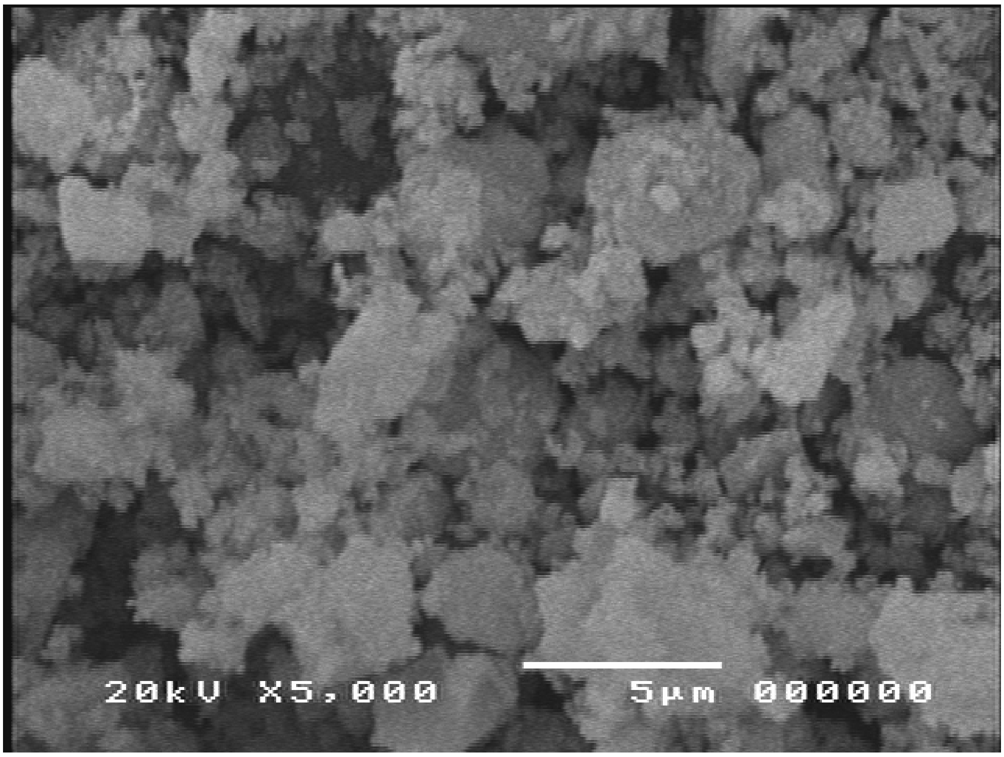

Fig 4(B) Cement with 1 % (w/w) $SnSO_4$ after hydration (SEM)

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