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Minerals as Cr (VI) Reducing Additives and their Impact 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. A common strategy to surmount this difficulty is to reduce hexavalent chromium in cement using a reducing agent in wet condition before putting to use cement-water paste.*

The objective of the present research work is to evaluate the effectiveness of various minerals as Cr (VI) reducing additives to Portland cement. The minerals used in the present study are bauxite, bentonite, attapulgite, china clay and jarosite.

The Cr (VI) levels were tested using 1,5- diphenylcarbazide method at 540 nm on an UV-Visible spectrophotometer (according to the EN-196-10 method); the same were confirmed using ICP-OES technique.

The physical testing of the cement mortar samples was carried out in order to understand the effect of these additives on cement quality.

The mineral jarosite, was found to be the most efficient additive for reducing Cr (VI) in cement and also, it was observed to be storage stable for the longest period (up to 90 days). XRD and SEM studies reveal that no phase alterations took place compared to the original cement sample. Thus, jarosite emerges as a good reducing agent for the reduction of hexavalent chromium in cement at 3 % (w/w) solid dosage form, on account of its reduction efficacy, good storage stability, without impacting the physical properties of cement and its low cost.

Keywords: *Cr (VI), ICP-OES, SEM, XRD, compressive strength.*

1. Introduction

Chromium is an unavoidable trace element present in the raw materials [1, 2] used in the manufacture of cement clinker. The oxidizing and alkaline burning conditions of the cement kiln form toxic 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, allergic reactions, and eczema [1, 2]. 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 less than 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 with respect to the period of time for which the reducing agents remain potent; BCA

(British Cement Association) member companies have initially declared shelf- life of cement with an additive as 61 days [3].

The reduction reaction that takes place when using ferrous sulphate as a chemical reducer for reduction of Cr (VI) in cement 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 sulphate [4] to that of chromate present in the cement.

Many compounds such as stannous sulphate [5], manganous sulphates [6] disulphides, polysulfides [7], catalyzed hydrazine compounds [8], hydroxyl amine and hydrazine compounds [9], sulphate dispersions [10] and aldehydes and carboxylic acids [11] have been recommended as additives for reduction of Cr (VI).

The present work is an attempt to study five minerals viz., bauxite, bentonite, attapulgite, china clay and jarosite as reducing agents for Cr (VI) in Portland cement. Bauxite is an aluminium rich mineral, whereas bentonite and attapulgite are clays comprising of aluminosilicate structure, with Na, K and Mg as main cationic components. China clay contains kaolinite as basic mineralogical phase with double layer silicate structure. Jarosite is the mineral composed of iron, calcium and aluminium sulphates.

Best two reducing additives viz., jarosite and bentonite among the five minerals studied, have been further evaluated for their influence on the physical parameters viz., normal consistency, setting time and compressive strength of cement. Some of the cement samples were also studied by XRD and SEM for phase alteration in cement samples with additives.

2. Materials and Methods

Minerals viz., bauxite, bentonite, attapulgite and china clay for the study were obtained from M/S Ashapura Minechem Ltd., Gujarat and the mineral jarosite was procured from M/S Hindustan Zinc Ltd.

The minerals in the powder form were used as supplied. All reagents/chemicals used were of analytical reagent grade from Merck. Type – I water was used throughout the work.

2.1. Incorporation of the Various Additives in Cement

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

The additives used were bauxite, bentonite, attapulgite, china clay and jarosite. Each of the additives in powder form were blended with the cement in 1.0 % (w/w), 2.0 % (w/w), 3.0 % (w/w), 4.0 % (w/w), and 5.0 % (w/w) dosage levels and used for performing the experiments. The details regarding the cement batches thus prepared are recorded in Table 1.0. The prepared samples were stored in doubly sealed polythene bags for the experimentation.

Table 1. *Cement batches prepared with various dosage levels*

Sr. No.	Type of Mineral additive	% Dosage (w/w)				
1	Bauxite	1	2	3	4	5
2	Bentonite	1	2	3	4	5
3	Attapulgite	1	2	3	4	5
4	China clay	1	2	3	4	5
5	Jarosite	1	2	3	4	5

2.2. Storage Stability Determination of Additives in Cement

The Cr (VI) contents in the samples stored in polythene bags 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 the spectrophotometric method using 1, 5-diphenylcarbazide reagent was employed [12]. The detailed methodology of the same is described in Sub-secs. 2.3.1 and 2.3.2. Cr (VI) in cement was estimated on 0, 8, 15, 30, 60 and 90 days.

2.3. Estimation of Water Soluble Cr (VI)

2.3.1. Preparation of Standard Calibration Curve for Estimating Cr (VI) 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 [13]. The volume in each flask was made to 100 mL with de-ionized water. The absorbance of each solution was measured at 540 nm on Shimadzu UV-2450-spectrophotometer.

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 at 540nm on Shimadzu UV-2450 spectrophotometer.

2.4. Evaluation of Physical Parameters of Cement

2.4.1. Determination of Standard Water Consistency and Setting Time for Cement Samples with and without Additives

The water consistency was determined using Vicat apparatus (IS: 4031 part 4, 1988 (BIS, 1988a)). Cement samples with and without additives 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 additives were tested for evaluation of setting time.

2.4.2. Determination of Compressive Strength

Cement with various additives at their respective dosage level were mixed with sand in 1:3 ratio and mixed with appropriate amount of distilled water (IS: 4031 part 4, 1988). The mortars were placed in steel moulds to form cubes having (dimension) of 70.6 mm^3. These cubes were de-moulded after 1 day and stored in type –I water at 27^0C at a relative humidity of 100%. The cubes were taken out of the water prior to testing. The compressive strength for each cube was determined at 1, 3 and 7 days as per IS: 4031 part 6, 1988.

2.5. Preparation of Hydrated Cement Samples with and Without Jarosite

Specimen samples, 20 g each were withdrawn from bulk prepared batch of cement with jarosite at 5% (w/w) and original cement sample. 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 7days by adding isopropyl alcohol and diethyl ether. The hydrated samples were heated at 105^0C for 1 hr., stored in self-sealing polythene bags and kept in a dessicator. Both cement with jarosite at 5% (w/w) dosage level and original cement hydrated for 7 days were prepared for carrying out XRD and Microscopic studies. In addition, original cement and cement with jarosite 5 % (w/w) dosage level in anhydrous condition were also subjected to XRD studies.

2.5.1. X-Ray Diffraction Studies

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

2.5.2. 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. Results and Discussion

3.1. Stability of Additives in Stored Cement Samples

The results of the stability studies with respect to time on the cement batches with Cr (VI) additives are presented in Table 2.0.

Table 2. *Studies on reduction efficacy and storage stability of Cr (VI) reducing additives*

Sr. No.	Sample Id	Concentration of Cr (VI) in ppm					
		0 day	8 days	15 days	30 days	60 days	90 days
	Original cement	18	18	18	18	18	18
1	Cement with 1% (w/w) bauxite	12	N P	N P	N P	N P	N P
2	Cement with 1% (w/w) bentonite	10	N P	N P	N P	N P	N P
3	Cement with 1% (w/w) attapulgite	12	N P	N P	N P	N P	N P
4	Cement with 1% (w/w) china clay	12	N P	N P	N P	N P	N P
5	Cement with 1% (w/w) jarosite	6.6	N P	N P	N P	N P	N P
6	Cement with 2% (w/w) bauxite	12	N P	N P	N P	N P	N P
7	Cement with 2% (w/w) bentonite	4.2	N P	N P	N P	N P	N P
8	Cement with 2% (w/w) attapulgite	9.5	N P	N P	N P	N P	N P
9	Cement with 2% (w/w) china clay	10	N P	N P	N P	N P	N P
10	Cement with 2% (w/w) jarosite	3.1	N P	N P	N P	N P	N P
11	Cement with 3% (w/w) bauxite	8.5	N P	N P	N P	N P	N P
12	Cement with 3% (w/w) bentonite	1.8	1.8	2.7	3.9	5.5	9.5
13	Cement with 3% (w/w) attapulgite	6.9	N P	N P	N P	N P	N P
14	Cement with 3% (w/w) china clay	6.5	N P	N P	N P	N P	N P
15	Cement with 3% (w/w) jarosite	0.5	0.5	0.5	0.5	0.6	0.8
16	Cement with 4% (w/w) bauxite	5.9	N P	N P	N P	N P	N P
17	Cement with 4% (w/w) bentonite	BDL	0.4	0.4	1.8	3.5	5.9
18	Cement with 4% (w/w) attapulgite	5.3	N P	N P	N P	N P	N P
19	Cement with 4% (w/w) china clay	4.8	N P	N P	N P	N P	N P
20	Cement with 4% (w/w) jarosite	BDL	BDL	BDL	0.4	0.7	0.8
21	Cement with 5% (w/w) bauxite	4.4	N P	N P	N P	N P	N P
22	Cement with 5% (w/w) bentonite	BD	0.4	0.4	2.0	3.2	5.5
23	Cement with 5% (w/w) attapulgite	3.4	N P	N P	N P	N P	N P
24	Cement with 5% (w/w) china clay	3.2	N P	N P	N P	N P	N P
25	Cement with 5% (w/w) jarosite	BDL	BDL	BDL	0.4	0.7	0.8

NP- Not Performed

BD- Below Detection Level

Bauxite, bentonite, attapulgite, china clay, and jarosite at 1 % (w/w) dosage level in cement were found to reduce Cr (VI) content of original cement from 18.0 ppm to 12.0, 10.0, 12.0, 12.0 and 6.6 ppm respectively. Thus, none of the mineral additives were found to be effective in reducing Cr (VI) content below 2.0 ppm at 1.0 % (w/w) dosage level.

Bauxite, bentonite, attapulgite, china clay, and jarosite at 2 % (w/w) dosage level in cement were found to reduce Cr (VI) content of original cement from 18.0 ppm to 12.0, 4.2, 9.5, 10.0, 3.1 ppm respectively. Evidently, the reduction in Cr (VI) levels is greater when the minerals are used at 2.0 % (w/w) dosage level as additives compared to the minerals when used at 1 % (w/w) dosage level. However, none of the mineral additives are found to be effective in reducing Cr (VI) content of cement below 2.0 ppm at 2.0 % (w/w) dosage level.

However, bentonite and jarosite at 3 % (w/w) dosage level have been found to be efficient in reducing Cr (VI) content below 2 ppm, in comparison to the additives using bauxite, attapulgite and china clay at 3 % (w/w) dosage level. Furthermore, jarosite at 3% (w/w) dosage level has been found to be storage stable up to 90 days (leachable Cr (VI) content was evaluated to be 0.8 ppm at 90 days). By contrast, 3 % (w/w) bentonite additive imparts storage stability to the cement upto 8 days only (leachable Cr (VI) content was evaluated to be 1.8 ppm at 8 days).

It can also be inferred that 4% (w/w) bentonite in cement (Cf. data at Sr. No. 17 in Table 2.0) is found to be storage stable up to 30 days (Cr (VI) content of the cement samples was determined as 1.8 ppm at 30 days). Lastly, it is clearly seen that the 5 % (w/w) bentonite additive in cement is storage stable up to 30 days (Cf. data at Sr. No. 22 of Table 2.0) like 4.0 % (w/w) bentonite additive.

The additive 4% (w/w) jarosite in cement reduces Cr (VI) more efficiently such that Cr (VI) content is below detection limit up to 15 days (Cf. data at Sr. No. 19 of Table 2.0). It is also observed that the additives viz., 4 % (w/w) jarosite and 5% (w/w) jarosite are storage stable up to 90 days.

3.2. Physical Properties of Cement Samples with and without Additives

3.2.1. Standard Water Consistency, Setting Time and Compressive Strength of Cement

Since both bentonite and jarosite at 4 % (w/w) and 5 % (w/w) dosage levels exhibited good storage stability, the standard water consistency and setting times for these two reducing agents were evaluated and the same are presented in Table 3.0.

These results show effects of additives on standard consistency and setting time. In case of original cement sample, the standard consistency was found to be 28.5 % and setting time value for IST 80 min. and for FST 170 min. In case of cement with 3% (w/w) betonite, the standard consistency increased from 28.5 to 33.2 thus affecting the hydration of the samples adversely. As a result, the values of IST (200 min.) and FST (445 min.) are extremely high compared to the values for the original cement.

Comparatively the values of standard water consistency in case of 3 % (w/w) jarosite, 4 % (w/w) jarosite and 5 % (w/w) jarosite were found to be 29.2, 31.2, and 33.1 respectively as against the standard water consistency of 28.5 % for the original cement.

In case of jarosite the water demand is increased as compared to original cement for all additions from 3 % (w/w), 4 % (w/w) and 5 % (w/w) jarosite, however, it is not leading to failure in failing of setting time test. The IST and the FST values have increased in comparison those to for the original cement from 80 min. and 170 min. to maximum of 210 min. and 340 min. respectively in case of cement with 5 % (w/w) of jarosite.

3.2.2. Compressive Strength Studies

Table 3.0 enlists the compressive strength values of cement samples with different additives. The compressive strength for original cement for 1 day, 3 days, 7days are found to be 26.0, 38.0 and 48.0 MPa respectively. In case of cement with 3 % (w/w) bentonite the compressive strength values are lowered slightly to 24.0, 33.0 and 45.0 MPa in comparison to values for the original cement at 1 day, 3 days and 7 days respectively. Lowering of the compressive strength values can be explained in terms of the increased water requirement as more and more bentonite mineral is incorporated in cement.

The compressive strength values with 4.0 % (w/w) bentonite additive in cement are further lowered to 21.0, 30.2 and 40.1 MPa respectively at 1 day, 3 days and 7 days. In case of 5 % (w/w) bentonite as an additive in cement brings down the compressive strength values to 18.0, 27.1 and 36.2 MPa at 1 day, 3 days and 7 days respectively.

In case of cement with 3 % (w/w) jarosite, the early strength i.e., at 1 day is found to be 28.1 MPa as compared to that for original cement of 26.0 MPa. This is attributed to the presence of sulphates in the mineral jarosite. However, the compressive strength values at 3 days and 7 days are nearly the same as those for the original cement sample. A similar trend in the values of compressive strength is noticeable in cement samples containing 4 % (w/w) jarosite or 5 % (w/w) jarosite as the additive. Thus, it can be concluded that addition of jarosite does not adversely affect cement performance.

Table 3. *Compressive strength of cement samples with Cr (VI) additives*

Sr. No	Sample	Standard water consistency	Setting Time		Cement strength		
			Initial setting time (IST)	Final setting time (FST)	1 day	3 days	7 days
		%	Min	Min	(MPa)		
	Original Cement	28.5	80	170	26.0	38.0	48.0
1	Cement with 3% (w/w) Bentonite	33.2	200	445	24.0	33.0	45.0
2	Cement with 3% (w/w) Jarosite	29.2	110	230	28.1	38.2	47.0
3	Cement with 4% (w/w) Bentonite	33.9	250	550	21.0	30.2	40.1
4	Cement with 4% (w/w) Jarosite	31.2	145	245	28.5	39.1	48.1
5	Cement with 5% (w/w) Bentonite	34.8	305	660	18.0	27.1	36.2
6	Cement with 5% (w/w) Jarosite	33.1	210	340	28.5	39.2	48.3

3.3. Studies of Hydrated Cement to Understand any Phase Alteration Due to the Additive

Since the cement sample with 5 % (w/w) dosage level of jarosite shows good efficacy with respect to Cr (VI) reduction, storage stability and good physical properties, further investigations using XRD and SEM techniques were carried out in order to understand any phase alterations during hydration of cement with and without jarosite.

3.3.1. 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, anhydrous cement with 5% (w/w) jarosite, hydrated original cement for 7 days and cement with 5% (w/w) jarosite hydrated for 7 days are presented in Figures 1.0-4.0 respectively.

The XRD pattern of anhydrous cement sample (Fig.1.0) gives peaks corresponding to different mineral phases present in hydrated cement (Fig.3.0). In addition to the mineral phases, the presence of calcium carbonate has also been detected.

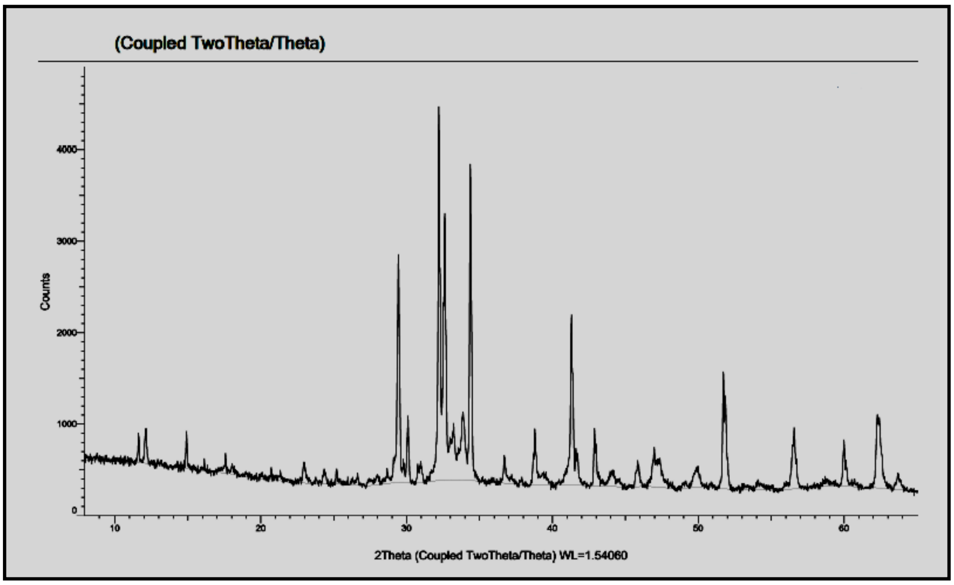

Fig 1. *X-ray diffractogram for anhydrous original cement.*

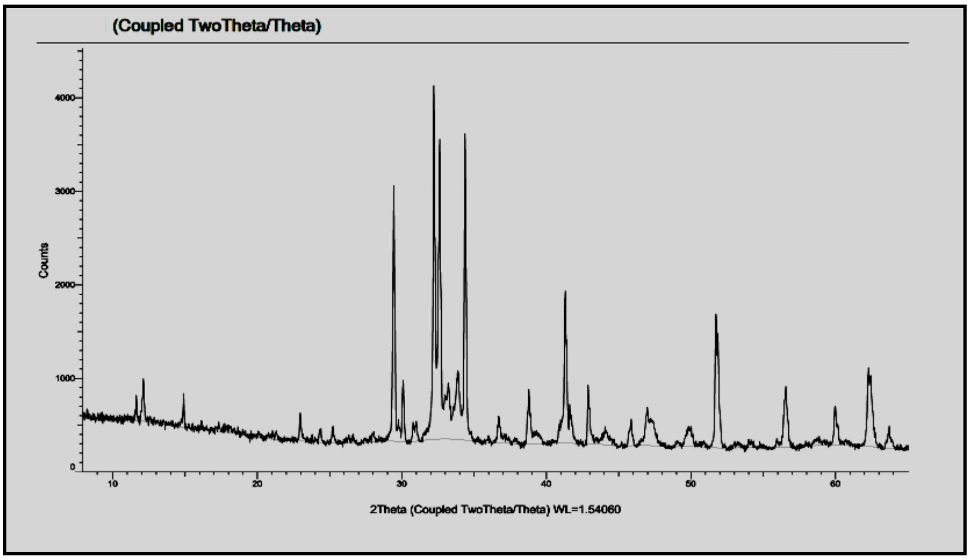

Fig 2. *X-ray diffractogram for anhydrous original cement with 5 % (w/w) jarosite.*

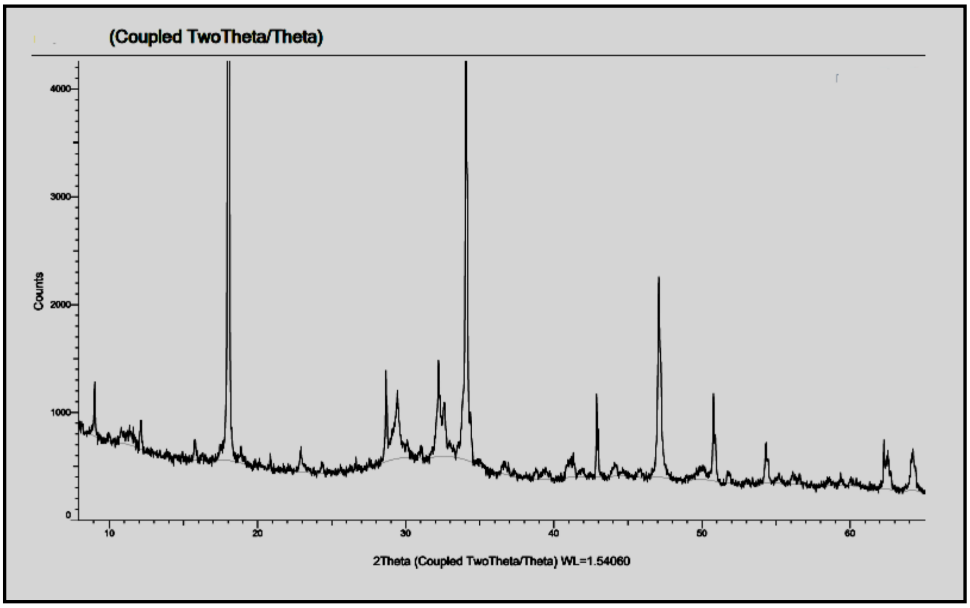

Fig 3. *X-ray diffractogram for 7 day hydrated original cement.*

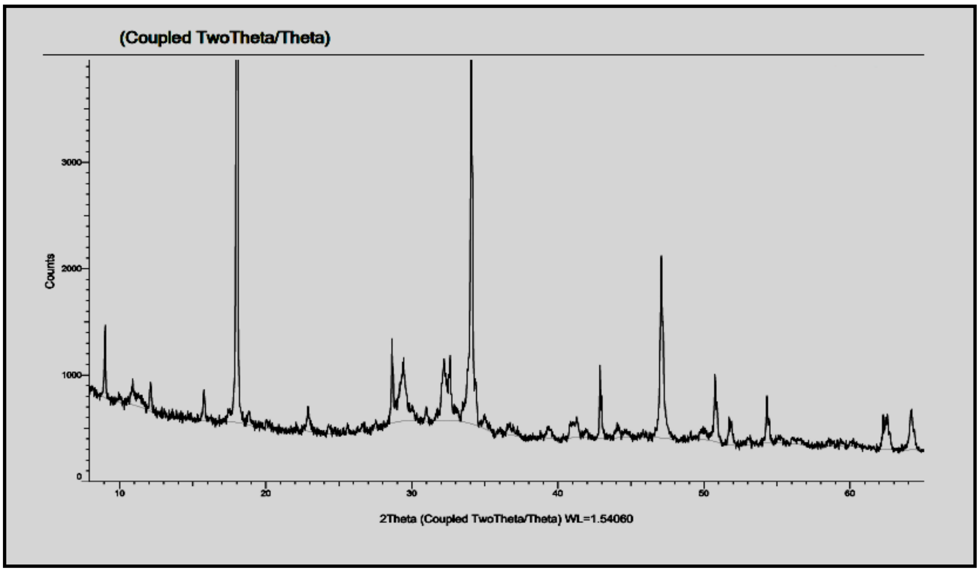

Fig 4. *X-ray diffractogram for 7 day hydrated original cement with 5 % (w/w) jarosite.*

When the hydration was allowed to occur at 7 days, the intensity of the mineral phases decreased and new diffraction lines due to formation of portlandite were observed at 2θ= 18.0, 47.0 and 51.0 (Cf. Fig.3 and Fig. 4). It is a well known fact that the calcium-silicate-hydrate (C-S-H) and ettringite formed during 1day of hydration are not crystalline in nature and have not been detected in the XRD pattern. However, portlandite peak is found to be of low intensity (Fig. 4.0) for cement with 5% (w/w) jarosite in comparison to that for the original cement sample (Fig. 3.0). This indicates that the additive jarosite retards the hydration of cement. Yet the compressive strengths of the sample of jarosite is similar as that of the original cement. Comparing Fig 1.0 and Fig. 2.0, it can be stated that no new peaks are seen in Fig. 2.0 due to the addition of 5 % (w/w) jarosite in cement. Likewise, comparing Fig 3.0 and Fig. 4.0, it can be inferred that no new peaks are observed in Fig.4.0 as a result of addition of 5 % (w/w) jarosite in cement in hydrated condition also.

3.3.2. Microscopic Studies

Microscopic studies were carried out only with the hydrated original cement and hydrated cement with 5 % (w/w) jarosite at 7 days and SEM images are depicted in. Fig.5.0 and Fig.6.0 respectively, which reveal well -hydrated products for both original cement and cement with 5 % (w/w) jarosite. More etringite formation could be seen in cement with 5 % (w/w) jarosite. Furthermore, there are no special products seen during hydration with the help of SEM studies (Cf. Fig.5.0 and Fig. 6.0). Lastly, no microstructural changes are observed due to addition of jarosite (Fig. 6.0).

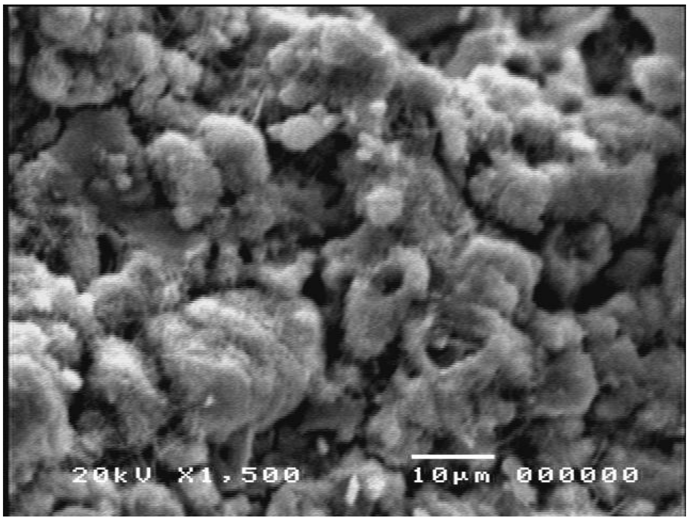

Fig 5. *SEM image for 7 day hydrated original cement*

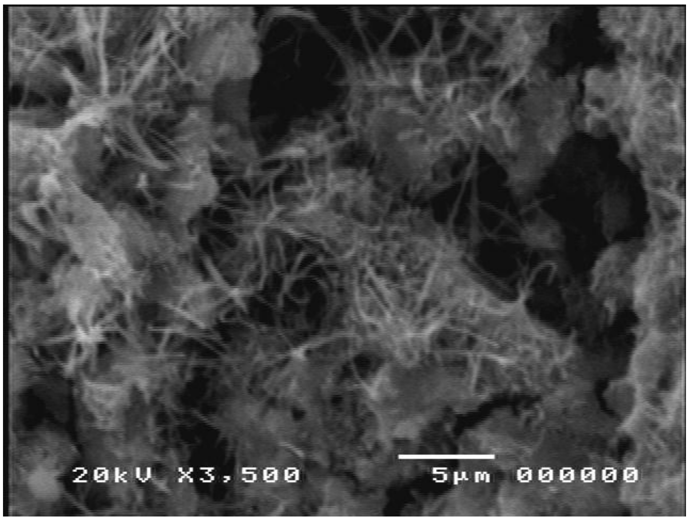

Fig. 6 *SEM image for 7 day hydrated original cement with 5 % (w/w) jarosite.*

4. CONCLUSIONS

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

1. The mineral, jarosite was found to be the best reducing agent at dosage levels i.e., 3.0% (w/w) for reducing Cr (VI) among all the mineral-based additives studied.
2. The data on setting time and compressive strength reveal that jarosite is the best additive among all the additives studied.
3. The additive viz., bentonite clay was found to possess good reducing properties at 4% (w/w), and 5% (w/w) dosage levels. However, the physical performance of the cement with bentonite clay as the additive was evaluated to be poor.
4. The early strength of the cement is increased with the use of jarosite as the additive. In case of other minerals the water requirement of cement is increased.
5. The investigative studies of hydrated cement with and without Jarosite have shown good agreement with each other.
6. The XRD and SEM studies indicate that no phase alteration takes place in case of the cement with 5 % (w/w) jarosite compared to the original cement.
7. Jarosite, being a low cost material, makes it economically attractive.

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