Extraction, Estimation and Reduction of Hexavalent Chromium in Indian Cement Samples

A

Thesis

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Chemistry

By

Devesh Kumar Sharma

(Registration No: 41200378)

Supervised

By

Dr Rekha Sharma

LOVELY FACULTY OF TECHNOLOGY AND SCIENCES

LOVELY PROFESSIONAL UNIVERSITY

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DECLARATION

“I hereby declare that the thesis entitled, “**Extraction, Estimation and Reduction of Hexavalent Chromium in Indian Cement Samples”** submitted for the degree Doctor philosopher in Chemistry, at Lovely Professional University, Punjab is my own original work and all ideas and references have been duly acknowledged. The research work has not been previously submitted to any other institution of the award of any other degree.

Signature of Candidate

Devesh Kumar Sharma
Reg. No. 41200378

CERTIFICATE

This is to certify that Mr. Devesh Kumar Sharma has completed the Ph.D. in Chemistry titled, “**Extraction, Estimation and Reduction of Hexavalent Chromium in Indian Cement Samples”** under my guidance and supervision. To the best of my knowledge, the present work is the result of his original investigation and study. No part of thesis has ever been submitted for any other degree or diploma.

The thesis is fit for the submission for the partial fulfillment of condition for the award of degree of Ph.D in chemistry

Signature of supervisor

(Dr. Rekha Sharma)
Associate Professor
Lovely professional university Punjab

ABSTRACT

In total 57 samples of eleven brands of Portland pozzolana cement (PPC) and 6 samples of two brands of ordinary Portland cement (OPC) were collected from different parts of India for estimation of hexavalent and total chromium content. Water soluble Cr(VI) was extracted using three different literature methods (Danish, European and German methods) and one in-house developed method. In in-house developed method, to ensure and complete extraction of Cr(VI), 2.0 gram of cement was taken in 100 ml distilled water and content were mixed after every day hours up to 5 days. The concentration of water soluble Cr(VI) and total chromium in these samples was found to be higher than the permissible limit (2 ppm).

For detection of Cr(VI), DPC was used as redox indicator, which causes reduction of Cr(VI) to Cr(III) by undergoing self oxidation. But the % age recovery of Cr(VI) obtained by use of DPC was found to be more due to interfering ions such as Fe(III). To remove this interference, Variamine blue dye (VB) was used first time for detecting Cr(VI) in cement sample. The determination is based on the reaction of hexavalent chromium with potassium iodide in an acid medium to liberate iodine. This oxidizes variamine blue to form a violet coloured species having absorption to maximum at 556 nm.

Concentration of sparingly soluble and insoluble Cr(VI) was also estimated by treating cement extract with sulphate and carbonate buffer. Energy-dispersive X-ray spectroscopy (EDX) and Infrared Spectroscopy (IR) confirmed the complete extraction of hexavalent chromium by sequential extraction process. Extracted Cr (VI) was determined by both methods (DPC and VB method). The validity of Varamine Blue method was thoroughly examined by comparing the results with standard DPC method as well as the accuracy of the method was checked using a standard reference material of National Institute of Standards & Technology (NIST), USA and SRM 2701 (Reference material from NIST, USA).

$FeSO_4.7H_2O$ and $SnCl_2.2H_2O$ as reducing agents were used first time in Indian cement samples. The effect of reducing agents ($FeSO_4.7H_2O$ and $SnCl_2.2H_2O$) on Cr(VI) concentration was observed. The determination of water soluble Cr(VI) after adding reducing agents was precisely conducted by in-house developed method using DPC reagent. Effect of additive’s form (crystalline and powder) was also observed. The qualitative information regarding reduction of water soluble Cr(VI) in hydrated cement paste and extracted solution was monitored by FTIR and UV-Visible Spectra. It was observed that the maximum reduction was found in hydrated

cement with $SnCl_2.2H_2O$. The effect of addition of reducing agents on the standard consistency, setting times and compressive strength of the cement mortar samples was checked. In addition, hydration properties of cement paste (with and without additives) were also investigated by TGA, SEM, FTIR and XRD. The excessive use of reducing agents with cement has shown significant retardation in early hydration, but required for storage stability and effectiveness.

To enhance the effectiveness of chromate reducing additives ($FeSO_4.2H_2O$ and $SnCl_2.2H_2O$) in hydrated cement as well as its storage for longer periods of time, a modified reducing agents (liquid detergent based) were prepared. The effectiveness of these modified reducing agents was evaluated with respect to their storage stability, reduction efficiency and hydration effect. The cement samples containing modified additives were stored in polythene bags and periodically, their Cr(VI) levels were tested through DPC method. The standard consistency, setting times and compressive strength were also checked to understand the effect of modified additives on cement quality. TGA, SEM, XRD and FTIR studies were used to understand their effect on hydration behavior.

To improves the hydration process of cement in the presence of reducing agents, six blended cement samples were prepared by agricultural waste (RHA and RTA). Cr(VI) leachability of pure OPC and RHA and RTA blended samples was checked using the standard DPC method. Use of reducing agents only in cement delayed the initial hydration process, as reducing agents might react with $Ca(OH)_2$ to form ettringite phases and decreases $Ca(OH)_2$ content. Initial as well later age hydration improved on addition of rice husk ash or rice tiller along with reducing agents. Amorphous silica of RHA and RTA reacted with $Ca(OH)_2$ to form calcium silicate hydrate which provides strength to the cement and improve the hydration. Microstructural changes in these samples were analyzed by TGA, SEM and XRD.

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(Devesh Kumar Sharma)

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The list of abbreviations

AAS	Atomic Absorption Spectroscopy
AdSV	Asorptive stripping voltammetry
ATILH	Association Technique de l'Industrie des Liants Hydrauliques
C-S-H	calcium silicate hydrate
C_3S	Tricalcium Silicate
C_2S	Dicalcium silicate
C_3A	Tricalcium aluminate
C_4AF	Tetracalcium alumino ferrite
DPC	Diphenylcarbazide
DPCA	Diphenylcarbazone
EPA	Environmental Protection Agency
EDTA	Ethylenediaminetetraacetic acid
ETAAS	Electrothermal atomic absorption spectrometry
FTIR	Fourier transform infrared spectroscopy
FIOSH	Federal Institute for Occupational Safety and Health
FPLC	Fast protein liquid chromatography
$FeSO_4$	Ferrous sulphate
HPLC	High performance liquid chromatography
ICP-MS	Inductively coupled plasma mass Spectrometry
$MnSO_4$	Manganese sulphate
$NaHSO_3$	Sodium hydrogen sulphite
$Na_2S_2O_8$	Sodium persulphate
Na_2CO_3	Sodium carbonate
$NaBH_4$	Sodium boro hydride
OPC	Ordinary Portland Cement
PPC	Portland Pozzolona Cement
PSC	Portland slag cement
PVDF	poly vinylidene difluoride

RHA	Rice Husk Ash
RTA	Rice Tiller Ash
SEM	Scanning electron microscope
SCTEE	Scientific Committee on Health and Environmental Risks
TG-DSC	Thermo gravimetric - Differential scanning calorimetry
TRGS	The Technical Rules for Hazardous Substances
TCLP	Toxicity Characteristics Leaching Procedure
UV	Ultra-Violet
XRD	X-ray diffraction
$Na_2S_2O_4$	Sodium hydrosulfite
MIBK	Methyl isobutyl ketone

Chapter-1

Introduction

1.1 Background

Cement is a powder which is mixed with water. It can cause allergic reactions in presence of trace metals such as Ni, Co, Pb, Cr etc and irritation on worker's skin due to highly alkaline pH of aqueous cement. Out of these trace metals; chromium is one of them, which causes toxic effect on worker's skin in their hexavalent form. The problems, related to human health, encourage the researcher to conduct more research in this field. Therefore, present research has been entitled, i.e. the extraction, estimation and reduction of hexavalent chromium in Portland cement.

Initially work on extraction, how to extract maximum percentage of soluble hexavalent chromium from hydrated cement phases because the industries and researchers are more concerned about water soluble hexavalent chromium due to high solubility consideration, but we can not ignore the sparingly and insoluble Cr(VI) also. Therefore we should be interested in the extraction of total hexavalent Chromium (soluble, sparingly and insoluble). After that, Cr(VI) species can be determined through diphenylcarbazide (DPC method), but this method suffer interference from ions (such as Mo(VI), Cu(II), Fe(III), Hg(II), and V(V)) which disturb the accuracy of results therefore need of an alternative for DPC reagent.

Apart from that, the reduction of hexavalent chromium in hydrated cement can be done through reducing additives (iron (II) and tin (II) salts), but these additives shows problem of stability and retards the initial hydration process, hence modification required in additives to enhance the storage stability and reduction efficiency. Reduction of Cr(VI) is not complete work to stop the further leaching of Cr(VI) from cement materials therefore it is tried to understand how can be stabilized or minimized the leaching of Cr(VI) after reduction.

Rice husk ash (RHA) and rice tiller ash (RTA) is used as stabilizing agent of Cr(VI). These are the great source of amorphous silica which can react with free lime and liberated lime during hydration and produced strengthen phase (calcium silicate hydrate). Thus we can solve the problems of Cr(VI) leaching and intial retardation in strength by using reducing additives and agricultural wastes (RHA/RTA) both as blended cement form. As a consequence this research may be beneficial for society and cement industries.

1.2 A brief history of cement

In ancient times, natural cement was used which was produced by burning a naturally occurring mixture of lime and clay [1]. In Roman times, cements were made from lime and pozzolana (a volcanic ash) mixed with ground brick and water. John Smeaton was a first person who discovered the cement. The Portland cement (OPC) was prepared and after that Patented by Joseph Aspdin in 1824. It had a colour similar to the white-grey limestone found on the Isle of Portland in Dorset, England. This method is still in use today [2, 3].

Portland cement was first produced commercially in India at Madras in 1904 as Indian Cement Company. At that time India had to import the cement from England. After increase in domestic demand, more cement unit was started in India. In 1924, production was 267000 tons in India. However, initially this production could not reduce the imports. Therefore, first cement manufacturers association in 1925 was formed as "Cement Manufacturers Association". It was followed by Associated Cement Companies Ltd. (ACC). After that many more companies were established. In 1950-51, there were 22 operating units in India were able to produce 3.3 million tons per year (http://www.gktoday.in/history-of-cement-industry-in-india/). As per Figure 1.1, India is the second largest producer of cement in the world (from India Brand Equity Foundation at www.ibef.org) and its consumption is around 400 million tons per year (available at https://en.wikipedia.org/wiki/Cement).

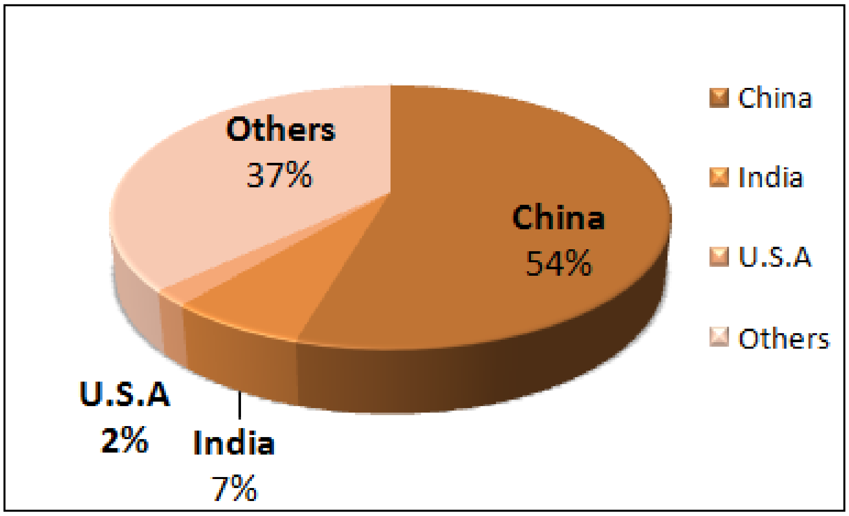


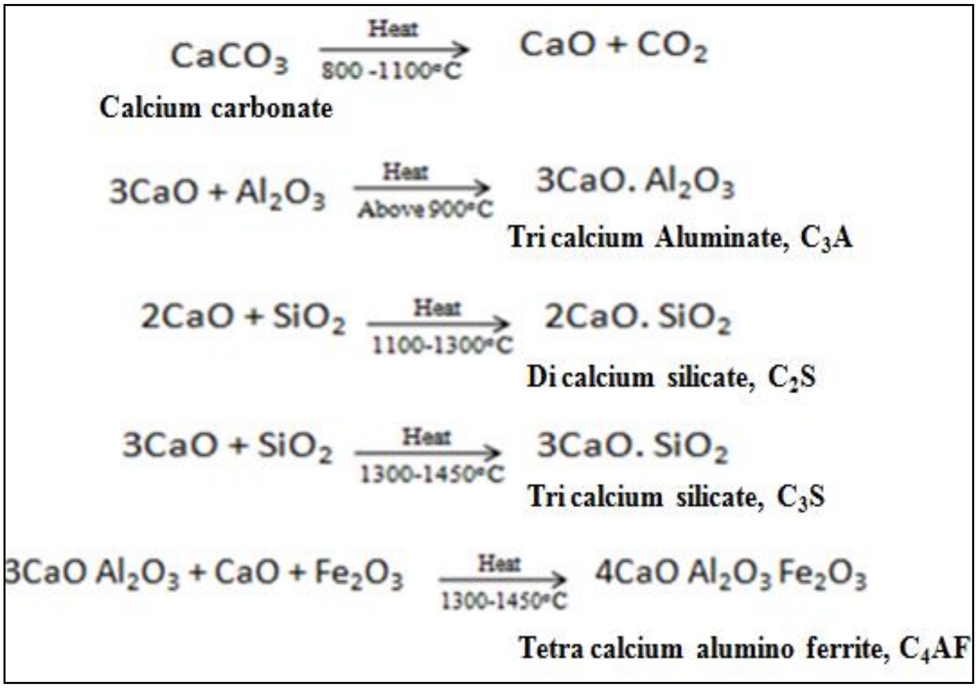
Figure 1.1: Cement production in world (https://en.wikipedia.org/wiki/Cement)

1.3 Cement

Portland cement is a composite material made by heating a mixture of calcareous (Insoluble calcium salts such as $CaCO_3$), argillaceous materials (such as clay), and iron oxide (Fe_2O_3) at temperature of around 1450˚C, this process is known as clinkerisation [3]. By this process, clinker is formed and it contains major portions such as CaO, SiO_2, Al_2O_3, Fe_2O_3 and minor portions such as MgO, K_2O and Na_2O. In clinkering, primary compositions are combined to each others to form calcium silicates, calcium aluminate and Tetracalcium aluminoferrite. These are the main phases of clinker. After that, gypsum ($CaSO_4.2H_2O$) is mixed up to 10%. It is added into the clinker before grinding, to stops cement from setting too rapidly [4]. In this way, a fine powder is obtained; known as Portland cement and used as building material for their strong linked properties with sand like materials or only with water.

1.3.1 Manufacturing of cement

Cement industries involves crushing, mixing and grinding of raw materials after that burning is done in kiln furnace in which thermal decomposition of calcite ore ($CaCO_3$), melting of Al_2O_3, Fe_2O_3 and formation of tricalcium aluminate (C_3A) phase is done from 800˚C to 1100˚C and the formation of dicalcium silicate phase (C_2S, belite) at 1100-1300˚C, tricalcium silicate (C_3S, alite) and tetra calcium alumino ferrite (C_4AF, ferrite) at 1300-1450˚C. The reaction involves in cement manufacturing are given in Scheme 1, after these reactions, cooling and crystallization of the various minerals phases, to form the clinker, the main constituents of clinker with its proportion as shown in Table 1.1 [1]. After that it is fed into a ball mill where it is ground into a fine powder and then gypsum is added to the clinker as a set retarder [4].



Scheme 1

Table 1.1: Major mineral constituents of clinker [1]

Name	Chemical Formula	Shortened Formulation	Percentage by weight
Tricalcium silicate (alite)	$3CaO.SiO_2$	C_3S	50-70
Dicalcium silicate (belite)	$2CaO.SiO_2$	C_2S	15-30
Tricalcium aluminate (celite)	$3CaO.Al_2O_3$	C_3A	5-10
Tetracalcium aluminoferrite (ferrite or brownmillerite)	$4CaO\cdot Al_2O_3\cdot Fe_2O_3$	C_4AF	5-15

As a result, an industry produces initially Portland cement (OPC) and after partial substitute of OPC with fly ash and slag and formed pozzolana cement (PPC) and slag cement (PSC). In addition, a few special types of cements are manufactured in India for special projects such as Oil Well Cement, Rapid Hardening Portland Cement, heat cement and Sulphate Resisting Portland Cement. Out of these types of cement, Portland pozzolana cement (PPC) is used commonly in India owing to high production of fly ash as industrial waste. The chemical and physical parameters of commonly used cement in India and their requirements as per Indian standards [5-9] are given in Table 1.2 and 1.3.

Table 1.2: Chemical characterization of Portland cement

Characteristic	**Requirements**				
	OPC 53 G (IS 12269)	OPC 43 G (IS 8112)	OPC 33G (IS 269)	PSC (IS 455)	PPC (IS 1489)
Lime Saturated Factor $\frac{CaO - 0.7\ SO_3}{2.8\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2}$	0.80-1.02	0.66-1.02	0.66-1.02	-	-
Al_2O_3/Fe_2O_3 (%), *Min*	0.66	0.66	0.66	-	-
Insoluble residue (%), Max	4.0	4.0	5.0	4.0	5.0
Magnesia (%), *Max*	2.9	6.0	6.0	8.0	6.0
Suphuric anhydride (SO_3), *Max*	3.5	3.5*	3.5	3.0	3.0
Sulphur content (sulphide) Max	-	-	-	1.5	-
Loss on ignition, percent by mass, *Max*	4.0	5.0	5.0	5.0	5.0
Chloride (%), *Max*	0.1	0.1	0.1	0.1	0.1
Alkali content %, max (for prestressed structures)	0.05	0.05	0.05	0.05	0.05
Alkali content %, max (for aggregates)	0.6	0.6	0.6	0.6	0.6

*Not more than 2.5 when C3A< 5, 3.0 when C3A> 5

Table 1.3: Physical properties of Portland cement

Characteristic	**Requirements**				
	OPC 53 G (IS 12269)	OPC 43 G (IS 8112)	OPC 33G (IS 269)	PSC (IS 455)	PPC (IS 1489)
Fineness, m^2/kg, *Min*	225	225	225	225	300
Soundness:					
a) By Le Chatelier method, mm, *Max* 10	10	10	10	5	10
b) By autoclave test method, percent, *Max*	0.8	0.8	0.8	0.6	0.8
Setting time:					
a) Initial, min, *Min*	30	30	30	30	30
b) Final, min, *Max*	600	600	600	600	600
Compressive strength, MPa:					
a) 72 ± 1 h, *Min*	27	23	16	16	16
b) 168 ± 2 h, *Min*	37	33	22	22	22
c) 672 ± 4 h, *Min*	53	43	33	33	33

1.3.2 Importance of cement

Portland cement is a building materials used for its strong bonding properties. It is used in the production of the many structures such as buildings, bridges, runways and roads etc. The regular demand for all of these cement structures, gradually more from the developing world, means that cement is the second most consumed material in the world after water. Besides this, it is used to stabilize the industrial waste such as fly ash and slag which are produced in very large amounts [10, 11]. In India, fly ash and slag both are produced in major quantity. The annual production of fly ash is about 131.09 million tons per annum, but about 73.13 million tons per annum has been utilized in production of blended cement and remaining in roads and agriculture etc [12, 13]. The Steel industries in India are producing about 24 million tones of blast furnace slag and 12 million tons of steel slag is being utilized. As per Figure 1.2, 30% fly ash and 5% slag are utilized in production of Portland pozzolana cement (PPC) and Portland slag cement (PSC) (Source: CEA annual report on fly-ash generation-utilization 2010-2011).

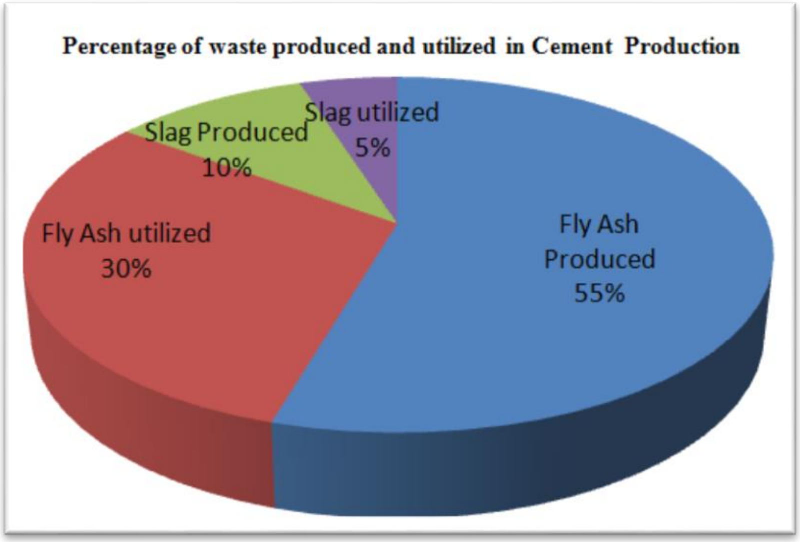


Figure 1.2: Utilization of industrial waste (Fly ash and Slag) [10, 22]

It can significantly reduce the release of toxic species and support for construction sustainability and development of using waste (industrial and domestic), reducing the consumption of natural resources and forming more resourceful materials [14-16]. About 20 million tons of rice husk ash (RHA) is produced annually in India during milling as a fuel in the boilers. This RHA is a huge environment danger causing damage to the land and the surrounding area in which it is discarded. In some countries except India, RHA is commonly used in production of cement. It may binds toxic metals in hydrated cement and minimizes the leaching of toxic metals in water reservoirs, but now days RHA is used as super-pozzolans in concrete also [17-20].

1.3.3 Health hazards of cement

Wet cement has adverse effects on workers health due to high alkalinity, exothermic reaction during hydration and contact sensitization causes a non-allergic form of dermatitis (irritant contact dermatitis). Apart from this, some metals like nickel, cobalt, lead and chromium are also present in cement which causes allergic type of dermatitis [21-24]. Out of these, chromium species (soluble hexavalent) are of prime concern as toxin and is harmful to the humans and its toxicity depends upon the route of exposure (Table 1.4) [23, 24].

Table 1.4: Hexavalent chromium exposure and diseases [23, 24]

Route of exposure	Mode of intake	Health hazards
Air	Breathing	Nasal irritation, nasal ulcer, respiratory tract cancer, lung cancer, tuberculosis, cough and cold, etc.
Water	Drinking and eating	Stomach cancer, diarrhea, bronchospasm and pneumonia, etc.
Dermal	Skin penetration	Dermatitis, irritation, skin lesions

Chromium is present in raw materials as clay, lime, ore and fuels used for the production of cement in which chromium level was found up to 300 ppm [22]. Naturally occurring Cr (III) is not initially harmful, because it is chemically stable but at high temperatures (occurring in cement rotary kilns during its production), this trivalent chromium oxidizes into hexavalent form [25]. This form of chromium is water soluble and can easily come in contact with the skin of the workers in construction field. It can enter into skin, where it is transformed into trivalent form and comes together with epidermal proteins leading to a general exasperation of the skin, known as cement dermatitis (Figure 1.3). Thus, it is both carcinogenic and allergic [21-24].

Therefore, European directive 2003 has enforced a law regarding to limit of Cr(VI). The cement should not have more than 2 ppm Cr(VI) in cement. Reducing additives can be used if its limit is more than 2.0 ppm [26]. Thus cement has harmful effect not only during its making, but also in the process of its utilization.

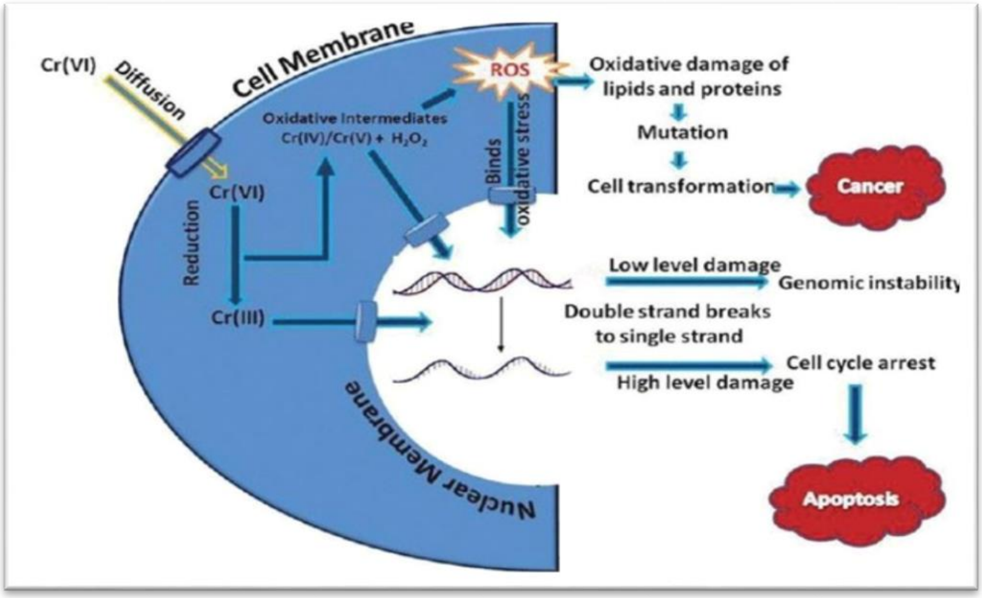


Figure 1.3: Possible mechanism of hexavalent chromium intracellular toxicity [21].

1.4 Chemistry of chromium species

Metallic chromium is a white, hard, brittle and lustrous metal that melts at 1903 ± 10°C. It is found in nature in the combined form as chromite ore ($FeCr_2O_4$), in which chromium is in the trivalent state [27]. The property of Cr is highly dependent on its oxidation state and generally exists in two forms i.e. hexavalent and trivalent form [28].The chromium species exhibits different behavior with respect to solubility, redox and complexation activities [29]. Cr(VI) is more mobile and soluble in aqueous meadium than Cr(III) therefore it is difficult to remove it from water [30]. It is, approximately 10 to 100 times more toxic than Cr(III) by the acute oral route [31]. Therefore Cr(VI) ion is accepted as the principal cause of toxicity and allergens or hypersensitivity through skin contact [32]. On the other hand, Cr (III) has been considered an important micronutrient in the human fast and widely used as a relating to diet supplement for humans and animals. Sometimes Cr (III) compounds can cause allergy in highly alkaline medium due to the formation of soluble chromium species [33].

As presented in Figures 1.4 and 1.5, the behavior of trivalent and hexavalent Chromium in aqueous medium is mainly affected by oxidation-reduction potential and pH of solutions [32, 34]. In acidic medium, the high redox (oxidation-reduction) potential of the trivalent and hexavalent Chromium couple is responsible for transformed into stable trivalent Cr. In contrast, under alkaline conditions the redox potential decreases. It indicates stabilization of Cr(VI). Thus, thermodynamically, Cr(VI) is present maximum in high pH range. At pH (from 0 to 4), Chromium (III) tends to form soluble hexacoordinate complexes, pH 4–6, Cr(III) tends to form hydrolysis products. At pH upper than 6, Cr(III) precipitates in the form of $Cr(OH)_3$, this precipitate is transformed into the soluble complex such as $Cr(OH)_4^-$ [35].

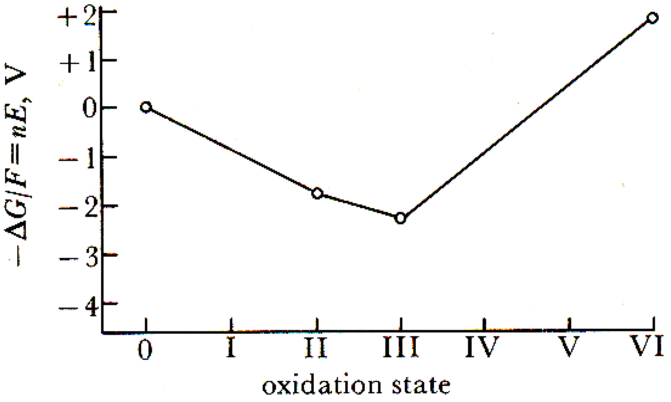


Figure 1.4: The oxidation state and reduction potential diagram for chromium [30]

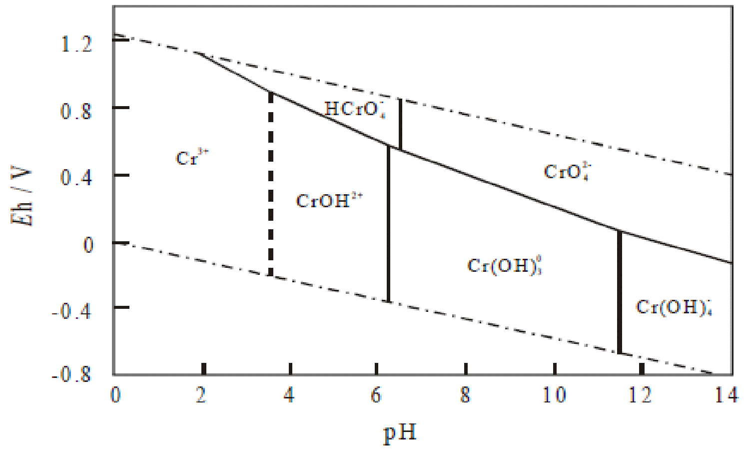
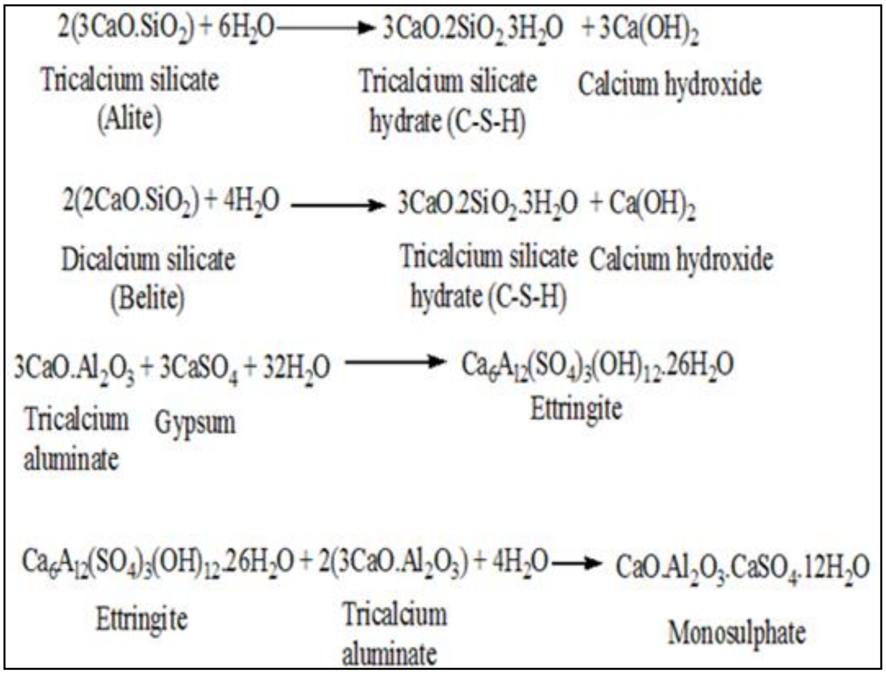


Figure 1.5: The redox potential and pH diagram for chromium species [35]

1.5 Chemistry of cement hydration

The main oxides of cement (CaO, SiO_2, Al_2O_3 and Fe_2O_3) are present in the form of four solid phases such as C_3S, C_2S, C_3A and C_4AF. Hydration of cement occurs when the cement is mixed with water. The cementing action of Portland cement is derived from the hydration reaction of four phases with water (given in Scheme 2) and about two-third of hydration is achieved in 28 days [36].



Scheme 2

Out of four phases, alite (Ca_3SiO_5, C_3S) is the most important constituent of Portland cement. It reacts quickly with water and provides early strength to the cement materials (cement mortar and concrete). When this phase hydrates, it forms calcium hydroxide and a solid calcium silicate hydrate (C-S-H) gel. Belite (Ca_2SiO_4, C_2S) is another important phase of cement which reacts relatively slowly with water and contributing less early strength. However, it contributes strength in later aging. The hydration of belite is much slower than alite therefore less calcium hydroxide (CH) is formed [37]. The structure of hydrated C_3S and C_2S (C-S-H) are similar to tobermorite and jennite [38, 39]. Aluminates phase ($Ca_3Al_2O_6$, C_3A) is beneficial in the cement manufacturing, where it forms a liquid during clinkering but it reacts rapidly with water and cause unwanted rapid setting. This problem can be suppressed by adding gypsum as a set-controller. Otherwise, aluminate decreases the final strength of cement [40]. Ferrite phase (C_4AF) is also similar to aluminates phase due to its initial rate of hydration is fast. Hydration process of this phase is intermediate in between alite and belite phase. The formation of ferrite phase during clinker formation is responsible for grey colour in cement [40]. In addition of calcium sulfate, it plays an important role in the cement hydration, not only as set retarder but also influenced the hydration of aluminates (C_3A) and ferrite (C_4AF) and help in formation of AFm and Aft phases. Besides this, aluminates reacts with gypsum ($CaSO_4 \cdot 2H_2O$) which forms the ettringite phase. After consumption of gypsum, alumiates reacts with ettringite and $Ca(OH)_2$ to form monosulfate [41, 42].

1.6 Effect of chromium

The presence of chromium at below 0.5% (by weight) concentration do not influence the belongings of clinker phases. However with rising concentrations of Cr up to 2.5%, the decomposition of C_3S (allite) occurs into C_2S (belite) phase and free lime [43-45]. Thus the occurrence of Cr in clinker formation influences the phase composition and restrains the tricalcium silicate (C_3S) formation. As a result, initial hydration of cement may be influenced due to the formation of calcium chromium compounds ($CaCr_2O_7$, $CaCrO_4$, $Ca_5(CrO_4)_3OH$, $CaCrO_4.2H_2O$, and $Al_2(OH)_4CrO_4$) [46, 47]; therefore several researchers have also been reported that the presence of chromium in cement decreases the compressive strength of cement mortar by increasing the porosity (as per figure 1.6) [48].

Apart from inhibition of hydration process of cement, chromium (in hexavalent form) has also adverse effect on human being and environment [49]. In contrast, the presence of Chromium (0.1%) in raw materials is responsible for reducing the viscosity of cement which makes easy grinding of clinker [45]. Although the presence of chromium (as trivalent form), during the clinkerization process increases corrosion resistance, durability of the cement as well as it accelerated the C_3S formation [46, 47].

Figure 1.6: XRD of hydrated cement without chromium (A) and with chromium (B) [48]

1.7 Chromium in cement

The presence of chromium in cement is obvious and the most frequently discussed forms in the cement industry are chromium (III) and Chromium (VI). Both consideration is required by which affected the properties of cement and cement materials and Cr(VI) also received the most attention regarding health issues [25]. During cement hydration, these forms (Cr (III) and Cr (VI)) unbalanced to each other, a short description of the trivalent and hexavalent states of chromium in clinker and cement provided below. Chromium (III) compounds such as chromic oxide, chromic sulfate, chromic chloride, and chromic potassium sulfate. Compounds with Cr (III) are most stable, having low solubility and reactivity therefore their impact on the environment and living systems is low [50]. Cr(VI) compounds such as Cr_2O_3, chromic acid, Na_2CrO_4, sodium dichromate, $K_2Cr_2O_7$, ammonium dichromate, zinc chromate, calcium chromate, lead chromate, barium chromate, and strontium chromate [51]. These are strong oxidizers and unstable. Its high solubility in water is related to health risks. Soluble Chromium (VI) can go through insecure skin and is transformed into Chromium (III), which combines with proteins to form the allergen that is foundation of sensitivity in certain people [51].

As per recent research, chromium compounds with different oxidation states were found in dry and hydrated cement as well as some chromium compounds were leached out during hydration [52]. The detail of chromium compounds (present in cement) is given in Table 1.5. Chromium compound with oxidation states of +3, +4.6, +5, and +6, respectively, were detected in the doped clinkers (Figure 1.7 a). $Cr^{4.6+}$ and Cr^{5+} in the form of $Ca_5Cr_3O_{12}$ and $Ca_5Cr_2SiO_{12}$, respectively, were noticed in both doped clinkers and mortars. The new kinds of chromium species as $Ca_5(CrO_4)_3OH$, $CaCrO_4$. $2H_2O$, and $Al_2(OH)_4CrO_4$ were also investigated in the hydrated mortar (Figure 1.7 b). But, in leached cement mortar the hexavalent chromium phases have not been detected (Figure 1.7 c). There are two reasons for this, firstly one is most of the concentration of Cr(VI) is leached out (due to high solubility) secondly its low concentration was not seen in XRD technique. In addition, SEM-EDS techniques are also suitable to confirm the presence of chromium species in the mortar samples (Figure 1.8) [52, 53].

Table 1.5: Various chromium species in cement [53]

Various Cr Species in cement	**Oxidation state**
Before hydration process following compounds are identified such as $Ca_6Al_4Cr_2O_{15}$, $Ca_5Cr_3O_{12}$, $Ca_5Cr_2SiO_{12}$, and $CaCr_2O_7$	+3, +4.6, +5, and +6
After the hydration process additional Cr compounds were identified such as $Ca_5(CrO_4)_3OH$, $CaCrO_4{\cdot}2H_2O$, and $Al_2(OH)_4CrO_4$	+4.6, +6, and +6
During cement hydration the following Cr compounds may be leached out such as $Ca_6Al_4Cr_2O_{15}$, $CaCr_2O_7$, $CaCrO_4{\cdot}2H_2O$, and $Al_2(OH)_4CrO_4$	+6

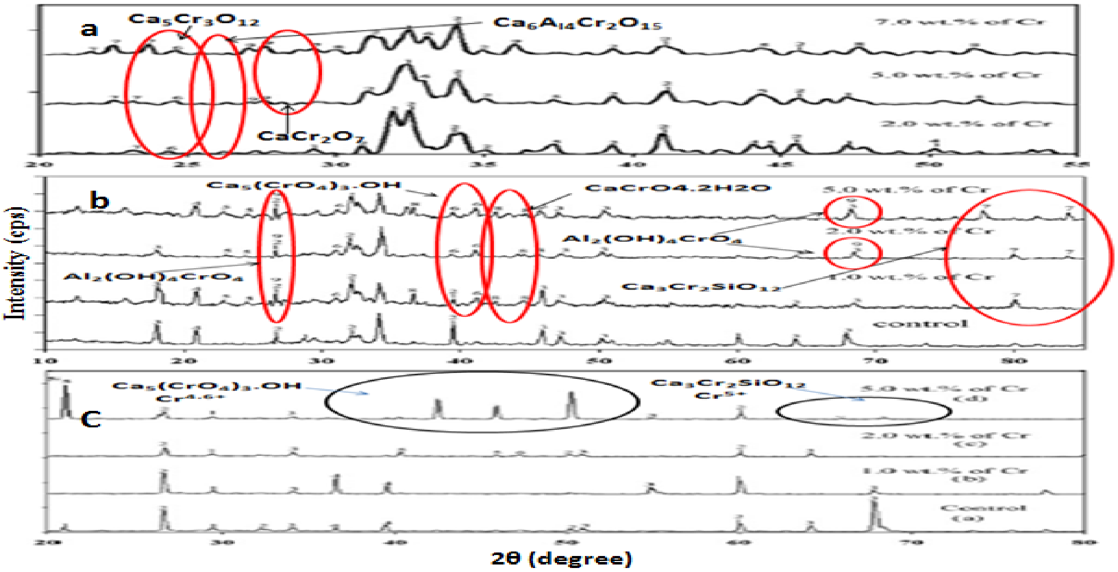


Figure 1.7: XRD patterns show, presence of chromium species in clinker, hydrated cement mortar and leached mortars at 28 days [53]

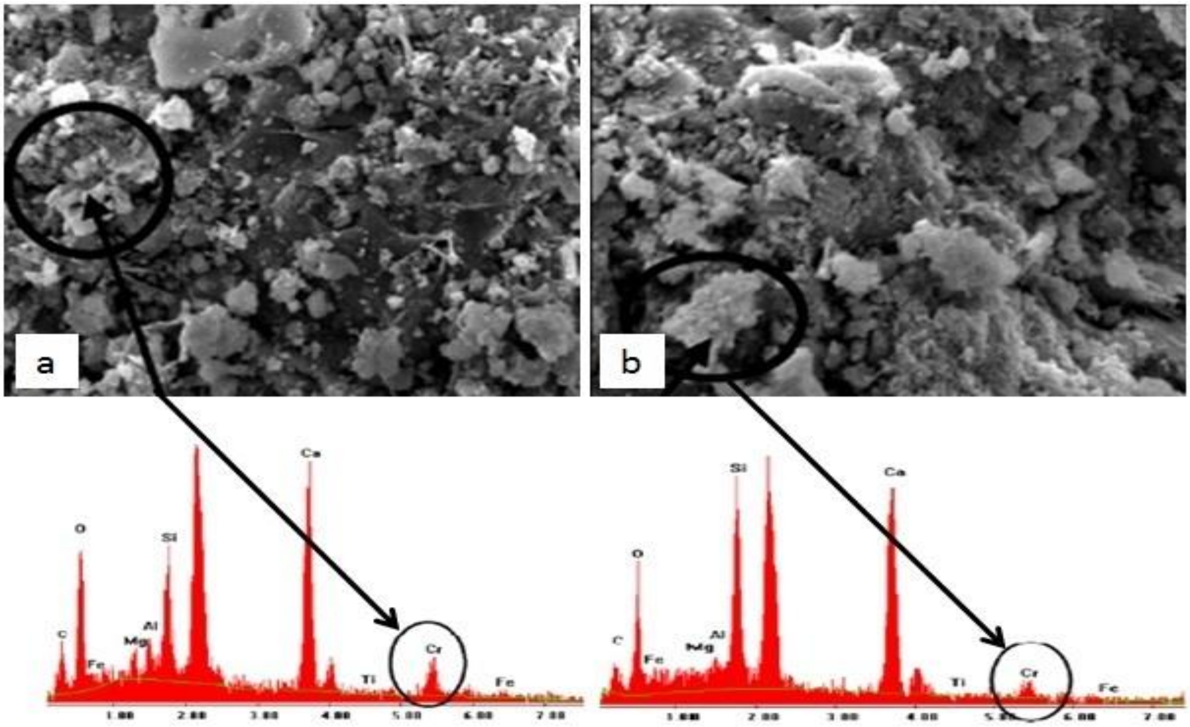


Figure 1.8: Surface morphology of hydrated cement at the age of 28 days: (a) 5.0 wt. % of Cr, (b) 2.0 wt. % of Cr [53].

Thus, the amount of Cr (VI) in clinker and cement can originate from raw material and additives as well as from manufacturing process [54, 55]. The details regarding potential sources of chromium in cement is given below.

1.8 Sources of chromium in cement

Chromium is a naturally occurring element and is found in mineral form (as iron chromite, $FeCr_2O_4$) [56]. The higher concentration of chromium is found from industrial pollution. The most common sources of chromium is cement producing plants, combustion of natural gas, oil and coal, metal finishing industry (chrome plating), chemical manufacturing industry, (dyes for paints, leather tanning, rubber and plastic products) etc [54-57]. As per US Geological Survey, Chromium ores are mined today from South Africa, Kazakhstan, India, Turkey and other countries about 52%, 14%, 10%, 8% and 16%. South Africa is a leading country in the production of chromite ore while India has 7th position in the world (Figure 1.9) [56, 58].

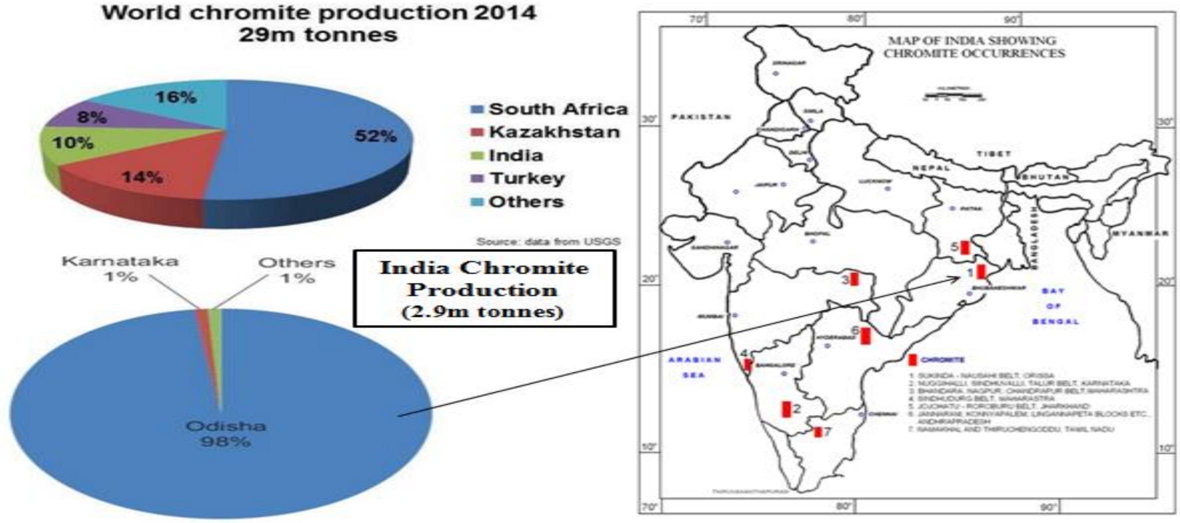


Figure 1.9: Chromite ore production (data from US Geological Survey) [58].

By this fact, the major source of chromium in cement product may be chromite ore. The present research has been made to show the interest in chromium estimation in cement due to the most attention regarding to health issues therefore the role of hexavalent chromium as a contact sensitizer in cement dermatitis has been known since 1950 [59, 60]. Chromium in cement comes from the raw materials (limestone, clay and gypsum), auxiliary materials (blast furnace slag, fly ash, silica sand, iron oxide, bauxite, and spent catalysts) and primarily fuel such as coal, oil as well as industrial by-products are also used as substituted fuel such as petroleum coke, used tires, impregnated sawdust, waste oils, lubricants and sewage, sludge, metal cutting fluids, and waste solvents [55]. These materials have chromium in the form of Cr(III), which is inert and insoluble, but during cement production, the Cr(III) can be oxidized partly into Cr(VI) and hexavalent chromium in hydrated cement in the form of chromate ion is water soluble [61, 62]. Chromium compounds have never been deliberately added to cement except in China to adjust concrete setting time, hence the cost of production is also decrease [63]. Thus the above sources of chromium could be a serious problem for cement producing companies in India where chromium is found at higher than permissible limit (2 ppm) [64].

First source of chromium (as Cr_2O_3) in the cement comes from raw materials such as lime stone, clay, shales and bauxites. Mr. Sprung has reported that it is up to 16 ppm in limestone, 100 ppm in clay and shales. Some of the auxiliary raw materials, such as bauxites may contain in between 0.04-0.40 ppm [65]. Mr. Sprung and Rechenberg have reported that it is up to 12 ppm Cr in limestone, 90 ppm in clay and shales. Mr. Bhatty has reported that it is up to 16 ppm in limestone, 200 ppm in clay/shale [66]. ATILH has reported that 20 ppm Cr in lime stone, 200 ppm in clay and marl, 110 in clay-schiste, 450 in iron oxide, 50000 ppm in mill scale, 40000 ppm in foundary sand, 250 in fly ash and 1100 in bauxite [67]. Mr. E. Erdem has reported that the presence of chromium in raw materials such as limestone contains 10.6 ppm, 8.0 ppm in clay 14.1 ppm in Fe-slag, 6.5 ppm in fire brick, 11.1 ppm in silica and 1.1 ppm in gypsum [68].

Second sources of chromium are fuels such as coal, tire-derived fuel are used in cement industry. Coals and oils are used in cement production, have chromium up to 80 ppm and 50 ppm. Third sources of chromium are magnesia-chrome kiln refractory brick [55]. Mr. Klemm is referred that if chrome refractory brick would expose to the clinker having reactive alkalies at high temperature and alkali chromates are formed. These (Potassium and sodium chromate) are highly soluble in water [69, 70]. Grinding mills is the fourth source of chromium because it is made up of chromium alloys and grinding in its mill can add chromium into cement [55].

Fifth source is additive such as gypsum, pozzolans, ground granulated blast furnace slag, mineral components, and cement kiln dust. ATILH has reported that from 3.3 to 33 ppm chromium in gypsum [71]. Kiln operation is the six source of hexavalent chromium formation, it can influence that how much Cr(VI) will form because during kiln operation, high temperature of kiln, high amount of free lime, alkalies and pressure of air causes oxidation of Cr (III) to Cr (VI). In the kiln, oxidizing atmosphere will play the largest role, with more oxygen in the burning zone leading to increase Cr(VI) formation [72].

Thus secondary additive (Industries waste) used as raw materials in cost-effective cement production are also responsible for enhancing chromium content in cement [71], therefore determination of chromium species is necessary before utilization of waste in cement production. The Cr(VI) content in the Portland cement may be varied from 0.2 to 40 ppm, depending on the origin of the cement [55, 64, 68]. Here, chromium content in cement raw materials from few research works is reported in Table 1.6.

Table 1.6: Reported Chromium Content in raw Materials used during cement production

Study	**Raw Material (Concentration in ppm)**								
	Limestone	Clay	Fuel				Fly ash	Bauxite	iron oxide
			Coal	Oil	Lignite	By product			
ATILH 2003 [80]	2.0-20.0	50-200	0-100	-	0-280	0-400	200-250	200-1100	20-450
Bhatty 1993[76]	1.2-16	90-109	5.0-80.0	-	-	-	-	-	-
Sprung and Rechenberg 1994 [75]	0.7-12	20-90	1.0-50.0	-	2.3-6.1	97	-	-	-
Sprung (1985) [83]	16	100	80	50	-	-	-	400- 4000	-

1.9 Status of chromium in cement samples of different countries

Since hexavalent chromium has adverse effect on human health, its determination in cement has been a prime concern of analyst in world over the years. A review of chromium contents in cement of different countries is given in Table 1.7

American cements showed variation of 0.03 to 30 µg/gram of Cr (VI) and 60 µg/gram of total chromium in cement samples [73, 74]. Recent studies on Ordinary Portland Cement (OPC) supplied by Assiut Cement (Cemex, Egypt) showed that the concentration of water soluble chromium was within permissible limit (below the 2.0 ppm) [75]. The concentration of hexavalent chromium varied from 0.02 to 200 µg/gram in German, Singapore, Norwegian and Swedish cements samples [76-79]. But recent study in Swedish cement showed decrease in water-soluble chromium [80].

In Slovak Republic, total chromium content in cement varied from 178.5 to 257.3 ppm and water soluble hexavalent chromium was found in range of 0.46 to 2.74 ppm [81-83]. In Australian Portland cements, total chromium, water soluble and sodium sulphate extractable chromate ranged from 49 to 99, 0.2 to 8.1 and 1.4 to 9.7µg/g respectively [84-86]. In Turkey, three types of cements (such as Portland, Portland Pozzolanic and Pozzolanic cement) were analyzed for chromium content. It was found that water soluble Cr (VI), total Cr (VI) and total Cr were in the range of 4.5 -17, 36.2 – 144.2 and 56.3 – 190.4 mg/kg respectively [68]. In Japan, Germany, Australia and Spain, Cr (VI) content in the Portland cement product was found to be varied from 0.2 to 40 ppm [87- 91].

In South Africa, total Cr in the portland cement was found to be 102 mg/kg and Cr(VI) was varied from 26.4 to 95.5 mg/kg [93]. The Korea Cement Industrial Association (KCIA) determined the content of Cr(VI) which varied from 2.17 to 4.44 mg/l. when these samples were analyzed as per Japanese Cement Association's testing method. It was found 25.5 mg/kg of Cr(VI) [94]. Various cement samples from the Bulgarian market were analyzed with respect to soluble Cr(VI) and its concentration was found from 0.9 to 3.0 mg/kg [95]. In Czech Republic, the soluble Cr(VI) contents in Poland cement was 2.5 mg/kg [96]. A study in Lithuania showed the content of Cr(VI) and total Cr from 13.1 to 26.3 and 54.4 to 108.6 mg/kg [97]. In Asian cement samples, the total chromium content was found from 15.9 mg/kg to 30 mg/kg and the soluble Cr(VI) content ranged from 3.6 mg/kg to 25.1 mg/kg [98]. The concentrations of chromium in different brands of Pakistani Portland cement was varied from 38 to 67 ppm [99]. Till now few study showed, there is correlation between total chromium and hexavalent chromium content in cement and few study did not showed these correlation.

Till now only one study had been conducted on Indian cement samples. In 2011, a study was made on Portland pozzolana cement. It showed that average concentration of water soluble chromium and total chromium concentration were found to be 18 ppm and 120 ppm respectively [100].

Table 1.7: Chromium concentration in cement as country wise

Country	Water Soluble Cr(VI) (mg/kg)	Total Chromium (mg/kg)	Reference
Slovak Republic	0.50 - 2.46	178.5 - 257.3	[81]
	0.46 - 6.38	-	[82]
	1.8	-	[83]
India	18	120	[112]
Turkey	4.5 – 17	56.3 - 190.4	[68]
South Africa	4.72 - 18.1	84 - 186	[93]
Australian	0.2 - 8.1	49 - 99	[84]
	1 – 18.5	-	[101]
Swedish	< 20	40 - 115	[80]
Spain	4.64 - 13.7	-	[85]
	0.9-24	-	[86]
France	1.0 – 9.0	57 - 102	[85]
	0.0591-15.3	-	[102]
U.S.A Cement	0.03-7.8	90.6-107	[70, 73, 103]
Germany	1-30	20-100	[88]
	0.1 – 20.3	40	[72, 104, 105]
Asia	3.6 – 25.1		[98]

Europe	0.003 – 20	-	[106]
Japan	6.4	58.4	[90]
	0.2 – 24	-	[107]
	6.3	67	[105]
Karlsruhe	-	30 – 70	[71]
South Korea	2.17 - 4.44	-	[94]
Lithuania	13.1-26.3	54.4-108.6	[97]
Pakistan	-	38-67	[99]
Bulgaria	0.9-3.0	-	[95]
Poland	2.5	-	[96]

1.10 Research Motivation

This research has been inspired to protect our body skin from irritations and eczema when cement having Chromium (VI) moves toward into contact with water therefore it is necessary to estimate the chromium from cement samples. Though the use of cement containing more than 2.0 ppm soluble Chromium (VI) in hydrated cement which was restricted by European Directives 2003/53/EC [26], but still there is no check in India.

As per literature, there is no method for sequential extraction of total hexavalent chromium from cement samples. It is required for the reason that toxicities may fluctuate for Chromium (VI) compounds of changeable solubility in water [108] therefore present research has focused on extraction and determination, not only soluble Cr(VI) but total Cr(VI) also such as water soluble, partially soluble and insoluble Chromium (VI).

In addition, there is no comparative study among extraction methods which are used to separate soluble Cr(VI) from hydrated cement and there is no method to extract the definite amount of water soluble Chromium (VI) from cement phase. Therefore present research has tried to develop a method for extraction of soluble Chromium (VI) without heating and chemical action and the triumphant application of wet method of analysis for inclusive extraction of total chromium also.

In determination of chromium, redox indicator such as Diphenyl carbazide reagent is used commonly which suffers ionic interferences during determination. Besides it some other reagents are either carcinogenic or less selective and time consuming [109]. These problems in determination of chromium in cement encourage adopting new chromogenic reagent. After estimation of chromium species, it is essential to reduce and stabilize the toxic Cr(VI). Therefore present research also focused on modification of the reducing agent to enhance its storage stability and reduce amount and cost as well as stabilization of toxic Cr(VI) has been done to utilize the agriculture waste materials (such as RHA and RTA).

1.11 Aims and objective of the study

Chromium is important among many trace elements present in Portland cements [28] because its toxic form such as Cr(VI) which can not completely stabilized in hydrated cement and it is leached. Its leachability was limited by the European countries regulations for Cr(VI) in wet cement so few methods for estimation of chromium concentration in cement are available but still no suitable method for complete estimation of total Cr(VI). Moreover, the reducing agents are used to reduce toxic Cr(VI) into non toxic Cr(III). It has disadvantage in terms of dosage, stability, high cost etc. Lack of systematic study of chromium in Indian cement samples imposes health risk to the workers. Thus keeping all these points in mind the following objective has been planned for present research work:

1. Complete extraction of total chromium (soluble and insoluble) and total hexavalent chromium (water soluble, partial soluble and insoluble) from Indian cement samples.

2. Estimation of chromium with Diphenyl Carbazide as well as with variamine blue (Redox indicator as well as chromogenic reagent) using UV-Visible Spectrophometer.

3. Reduction and Stabilization/solidification of hexavalent chromium in hydrated cement samples by modification of reducing agent or by utilization of waste material such as rice husk ash and rice tiller ash (free from hazardous element) in cement.

4. To study the effect of reducing additives or stabilizing mixture (RHA and RTA) on soluble Cr (VI) level, leachability of hexavalent chromium and cement performance by using UV-Visible, FTIR, TG-DSC. SEM, XRD.

Thus present research work will be helpful to the cement industry to find out the concentration of hexavalent chromium with accuracy so that some steps can be taken to reduce the Cr(VI) and decrease the health risk of the cement workers by adopting chromium reducing additives.

1.12 Organization of thesis

The structure of this dissertation is outlined below

Chapter 2: Literature review
Chapter 3: Experiment
Chapter 4: Extraction and Estimation of chromium from hydrated cement
Chapter 5: Influence of Hexavalent Chromium Reducing Agents
Chapter 6: Effect of Modified reducing agent (with liquid detergent)
Chapter 7: Effect of RHA-RTA along with reducing agents
Chapter 8 Conclusions
Chapter 9 References
Appendix 1
Appendix II
Appendix III

Chapter-2

Literature Review

In this chapter, concise literature survey of various methods of estimation of chromium, reduction and stabilization of hexavlent chromium and effect of reducing agent on hydration of cement is given. The point wise discussion is following:

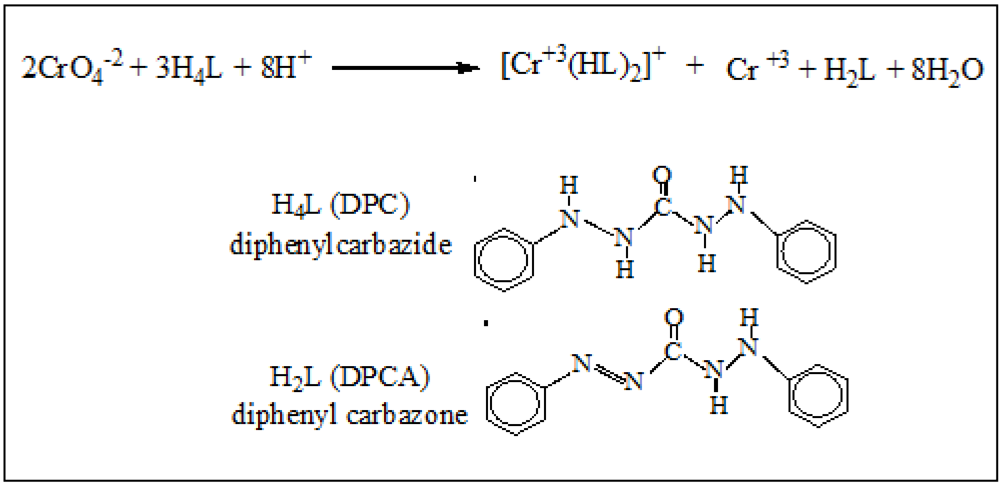
2.1 Chromium estimation in cement

A number of methods for extraction and detection of hexavalent chromium is available in literature. These methods are described as follows:

In 1957, Robert G. Keenan M.S. & Vernon B. Perone [73] developed a quantitative spectrographic method for the estimation of hexavalent chromium, Cr(VI). In this process, 50 g of Portland cement sample was added to 100 ml double-distilled water and shake for 30 minutes in a mechanical shaker. The suspension was filtered with suction. Residue was washed with 5-10 ml of double distilled water. Washings were added to filtrate. Residue had been given the same treatment and the filtrates from the two washings were diluted. Both the filtrate was analyzed separately using spectrophotometer. Residue was also analyzed for its contents. For total Chromium, 1.0 g sample was ground with 4.0 g of anhydrous sodium carbonate (Na_2CO_3), 2.0 g of anhydrous potassium carbonate (K_2CO_3) and 0.5 g of potassium nitrate (KNO_3). The resulting mix was transferred to a covered platinum crucible, heated for one hour to fusion, The crucible was cooled to room temperature, moved with 40-50 ml of double distilled water in a beaker and 5 drops of redistilled ethyl alcohol (to reduce any manganate present), heating was continued an additional 8 hours until only a light colored residue remained. The liquid was filtered throughout Whatman No. 42 filter paper. The insoluble material was washed with 4 or 5 ml portions of hot, 1% sodium carbonate (Na_2CO_3) solution. The filtrate was diluted to 250 ml and reserved for the estimation of total chromium.

In DS 1020 method (1984) [110], 25.0 g of cement was mixed with 25 g water and stirred for 15 minutes. The slurry formed was filtered and after appropriate dilution, soluble Cr(VI) content was estimated using DPC method. In DPC method [111, 112], extracted solution was acidified (pH 2.1 to 2.5) and adjusted to final volume. Then 0.25% (w/v) solution of Diphenylcarbazide (DPC) was added. DPC causes reduction of water soluble Cr (VI) to non soluble Cr (III) by itself undergoing oxidation (Scheme 3). Thus

DPCA and Cr (III) formed a magenta-colored complex. This concentration of complex was calculated by the spectrophotometer with a maximum absorption at 540 nm.



Scheme 3: Reaction of DPC with Chromate ion in acidic medium

In TRGS 613-2002 method [113], 10.0 g of cement sample was mixed with 40 ml of water stirred for 15 min at 300 rpm using a mechanical shaker and then filtered. The extracted solution as water soluble Cr(VI) was detected through standard DPC method [111, 112].

A mortar-based extraction procedure [114] was developed for water soluble Cr(VI) by the French cement industry R&D Association, ATILH, 2003 by a slight modification was done in TRGS 613, where cement samples were homogenized, suspended in deionised water in 1:1 and stirred for 15 minutes to form slurry. The slurry was vacuum filtered. Filtrate was analyzed directly without dilutions by standard DPC method [111, 112].

In 2003, S.S. Potgieter et al [93], devised a method to determine chromium species in cement. In case of water soluble Cr(VI), 0.2 g of cement was added into 25.0 ml of deionized water, boiled for 10 min, cooled and treated for 2 min in an ultrasonic bath and filtered. After appropriate dilution, soluble Cr(VI) content was estimated. For total Cr(VI), the cement was treated with a 0.1 M sodium carbonate (Na_2CO_3) solution for 2-3 min in an ultrasonic bath and filtered. Heating period was diversed to complete Cr(VI) dissolution and total chromium content was estimated by dissolving 0.5 g of cement with 1.0 ml of deionized water (H_2O) and 10.0 ml of 6 M nitric acid (HNO_3).

Samples were heated until all the excess acid evaporated, diluted again with 1% nitric acid (HNO_3) solution and filtrated. The final volume was made up to 100.0 ml with used water. In Another way, 0.2 g cement sample was mixed with 10.0 ml of 0.1 M sodium carbonate (Na_2CO_3) solution. After filtration, the wet filter paper was placed in 10.0 ml of 6 M nitric acid (HNO_3) solution. Thus chromium species were detected through electro thermal atomic absorption spectrometry.

For the selective extraction of hexavalent chromium Cr(VI), Panichev et al (2003) developed the Cr(VI) extraction by using solution of sodium carbonate (Na_2CO_3) which is most efficient as compared to other extraction process used water and CO_2.The ETAAS was used for the estimation of Cr(VI) [115, 116].

The Maximum extraction of Cr(VI) from cement was detected by Ellis and Freeman's method (1986), in which Na_2SO_4 solution was used to extract Cr(VI) from cement [101], but this method resulting in formation of large amount of insoluble residue. Thus it proved not to be a very reliable method [107]. Another direct and precise method for the leaching of total Cr(VI) in cement samples was given by Yamaguchi et al., 2006. In which, 1.00 g sample was digested with 10 ml HCl and neutralization with NH_4OH. In this method, Fe(III) was removed because it causes interference in detection of chromium by DPC method [107].

A selective extraction method was given by Janez Scancar et al, (2005) [102] In which the leached chromium was treated with HCl to form Cr(VI) - HCl complex and it was extracted by Methyl isobutyl ketone (MIBK). L-ascorbic acid was added to remove the interference caused by chromium (III) MIBK soluble species. After extraction of Cr(VI), detection was done by HPLC-ICP-MS, FPLC-ETAAS, and spectrophotometer. When a reducing agent was added in cement, selective extraction procedure could not be applied due to gel formation in organic phase. Therefore oxidizing agent (such as $Na_2S_2O_8$) was executed to remove the interfering effect of iron salts as a reducing agent therefore ortho phosphoric acid (H_3PO_4) was used for the removal of interfering ferric ion during analysis. These implementations had been taken in European method, known as EN 196-10: 2006 [117]**.** It was a combination of Danish and ATILH method, where water-soluble chromium (VI) was extracted by making a paste of cement, sand and water

(1:3:0.5) in mixer, followed by vacuum filtration through the glass filter and then detected by standard DPC method [111, 112].

Wladiana Oliveira Matos et al (2009) [118] verified the applicability of the alkaline extraction of Cr(VI) using solution of Na_2CO_3. In this study, taking 200 mg of sample and added into 10 mL 0.10 mol L^{-1} $Na_2 CO_3$ solution, kept under boiling for 10 min in a sand bath, then cooled to room temperature and adjusted to 14 ml with water. The mixture was centrifuged (4000 rpm) for 10 min. After that, 1,5-diphenylcarbazide reagent was added into extract by adjusting pH=1 after that Cr (VI) was determined by molecular absorption spectrophotometer. In determination of total chromium, the cement samples were decomposed by fusion in which 100 mg of sample was weighed in a platinum crucible with added 600 mg of melting mixture [Na_2CO_3 , 30%; K_2CO_3 30% and H_3BO_3, 40% by weight]. The mixture was first heated in a Bunsen burner until molten mass turning into a transparent liquid fluid. After cooling to room temperature then the sample was heated in oven at a temperature of 1000°C for an approximate period of time for 1 h, after cooling, the mixture was dissolved in 20 ml of HCl 1: 1 (v/v) with warming in a sand bath. After filtering, the total chromium was determined from filtered solution by FAAS.

Khmiri et al. (2009) [119] developed methods for chromium estimation in Portland cement. For total Cr(VI), 0.5 g cement sample was treated with 5 ml HCl and 3 ml of 6M HNO_3 then diluted with 20 ml of 20% HCl solution after that 0.1M sodium carbonate (Na_2CO_3) solution was added. The mixture was heated for 10 min, cooled and treated for 2 min in an ultrasonic bath. In determination of total chromium, 0.5 gram cement samples was taken in a beaker and added to 1.0 ml water, 5 ml con HCl and 3 ml of 6M HNO_3, The mixture was heated until the excess acid evaporated, then cooled and diluted with HCl solution. After appropriate chromium dissolution, total Cr(VI) and total Cr were analyzed through AAS (atomic absorption spectrometry). In case of water soluble Cr(VI) determination, 50 gram cement sample was taken and added to 50 ml deionised water. The mixture was agitated for 15 min and filtered. Ten drops of diphenylcarbazide were added into the filtrate and the concentration of soluble Cr(VI) may be measured by spectrophotometer at wavelength 540 nm.

Eva Margui et al, [120] produced activated layer method for Cr(VI) estimation. That layer consisting of a commercial poly vinylidene difluoride (PVDF) film soak with organic solution of 0.5M of Aliquat 336 was prepared. This layer was kept in contact with aqueous solution of cement leachate (at pH 2) with continuous stirring for two hours. Hexavalent chromium got entrapped in this layer via anion exchange mechanism. The loaded activated layer was washed with deionized water before analysis. Detection was done with Wavelength-Dispersive X-ray Fluorescence Spectrometry.

Erika Panaščikaitė et al (2011) [97] developed a simple and fast procedure trace determination of Cr(VI) and Cr(III) in cement by catalytic adsorptive stripping voltammeter (CASV) with the use of mercury drop electrode. In this method 0.1 gram of dry cement was taken and added to 50 ml of distilled water for 24 hours then 0.1 ml of this solution was taken into an electrochemical cell containing solution, 0.15 mol L^{-1} CH_3COONa, 5 m mol L^{-1} DTPA and 0.7 mol L^{-1} $NaNO_3$ and adjusted the pH up to 6. The electrochemical reduction of Cr(VI) to Cr(III) at a mercury drop electrode in the presence of DTPA ligand, and the adsorption of the Cr(III)–DTPA complex. Accumulation of this complex was carried out at potential from –0.9 V to –1.4 V. Total chromium is determined after the quantitative oxidation of Cr(III) to Cr(VI) by addition of 0.1–0.3 mmol/L of permanganate ions to the cement extracts. The concentration of Cr(III) is evaluated as the difference between total chromium and Cr(VI).

Rina S. Vaity (2011) [64, 100] determined the chromium in Portland pozzolana cement samples. For water soluble Cr(VI), 10 g of cement (PPC) was taken in a 250 ml glass beaker and 40 ml of deionised water was added to it. The slurries were stirred using a magnetic stirrer for 20-30 min and then filtered through vacuum filtration unit. In filtrate, 2 ml 6N H_2SO_4 (sulphuric acid) were added followed by 2 ml of 0.25% 1,5-diphenyl carbazide reagent. The absorbance of the solution was measured through spectrophotometer. In case of total Cr determination, 1 gram of lithium metaborate was used to fuse 0.5 g of cement sample in platinum-gold alloy crucible. The fusion was carried out at approximately 1000^{o}C on a bunsen burner. The glass beads formed and put for cooling and quenching. The beads were transferred into a glass beaker containing 100 ml water and 15 ml nitric acid for complete dissolution. The solutions were put on ICP-OES to determine the absorbance of chromium.

E. Erdem (2011) [68] determined the chromium content in cement samples. For soluble Cr(VI), 25 gram cement and 25 mL distilled water were mixed and agitated for 15 min and filtered. After that soluble Cr(VI) was determined from filtrate (extract) through DPC spectrophotometer method [111, 112]. In determination of total Cr(VI), 0.2 g of cement was treated with 10.0 mL of a 0.1 M sodium carbonate (Na_2CO_3) solution then boiled it for 10 minutes. After cooling, it was treated for 2 min in an ultrasonic bath and then filtered. For the determination of total chromium, 0.2 g cement sample was treated with 10.0 mL of 0.1 M Na_2CO_3 (sodium carbonate) solution. After cooling, the sample was completely dissolved in 10.0 mL of a 6 M HNO_3 (HNO_3) solution.

K. A. Idriss et al (2013) [75] produced a method for Cr(VI) determination in the presence interfering ions (Fe^{3+} and Ti^{4+} ions). In this method direct spectrophotometric determination of Cr(VI) has been carried out in presence of 1, 2, 5, 8 Tetrahydroxyanthraquinone, (Quinalizarin) at pH 1.5. Perchloric acid was used to adjust the pH of solution. For soluble Cr(VI) extraction, TRGS 613 procedure was used. After that, cement extract was taken into 25 mL calibrated flask and add 5.0 mL of Quinalizarin. Adjusted the pH to 1.5 and diluted with ethanol solution. Finally, measure the absorbance value at 565 nm. For total Cr(VI), 0.5 gram cement was taken and dissolved it into hydrochloric acid, after digestion, diluted with distilled water. To take cement extract solution (0.5 - 1.0 mL) into a 25 mL calibrated flask and added 12.5 mL of Quinalizarin and adjusted the pH to 1.5. This research devised the determination process of chromium in presence of Fe^{3+} and Ti^{4+} ions, both are interfered seriously during analysis which was overcome by using derivative ratio spectra-zero crossing method.

Pawel Zajac et al (2014) [96] developed a method by using catalytic adsorptive stripping voltammeter with Diethylenetriaminepentaacetic acid (DTPA) and nitrate and applied for the determination of chromium (VI) and total chromium in the extracts from cement. In this method leaching of Cr(VI) from cement was performed according to European Standard PN-EN 196-10:2008. The oxidation of Cr(III) present in the extract samples to Cr(VI), which is necessary for the CAdSV determination of total chromium. The oxidation of Cr(III) into Cr(VI) through UV-irradiation procedure. After that 0.5 mL of the diluted extract was mixed in a voltammetric vessel with 1 mL of 2.5 M KNO_3, 0.5 mL of 2M acetic buffer, 0.5 mL 0.2 M DTPA and 7 mL of water. The solution was left to settle for 30 min then it was deaereated with pure argon for 7 minutes. Quantitative measurements were performed by means of the differential pulse mode (DPV).

Soluble Cr(VI) is also extracted through sulfuric acid or sodium carbonate solution but this type of extraction process does not give accurate result due to pH considerations. In acidic medium the Cr(VI) may be converted into Cr(III) in presence of Fe(II) ion. Extraction with 1% Na_2CO_3 has been used to overcome the problems of extraction with 0.5 M H_2SO_4, because using an alkaline (Na_2CO_3) extraction solution diminishes the potential for hexavalent Cr to go through redox reaction with, for example, Fe(II) salt. However, 1% Na_2CO_3 solution may not firmly determine only water-soluble Cr(VI), as this medium (alkaline) might be expected to dissolve insoluble Cr(VI) to some extent. The use of an ammonium buffer ($(NH_4)_2SO_4$ and NH_4OH) has been proposed as an substitute medium for the extraction of soluble forms of Cr(VI) but this buffer offers to dissolve sparingly (partial) soluble Cr(VI) species also.

As per literature, it is concluded that these methods demanded a revision in extraction and determination techniques of chromium. Cement industries have interest to determine only water soluble Cr(VI) due to its high toxicity in aqueous environment [55]. The extraction (removal) of water soluble Cr(VI) may be affected by the ratio of water/cement, speed of mixer or magnetic stirrer with respect to time [95]. During extraction if low water/cement ratio and short time of mixing occurs, the soluble Cr(VI) may not completely leached out, During mechanical mixing and heating, the chance of Cr(III) may be transformed into Cr(VI). Total Cr(VI) may be also leached (extracted) by mixing of some chemicals like acetic acid (CH_3COOH), hydrochloric acid (HCl) and sodium carbonate (Na_2CO_3) [68, 93]. Recently the extraction of Cr(VI) has been done by activated layer and MIBK method, where the Cr(VI) get separated from interfering elements like Manganese (Mn), Iron (Fe), and Calcium (Ca) before detection [102]. But the extraction with MIBK reagent has a disadvantage as it forms gel with leached cement. Extraction of total chromium involves digestion through HNO_3, Na_2CO_3 and Na_2O_2 [68, 93]. After extraction, determination of chromium is very challenging task due to the presence of foreign ion which interfere as positively and negatively [109].

There are many varieties of the instrumental techniques for Cr(VI) determination [68, 93, 102, 121] out of these, diphenylcarbazide - spectrophotometric methods or adsorptive stripping voltammetry (AdSV) with Cr(III)–diethylenetriammine-pentaacetic acid (DTPA)–NO_3 are helpful financially for industries [64, 68, 81, 96, 97] These methods are based on the different capability of complex formation with Cr(III). In case of hyper-techniques (such as HPLC and IC) which involves simultaneously separation and estimation of Cr(III) and Cr(VI) both. Diode array detection is based on the chelating agent (ammonium pyrrolidine dithiocarbamate) [121]. Thus chromatographic techniques is very useful because it can separate not only Cr(III) and Cr(VI), but also forms of Cr(VI) such as CrO_4^{-2} and $Cr_2O_7^{-2}{}_7$. These methods are not economical for cement industries.

In multi-element determination, ICP-AES and the AAS methods require the use of costly apparatus so they are not always available easily for industrial laboratories [121, 122]. The Graphite furnace atomic absorption spectrometry (GFAAS) method has the suitable sensitivity; however, the presence of huge amounts of sodium (Na) and calcium (Ca) ions in the leaching solutions may create some problems with precise determination of chromium (Cr). Although these sophisticated techniques can detect chromium (Cr) in very low concentration with high correctness, precision, and selectivity but the cost of instruments is high. On industrial level use of these techniques is not possible. Thus spectroscopic techniques are still the most used methods for the determination of Cr(VI) in cement extracts. Therefore European Union (EU) prescribed UV/VIS spectrophotometry is best for Cr(VI) determination in cement. There are three standard methods (such as DS1020, TRGS 613, EN 196-10) for soluble Cr(VI) determination, those are based on UV/VIS spectrophotometry [110, 113, 117].

For estimation of total Cr by spectrophotometry method based on oxidation of chromium species into hexavalent form, after that Cr(VI) can be determined by most widely used reagent such as diphenylcarbazide (DPC method) but it bears severe interference from Fe(III), Mo(VI), Cu(II) and Hg(II) and as a result it makes high blank value [109]. Besides it, other reagents, like, phenylarsenazo, 4-(2-pyridylazo) resorcinol, gallacetophenone oxime, citrazinic acid, trifluoroperazine hydrochloride, and leuco xylene cyanol FF are either carcinogenic or less selective and time consuming [109, 122]. Thus, there is a need of simple and sensitive reagent for estimation of concentration of Cr(VI) with mimimum ionic interference. As per American Conference of Governmental Industrial Hygienists (ACGIH), The toxicity of Cr(VI) compounds is varied and depends on the solubility of the Cr(VI) compound. Owing to difference in toxicity of Cr(VI) species, there is rising interest in the ability to separately determine not only soluble Cr(VI) as well as sparingly soluble and insoluble Cr(VI) compounds. Previously this type of work has been done with air samples and it is not done with cement samples [123]. The estimation of chromium in cement samples included the extraction process is given in Table 2.1.

Table 2.1: Extraction process and determination techniques of Cr from cement

Extractable Fraction	**Sample types**	**Extraction process**	**Detection techniques**	**Ref.**
Soluble Cr(VI)	Cement	50 g cement + 100 ml water and stirred for 30 min.	DPC Spectrophotometer	73
Total Cr	cement, cement Residue after washing	1.0 g cement + 4g Na_2CO_3, 2 g K_2CO_3, 0.5 g K_2NO_3 + 40-50 ml water + heated.	DPC Spectrophotometer	73
Soluble Cr(VI)	Cement	25 g cement + 25 g water and stirred for 15 minutes	DPC Spectrophotometer	110
Soluble Cr(VI)	Cement	10 g cement + 40 ml water and stirred for 15 minutes at 300 rpm (TRGS 613)	DPC Spectrophotometer	113
Soluble Cr(VI)	Cement, cement materials	0.2 g sample + 25 ml water + boiled (10 min) + ultrasonic bath (2 min).	Electro-thermal atomic absorption spectrometry (ETAAS)	93

Total Cr(VI)	Cement, cement materials	0.2 g sample + 10 ml 0.1 M Na_2CO_3 + boiled (10 min) + ultrasonic bath (2 min)	ETAAS	93
Total Cr	Cement, cement materials	0.5 g sample + 1.0 ml water + 10 ml 6M HNO_3 + heated	ETAAS	93
Total Cr	Cement, cement materials	0.2 g sample + 10 ml 0.1 M Na_2CO_3 + we filtered paper + 10 ml 6M HNO_3.	ETAAS	93
Soluble Cr(VI)	Cement	25 g cement + 25 ml distilled H_2O + agitated for 15 min + filtered	DPC spectrophotometer	68
Total Cr(VI)	Cement	0.2 g sample + 10 ml 0.1 M Na_2CO_3 + boiled (10 min) + ultrasonic bath (2 min)	DPC spectrophotometer	68
Total Cr	Cement	0.2 g sample + 10 ml 0.1 M Na_2CO_3 + we filtered paper + 10 ml 6M HNO_3.	DPC spectrophotometer or AAS	68
Cr(VI)	Cement	Cement treated with Na_2SO_4 solution	DPC method	101
Total Cr(VI)	Cement	1.00 g cement + 10 ml HCl + neutralization with NH_4OH	DPC method	107
Soluble Cr(VI)	Cement	20 ml cement extracts (from TRGS 613 procedure) + 2 ml of con HCl + 5 ml MIBK	Flame atomic absorption spectrometry FAAS	102
Soluble Cr(VI)	Cement	Cement extract (from TRGS 613) + Cr(VI) separated by Ion pac CGSA guard column.	HPLC-ICP-MS	102
Soluble Cr(VI)	Cement	Cement extract (from TRGS 613) + Cr(VI) separated by	FPLC-ETAAS	102

		anion exchange column mono QHR 5/5.		
Soluble Cr(VI)	Cement	Cement, sand, water (1:3:0.5) + mixing + filtered	DPC Spectrophotometer	117
Total Cr(VI)	Cement	200 mg sample + 10 mL 0.10 mol L $^{-1}$ Na_2CO_3 + boiling for 10 min + centrifuged (4000 rpm)	DPC Spectrophotometer	118
Total Cr	Cement	100 mg of sample + platinum crucible + 600 mg melting mixture (Na_2 CO_3, 30%; K_2 CO_3 30%, H_3 BO_3, 40%) + heated up to 1000°C (1 hour)	FAAS	118
Soluble Cr(VI)	Cement	50 g sample + 50 ml water + agitated (15 min)	DPC Spectrophotometer	119
Total Cr(VI)	Cement	0.5 g sample + 5 ml con HCl + 3 ml 6M HNO_3 + diluted + titrated with Na_2CO_3 +added 10 ml Na_2CO_3 + heated	FAAS	119
Total Cr	Cement	0.5 g dried sample + 1ml water+ 5 ml con HCl + 3 ml 6M HNO_3 + heated + diluted	FAAS	119
Water soluble Cr(VI)	Cement, clinker	Activated layer (PVDF) + cement leachate (at pH 2) + stirring for two hours + washed with deionized water	Wavelength-Dispersive X-ray Fluorescence Spectrometry	120
Water soluble Cr(VI)	Cement	0.1 g cement + 50 ml water = leachate, take 0.1 ml aliquot into electrochemical cell (having CH_3COONa + DTPA	Catalytic adsorptive stripping voltammetry	97

		+ $NaNO_3$).	(CASV)	
Total Cr	Cement	10 ml cement extract + $KMnO_4$ solution, take 0.1 ml aliquot into the electrochemical cell	(CASV)	97
Water soluble Cr(VI)	Cement	5.0 ml cemnt extract (from TRGS 613 procedure) + 5 ml QINZ (0.001M) + 0.2 M perchloric acid	Direct Spectrophotometry	75
Total Cr(VI)	Cement	0.5 g sample + hydrochloric acid + dilution = take 0.5 - 1.0 mL aliquot + 12.5 mL QINZ (0.001 M).	Direct Spectrophotometry	75
Water soluble Cr(VI)	Cement, fly ash	0.5 ml cement extract (from EN196-10 method) + diluted + 1 ml 2.5 M KNO_3+ 0.5 ml 2M acetic buffer + 0.5 ml 0.2 M DTPA + 7 ml water	Catalytic adsorptive stripping voltammetry	96
Total Cr(VI)	Cement, fly ash	0.5 ml cement extract (after UV-irradiation procedure) + diluted + 1 ml 2.5 M KNO_3+ 0.5 ml 2M acetic buffer + 0.5 ml 0.2 M DTPA + 7 ml water	CASV	96
Water Soluble Cr (VI)	Cement	10 g sample + 40 ml water + 20 min stirring with a magnetic	DPC Spectrophotometer	64
Total Cr	Cement	Fussion with lithium metaborate, water & nitic acid in platinum-gold alloy Crucible at 1000°C	ICP-OES	64

2.2 Chromium speciation in cement materials

Apart from the estimation of chromium species in cement powder, estimation of chromium species from cement materials (mortar and concrete) is also important because of Cr(VI) can be leached from cement materials such as water reservoirs and transport pipes. Therefore leaching test for cement materials is required.

Leaching is the process by which contaminants (toxic metal ions) are transferred from a solid cement matrix into aqueous solution. Leaching test such as EA NEN 7375:2004 and TCLP method 1311 (U.S. EPA) were used commonly [124, 125] but the static tank method is also used now days, In this method samples as paste, mortar or concrete are in a tightly closed plastic bottle with distilled water or a weak solution of acid (pH = 4) [126]. Another leaching process such as DEV-S4 and EPA method (Environment Protection Agency) are also related with mortars and concretes [127]. The leaching rate of chromium was decreased as per contact time increased [17, 128]. After leaching process, chromium was determined through an ICP-OES (inductively coupled plasma-optical emission spectrometer), atomic absorption spectrometer (AAS) and a UV–Visible spectrometer [129, 127].

As per EPA, Samples were ground to powder form and dipped into 200 ml water and mixed in a rotary shaker at 30 rpm for 18 h. After filtration, Cr(VI) was determined from the filtrate by atomic absorption spectrometer (AAS) [124, 130-135]. For complete leaching of chromium, Batch leaching experiments have been used in cement treated soil to cover a wide range of pH (from 2.0 to 12.0) [136, 137]. In this method, the sample was leached with 1M NaOH and the leached solutions were then analyzed the chromium [138]. Cr(VI) was not detected at pH < 2.5, which may be recognized to absorption of Cr(VI) into the soil surface or its reduction by organic matter or ferrous ions. A considerable amount of Cr(VI) was extracted between pH 4.5 to 12. It has been found that cement treated soils do leach hexavalent chromium [62] therefore it is essential to reduce or stabilized toxic Cr(VI). Sodium carbonate is successfully used for the leaching of hexavalent chromium, not only in cement but also in the raw materials of cement [93]. In a research work, de-ionized water, Na_2CO_3 solution and HNO_3 solution as used to extract soluble Cr(VI), total Cr(VI) and total Cr from cement materials. Alkaline leaching was done to leachate total Cr(VI) from cement samples but in a very basic environment (above pH 12), the chance of Cr(III) may be transformed into Cr(VI) as well as Na_2CO_3 solution is able to convert all insoluble Cr(VI) to soluble form therefore higher values will be obtained for hexavalent chromium [93].

TCLP (toxicity characteristic leaching procedure) were carried out on the hydrate cement pastes [133]. In this procedure, a sample was ground to a powder form and immerged into water in acidic solution and its contents were agitated in a rotary shaker for 18 h. The leached solution was analyzed the Cr(VI) contents by colorimetric tests [43, 139]. The results pointed out the importance of the shaking time and the fineness of the specimens in Cr(VI) leaching procedure [62, 140]. In Ellis and Freeman's method, Na_2SO_4 solution was used to leach the Cr(VI) from cement samples. However, this method left a large amount of insoluble residue, so it is hard to believe that all of Cr(VI) in the cement was dissolved [107].

Yamaguchi et al.,(2006) was optimized the procedure, in this case 1.00 g cement sample was digested with 10 ml HCl and the solution was neutralized using NH_4OH followed by filtration to remove Fe which interferes with diphenylcarbazide method of analysis [107].

In Japan, It was found that the leachability of Cr(VI) from soils stabilized by cement was high in some cases [107]. The amount of metal ions in leachant solution depended on the amount and kind of the immobilized metals in soil. Therefore it is essential to do more research on the leaching process [126, 129].

Yu et al. (2005) reported that leachability of heavy metals depends largely on the leachant pH and the leaching test method. The leaching of heavy metals is enhanced at lower pH. Therefore tank method may leach less heavy metal as compared to the shacking test method [127].

Palomo and Palacios (2003) have been used Portland cement and fly ash as stabilizing agents to minimize the Cr(VI) leaching and found that the formation of $CaCrO_4$, which is highly insoluble, in a cement system accounted for low Cr(VI) leachability while high Cr(VI) leachability with respect to fly ash, indicated the formation of soluble Na_2CrO_4 [141]. This study was also supported by Wang and Vipulanandan (2000). They had concluded that the immobilization of Cr(VI) was achieved due to formation of $CaCrO_4.2H_2O$ in hydrated phase [48]. Weng and Robson B. Lokothwayo

[2007] gave a method, where the solid samples (concrete) were treated with Na_2CO_3 to solubilize all compounds of Cr(VI) and then detected by AAS and Adsorptive stripping voltammetry (AdSV) [134].

Suthatip Sinyoung et al (2011) investigated the behavior of chromium during the leaching of cement mortar and found that chromium species such as $Ca_6Al_4Cr_2O_{15}$ (trivalent form) and $CaCr_2O_7$, $CaCrO_4\cdot 2H_2O$, and $Al_2(OH)_4CrO_4$ (in hexavalent form) were leached during leaching tests (TCLP method 1311) whereas other species remained in the mortar. The amounts of leached chromium from concrete cubes were higher than the allowable value (5mg/L) [53].

Neeraj Jain (2011) investigated the effect of Cr(VI) on solidification with rice husk ash (RHA) blended cement [17]. In this research the leaching tests were conducted for 28, 90, 180, and 360 days-old hydrated samples using the EPA standard toxicity characteristics leaching procedure (TCLP). In this work, 10 gram samples were ground to powder form (<0.5mm) and added into 200 mL of water or acetic acid solution in a plastic bottle. The contents were agitated in a rotary shaker at 30 rpm for 18 h, the leachates were filtered through a 0.45 μm membrane filter. After that leached solutions were used for determination of Cr (VI) by atomic absorption spectrometer (AAS) [17]. Thus, the leachability of Cr(VI) from solidified cement mixtures depends on the chromium content in cement, leaching time and leachant pH. Carbonation of cement mortars may enhance the leaching of chromium ions but the presence of slag, limestone and marble dust in cement decreases the leaching of Cr(VI) because of immobilization of Cr(VI) in blended cement. The research related to leaching of chromium from cement mortar and concrete with their methods are given in Table 2.2.

Table 2.2: Estimation techniques of chromium from cement mortar and concrete cube

Extractable Fraction	**Methods**	**Physical process**	**Detection technique**	**Ref.**
Cr (VI)	U.S.EPA 1311	10 g hydrated samples + polypropylene bottles + 200 ml extraction fluid (0.1M acetic acid with pH 2.88±0.1) + The bottles were tumbled at 30 rpm in a rotary extractor at room temperature for 18 h + filtered with glass-fiber filter paper + preserve the sample with nitric acid.	Atomic absorption spectrometer (AAS)	17, 53, 124
Total chromium And Cr(VI)	EA.NEN 7375: 2004 Or Tank test method	Cylindrical specimens were wrapped with cling film + leachants (H_2SO_4 + HNO_3 + deionized H_2O) + Curing for 28 days + adjust the pH 3 (synthetic acid rain) and 7 (natural solution) + filtered through membrane filters	Inductively coupled plasma-optical emission Spectrometer And UV–visible spectrometer at a wavelength of 540 nm	125, 53, 142
Soluble Cr(VI)	JSCE Standard G575-2005	Concrete + immersed leachant (water) + left for 24 hour + filtered by suction	Diphenylcarbazide Absorptiometry	143, 144
Soluble Cr(VI)	DEV-S4 method	Shaking with water + suitably prepared chips + clear filtrate + adjust pH	Diphenylcarbazide Absorptiometry	127
Cr(VI)	Batch leaching	Sample + 1M NaOH + leached solutions + amount of Cr(VI) were leached between pH 4.5 to 12.	X-ray spectromicroscopy	136, 137
Total Cr(VI)	Yamaguchi’s method	Digestion of 1.00 g sample + 10 ml HCl + neutralized	diphenylcarbazide	107

		using NH_4OH	method	
Cr(VI)	Surface leaching (sprayed and immersed)	Exposed surface was treated with deionised water over a period of 5 days + The leachate was refrigerated at 4°C	Adsorptive Stripping Voltammetric methods (AdSV)	134
Cr(VI)	modified tank method	125 cm^3 concrete cubes + stirred deionized water + adjusted pH + magnetic stirrer + leachate solution was sampled at 24 hours.	ADSV	134
Cr(VI)	DIN-38414 S4	Similar to the TCLP, but it uses distilled water in a proportion of L/S = 10 for 24 hr	AAS and diphenylcarbacide photometric method	145
Cr(VI)	SW-846 method 1311	pulverized sample is extracted with acid solutions with a liquid/solid proportion of L/S = 20 for 18 hr	AAS and diphenylcarbacide photometric method	146

2.3 Reduction of hexavalent chromium in hydrated cement

The utilize of Cr(VI) reducers in cement is appeared because of tremendous toxicity of Cr(VI) which arises skin irritation and allergic eczema to cement workers [55]. The leachability of Cr(VI) from hydrated cement was limited by the European countries regulations, according to this the allowed level of Cr(VI) in dry cement is up to 2 ppm [26]. For the reduction of toxic Chromium (VI) into non toxic form Chromium (III), a number of reducing additives like iron (II) salts in the form of hepta hydrate and monohydrate, sulphur compounds as metabisulphite ($S_2O_5^{2-}$), sulphite (SO_3^{2-}), thiosulphate (S_2O3^{2-}), $Na_2S_2O_4$, $NaHSO_3$, tin salts (as $SnSO_4$, $SnCl_2.2H_2O$), antimony (III) compounds, NH_2 based species (as N_2H_4, NH_2OH), ammonium ferrous sulphate, $MnSO_4$, FeS, solid lignin (SL), EDTA, $NaBH_4$ etc have been studied [147-154]. Among these reducing additives, salts of iron, tin and antimony are generally used [55].

In alkaline medium, redox couple for Cr^{+6}/Cr^{+3} is -0.12V and those additives have redox couple less than -0.12V in basic medium can act as Cr(VI) reducers [149, 155-

157]. Redox couples of commonly used reducing additives and various advantages and disadvantages of these reducing additives are given in Table 2.3 and 2.4.

Table 2.3: Redox couples of reducing additives for hexavalent chromium [158-161]

Redox couple	**Half-reaction**	**Redox potential in alkaline solution E (Volt)**
Cr^{+6}/Cr^{+3}	$CrO_4^{2-} + 3e^- + 4H_2O \rightarrow Cr(OH)_3 + 5OH^-$	– 0.12
Fe^{+3}/Fe^{+2}	$Fe(OH)_3 + e^- \rightarrow Fe(OH)_2 + OH^-$	– 0.56
$Sn^{+4/}Sn^{+2}$	$Sn(OH)_6^{2-} + 2e^- \rightarrow Sn(OH)_2 + 4OH^-$	– 0.96
Sb^{+5}/Sb^{+3}	$SbO_3^- + H_2O + 2e^- \rightarrow SbO_2^- + 2OH^-$	– 0.59
$N_2O_2^{1+/}NH_2^{1-}$	$N_2O_2^{2-} + 6H_2O + 4e^- \rightarrow 2NH_2OH + 6OH^-$	– 0.73
SO_4^{2-}/SO_3^{2-}	$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{-2} + 2\ OH^-$	– 0.92

Table 2.4: Advantages and disadvantages of reducing additives for hexavalent chromium

Reducing agent	**Advantages**	**Disadvantages**	**Reference**
Ferrous sulphate [$FeSO_4.7H_2O$ and $FeSO_4.H_2O$]	Cheap, easily, available, cements set retarder.	high dosage required, hygroscopic material, have side effects like spots on concrete, and affect on cement quality	[155, 161, 162]
Tin(II) salts	Long lasting Cr (VI) reduction, Higher reduction efficiency over iron salts.	High cost, difficult to amount, very, may affect cement quality	[163-167]
$NaBH_4$	Good reducing properties	Create adverse effect on Cement’s physical properties.	[100]
$MnSO_4$ and EDTA	Good reducing properties	Poor storage stability	[100]

Amine –based	Dosage efficiency, storage stability, operability at higher temperature	No longer storage stability , use of oxygen scavenger and metal chelating agent required, may affect cement quality	[149]
Antimony(III) compounds	Sb(III) is stable at alkaline pH, unaffected by moisture and high temperatures and free lime, no effect on the properties of the cement, high storage stability	Costly for accelerating reduction, use of antioxidant, pH adjusting agent and complexing agent such as sodium gluconate required, may affect cement quality	[168]
$Na_2S_2O_4$ and $NaHSO_3$	Favorable at the time of consumption, no storage stability	Alkali–Silica reaction may create distorted effect on cement, Sulphide were not preferred due to bad smell, Cause storage problem in humid atmosphere	[68, 169]
Silica lignin	Consumption of waste materials, this reduces environmental problems, will be beneficial.	Used with low content of Chromium (VI) and raise the strength of cements materials by decresing water/ cement ratio.	[68]

2.4 Brief discussion on chromium reducing additives

2.4.1 Ferrous Sulphate

In 1969, instead of gypsum, ferrous sulphate was used as set retarder to control the setting time of the cement [170]. Later on it was used for reducing water soluble chromate present in cement [154, 171]. Now a day, ferrous sulphate is widely used as reducing agent in cement industries due to its availability and relatively low cost [172]. It is mixed with cement during manufacturing process [173]. The following reaction occurs during hydration of cement [159]:

$$CrO_4^{2-} + 3Fe(OH)_2 + 4H_2O \longrightarrow Cr(OH)_3 + 3Fe(OH)_3 + 2OH^-$$

But the use of ferrous sulfate as reducing agent has certain drawbacks. Under humid atmosphere and high temperature, Fe (II) salts get oxidized into Fe (III) salts and hence more than calculated (stochiometric) quantity is required [69, 70, 174]. Moreover it has less durability for storage and if it is used in excess, quality of cement get retarded (delay in setting time) [170]. It increases water demand, long setting time, lower concrete strength and possible discoloration [68]. Dosing and feeding process as well as storage condition can influence the effectiveness of the reducing agent in the cement mill due to thermal, mechanical and chemical stress, which can accelerate the chemical reaction of the reducing agent and decrease its effectiveness [55].

Ferrous sulphate heptahydrates are particularly effective if added to cement in granular form or by coating particles with an oxidation-preventing material. However, this step introduces additional costs [55, 175 and 176]. Ferrous sulfate with “green salt” (waste product from titanium dioxide manufacture) and gypsum was also used as ferrogypsum [70, 177]. Use of acidifying agent enhances the storage life of ferrous sulphate as reducing agent. The use of a liquid carrier (sulphate dispersive ferrous sulphate) offers greater accuracy and convenient transportation as compare to dry materials because it eliminates the opportunity for human inhalation of chemical dust and enhances the storage stability [177]. Therefore co-additive such as anti-oxidant/or oxygen scavenger [178, 179] and viscosity modify agents are used with liquid carrier [180, 181].

The metallic sulphate particles coated gelatine are useful for stabilization of ferrous sulphate (storage period enhances upto 12 months) [182-185].

According to Robson B. Lokothwayo [134], The ferrous sulphate heptahydrate recommended high dosage (0.5% by mass) in reduction of Cr(VI) whereas monohydrate quantity has been reduced to 0.3 % by mass, it means monohydrate is more effective than heptahydrate. The water requisited for all types of cement is considerably increased. Monohydrate seems to involve more water than heptahydrate as well as both hydrate delayed the initial setting time of Portland cement. Heptahydrate maintains its outstanding efficiency for 6 months. In opposing, the monohydrate was insightful against storage in cement mixes. After 3 months the required reduction of chromium (VI) to 2 ppm was no longer reached [169].

Ferrous sulfate in concrete had successfully reduced Cr(VI) to a certain extent. Cr(VI) was reduced by more than 50 % by addition of 0.13 % ferrous sulfate. However, with an increase of the amount of the reducing agent, reducing efficiency deteriorates. The reason could be due to the precipitation of $Fe(OH)_2$ and reduction of the surface active sites for the reaction. 0.35 % (w/w) iron sulfate was enough to reduce 20 mg Cr(VI) / kg cement. The difference with the results of this work could be due to the different types of cement used and the different environmental conditions (e.g. climate) which also contribute to the redox chemistry of chromium. it is possible that ferrous sulfates doesn’t achieve 100 % reduction of Cr(VI) in South African cement and concrete because the factors affecting the reaction are more severe (UV, temperatures, Mn levels) [169].

2.4.2 Stannous salts

Redox potential of Sn(IV)/Sn(II) is more negative therefore small amount is required as compare to ferrous sulfate [202]. The reaction is given below to exhibit the reduction process.

$$2CrO_4^{2-} + 3Sn(OH)_2 + 2OH^- + 8H_2O \longrightarrow 2Cr(OH)_3 + 3Sn(OH)_6^{2-}$$

But stannous salt shows precipitation reaction in presence of traces of water and excess lime and forms unstable stannous hydroxide [208].

$$SnSO_4 + CaO + H_2O \longrightarrow Sn(OH)_2 + CaSO_4$$

$$SnCl_2 + CaO + H_2O \longrightarrow Sn(OH)_2 + CaCl_2$$

Due to this, stannous salts are not profitable when used during grinding of clinker with high amount of free lime [155, 164, 156, 186 and 168].

Stability of tin (II) salts can be enhanced when present in liquid carrier such as water, glycol, glycerol, acetate salt, phenol, chloride salt, sugar, dispersants, lignin as a colloidal suspension of tin (II) hydroxide $Sn(OH)_4^{2-}$ [151-155]. Use of antioxident such as Hydroquinone derivatives, 2,6-di(t-butyl)-4-methylphenol (BHT), 2,2'-methylene-bis(6-t-butyl-pcresol), triphenylphosphite, tris-(nonylphenyl)phosphate, dilaurylthiodipropionate, sulfur dioxide, trihydroxy butyrophenone, and butylated hydroxy anisole can enhance the stability of Sn(II) salts. An alternate of antioxidants is oxygen scavenger such as ethylenically unsaturated hydrocarbon derivatives and co additive i.e transition metal catalyst, enediols, ascorbate, alkali metal carbonate as well as a new series of hydroxylamine and hydrazine salts and derivatives [187, 188]. A water soluble complex has been formed by reaction of tin (II) compound and sodium gluconate. This complex has greater stability in acidic and alkaline solution [184].

2.4.3 Antimony compounds

Antimony (III) compounds such as antimony (III) oxide, inorganic salts, coordination compounds (e.g. antimony (III) chelate with a ligand), organometallic compounds of antimony (III) or a mixture are also used as reducing agents for chromium (VI). These can be added to cement in powder and/or in a liquid additive form [156-160, 189]. Redox reaction of antimony (III) compound is given below:

$$SbO_3^- + H_2O + 2e^- \longrightarrow SbO_2^- + 2OH^- , E\ (Sb^{5+}/Sb^{3+}) = -0{,}59\ V$$

Use of antimony (III) compounds for the reduction of hexavalent chromium in cement is advantageous because its reduction potential lies in between iron and tin [190, 191]. Antimony trioxide is soluble only at very low or very high pH value this means that if dispersed in cement during grinding, the reducing agent is not affected by moisture even after prolonged storage. Antimony (III) oxide is thermally stable up to 600°C and also not effected by free lime [168]

2.4.4 Amine based compounds

Hydroxylamine and hydrazine salts are better reducing agent than ferrous sulfate due to dosage efficacy, storage stability and thermal stability [149]. Hydroxylamine derivatives are more soluble and less reactive towards oxygen under alkaline conditions. They can coordinate with chromate ion and reduced them to Cr (III). Oxygen scavengers such as quinone, hydroquinone, ascorbic acid’s salt, sodium sulphite, sodium bisulphite etc have been known for improving the reducing kinetics of hydrazine [187, 188 and 192]. The only disadvantage with hydroxylamine is their volatile nature thus cannot be used at higher temperature [193, 194].

2.4.5. Other reducing additives

Manganese, zinc and aluminum salts are also effective reducing agent with respect to thermal stability [69, 70, 194 and 195]. These additives are also present in slag cement therefore Portland slag cement is used, not only as cement admixture but also act as Cr(VI) reducers [196]. Other reducing additives such as Sodium dithionate, EDTA, alkaline metal, alkaline earth metal, disulphide, polysulphides, thiosulfate, metabisulfite, and ascorbic acid were also used. These additives could not reduce Cr(VI) completely due to their rapid deterioration with storage [100, 85, 197 and 198]. The effect of reducing additives on Cr(VI) was monitored by spectrophotometer [64, 100]. Dosing of reducing additives is very typical problems because it depends upon the Cr(VI) level as well as cement grinding, handling and storage condition for example dosing of ferrous sulphate is needed higher during packaging of cement whereas theoretically it should require very low amount. Besides this, dosing depends on the form and method of addition [181]. The short description about chromate reducing additives as well as dosages effect on Cr(VI) content are given in Table 2.5 and 2.6.

Table 2.5: About Cr(VI) reducing additives, used in cement

Reducing additives	Reduction efficiency	Stability	Product Form	Cost per kg Reducing Agent	Reference
$FeSO_4$	Low	3 – 6 month	Solid as Hydrate	Low	[70]
$SnSO_4$	Very high	6 - > 12 month (as solid)	Solid	High	[199]
$SnCl_2$	High	3 - 6 month	Solution Dispersion	High	[167]
Sb_2O_3	Medium	12 month	Solution Dispersion	Medium	[200]
Na_2S	Medium	3 month	Solution	Medium	[200]
$MnSO_4$	High	Above 6 month	Solid	Meadium	[70]
Aluminum Powder	Medium	Above 6 month	Solid	Medium	[70]
Zinc (II) Salts	Medium	Below 6 month	Solid	Medium	[194]
Sodium thiosulfate	High	deteriorated rapidly with storage	Solid	High	[70]
Sodium metabisulfite	High		Solid	High	[70]
Ascorbic acid	Low		Solid	Medium	[70]

Table 2.6: Effect of reducing additives on soluble Cr(VI) content

Reducing agents	Dosage (%)	Cr (VI) content (ppm)		Reference
		Before	After	
H_3SbO_3	0.04	7.10	0.0	[100, 149, 156, 157, 180, 199, 201, 162-168]
$FeSO_4. 7H_2O$	2.0	6.10	0.25	[189-201, 165-168]
$FeSO_4. 7H_2O$	0.35	20.0	0.0	[180]
$FeSO4. 7H_2O$	0.25	15.0	0.0	[68, 180]
$C_6H_8O_6$	5.0	15.0	6.0	[169]
$Na_2S_2O_3$	5.0	15.0	9.0	[169]
$Na_2S_2O_4$	0.2	15.0	0.0	[169]
$Na_2S_2O_5$	5.0	15.0	9.0	[169]
$Fe(NH_4)_2(SO_4)_2.6 H_2O$	0.50	15.0	0.0	[169]
$Na_2S_2O_4$	0.10	17	< 2.0	[169]
$SnCl_2.2H_2O$	0.036	17	< 2.0	[155-157, 199, 180, 201,162]
$NaHSO_3$	0.28	17	< 2.0	[68, 169]
$N_2H_4.H_2O$	0.24	17	< 2.0	[149, 169]
$FeSO_4.7H_2O$ (HH)	0.16	17	< 2.0	[68]
$FeSO_4. H_2O$ (MH)	0.14	17	< 2.0	[68]
Solid lignin (SL)	0.44	17	< 2.0	[68]

SL/MH (1:3)	0.24	17	< 2.0	[68]
SL/MH (3:1)	0.27	17	< 2.0	[68]
$NaBH_4$	1.0	18	0.0	[115]
$SnSO_4$	1.0	18	0.0	[100]
$MnSO_4$	1.0	18	0.3	[100]
EDTA	1.0	18	4.3	[100]
Synchro100 ($SnSO_4$)	0.012	5.0	0.0	[180]
MA.P.E/Cr06	0.0075	1.0	0.0	[157]
MA.P.E/Cr05 LV (based on Sb_2O_3)	0.005	1.0	0.0	[157]
$SnSO_4$ (Powder)	0.0015	1.0	0.0	[156-160]
$SnCl_2$ + gluconate	0.035	3.5-5.0	0.3	[187]
Sb(III) compound	0.02	7.8	<0.5	[156, 169, 82, 190]
Hydroxyl amine	0.03	10	1.0	[149]

Now, It has been cleared from various studies that ferrous sulfate has poor dosage efficiency in reducing Cr(VI) [202, 203]. Therefore it is used in excess by which water demand and delayed the setting time of cement materials. [180]. as per recent study, it was cleared that a chelating agent such as EDTA when added in cement increased its compressive strength. However $SnSO_4$ or $MnSO_4$ in cement retarding the hydration process. $NaBH_4$ was also found to be failure in setting time test [100].

2.5 Stabilization of Cr(VI)

Hazardous waste disposal is a major issue in the world for limited sites because it is matter of cost, technology and strict environmental conditions. The wide spread use of chromium has often polluted the soils and water. If chromium is found in the form of soluble Cr(VI), it will be toxic in trace amount [21, 51]. It is generated from steel and other alloy’s production, chrome plating, pigments and leather tanning industries [204, 205]. Cement-based stabilization technique is widely used to minimize the handling and disposal problems of hazardous waste as well as reduced the leachability of toxic metals such as Cr(VI) [14, 206-208]. Besides hazardous waste, waste materials such as rich husk ash, marble dust, fly ash, slag etc which are stabilized into the Portland cement, should exhibit hydraulic reaction with cement. US EPA (The United States environmental protection agency) has identified that stabilization technique is very useful to handle the hazardous waste [209].

In India marble dust, rice husk ash, fly ash, bagasse ash and blast furnace slag from industries are available as wastes in million tones and these are an environmental hazard due to disposal problems [210]. For the marble dust, it is a filler material having similar properties like limestone and its presence in cement improves the hydration. According to recent study by Neeraj Jain 2015, marble dust blended cement has been utilized to stabilize the toxic Cr(VI) [211]. Rice husk ash (RHA) and fly ash both have high amount of amorphous silica, thus these can be utilized in cement having higher value of lime and alumina. [212]. This is a siliceous material react that react with calcium hydroxide (free lime) in the presence of water and both are converted into hydrated phase like calcium silicate hydrate (C-S-H) which provides strength to the cement materials. As well as incorporation of RHA in concrete increases compressive strength and decreases the leachability of toxic metals [213, 214].

Bagasse ash is the waste generated by the combustion of sugar cane bagasse. It contains not only silica as a major component but also keeps other oxide and unburned carbon. The use of bagasse ash in cement is, not only improves the mechanical properties of cement materials but stabilizes the waste (heavy metals) also [215-221]. As per recent study by M.A. Tantawy et al 2011, the use of bagasse ash with cement is suitable to minimize the problem of disposal as well as improve the durability of concrete under aggressive environment [222-224].

Slag is a non-metallic product having silicate and alumino-silicates of lime. It is produced from steel manufacturing plant. Now days slag is used in production of Portland slag cement (PSC). This type of cement contains 45-50% slag, 45% – 50% clinker, and 3-5% gypsum. This is most suitable cement for mass construction because of its low heat of hydration [225]. Portland slag cement is very effective in reduction and stabilization of Cr(VI) because initially it reduces the Cr(VI) into Cr(III) through sulphide ion, present in slag. By which, Portland slag cement decreases the leaching of Cr(VI) from hydrated cement materials [226, 227].

In India, power plant burns coal and produces fly ash as a waste. Fly ash is one of the most common binders in waste stabilization formulations. In its two kinds of mixture (such as Portland cement plus fly ash and fly ash plus lime) was used. As per M. Rodrfguez-Piñero et al, 2011, the stabilization of a waste with heavy metals was studied in hydrated cement and stabilization of heavy metals was done with fly ash as binding agent. To meet the EPA limits for chromium TCLP test, it is essential to first reduce the Cr(VI) into Cr(III) [228]. Only fly ash could not stabilize the Cr(VI) because of it showed high leachates amounts of Cr(VI) which exceeded the acceptable level for disposal according to EU Decision 2003/33/EC. Therefore fly ash was mixed with MgO in different ratios and to stabilize the toxic Cr(VI). Further leaching test (EN 12457-2) was done to check the stability of the stabilized mixtures [229]. Thus 5% MgO blended fly ash as a stabilizing mixture was accepted for disposal in landfills to minimize the leaching of heavy metals. It might be used in Chromium stabilization also. Partial replacement of cement by zeolite could improve the properties of concrete and decrease the leaching of soluble chromates as it reduces the porosity of blended cement paste [54, 230].

Neeraj Jain (2011) prepared a composition of rice husk ash with cement that was used to stabilize the Cr(VI) and It was found through TCLP test that RHA-blended samples show high retention capacity for Cr(VI) as compared to cement only. Thus rice husk ash-blended cement is good binder to stabilize the high concentration of toxic Cr(VI) [17].

Chromate reducing additives such as iron sulphate act as effective Cr(VI) reducer in acidic condition but not in highly alkaline medium therefore it is not possible to reduce Cr(VI) completely in hydrated cement. If ferrous sulphate is used as Cr(VI) reducer with cement then required high dosage. This excess amount of reducers retards the hydration process as well as decreases the compressive strength of cement materials. Information regarding to stabilization of chromium is given in Table 2.7.

Table 2.7: Dosage and stabilizing efficiency of using waste in cement

About researchers	Sample type	Medium	Leached values of Cr(VI) in mg/L (US-EPA allowable limit (5mg/L)			
			28 days	90 days	180 days	360 days
Neeraj Jain 2011 [17]	OPC +20% RHA+ 1000 mg/l Cr(VI)	Water	10	4	-	-
		Acid	55	26	-	-
	OPC +20% RHA+ 2000 mg/l Cr(VI)	Water	11	6	-	-
		Acid	20	15	-	-
	OPC +20% RHA+ 3000 mg/l Cr(VI)	Water	8	4	-	-
		Acid	35	17	-	-
Neeraj Jain 2015 [211]	OPC + 1000 mg/l of Cr (VI)	Acid	5	3	BDL	BDL
		Water	BDL	BDL	BDL	BDL
	OPC + 2000 mg/l of Cr (VI)	Acid	22	17	15	12
		Water	15	13	12	8
	OPC + 3000 mg/l of Cr (VI)	Acid	30	25	23	16
		Water	5	22	17	10
	OPC + Marble dust (40% + 1000 mg/l of Cr (VI)	Acid	8	5	3	BDL
		Water	5	3	BDL	BDL
	OPC + Marble dust (40% + 2000 mg/l of Cr (VI)	Acid	25	23	17	12
		Water	18	15	13	10
	OPC + Marble dust (40%)+	Acid	38	18	21	16

	3000 mg/l of Cr (VI)	Water	32	27	20	12
M. Rodrfguez-Piñero et al 2011 (228)	Waste + fly ash (1:1) + Portland cement (alkaline paste, pH =12.4)	Acid	39^*	-	-	-
	Waste + fly ash (1:1) + Portland cement + 4eq/kg H_2SO_4+ 10% $FeSO_4$ (of waste), at pH 6.83	Acid	ND^*	-	-	-
Pal et al (231)	100 gram hazardous soil (untreated) at pH 11	Acid	$138^\#$	-	-	-
	hazardous soil (treated) 100 gram soil+ 3 gram $Na_2S_2O_4$ + cure for 9 h + blended 25 ml (20% H_3PO_4) + cure for 3 hour (pH = 7)	Acid	BDL (0.2)	-	-	-

* 18 hour curing time, # 12 hour curing time

2.6 Effect of reducing additives on cement

Reduction of toxic Cr(VI) into nontoxic form Cr(III) is essential, a number of reducing additives are available but out of them iron and tin salts are commonly used [55]. High quantity of reducing additives is required during grinding and packaging to get the beloved result. Due to overamount, the hydration of cement is affected [55, 134]. In hot weather, these additives are used in cement and control the rapid setting [232]. It has been reported that when the temperature of cement paste (w/c ratio of 0.6) is increased from 27^{o}C to 45.5^{o}C, the setting times are reduced up to half [4]. But the problems are decrease of slump, formation of cold joints, plastic shrinkage, crakes, enhanced permeability and compressive strength of cement materials are decreased [55, 196, 233-235]. Thus, these additives are, not only used as reducing additives but also used as set retarder [196].

The problem of Cr reducers such as effectiveness, economy and handling methods are mainly discussed and motivated by the researchers to improve its efficiency [55, 68, 232]. However, the presence of excess Cr reducers in cement affects negatively the properties of hydrated cement. It is added in plenty during cement production because of its stability is not good. The study of few researcher works with respect to standard consistency, setting time and compressive strength are given in Table 2.8.

Table 2.8: The effects of various additives on consistency, setting time and strength

Sample	**Standard water consistency (%)**	**Setting time (min)**		**Compressive strength of cement mortar (MPa)**						**Ref.**
		Initial (IST)	Final (FST)	1 day	2 days	3 days	7 days	28 days	90 days	
Original cement sample	29.0	165	225	20.5	-	35.6	48.5	-	-	100
Cement with 1% (w/w) $NaBH_4$	31.5	Failed	Failed	-	-	-	16	-	-	
Cement with 1% (w/w) $SnSO_4$	28.0	420	Failed	29.9	NA	49.7	65.0	NA	NA	
Cement with 1% (w/w) $MnSO_4$	28.5	130	175	27.0	NA	43.2	53.7	NA	NA	
Cement with 1% (w/w) EDTA	30.0	170	230	21.0	NA	37.0	50.0	NA	NA	
Original cement	28.5	80	170	26.0	NA	38.0	48.0	NA	NA	236
Cement with 3% (w/w) Bentonite	33.2	200	445	24.0	NA	33.0	45.0	NA	NA	
Cement with 3% (w/w) Jarosite	29.2	110	230	28.1	NA	38.2	47.0	NA	NA	
Cement with 4% (w/w) Bentonite	33.9	250	550	21.0	NA	30.2	40.1	NA	NA	
Cement with 4% (w/w) Jarosite	31.2	145	245	28.5	NA	39.1	48.1	NA	NA	

Cement with 5% (w/w) Bentonite	34.8	305	660	18.0	NA	27.1	36.2	NA	NA	
Cement with 5% (w/w) Jarosite	33.1	210	340	28.5	NA	39.2	48.3	NA	NA	
CEM I class 42,5R (w/c = 0.4)	NA	NA	NA	NA	29.1	41.3	NA	53.0	NA	237
$FeSO_4$ 1 %	NA	NA	NA	NA	21.7	44.1	NA	56.0	NA	
$FeSO_4$ 5%	NA	NA	NA	NA	16.5	34.3	NA	43.9	NA	
$FeSO_4$ 10%	NA	NA	NA	NA	8.0	17.7	NA	22.0	NA	
$MnSO_4$ 1%	NA	NA	NA	NA	27.9	43.6	NA	60.4	NA	
$MnSO_4$ 5%	NA	NA	NA	NA	18.6	36.3	NA	55.1	NA	
$MnSO_4$ 10%	NA	NA	NA	NA	14.1	24.2	NA	32.6	NA	
$SnSO_4$ 1 %	NA	NA	NA	NA	15.3	41.3	NA	57.1	NA	
$SnSO_4$ 5 & 10 %	The samples with 5 and 10 % additives are not hardened after 2 days									
CEM I 42.5R	NA	NA	NA	NA	NA	21.8	34.2	44.6	50.1	68
MH*	NA	NA	NA	NA	NA	21.6	36.7	49.1	54	
MH	NA	NA	NA	NA	NA	21.7	37.5	48.9	54.5	
SL	NA	NA	NA	NA	NA	23.1	33.8	45	50.4	
HH	NA	NA	NA	NA	NA	23.4	33.8	48.5	53.8	
MH/SL:1/3	NA	NA	NA	NA	NA	28.5	38.8	47.4	54.8	
MH/SL:3/1	NA	NA	NA	NA	NA	25.7	37.5	47.6	55.7	
MH/SL:1	NA	NA	NA	NA	NA	22.3	35.2	44.5	50.7	

$FeSO_4$ 2000, mg/l	NA	NA	NA	NA	NA	NA	21.6	33.7	44.12	238
$FeSO_4$ 2500, mg/l	NA	NA	NA	NA	NA	NA	20.6	31.7	43.14	
$FeSO_4$ 3000, mg/l	NA	NA	NA	NA	NA	NA	18.6	27.7	38.24	
Slag cement	NA	NA	NA	NA	NA	16	28	33	NA	239
$SnSO_4$ 0.5 gram	NA	NA	NA	NA	NA	16.5	31.5	41	NA	
$SnSO_4$ 1.0 gram	NA	NA	NA	NA	NA	13	30.5	37	NA	
$SnSO_4$ 3.0 gram	NA	NA	NA	NA	NA	NA	32	33	NA	
Slag cement	131(ml)	297	364	NA	NA	NA	NA	NA	NA	
$SnSO_4$ 2.5 gram	129	855	937	NA	NA	NA	NA	NA	NA	
$SnSO_4$ 5.0 gram	128	1220	1396	NA	NA	NA	NA	NA	NA	
$SnSO_4$ 15.0 gram	134	1812	2116	NA	NA	NA	NA	NA	NA	

MH* = Ferrous sulphate hepta hydrate (HH) was calcined in an oven at air atmosphere, MH = HH was calcined in an oven where the flow rate is 25 ml/min inert N_2 gas, solid lignin (SL)

According to R. S. Vaity & J. K. Verma study in 2013 [100], The early strength of the cement, was not influenced much as compare to control in presence of reducing additives such as $SnSO_4$, $MnSO_4$, EDTA except $NaBH_4$. This study concluded that the $SnSO_4$ was found to be the best Cr(VI) reducing agent at 1.0% (w/w) with respect to time and storage stability but there is a problem about its delaying in setting time as well as its strength is reduced comparatively Portland cement. The setting time of slag cement with $SnSO_4$ is increased about 3-9 times as per experimented by Yang Gao, Zhigang Song [239]. By which the strength of cement mortar becomes weaker in the early days, but stronger in the later days, thus stannous sulphate salt is a good retarder. According to J.

Hills and J.H. Sharp in 2003 [240, 241], it was given that tin chloride (more than 2%) reduces the cement hydration in early days, this was also confirmed by XRD. The XRD patterns of the cured OPC in the presence of tin (II) chloride showed that reduction in intensities of portlandite and other important peaks was appeared (due to the formation of additional hydrated product) whereas according to Nabajyoti Saikia in 2011, tin chloride (up to 1%) could promote the hydration [242].

Minerals based additives such as bauxite, bentonite, attapulgite, china clay and jarosite were used in cement to reduce Cr(VI), This study was done by R. S. Vaity & J. K. Verma in 2014 [236]. Among additives, jarosite was found to be the good Cr(VI) reducer and it did not influence the properties of cement. No phase alteration was seen by XRD and SEM.

As per Wiesława Nocun´-Wczelik et al (2014) [237], Additives such as $FeSO_4$, $SnSO_4$ and $MnSO_4$ (more than 1%) were added to cement, the compressive strength is decreased in early days. Cement with 5-10% $SnSO_4$ is retarded setting time strongly however the strength is increased after 7 days whereas cement with $MnSO_4$ additives increased it highly. Sulphate salts are participated in ettringite phase formation. Among them, iron sulphate is well visible in XRD and SEM techniques as compare to $SnSO_4$ and $MnSO_4$. Gypsum content was detected much in case of $SnSO_4$ blended cement. In presence of iron sulpahte, long ettringite crystals was seen while $MnSO_4$ produced manganese hydroxide and $SnSO_4$ formed plate like crystals of Ca-Sn compounds. Thus the behavior of sulphate salts is different one another.

2.7 Effect of stabilizing additives on cement materials

According to Robson B. Lokothwayo, [134], ferrous sulfate hepta hydrate ($FeSO_4.7H_2O$) and humic acids (HA) were used to minimize the leaching of Cr(VI) from concrete cube. Humic acid was reported to have high binding capacity to chromium (243, 244), but it delayed the setting time and lowered the strength of concrete as well as it increases the Cr(VI) elution because it increases the porosity and resulted in enhanced surface area for the leaching of chromium. Thus study has been concluded that Reduction of Cr(VI) does not possible with humic acid, due to highly alkaline pH of cement paste (Geelhoed, 2002) [245]. Thus humic acid is not a suitable stabilizing and reducing agent for chromium species.

Ferrous sulfate is a highly effective Cr(VI) reductant [169, 246, 247, 248], if it is used with concrete. Study showed that it has no technical effect on the properties of cement [169] but its excess quantity may result in lower the setting time and concrete strength, expansion, and possible internal sulfate attack, increased water demand and possible concrete discoloration [180]. Fly ash is one of the most common binders in waste stabilization formulations, mainly in the form of Portland cement plus fly ash [207]. The stabilization of a steel-making waste with substantial proportions of Cd, Pb, Zn and Cr was studied. The stabilization of heavy metals (Cd, Pb, Zn etc) has been achieved by fly ash [228].

The addition of Cr(VI) retards the setting time of Portland cement due to the formation of calcium chromate which has a low solubility in water [48, 248]. This retardation problem has been controlled through the addition of marble dust. Thus Marble dust is used to cancel the retardation effect as well as act as good binder or stabilizer of Cr(VI). The strength of Cr(VI) having marbles dust blended cement is showed that the low decrease in the strength at early age [249]. According to a recent research study tell us that saturated zeolite having toxic metals creates a problems of leaching of toxic metals in aqueous medium so they were stabilized in cement and nothing were found. It is cleared from TCLP test; cement (itself) is one of the best binding agents for waste materials [250].

A byproduct (known as bagasse ashes) from sugar mills contains high silica levels (about 60% of the total weight). Silica possesses binding properties in the presence of water and calcium hydroxide as well as bagasse ashes can replace sand in the production processes of cement-derived materials. Thus its use with cement becomes economically and environmentally interesting [251]. Hydration characteristics with stabilization of Cr(VI) in bagasse ash blended cement were improved the compressive strength at later ages but the rate of precipitation of $CaCrO_4$ decreases due to the pH of bagasse ash blended cement paste was minimised during pozzolanic action. FTIR, XRD and SEM results indicate that calcium silicate hydrate formed by the pozzolanic action of bagasse ash blended cement was differs in its nature from that formed by hydration of OPC. It was suggested that the blended cement which restrain 15–20% bagasse ash, can be used successfully for stabilization of Chromium (VI) up to 13,000 ppm [220-224].

The ash of peanut husks was used in cement like that pozzolana but its result would be wrong due to the presence of little high alkali content. It can be added to cement up to 15% without altering the mechanical properties of compressive strength of mortars. Thus, the addition of peanut husk ashes in cement is used to decrease the environmental pollution [252].

In present research, rice husk ash and rice tiller ash are used as Cr(VI) stabilizing agent therefore a short description of their literature is also given below

2.7.1 Effect of RHA on cement properties

Rice husk is formed in millions of tons per year as a throw away material and has generally been inclined of by dumping or burning, it is used in the civil construction field may be a good solution to its disposal as waste [253]. In the past decades the utilization of cement is elevated in structural construction for making concrete in the developing countries like India.

The raw materials used in making of cement will be minimized in larger extent therefore for coming years there is a need of other materials for partial replacement of cement. RHA has a good pozzalanic property like cement, so it can be used with cement. Rice husk ash (RHA) is used as supplementary material for cement mortar and concrete because it improves the physical and mechanical properties of cement such as improve workability, reduces heat evolution, thermal cracking, plastic shrinkage, strength development, modifying the pore-structure, minimizes alkali-aggregate reaction, reduced bleeding and segregation, high conflict to chemical attack and low transmission rate of chloride ions resulting in a higher conflict to corrosion of steel in concrete [254, 255].

These above properties are difficult to achieve by the use of pure Portland cement. Besides these merits of RHA, it is also used to stabilize the toxic metals [17]. The characteristic chemical composition and physical Properties of RHA are given in Table 2.9 and 2.10 [254, 256, 257].

Table 2.9: Chemical properties of RHA (Wt. %)

Constituents	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Loss on ignition
Mehta (1992) [294]	87.2	0.15	0.16	0.55	0.35	0.24	1.12	3.68	8.55
Zhang et al. (1996) [298]	87.3	0.15	0.16	0.55	0.35	0.24	1.12	3.68	8.55
Bui et al. (2005) [299]	86.98	0.84	0.73	1.40	0.57	0.11	2.46	-	5.14
C.Marthong (2012) [300]	75.0	1.29	0.78	3.3	0.22	-	0.4	1.50	3.67
M.U Dabai et.al (2009) [301]	68.12	1.06	0.78	1.01	1.31	0.137	-	21.23	18.25
S.ramesh & S.kavitha (2014) [302]	80-90	1-2.5	0.5	1-2	0.5-2.0	-	0.2-0.5	0.2	-
Chatveera, et.al, 2009	92.5a	1.2	2.1	0.9	0.4	0.1	2.0	0.0	0.9
	88.5b	1.1	2.0	0.9	0.4	0.1	2.6	0.0	0.9
Ganesan, K, et. al, 2008 [303]	87.32	0.22	0.28	0.48	0.28	-	1.02	3.14	2.10
Givi, N.A. et.al , 2010 [304]	87.6	0.68	0.93	1.30	0.35	-	0.12	2.3	-
Chindaprasirt, P. and S. Rukzon, 2008 [305]	93.2	0.40	0.1	1.1	0.1	0.9	0.1	1.3	3.7

Ismail, M.S, et al 1996 [306]	80	3.93	0.41	3.82	0.25	0.78	0.67	1.45	8.65
De Sensale, G.R., 2006 [307]	87.2	0.15	0.16	0.55	0.35	0.32	1.12	3.6	6.55

Table 2.10: Physical properties of RHA (Wt. %)

Physical properties	Specific gravity (g/cm^3)	Mean particle size(µm)	Fineness: passing 45µm (%)	Moisture content % by weight	Blaine fineness
Mehta (1992) [294]	2.06	-	99	-	-
Zhang et al. (1996) [298]	2.06	-	99	-	-
Bui et al. (2005) [299]	2.10	7.4	-	-	-
C.Marthong (2012) [300]	2.53	-	-	2.15	-
S.ramesh & S.kavitha (2014) [302]	-	< 45	-	-	-
Ganesan, K, et. al, 2008 [303]	2.30a	-	-	-	4750 cm^2/gram
	2.27b	-	-	-	5750 cm^2/gram
Givi, N.A. et.al , 2010 [304]	2.06	2.50	-	-	36.47 m^2/kg

Chindaprasirt, P. and S. Rukzon, 2008 [305]	2.23	10.0	-	-	11200 cm^2/gram
Ismail, M.S, et al 1996 [306]	2.11	-	-	-	-
De Sensale, G.R., 2006 [307]	2.06	8.0	-	-	28800 m^2/kg Nitrogen absorption

a, b - RHA obtained from electric power station and rice mill respectively

It is observed from Table 2.9 that RHA contains large amount of silica (more than 80%) which is an effective constituents for pozzolanic actitivity. These types of ashes show a lower loss of ignition. Specific gravity of RHA is lower than OPC and its fineness is much greater than of OPC therefore it is important for the production of denser and durable concrete [258]. Above study shows that partial replacement of cement through rice husk ash (RHA) provides a good strength to concrete. The compressive strength of 20 % RHA blended cement after 90 days was found to be in control [259]. After reviewing the research articles the details of effect of rice husk ash on cement properties are given in Table 2.11 and 2.12.

Table 2.11: Effect of rice husk blended cement on cement mortar cube

Cement	RHA	W/B ratio	Setting time		Compressive strength (N/mm^2)						Ref.
%	%		Initial	Final	1 day	3days	7days	14days	28days	90 days	
100	0.0	0.53	-	-	11.6	20.9	27.2	--	37.0	--	260
95	5.0	0.53	-	-	12.0	22.1	27.4	--	38.9	--	
90	10	0.53	-	-	12.8	24.4	27.8	--	42.8	--	
85	15	0.53	-	-	13.8	28.9	29.3	--	46.7	--	
80	20	0.53	-	-	12.2	24.8	28.3	--	39.8	--	
75	25	0.53	-	-	11.7	23.6	27.6	--	38.3	--	
70	30	-	-	-	11.1	20.7	27.4	--	37.0		
35	65	-	-	-	10.4	18.4	26.4	--	36.0		
100	0.0	0.40	-	-	-	-	-	27.3	36.8	42.3	259

95	5.0	-	-	-	-	-	-	25.7a; 27.4b	38.7a; 39.9b	43.5a; 45.8b	
90	10	-	-	-	-	-	-	25.1 a; 28.3 b	40.6 a; 43.8	46.1 a ; 51.2 b	
85	15	-	-	-	-	-	-	23.7 a; 25.9 b	37.9 a; 39.1	42.7 a;44.4 b	
80	20	-	-	-	-	-	-	21.5 a; 24.4	36.7 a; 38.3	41.3 a; 42.8 b	
100	0	-	122	183	16.00	25.70	28.00	32.30	41.00	-	212
90	10	-	136	227	12.60	14.20	22..10	28.50	36.30	-	
80	20	-	154	255	6.70	10.40	18.6 0	24.30	30.20	-	
70	30	-	165	275	4.20	8.60	16.3 0	22.40	24.00	-	
60	40	-	213	350	2.00	6.20	14.4 0	18.20	20.30	-	
50	50	-	281	402	0.90	4.10	9.20	11.50	14.00	-	

a RHA passing #200 sieve; b RHA passing #325 sieve

Table 2.12: Effect of rice husk blended cement on cement concrete cube

Cement	RHA	W/C	Setting time		Compressive strength (N/mm^2)						Ref.
%	%	ratio	Initial	Final	1day	3days	7days	14days	28days	90 days	
100	0.0	0.53	-	-	-	-	27.2	32.3	37.1	38.3	260
95	5.0		-	-	-	-	27.6	34.2	40.0	43.3	
90	10		-	-	-	-	28.0	35.3	41.3	44.8	
85	15		-	-	-	-	29.3	36.0	41.8	45.7	
80	20		-	-	-	-	29.7	39.3	42.5	46.0	
75	25		-	-	-	-	28.7	36.1	38.8	43.0	
70	30		-	-	-	-	27.4	33.5	37.6	37.8	
35	65		-	-	-	-	25.7	31.1	35.1	37.2	

95	5	0.40	-	-	-	-	27.4	-	39.9	48.0	259
90	10		-	-	-	-	28.3	-	43.8	51.2	
85	15		-	-	-	-	25.9	-	39.1	44.4	
80	20		-	-	-	-	24.6		38.3	42.8	

Supplementary use of RHA in cement or concrete is not a new technique but it was started since early 1970 [253]. RHA has been used in concrete up to 30 % by weight of OPC. The use of RHA in mortar and concrete is more significant to improve the porosity and chloride induced corrosion resistance as well as reduces the plasticity and increases moisture content of soil [261, 262]. In case of black rice husk ash which has been used to improve the sulphate resistance of concrete [263]. According to recent study, rice husk ash is partly used to replace OPC for stabilization of Cr(VI). The study confirms that the presence of much Cr(VI) in cement retards setting times of cement sample but this retardation is controlled with the use of rice husk ash. During TCLP tests, RHA-blended samples show high retention capacity for Cr (VI) as compared to control in acidic pH=3. This retention may be due to the addition, substitution (Cr-CSH, Cr ettringite), or precipitation of new components [17].

The effect of Cr(VI) on RHA blended cement was investigated in 2011 by Neeraj Jain [17]. It was found that retardation in setting time was observed [48, 264, 265]. Therefore 8% strength is lost in RHA blended cement having Cr(VI) as compare to RHA blended cement without Cr(VI). Similarly minor loss in strength was found also in RHA blended cement as compare to OPC. The addition of rice husk ash in OPC minimizes the negative effect of Cr(VI) [17]

2.7.2. Utilility of Rice straw (Rice tiller)

Rice straw is the most abundant agricultural waste in the world. This is a by-product of the rice [266]. It is used as a source of feed for animals. It is a rich source of cellulose (polysaccharides), lignin and silica content. Rice straw produces more smoke therefore less desired as fuel for cooking [267]. Straw of rice is a better means of thatching than feed. Often people use it as manure in soil by its ash form as well as it is used in its original state in the field. Now days uses of rice straw in production of fiber, bio fertilizer, combustion for electricity generation etc. The rice straw is disposed easily in open field due to a quickly and cost effective means of burning. On the other hand it's burning in the open field is harmful as air pollution and decreases the fertility of soil [268]. International Rice Research Institute (IRRI) tells us that the increasing in rice production amount 1.5% per year therefore byproduct of rice (RHA and RSA or RTA) is also increased. Increasing quantity of byproduct is a burning problem before us how to dispose it and how to use it for beneficial purpose [269]. For it, rice straw ash or rice tiller ash has been using in cement for stabilization of Cr(VI) and making cost effective blended cement.

Chapter-3

Experiment

3.1 Experimental Techniques

3.1.1 UV-Visible Spectrophotometer: Estimation of Cr(VI) was done by HACH Spectrophotometer (DR/2010, USA made) with quartz cell (1cm). Absorbance (or optical density) of solutions was obsereved at 540 nm (wavelength).

3.1.2 Thermo-gravimetric analysis: Hydration properties of representative cement samples were carried out by Thermo-gravimetry analysis at Perkin Elmer STA 6000. The analysis was carried out in the temperature ranges from room temperature to 700˚C with 10˚C/min (heating rate) under inert atmosphere (N_2 gas was used).

3.1.3 SEM (Scanning Electron microscopy): Microstructural images of Portland cement sample (hydrated) as **S1, S2, S4, S5, S7, S10, S13, S16, S19, S22** and **S25** were recorded with the help of JEOL Model JSM - 6390LV, scanning electron microscopy.

3.1.4 XRD (X-ray diffraction method): X-ray diffractogram of cement samples (hydrated) as **S1, S2, S4, S5, S7, S10, S13, S16, S19, S22** and **S25** were recorded by Bruker Model D8 Advance, AXS D8, X-ray diffractometer equipped with a Si(Li)PSD detector including X-ray source of Cu Kα radiation (λ= 1.5418 Å) was used.

3.1.5 FTIR (Fourier Transform Infrared Spectroscopy): FTIR spectra of hydrated cement samples (**S1, S2, S4, S5, S7, S10, S13, S16, S19, S22, S25 and P1**) taken using in the Shimadzu-84005 spectrometer using the KBr pellets technique. Spectra of IR were recorded in the range of 4000–400 cm^{-1} at 4 cm^{-1} resolution with an interferogram of 32 scans.

3.1.6 EDS (Energy-dispersive X-ray spectroscopy): EDS spectra of hydrated cement samples (**S1, S2, S4, S5, S7 and P1**) were performed with a JEOL Model JED – 2300.

3.1.7 Other used instrument: A pH meter as well as conductometer was used to monitor the pH of the solutions and conductivity of used distilled water. A digital balance was used for weighing all the reagents. Physical parameters such as consistency and setting time of twenty five cement samples (from **S1-S25**) were determined with Vicat apparatus as per IS:4031 part 5, 1988. Compressive strength of twenty five cement samples (**S1-S25**) was also determined through Compression Testing Machines (AIM 302 - AIM 320), Aimil Ltd. (Civil Engineering Material Testing), India as per IS: 4031 part 4, 1988.

3.2 Materials used

$K_2Cr_2O_7$, KI, KBr, CH_3COONa, C_2H_5OH, phthalic anhydride, ammonium sulphate, ammonium hydroxide, sodium carbonate, sodium hydroxide, H_2SO_4 and Chromium reducing agent ($FeSO_4.7H_2O$ and $SnCl_2.2H_2O$) used in present study were of analytical grade and procured from Merck (India). Diphenylcarbazide (as DPC), Varaimene blue B base (VB) were purchased from Himedia chemicals (Mumbai) and TCI Chemicals Pvt. Ltd respectively. Distilled H_2O was used for dilution. Liquid detergent (Eazee Brand) was used in preparation of reducing admixture. Husk ash (from rice as RHA) was collected from local rice mill and rice tiller ash (RTA) was collected from agricultural land.

3.3 Samples collection

In total 63 samples were collected from various region of India (Table 3.1). Sample collections were done throughout the years (2014-2015), samples were either of Portland pozzolana cement (PPC) or Ordinary Portland cement (OPC 43G). Eleven brands of pozzolana cement which are used commonly in India were collected from cement shops in Uttar Pradesh, Madhya Pradesh and Punjab and only two brands of OPC (43G) cement were collected from construction sites (Plant of Oriental Infrastructure Pvt Ltd at District Etawah) in Uttar Pradesh because of their unavailability at cement shops. Sampling record was maintained in a Performa and some pictures of sampling and testing laboratory are also given in Appendix I. Sampling details of individual samples is given in Table 3.2.

Table 3.1: Sampling details

Cement types	No. of brands	Sample ID	No of samples
OPC 43G	Brand 1	OPCA	3
	Brand 2	OPCJ	3
PPC	Brand 1	PPCA	9
	Brand 2	PPCJ	12
	Brand 3	PPCU	12
	Brand 4	PPCAm	3
	Brand 5	PPCB	3
	Brand 6	PPCBlc	3
	Brand 7	PPCSU	3
	Brand 8	PPCBS	3
	Brand 9	PPCM	3
	Brand 10	PPCJk	3
	Brand 11	PPCP	3
Total Samples (6 OPC + 57 PPC)			63

Table 3.2: Sampling details of individual samples

S. No	**Sample ID**	**Cement Types**	**Manufacturing Weak/year**	**Date of sampling**
1	PPCA01	PPC	23/2014	06/06/2014
2	PPCAm02	PPC	21/2014	06/06/2014
3	PPCJ03	PPC	21/2014	06/06/2014
4	PPCA04	PPC	23/2014	07/06/2014
5	PPCB05	PPC	20/2014	08/06/2014
6	PPCU06	PPC	22/2014	08/06/2014
7	PPCBlc07	PPC	22/2014	08/06/2014
8	PPCA08	PPC	22/2014	08/06/2014
9	PPCJ09	PPC	22/2014	08/06/2014
10	PPCSU10	PPC	22/2014	09/06/2014
11	PPCJ11	PPC	22/2014	11/06/2014
12	PPCP12	PPC	22/2014	11/06/2014
13	PPCU13	PPC	22/2014	11/06/2014
14	PPCU14	PPC	22/2014	12/06/2014
15	PPCBS15	PPC	22/2014	12/06/2014
16	PPCM16	PPC	22/2014	12/06/2014
17	PPCJ17	PPC	23/2014	12/06/2014
18	PPCU18	PPC	23/2014	12/06/2014
19	OPCJ4319	OPC	24/2014	14/06/2014

20	PPCJk20	PPC	23/2014	18/06/2014
21	OPCA21	OPC	23/2014	20/06/2014
22	OPCJ4322	OPC	48/2014	12/12/2014
23	OPC43A23	OPC	48/2014	12/12/2014
24	PPCJ24	PPC	47/2014	12/12/2014
25	PPCA25	PPC	48/2014	15/12/2014
26	PPCMy26	PPC	48/2014	15/12/2014
27	PPCU27	PPC	49/2014	15/12/2014
28	PPCP28	PPC	49/2014	15/12/2014
29	PPCU29	PPC	48/2014	19/12/2014
30	PPCBS30	PPC	49/2014	19/12/2014
31	PPCM31	PPC	48/2014	19/12/2014
32	PPCJ32	PPC	48/2014	19/12/2014
33	PPCU33	PPC	48/2014	19/12/2014
34	PPCA34	PPC	49/2014	27/12/2014
35	PPCAm35	PPC	50/2014	27/12/2014
36	PPCJ36	PPC	50/2014	27/12/2014
37	PPCB37	PPC	49/2014	28/12/2014
38	PPCU38	PPC	50/2014	28/12/2014
39	PPCBlc39	PPC	50/2014	28/12/2014

40	PPCA40	PPC	50/2014	28/12/2014
41	PPCJ41	PPC	50/2014	28/12/2014
42	PPCJk42	PPC	49/2014	2/12/2014
43	OPCJ4343	OPC	14/2015	02/05/2015
44	OPCA4344	OPC	13/2015	03/05/2015
45	PPCJ45	PPC	13/2015	03/05/2015
46	PPCA46	PPC	14/2015	04/05/2015
47	PPCMy47	PPC	14/2015	04/05/2015
48	PPCU48	PPC	13/2015	04/05/2015
49	PPCP49	PPC	13/2015	04/05/2015
50	PPCJk50	PPC	12/2015	05/05/2015
51	PPCU51	PPC	13/2015	08/05/2015
52	PPCBS52	PPC	12/2015	08/05/2015
53	PPCM53	PPC	14/2015	08/05/2015
54	PPCJ54	PPC	15/2015	08/05/2015
55	PPCU55	PPC	14/2015	08/05/2015
56	PPCA56	PPC	15/2015	22/05/2015
57	PPCAm57	PPC	15/2015	22/05/2015
58	PPCJ58	PPC	15/2015	22/05/2015
59	PPCB59	PPC	13/2015	24/05/2015

60	PPCU60	PPC	14/2015	24/05/2015
61	PPCBlc61	PPC	14/2015	24/05/2015
62	PPCA62	PPC	13/2015	24/05/2015
63	PPCJ63	PPC	50/2014	28/12/2014

3.4 Preparation of Solutions

3.4.1 Diphenylcarbazide solution, DPC (0.25%): DPC solution was prepared by dissolving 1.0 gram diphenyl carbazide (DPC) in 75 ml ethanol. To this was added 5 gram phthalic anhydride and 6 drops of concentrated H_2SO_4 and made up to 100 ml with ethanol. The prepared solution was store in an ambered bottle.

3.4.2 Variamine blue dye solution, **VB (0.05%):** VB solution was prepared by dissolving 0.05 gram in 25 ml absolute alcohol and then the volume was made 100 ml using distilled water.

3.4.3 Potasium iodide solution, KI (2.0%): KI Solution was prepared by dissolving 2.0 gram potassium iodide in distilled water and diluting it up to 100 ml.

3.4.4 Sodium Acetate solution, CH_3COONa (16.4%): CH_3COONa solution was prepared by dissolving 16.407 gram sodium acetate in distilled water and diluting the solution to 100 ml in a volumetric flask.

3.4.5 Buffer Solution: Ammonium buffer solution was prepared by dissiolving 6.6% (w/v) ammonium sulfate and 1.75 % (w/v) ammonium hydroxide solution similerly a carbonate buffer solution is prepared by dissolving 3% (w/v) sodium carbonate and 2% (w/v) sodium hydroxide solution.

3.4.6 Prepartion of standard Cr(VI) solution and calibration curve: Prepartion of stock solution of $K_2Cr_2O_7$ and its dilutions. Stock solution of $K_2Cr_2O_7$ (1000 ppm) was prepared by dissolving 0.2829 gram of $K_2Cr_2O_7$ in distilled water and diluting into 1.0 L volumetric flask. Samples solution solution of 0-10 ppm concentration were prpared by diluting the stock. After that analyzed the absorbance of each standard solution through DPC, 10 ml of each solution from 0-10 ppm was taken into 100 ml measuring volumetric flask. To each solution was added 2-3 ml conc. H_2SO_4 followed by 2.5 mL of 0.25% diphenylcarbazide and the volume was made to 100 ml with distilled water. pH of each solution was adjusted (near 2.5) and kept undisturbed for 5 to 10 min for full colour development (pink or magenta color). Absorbance of all the reference solutions was measured with the spectrophotometer. A graph was plotted between concentration (on the X axis) and absorbance (on the Y Axis). A straight line was observed, which is taken as calibration curve for finding Cr(VI) concentration in unknown samples (Figure 3.1). Data for absorbance of $K_2Cr_2O_7$ solutions is given in Appendix II.

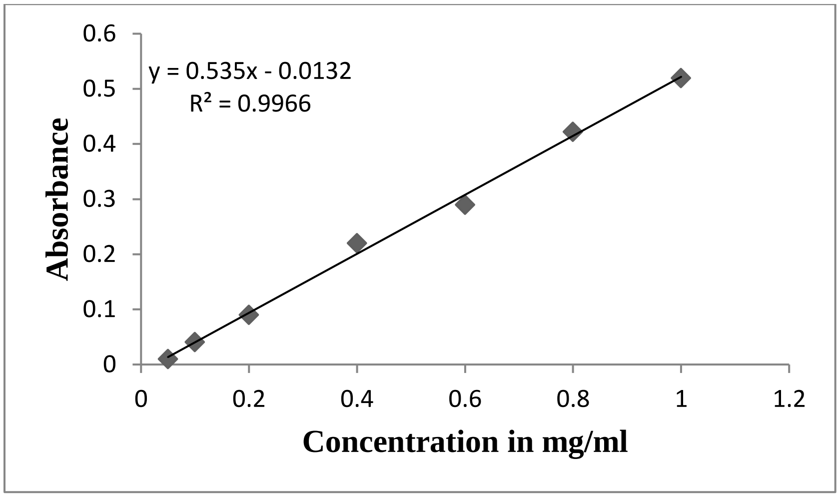


Figure 3.1: Calibration curve for Cr(VI)

3.5 Extraction of water soluble Cr(VI)

Water soluble Cr(VI) leached out from cement samples when suspended in water. Various methods of extraction of Cr(VI) are available in literature. Out of these commonly used literature methods were used and a new method was also developed. These methods are described below

3.5.1 In-house developed method

2.0 g cement was taken in a 250 ml beaker and 100 ml distilled water was added to it. The contents were thoroughly mixed with a glass rod. The beaker was covered with a watch glass. The contents were mixed intermittently after every day hour. This process was continued for five days. The contents were filtered with two times washing through

Whattman 42 in a 100 ml volumetric Flask. Filtrate was used to detect Cr(VI) concentration. The optimization of method was done by performing extractions at various cement (g) / water (ml) ratios (Such as 2/25, 2/50, 2/75, 2/100 and 2/125) and the maximum leaching of water soluble Cr(VI) from hydrated cement was observed at cement (g) / water (ml) ratio of 2/100. The results of Optimization are given in Appendix III.

3.5.2 Danish standard method (DS 1020): 25.0 g of cement was mixed with 25 g water and stirred with magnetic stirrer for 15 minutes. The slurry formed was thus filtered and used for determination of Cr(VI) concentration [110]

3.5.3 German regulatory method (TRGS 613): 10.0 g of cement sample was mixed with 40 ml of water in 250 ml glass beaker and stirred for 15 min in magnetic starrier then the sample was filtered and checked for Cr(VI) [113].

3.5.4 European method (EN196-10): 25g of cement and 75 gram Indian standard sand (Ennore, conforms to BIS: 650-2005) was taken in a 500 ml stainless steel mixer and 12.5 ml distilled water was added to it. The contents were thoroughly mixed in a mixer. This process was continued only for 90 sec. After that Vacuum filtration has been done and filtrate was detected for Cr(VI) concentration [117].

3.5.5 Extraction of sparingly soluble Cr(VI) species

Residue left after extraction of water soluble Cr(VI) from in-house developed method, was transferred to a 250 ml glass beaker. To it was added, 40 ml of ammonium sulfate buffer (0.05 M ammonium sulfate and 0.05 M ammonium hydroxide) and contents were stirred for 30 min. Filtrate obtained after stirring was used to estimate partially soluble chromium [14].

3.5.6 Extraction of insoluble Cr(VI) species

To the Residue obtained after extraction of sparingly soluble Cr(VI), was added 40 ml of carbonate buffer (3% (w/v) sodium carbonate and 2% (w/v) sodium hydroxide) in 250 ml glass beaker. The reaction mixture was stirred for 30 min and then filtered. Total Cr(VI) was calaculated by adding soluble, partially soluble and insoluble Cr(VI).

3.6 Extraction of Total Chromium

2.0 g of cement sample was taken in a platinum crucible. To it was added 6-8 g sodium carbonate. The contents were thoroughly mixed with a glass rod. The crucible was kept in a Muffle Furnace at ambient temperature. Then temperature was raised to 1050˚C. The fusion was carried for 20 minutes. After this the crucible was cooled to room temperature and transferred to a 250 ml beaker. To it was added about 40 ml of water followed by 15 ml of concentrated sulphuric acid. The beaker was heated on a hot plate at low temperature till the mass inside was completely dissolved. The solution was then filtered through Whatman No 42 filter paper in a 100ml volumetric Flask. Washing was done 4 times with hot distilled water.

3.7 Estimation of chromium

Estimation of chromium concentration has been done by two methods.

3.7.1 Reference method (DPC method)

Extract of all sixty three cement samples, were tested for water soluble Cr(VI) and total chromium. To the extract of each sample, 2.5 ml of 1, 5 dipenylcarbazide solution and sulfuric acid was added and pH was maintained at 2.1 to 2.5 [111]. The solution was then made up to 100 ml with distilled water. DPC causes reduction of Cr (VI) to Cr (III) by itself undergoing oxidation. Thus DPCA and Cr (III) formed a magenta-colored complex (Figure 3.2) [112]. A blank was made using all the reagents except the sample. Absorbance of all the solutions and blank was recorded using Spectrophotometer. From the absorbance corresponding concentration in mg/kg was found from the calibration curve. In case of total chromium estimation phosphoric acid (5 ml of 1:3) was also added followed by DPC reagent. This was added to prevent the positive interference from ferric ion.

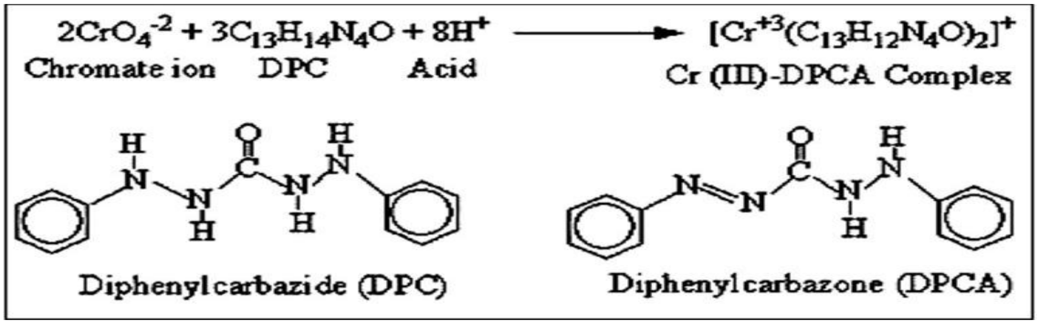


Figure 3.2: Magenta-colored complex (Cr(III) + DPCA) formation

3.7.2 VB method (Proposed method)

This method was applied on five OPC sample (same brand) and six PPC sample (diiferent brands). The samples details are given in Table 3.3. To the extract of cement samples, potassium iodide was added (1 ml of 2% w/v) followed by the addition of sulphuric acid (1.0 mol/L, 1 ml). Now the iodide ion in acidic meadium converted into yellow color iodiene by chromate ion, present in cement extract. Oxidation process was effective in the pH range 1.0 to 1.5. To this solution variamine blue (0.05%, 0.5 ml) and 2 ml of 2 mol/L sodium acetate solution (as Buffer solution) was added. The resulting solution was kept for 10-15 minutes to ensure the completion of reaction (appearance of violet colour) [109]. Reaction of varamine blue dye with iodiene is given in Figure 3.3. After that the absorbance of sample was measered at 556 nm as well as corresponding concentration was also calculated through calibration graph (Figure 3.4). Calibration data is given in Appendex II. The concentration of Cr(VI) can be calculated using the following formula: $C_{(Cr(VI))} = C\ V_1/M\ V_{2,}$ Where $C_{(Cr(VI))}$ is the concentration of hexavalent chromium (ppm), C is the concentration of Cr(VI) in µg/ml, V_1 is the volume of water in which the original sample is suspended, V_2 is the volume of filtrate which is transferred to the volumetric flask, cm^3. M is the mass of the cement sample.

Table 3.3: Samples used for Varamine Blue method

Sample ID	Cement types	Weak/year of Manufacturing
O1	OPC	40/2014
O2	OPC	42/2014
O3	OPC	01/2015
O4	OPC	04/2015
O5	OPC	05/2015
P1	PPC	23/2015
P2	PPC	22/2015
P3	PPC	21/2015
P4	PPC	22/2015
P5	PPC	21/2015
P6	PPC	21/2015

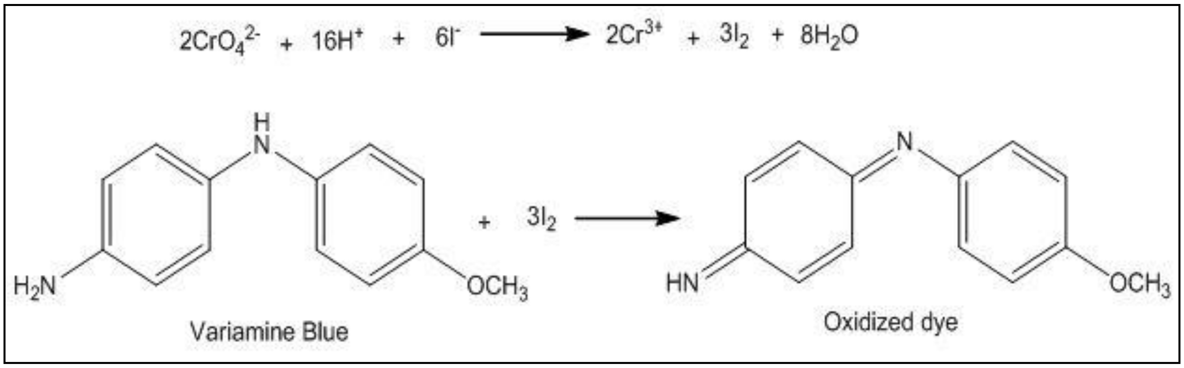


Figure 3.3: Oxidation of Variamine Blue (VB) by liberated Iodine (I_2).

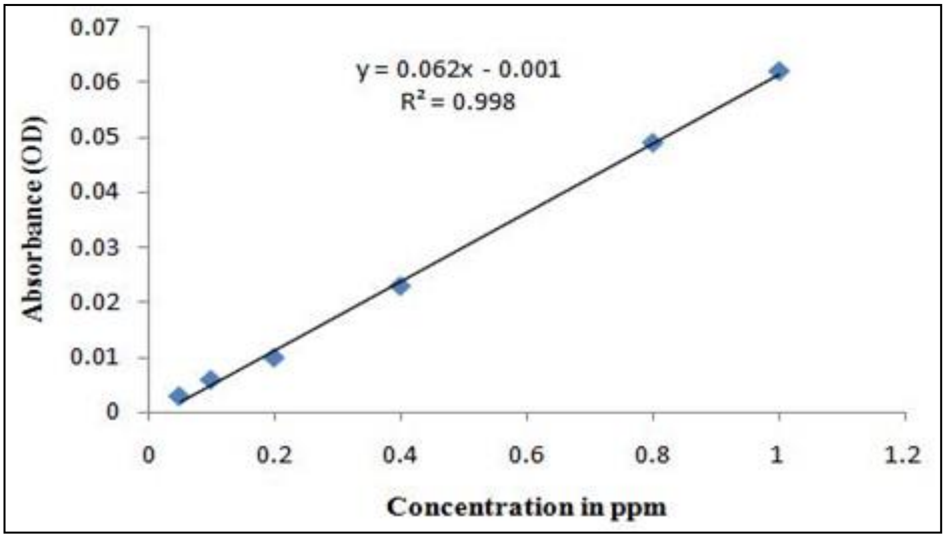


Figure 3.4: Calibration graph

3.8 Reduction of Water soluble Chromium (VI) in Hydrated Portland cement

3.8.1 Reduction with $FeSO_4.7H_2O$ and $SnCl_2.2H_2O$

Reducing agents ($FeSO_4.7H_2O$ and $SnCl_2.2H_2O$) were blended in cement samples in different proportions (0.1, 0.5 and 1.0%). Now the water soluble Cr(VI) has been extracted from them through in-house developed method and was estimated by DPC method. The samples details for this experiment are also given in Table 3.4.

Table 3.4: Sample's information

Sample ID	Cement samples
S1	Only OPC 43 Grade cement
S2	Cement with 0.1% $FeSO_4.7H_2O$
S3	Cement with 0.5% $FeSO_4.7H_2O$
S4	Cement with 1.0% $FeSO_4.7H_2O$
S5	Cement with 0.1% $SnCl_2.2H_2O$
S6	Cement with 0.5% $SnCl_2.2H_2O$
S7	Cement with 1.0% $SnCl_2.2H_2O$

3.8.2 Preparation of modified reducing agent (with liquid detergent)

The storage stability of $FeSO_4.7H_2O$ and $SnCl_2.2H_2O$ is less because bivalent metal ions get easily oxidized by atmospheric oxygen, alkali and free lime [55, 164, 270]. Therefore reducing agents mixed with liquid detergent to form paste, which when dried form a layer on the surface of reducing agent. For this, 250 g reducing agent were mixed with 25 g liquid detergent with glass rod until the homogeneous mixture was formed. The reducing mixture was dried at 45˚C for 15 minutes and then stored in an air tight container. Then mixture was added to the cement sample in different proportions. The detail of samples prepared by adding liquid detergent blended reducing agents is given in Table 3.5.

Table 3.5: Sample Information

Sample ID	About cement samples
S8	Cement with 0.1% liquid detergent blended $FeSO_4.7H_2O$
S9	Cement with 0.5% liquid detergent blended $FeSO_4.7H_2O$
S10	Cement with 1.0% liquid detergent blended $FeSO_4.7H_2O$
S11	Cement with 0.1% liquid detergent blended $SnCl_2.2H_2O$
S12	Cement with 0.5% liquid detergent blended $SnCl_2.2H_2O$
S13	Cement with 1.0% liquid detergent blended $SnCl_2.2H_2O$

3.8.3 Addition of RHA-RTA along with reducing agent

Twelve blended cement compositions (**S14-S25**) were prepared by adding agricultural waste (RHA and RTA) to the cement along with reducing agent in different proportions. A detail of samples prepared by mixing either only RHA or RTA or mixture of RHA and RTA with reducing agents is given in Table 3.6.

Table 3.6: Detail of sample prepared

Sample ID	Samples details
S14	Cement with 0.1% $FeSO_4.7H_2O$ (blended with 10% RHA)
S15	Cement with 0.5% $FeSO_4.7H_2O$ (blended with 10% RHA)
S16	Cement with 1.0% $FeSO_4.7H_2O$ (blended with 10% RHA)
S17	Cement with 0.1% $SnCl_2.2H_2O$ (blended with 10% RHA)
S18	Cement with 0.5% $SnCl_2.2H_2O$ (blended with 10% RHA)
S19	Cement with 1.0% $SnCl_2.2H_2O$ (blended with 10% RHA)
S20	Cement with 0.1% $FeSO_4.7H_2O$ (blended with 5% RHA and 5% RTA)
S21	Cement with 0.5% $FeSO_4.7H_2O$ (blended with 5% RHA and 5% RTA)
S22	Cement with 1.0% $FeSO_4.7H_2O$ (blended with 5% RHA and 5% RTA)
S23	Cement with 0.1% $SnCl_2.2H_2O$ (blended with 5% RHA and 5% RTA)
S24	Cement with 0.5% $SnCl_2.2H_2O$ (blended with 5% RHA and 5% RTA)
S25	Cement with 1.0% $SnCl_2.2H_2O$ (blended with 5% RHA and 5% RTA)

3.9 Storage stability test

The prepared twelve cement samples (from **S2 to S13**) having reducing additives were stored in airtight bags for further test. The Chromium (VI) in these samples was determined through DPC method at proper time i.e. 0, 8, 15, 30, 60 and 90 days interval. This experiment was done to examine the stability efficiency of agents with respect to time.

3.10 Evaluation of Physical and mechanical parameters of cement

The standard consistency (IS: 4031 part 4, 1988a) and setting time (IS:4031 part 5, 1988b) of cement samples were determined by Vicat apparatus. Cement mortar was prepared by adding 200 g cement samples (from **S1 to S25**) with 600 gram three types sand (TAMIN, from 0.09 to 2.0 mm) then added water (w/c = 0.40). Steel moulds (70.6 mm^3 in dimension) were used to prepare mortars cubes (Figure 3.5). Cubes were demoulded after 1 day. After that, mortars were stored in water (100% humidity) at 27˚C. Periodically, theses cubes were taken from cured tank. First dried it and then compressive strength of cubes were determined at 3, 7 and 28 days as per IS: 4031 part 6, 1988.

Figure 3.5: About mortar cubes (a) Mixing procedure (b) moulding procedure (c) vibrating machine (d) concrete cubes testing machine (e) tested cubes

3.11 Leaching test

Nineteen cement samples (**S1-S7** and **S14-S25**) having only reducing additives as well as both reducing and stabilizing agent except **S1**, were used to make cement mortar for leaching test. This test has been done in two ways.

3.11.1 Proposed test method: Cement mortar was cured in 250 ml of distilled water (pH = 6.5) for 90 days in a closed chamber. Cured water was replaced periodically (after 3, 7, 14, 28, 60 and 90 days) to determine the leached Cr(VI).

3.11.2 Standard test method: TCLP (toxicity characteristics leaching procedure) were performed with 28 days cement (hydrated) by the EPA standard [124-126]. Leaching test were carried out in distilled water (pH = 6.5). Samples were crused to fine powder (size <0.5mm). To examine the leachable Cr(VI), taking 10 grams powder and 200 ml water to dissolve in 500 ml glass beaker and agitated for 18 h in a mixer at 30 rpm. The extract or leachates were filtered from 0.45μm filter paper and estimated the Cr(VI) concentration.

3.12 Hydration study

For hydration study modified cement samples were mixed in water (w/c = 0.40). A material (cement + water) was mixed carefully, formed a paste. It was put airtight in polythene bags. Hydration without curing was started and continued at 28 days. These samples were analyzed from TGA (Thermo-gravimetric analysis), SEM (Scanning Electron Microscopy), XRD (X-ray Diffraction method) and FTIR (Fourier Transform Infrared Spectroscopy).

Chapter-4

Extraction and Estimation of Chromium from hydrated cement

In this chapter, four types of extraction process including European method (EN196-10), Danish method (DS1020), German method (TRGS 613) and in-house developed method were used to extract water soluble chromium (VI). Estimation of chromium (VI) was done by standard Diphenyl cabazide (DPC) as detecting reagent.

4.1 Estimation of Chromium by DPC method

Extraction of soluble Chromium (VI) for 63 cement samples were done using European, Danish, German and in-house developed method (five days extraction method) and estimated by using standard DPC method [111, 112]. However extraction for estimating total chromium was done only by in-house method where before extraction cement samples was fused with Na_2CO_3 at high temperature (1080˚C) [93]. All the Chromium in different oxidation state get oxidized and converted into Cr(VI) which was then extracted and determined for total Chromium by DPC method [111, 112]. Calibration curve (Cr reference solution) for this analysis was prepared from 0.05 to 1.0 ppm with reagent blank. The absorbance of each of these solutions was measured at the wavelength (λ = 540 nm).

The concentration of Chromium (VI) and total Chromium was calculated from calibration curve and given in Table 4.1. It has been observed that the concentration of Chromium (VI) in various samples is different and higher than the permissible limit (2.0 mg/kg) [26]. The variation is also observed among the different methods, used for extraction (Table 4.2). Trends in concentration of Cr(VI) in PPCBlc (**C40-C42**), PPCSU (**C43-C45**), PPCJk (**C52-C54**), PPCAm (**C34-C36**), PPCJ (**C1-C12**) and PPCA (**C25-C33**) is found to be similar by all the four methods used for extraction, however slight variation has been observed in other brands PPCM (**C49-C51**), PPCB (**C32-C34**), PPCP (**C55-C57**), PPCBS (**C46-C48**) and PPCU (**C13-C24**) by these methods. Variation among four methods was observed in same brand which can be due to the following reason:-

(i) Different dilution used: Extraction depends upon water/cement ratio. On dilution cement phases merged very well in water and all the water soluble Cr(VI) comes in water after a certain time [64, 68]. In-house developed method used more dilution i.e. 100/2 (w/c) as compare to German method (40/10), Danish method (25/25) and European method (12.5/25).

(ii) Time period used for extraction: It may be one of reason for variation in soluble Cr(VI) concentration. Cement is a mixture of different ingredient; it is prepared at high temperature clinker process [134]. Therefore hexavalent chromium takes more time to come into the form of leachant. Out of four methods, in-house developed method has been taken 5 days for maximum leaching. But another methods have minimum time of extraction (i.e. upto 15 min) so they required fast mixing and heating, thus there is a possibility of chromium transformation from sparingly soluble and insoluble Chromium (VI) and Chromium (III) into soluble Chromium (VI) form. This can be one of the reasons for higher concentration of soluble Chromium (VI) in German method (TRGS 613).

(iii) Mixing rate: Mixing rate round per minutes is main parameters for Cr(VI) extraction. The mixture of cement and water was stirred with gloss rod in In-house method, whereas other methods used stainless steel mixer or magnetic stirrer for mixing the cement paste with different rates (round per minutes). This mixing rate is 3000 round per minutes in European method (EN196-10) whereas in Danish and German method, it is 300 rpm [110-113].

Table 4.1: Chromium in hydrated cement

S. No	**Sample ID**	**Sample Coding**	**Water soluble Cr (VI) in mg/kg or ppm**				**Total Chromium (ppm)**
			European Method (EN196-10)	**Danish Method (DS 1020)**	**German Method (TRGS 613)**	**In-house Method**	
1	PPCJ03	**C1**	12.32	11.55	14.00	12.56	85
2	PPCJ09	**C2**	16.87	15.65	18.02	16.00	117
3	PPCJ11	**C3**	13.18	11.12	15.00	14.67	111
4	PPCJ17	**C4**	14.00	12.90	16.32	13.67	92

5	PPCJ24	**C5**	16.98	15.87	18.44	18.97	112
6	PPCJ32	**C6**	11.18	11.12	14.00	14.67	110
7	PPCJ36	**C7**	18.78	16.98	20.09	16.94	131
8	PPCJ41	**C8**	20.76	18.97	21.00	21.00	123
9	PPCJ45	**C9**	09.32	8.55	11.00	12.56	98
10	PPCJ54	**C10**	18.71	16.98	20.09	16.94	131
11	PPCJ58	**C11**	10.08	10.00	11.69	11.24	120
12	PPCJ63	**C12**	15.98	13.86	16.65	15.09	128
13	PPCU06	**C13**	14.56	14.33	15.09	13.56	98
14	PPCU13	**C14**	16	17.3	16.86	16.54	99
15	PPCU14	**C15**	15.66	12.35	16.99	14.98	107
16	PPCU18	**C16**	22.66	20.00	25.68	20.77	140
17	PPCU27	**C17**	14.51	14.32	15.99	16.00	99
18	PPCU29	**C18**	11.98	11.20	13.76	13.79	121
19	PPCU33	**C19**	15.38	14.44	17.36	16.30	112
20	PPCU38	**C20**	13.00	11.90	13.32	13.88	102
21	PPCU48	**C21**	14.53	13.33	15.39	14.96	108
22	PPCU51	**C22**	21.55	18.78	22.34	19.33	125
23	PPCU55	**C23**	21.56	18.78	22.34	19.35	125
24	PPCU60	**C24**	14.56	14.33	15.09	13.56	98
25	PPCA01	**C25**	10.56	09.45	12.32	11.88	102
26	PPCA04	**C26**	10.08	10.00	11.69	11.00	110
27	PPCA08	**C27**	12.98	11.23	15.60	13.78	120
28	PPCA25	**C28**	19.78	19.00	21.09	20.23	119
29	PPCA34	**C29**	32.22	31.22	36.87	35.97	177

30	PPCA40	**C30**	24.65	23.67	25.00	25.73	143
31	PPCA46	**C31**	12.08	12.00	14.39	14.00	109
32	PPCA56	**C32**	14.22	12.90	16.32	13.67	100
33	PPCA62	**C33**	10.08	10.00	11.69	11.00	120
34	PPCAm02	**C34**	09.00	09.00	10.46	09.65	119
35	PPCAm35	**C35**	16.16	15.35	16.99	15.98	111
36	PPCAm57	**C36**	22.66	20.00	25.68	20.72	140
37	PPCB05	**C37**	15.98	13.86	16.65	15.09	108
38	PPCB37	**C38**	25.57	23.18	26.34	25.33	147
39	PPCB59	**C39**	15.98	13.86	16.65	15.09	108
40	PPCBlc07	**C40**	20.89	19.35	23.00	19.68	128
41	PPCBlc39	**C41**	29.76	28.90	32.68	32.00	165
42	PPCBlc61	**C42**	21.80	19.35	23.33	19.68	128
43	PPCSU10	**C43**	27.98	24.99	30.45	25.87	139
44	PPCSU26	**C44**	24.98	23.87	24.00	25.33	144
45	PPCSU47	**C45**	15.92	13.76	15.65	15.79	118
46	PPCBS15	**C46**	18.78	16.98	20.09	16.94	131
47	PPCBS30	**C47**	16.77	16.65	18.62	17.00	122
48	PPCBS52	**C48**	14.00	12.90	16.32	13.67	92
49	PPCM16	**C49**	21.55	18.78	22.34	19.33	125
50	PPCM31	**C50**	26.88	25.99	28.45	28.80	136
51	PPCM53	**C51**	15.66	12.35	16.99	14.98	107
52	PPCJk20	**C52**	19.76	16.93	21.39	17.66	113
53	PPCJk42	**C53**	25.89	24.00	26.26	25.96	149
54	PPCJk50	**C54**	18.78	16.98	20.09	16.94	131

55	PPCP12	**C55**	17.37	15.44	19.36	16.30	126
56	PPCP28	**C56**	21.89	19.95	23.67	20.12	128
57	PPCP49	**C57**	15.66	12.35	16.99	14.98	107
58	OPCJ4319	**C58**	27.55	26.87	29	26.73	151
59	OPCJ4322	**C59**	29.76	29.45	31.56	30.88	178
60	OPCJ4343	**C60**	19.66	18.42	17.42	20.58	130
61	OPCA21	**C61**	25	23.76	27.16	25.86	148
62	OPC43A23	**C62**	32.67	33	33.89	34.98	184
63	OPCA4344	**C63**	15	14	15.46	13.65	158

Variation in concentration of Chromium within different brands of PPC or OPC cement can be due to raw material used or cement manufacturing conditions. The chromium concentration changes with percentage of clinker and additives [55]. PPC cement is produced by replacing clinker from fly ash and it can also increase the Chromium. For total Cr concentration in different brands of PPC samples, the decreasing order of chromium concentration follows the sequence: PPCBlc (**C40-C42**) > PPCSU (**C43-C45**) > PPCJK (**C52-C54**) > PPCAm (**C34-C36**) > PPCM (**C49-C51**) > PPCB (**C32-C34**) > PPCP (**C55-C57**) > PPCA (**C25-C33**) > PPCBS (**C46-C48**) > PPCJ (**C1-C12**) > PPCU (**C13-C24**). The highest concentration of water soluble Chromium (VI) and total Chromium both was found in PPCBlc (**C40-C42**) samples. Therefore there is a correlation between water soluble Cr(VI) and total Chromium (Figure 4.1) except few samples.

Table 4.2: The decreasing order of Cr (VI) in various brands of PPC samples

Method’s Name	Water Soluble Cr(VI)
European Method	PPCBlc> PPCSU> PPCJK> PPCM> PPCB > PPCP >PPCU> PPCBS > PPCAm> PPCJ> PPCA
Danish Method	PPCBlc> PPCSU> PPCJK> PPCM> PPCB > PPCP > PPCBS PPCU> > PPCAm> PPCJ> PPCA
German method	PPCBlc> PPCSU> PPCM > PPCJK > PPCP > PPCB > PPCBS PPCU> > PPCAm> PPCJ> PPCA
In-house-devised method	PPCBlc> PPCSU> PPCM > PPCJK > PPCB > PPCP > PPCU > PPCBS > PPCAm> PPCJ> PPCA

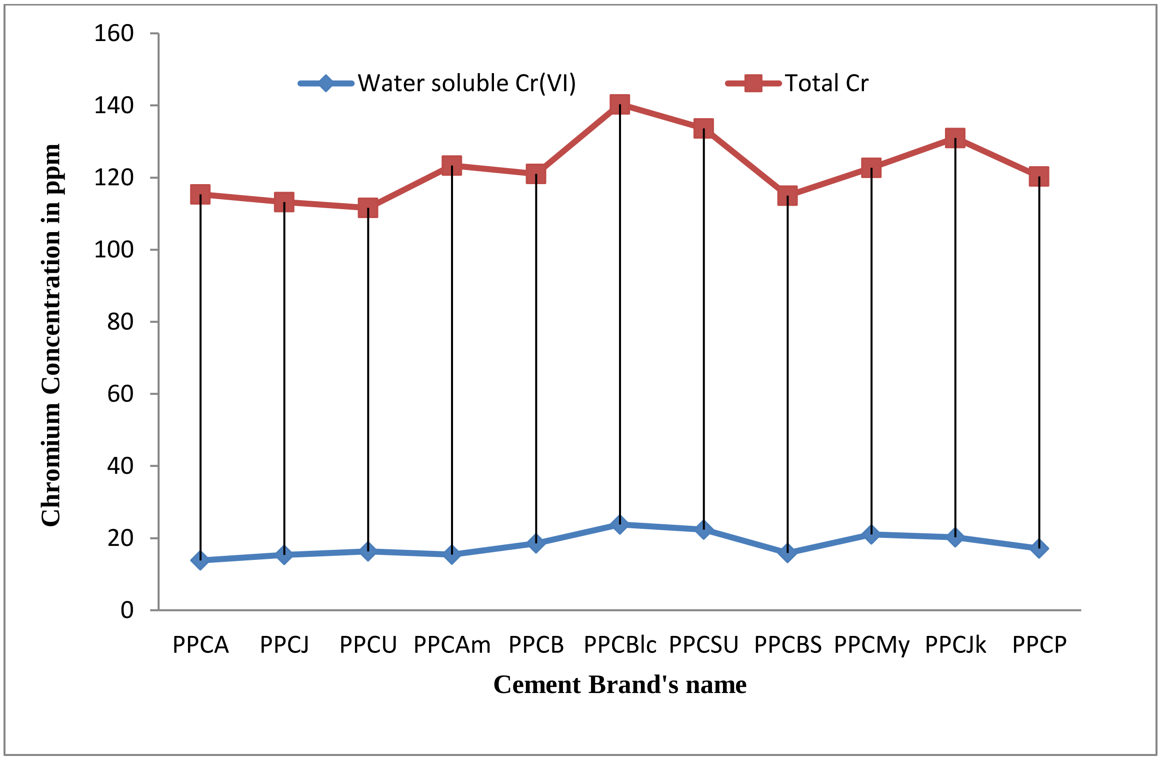


Figure 4.1: Correlation diagram in between water soluble Chromium (VI) and Total Cr

A comparison of average value of water soluble Chromium (VI) obtained by four methods is given in Table 4.3. It has been observed that, in eleven brands of PPC samples the average content of soluble Chromium (VI) calculated using four methods ranges from 12.16 to 14.55 ppm in PPCA samples, 13.63 to 16.36 (PPCJ), 15.26 to 17.73 (PPCU), 14.78 to 17.71 (PPCAm), 16.97 to 19.88 (PPCB), 22.53 to 26.34 (PPCBlc), 20.87 to 23.37 (PPCSU), 15.51 to 18.34 (PPCBS), 19.04 to 22.59 (PPCM), 19.3 to 22.58 (PPCJk) and 15.91 to 20.01 ppm in PPCP cement. In OPC samples, it varied from 23.59 to 25.50 ppm in OPCA sample whereas 24.91 to 25.55 ppm in OPCJ samples.

For amongst the four methods (German method, European method, In-house method, Danish method) used. German methods showed higher concentration of water soluble Cr(VI) than others methods due to 300 rpm mixing with high dilution, whereas Danish method showed lower concentration may be due to w/c ratio. In case of European method, water cement ratio was nearly 0.50 below the Danish method yet it provides higher concentration than in-house method and Danish method, because European method used 3000 rpm which is higher than others method. In European method sand was also added. Thus there is chance of increasing of Cr(VI).

Table 4.3: Average values of water soluble Cr(VI) in different Brands of PPC samples

Brand's name	Water soluble Cr(VI) in ppm							
	European Method		Danish Method		German Method		In-house method	
PPC samples	Avg^{e}.	Stdv^{n}.	Avg^{e}.	Stdv^{n}.	Avg^{n}.	Stdv^{n}.	Avg^{e}.	Stdv^{n}.
1.PPCA	13.04	2.98	12.16	2.92	14.55	2.94	13.81	2.78
2.PPCJ	14.85	3.72	13.63	3.26	16.36	3.3	15.36	2.81
3.PPCU	16.62	3.34	15.26	2.63	17.73	3.71	16.33	2.41
4.PPCAm	15.72	6.51	14.78	5.52	17.71	7.64	15.45	5.55
5.PPCB	19.18	5.54	16.97	5.38	19.88	5.59	18.5	5.91
6.PPCBlc	24.15	4.88	22.53	5.51	26.34	5.5	23.79	7.11
7.PPCSU	22.96	6.28	20.87	6.19	23.37	7.42	22.33	5.67
8.PPCBS	16.52	2.4	15.51	2.27	18.34	1.9	15.87	1.91

9.PPCM	21.36	5.61	19.04	6.82	22.59	5.73	21.04	7.07
10.PPCJk	21.48	3.85	19.3	4.07	22.58	3.25	20.19	5.01
11.PPCP	18.31	3.22	15.91	3.82	20.01	3.39	17.13	2.67
OPC samples								
1.OPCA	24.22	8.86	23.59	9.50	25.50	9.33	24.83	10.7
2.OPCJ	25.66	5.31	24.91	5.77	25.99	7.53	26.06	5.18

4.1.1 Verification of method

The recognition limit of planned method was deliberated based on three times the standard deviation (Stdv^n) of three runs of the blank solution. The recognition (detection) limits were initiated 0.5 mg/L and 0.7 mg/L for chromium (water soluble hexavalent Cr and total chromium). The calibration graph was found linear and depicted by the equation y = 0.535x - 0.013, where x is the Cr concentration and y is the integrated absorbance. The curve show good linearity with a correlation constant (coefficient) of 0.996. Reference cement (SRM - 886a and SRM 2701) from National Institute of Standards & Technology, USA, was taken from shanker laboratory, Delhi to ensure the accuracy of results. The reference sample using the Na_2CO_3 leaching procedure which was in concurrence with the certified value (% age total chromium was 26 ± 0.13 ppm found and 24 ± 0.08 ppm was certified) and water soluble chromium was 1.5± 0.04 ppm found and 1.0 ± 0.002 ppm was certified. As per regulations water soluble Cr(VI) should not more than 2.0 ppm [14]. Samples was inspected three times and brought to have a good conformity in repeatability and reproducibility in proposed method. It was found, the total Cr recovered from sample containing 74 ppm chromium was found be 80±2.3 ppm and water soluble Cr(VI) from sample containg 51 ppm was 53±2.3 ppm. The percentage recovery for total chromium and water soluble Cr(VI) was found to be 108.10±2.4 ppm and 103.92±3.3 respectivily (Table 4.4).

Table 4.4: Recovery of Total Cr and soluble Chromium (VI)

About Sample	**Concentration in ppm**	
	Total Cr	Soluble Cr(VI)
Initial values of NIST sample	24 ± 0.08	1.0 ± 0.002 ppm
Concentration spiked# (ppm)	74	51
Concentration calculated (ppm)	80±2.3	53±2.3
% Recovery	108.10±2.4	103.92±3.3

Average value ±standard dev^n (three determinations), # 50 ppm concentration solution of each Cr(VI)/Cr(III) was added to NIST sample.

As a higher percentage of recovery thus obtained indicate interference from metal ions (such as Mo(VI), Cu(II), Fe(III) etc) [109]. To minimize this interference Variamine blue dye as chromogenic reagent was used on selected eleven cement samples (six PPC and five OPC samples). Earlier Varamine blue dye (VB) has been used for detection of Cr(VI) in industrial effluents, steels, alloy, water, soil samples. This method was used the detection of Cr(VI) from cement samples for the first time. Samples details are given in Table 3.3.

4.2 Estimation of total Cr(VI) in PPC samples by Varamine Blue method

Six brands of Portland pozzolana cement (**P1-P6**) has been used for estimation of water soluble Cr(VI) using Variamine blue dye as chromogenic reagent. The extraction of chromium (soluble) for estimation in cement was done by in-house developed sequential extraction process [123].

4.2.1 Analtical parameters

The estimation was done in aqueous solutions for soluble Chromium (VI) by HACH spectrometer through making a calibration plot. The calibration graph (Figure 3.6) is linear and can be explained by equation: $y = 0.062x - 0.001$. In this equation y is integrated absorbance and x is analyte concentration. The regression value obtained from the calibration is 0.998. The detection limit ($D_L = 3.3\sigma/S$) and quantification limit ($Q_L = 10\sigma/S$) of Cr(VI) were found to be 0.05 and 0.16 μg/ml, where σ = standard deviation of blank samples (five determination) and S = slope of calibration curve.

4.2.2 Validation of proposed method

SRM 2701 Hexavalent Cr in contaminated Soil" from National Institute of Standards and Technology, USA was used for revalidating the values obtained by the proposed method (Table 4.5).

Table 4.5. Determination of Cr(VI) in standard sample (SRM 2701 from NIST)

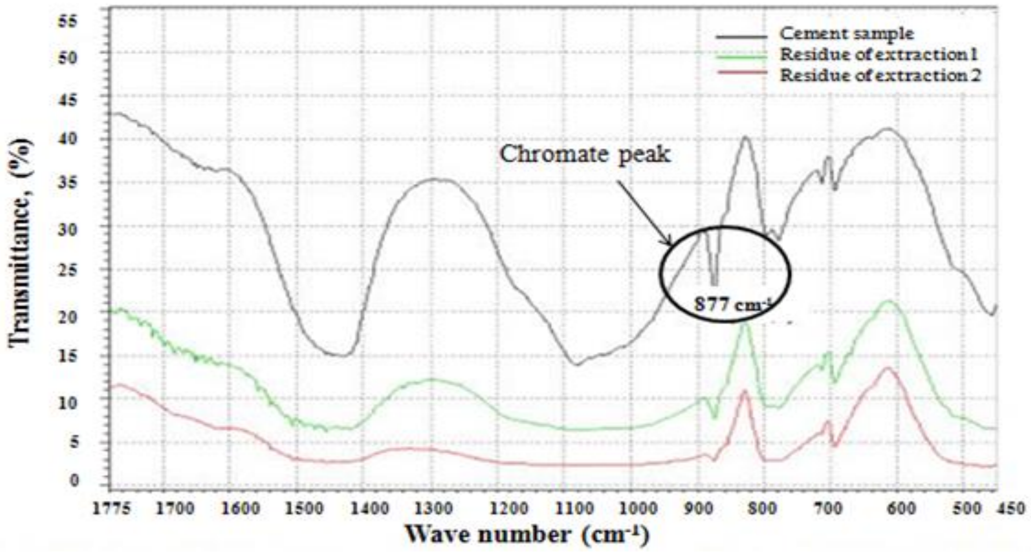
	Hexavalent chromium in SRM 2701 (in ppm)				Recovery	RSD	T -test	F- test
	Water soluble	Sparingly soluble	Insoluble	Total	(%)	(%)		
Certified value	-	-	-	551.12±34.5	-	-	-	-
Proposed method	125±2.74	115.2±8.70	309.2±14.45	549.4±25.89	99.69	4.7	0.93	0.97
Reference method	126±3.67	114.6±2.97	309.2±14.45	550.8±29.58	99.94	5.3		

For complete leaching of water soluble hexavalent chromium, five day extraction procedure was followed. Long stirring in water ensured the extraction of some hexavalent chromium that was present in solid phases of cement. Sparingly soluble Cr(VI) was extracted by treatment of residue of extraction 1 with ammonium sulfate buffer, however the insoluble chromium was extracted using carbonate buffer (3% (w/v) sodium carbonate and 2% (w/v) sodium hydroxide). Sequential extraction of total Cr(VI) (soluble, sparingly soluble and insoluble) was ensured by FTIR and EDS, the details are given below

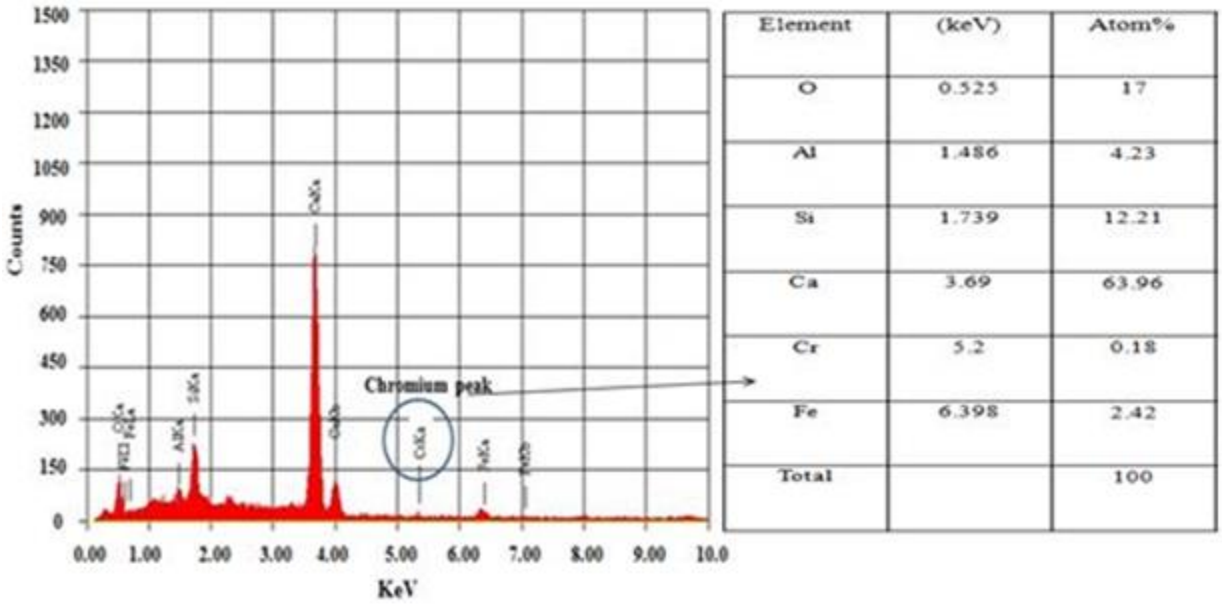
Discussion on IR Spectra: In the IR spectrum [273], bands for CO_3^{2-} ion appeared at 1425, 1497, 875 and 732 cm^{-1} and for chromate ion in the range 850-950 cm^{-1} (specially for $ZnCrO_4$ and $CaCrO_4$) [81, 274]. IR spectrum of cement sample PPC1 show band at 877 and 1430 cm^{-1} (Figure 4.2). The intensity of these bands decreased after the extraction of water soluble and spirangly soluble Cr(VI) (residue of extraction 1 and 2 respectively). Decrease in intensity of band at 877 cm^{-1} can either be due to leaching of hexavalent chromium in extraction process or reduction in carbonate concentration (due to formation of carboxyaluminates [275, 276] or replacement of carbonate by sulphate ion in Aft (alumina ferric oxide tri-sulfate) and AFm (alumina ferric oxide mono-sulfate) phases) [1, 277].

Since vibrational bands for carbonate and chromate band appeared in the range, 870-880 cm^{-1}, it is difficult to get a distinct information regarding decrease in concentration of chromate ion by IR only. It can be used as supporting data to other techniques like EDX and UV-Vis spectrophotometer.

Discussion on EDS spectra: Extraction of hexavalent chromium was also confirmed by EDS spectra of sample P1 and the residues left after extraction 3. Generally chromium gave a peak in range of 5.0 to 6.0 KeV in EDS spectrum [128]. In sample P1, this peak appeared at 5.2 KeV in its EDS spectrum (Figure 4.3), however this appeared as very weak peak after extraction 3. (Figure 4.4)

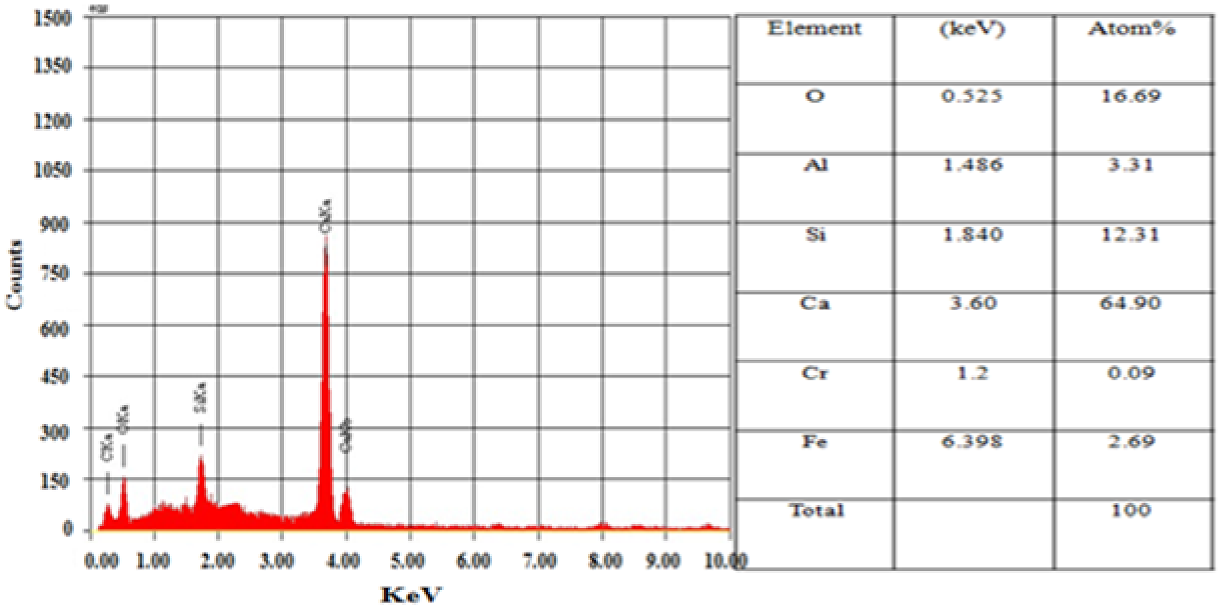


Fgure 4.2: overlay of IR spectrum of sample P1 and its residue after extraction 1 and 2



Element	(keV)	Atom%
O	0.525	17
Al	1.486	4.23
Si	1.739	12.21
Ca	3.69	63.96
Cr	5.2	0.18
Fe	6.398	2.42
Total		100

Figure 4.3: EDS spectrum of cement paste before sequential extraction



Element	(keV)	Atom%
O	0.525	16.69
Al	1.486	3.31
Si	1.840	12.31
Ca	3.60	64.90
Cr	1.2	0.09
Fe	6.398	2.69
Total		100

Figure 4.4: EDS spectrum of cement paste after sequential extraction

Variamine Blue method was applied to filtrates of extraction 1, 2 and 3 of six different samples of Portland pozzolana cement for estimation of water soluble, sparingly soluble and insoluble hexavalent chromium. To check the accuracy of proposed method, all the six cement samples were also tested for their water soluble, sparingly soluble and insoluble hexavalent chromium content using standard DPC method (results are given in Table 4.6 - 4.8).

Table 4.6: Determination of water soluble Cr (VI) in various Cement samples

Sample ID	Soluble Cr(VI) Added* (ppm)	Proposed method			Reference method			T-test	F-test
		Soluble Cr(VI) Found	RSD (%)	Recovery (%)	Soluble Cr(VI) Found	RSD (%)	Recovery (%)		
P1	-	23±1.58	6.9	-	24±2.12	8.8	-	0.42	0.58
	2	24.7±1.07	4.4	98.64	25.4±1.90	7.1	98.23	0.38	0.33
P2	-	20±1.64	8.3	-	20±1.92	9.5	-	0.84	0.77
	4	23.58±1.57	6.7	98.25	24.3±0.97	4	101.25	0.41	0.38
P3	-	23±2.49	10.8	-	26±1.52	5.9	-	0.07	0.36
	6	28.7±1.11	3.9	99.1	32.2±1.68	5.2	100.63	0.01	0.44
P4	-	26±2.63	10.21	-	29±3.02	10.38	-	0.1	0.79
	8	33.9±2.10	6.2	99.71	36.4±2.42	6.7	98.32	0.12	0.79
P5	-	17±1.92	11.3	-	18±2.17	11.91	-	0.49	0.82
	10	27.1±1.05	3.86	100.44	27.6±1.19	4.33	98.57	0.52	0.81
P6	-	19±1.49	7.83	-	20±2.35	7.22	-	0.47	0.40
	12	31.1±2.25	11.73	100.32	31.8±1.35	4.25	99.38	0.57	0.35

*Added as sodium chromate (Na_2CrO_4), a Mean ± standard deviation (n = 5). [a]Tabulatedt-value for 8 degrees of freedom at 5% level of significance is 2.306.[b]Tabulated F-value for (4,4) degrees of freedom at *P* (0.95) is 6.39.

Table 4.7: Determination of Sparingly soluble Cr (VI) in various Cement samples

Sample ID	Sparingly soluble Cr(VI) Added* (ppm)	Proposed method			Reference method			T-test	F-test
		Springle soluble Cr(VI) Found	RSD (%)	Recovery (%)	Springle soluble Cr(VI) Found	RSD (%)	Recovery (%)		
P1	-	10±1.48	14.5	-	11±1.58	14.37	-	0.43	0.20
	2	24.7±1.07	10.3	99	25.4±1.90	11.31	100.77	0.19	0.72
P2	-	15±1.14	7.81	-	15±2.07	14.2	-	1.00	0.27

	4	18.9±0.93	4.89	99.58	18.8±0.84	4.45	98.95	0.84	0.85
P3	-	13±1.19	8.91	-	14±1.92	13.55	-	0.46	0.38
	6	18.8±0.96	5.09	98.73	20.2±1.19	5.92	100.8	0.08	0.68
P4	-	15±1.33	9.01	-	16±1.30	8.05	-	0.12	0.97
	8	22.8±1.04	4.55	99.13	23.7±1.65	6.99	98.7	0.35	0.39
P5	-	11±0.23	2.04	-	11±1.62	14.73	-	0.72	0.00
	10	20.9±0.91	4.37	99.52	21.2±2.59	12.21	100.95	0.82	0.07
P6	-	14±1.92	13.94	-	13±1.48	11.59	-	0.39	0.63
	12	26.1±1.87	7.18	100.31	25±1.87	7.5	99.84	0.37	1.00

*Added as Calcium chromate

Table 4.8: Determination of Insoluble Cr (VI) in various Cement samples

Sample ID	Insoluble Cr(VI) added (ppm)	Proposed method			Reference method			T-test	F-test
		Insoluble Cr(VI) Found	RSD (%)	Recovery (%)	Insoluble Cr(VI) Found	RSD (%)	Recovery (%)		
P1	-	ND	-	-	ND	-	-	-	-
	2	1.94±0.36	18.8	97	2.08±0.26	12.44	104	0.5	0.52
P2	-	11±1.36	12.49	-	10.5±1.6	14.2	-	0.64	0.74
	4	14.7±1.32	9	98	14.8±1.97	13.3	98.8	0.9	0.45
P3	-	ND	-	-	ND	-	-	-	-
	6	5.94±0.99	16.7	99	6.18±0.81	13.17	103	0.69	0.71
P4	-	ND	-	-	ND	-	-	-	-
	8	8.02±0.93	11.64	100.25	8.1±0.82	10.11	101.25	0.89	0.8
P5	-	8±0.78	9.48	-	10.30±1.10	10.64	-	0.01	0.53
	10	18.4±0.81	4.43	102.4	21.2±2.58	12.2	106	0.07	0.05
P6	-	10±0.74	7.49	-	11.1±1.43	12.9	-	0.15	0.23
	12	21.94.1±1.9	8.5	99.72	23.4±2.12	9.1	101.8	0.28	0.81

*Added as lead chromate ($PbCrO_4$)

A comparison of proposed method with standard method using parametric tests (T and F test) given in Tables 4.6 - 4.8. The percentage of relative standard deviation (RSD) and percentage of recovery was also metioned in the tables. The percentage recoveries in six cement samples (from **P1 to P6**) were spiked with known concentration of hexavalent chromium. A null hypothesis indicate that both the adopted methods (DPC and VB method) are valid and are in close agreement for determination of Cr(VI). The calculated values were compared with the tabulated value at a proper degree of freedom [278] and results indicate reliability of these methods from 2 to 12 ppm concentration [109]. At a 95% confidence level, the calculated T- and F-values do not exceed the theoretical values (Table 4.6-4.8) indicating no significant difference between the proposed and the reference method. Consequently, the developed method is as accurate and precise as that of reference method (Figure 4.5).

No insoluble chromium was detected by both the methods for samples, **P1, P3** and **P4**. Results obtained by proposed method were in good agreement with standard method except for sample **P3** and **P4**, where concentration of water soluble Cr(VI) by proposed method was found to be less than that of obtained by standard method. Concentration of water soluble and sparingly soluble Cr(VI) was found to be maximum in sample **P4** and minimum in **P5** by both the methods. It was observed that in Portland pozzolan cement samples, 54-55% of the total hexavalent chromium was water soluble. The percentage of sparingly soluble and insoluble Cr(VI) was found to be 30% and 10% respectively. Although, the industries and researchers are more concerned about water soluble hexavalent chromium, sparingly and insoluble Cr(VI)) are also toxic [279]. Thus detection of all type of Cr(VI) in cement sample is necessary for the safety of workers.

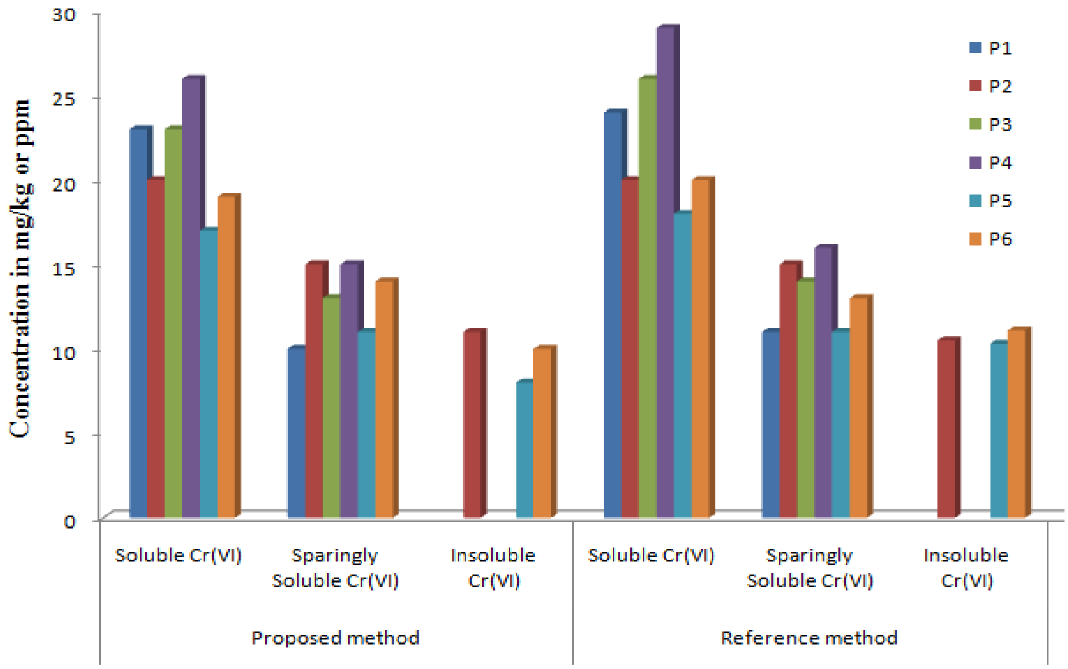


Figure 4.5: Concentration of Cr(VI) found by proposed method and reference method for samples **P1-P6**.

4.3. Determination of water soluble Cr(VI) in OPC samples by Varamine Blue method

The accuracy of the varamine blue method has been checked using a standard reference material (OPC) of National Institute of Standards & Technology (NIST), USA, and found to be in permissible limits. The varamine method was applied for quantitative determination of water soluble Cr(VI) in five OPC samples (**O1-O5**) of ACC brand and results obtained were given in Table 4.9. High concentration of Cr(VI) was found by DPC method as compare to proposed method (Varamine blue method) (Figure 4.6).

Table 4.9: Water soluble Cr(VI) in Ordinary Portland cement samples

S. No	**Sample ID**	**Water Soluble Cr(VI) (ppm)** Average (n=5 replicate) ± Standard deviation			
		VB	**RSD**	**DPC**	**RSD**
1	OPC NIST	0.98±0.03	3.06	1.09±0.02	1.8
2	**O1**	31±0.5	1.6	33±1.5	4.5
3	**O2**	27±0.9	3.3	30±1.9	6.3
4	**O3**	28±0.7	2.5	34±2.5	7.4
5	**O4**	32±0.5	1.6	33±2.0	6.06
6	**O5**	36±0.8	2.2	40±1.2	3.0

RSD: Relative standard deviation

4.3.1 Validation of method

The percentage of recovery of various Cr(VI) spiked solutions as well as their relative standard deviation, relative error and parametric test (t and f test) were also calculated to express the validation of proposed methods (results are given in Table 4.10). Results were compared statistically for the validity of the proposed method. All the experiment were performed at least five times, and student's t test and f test methodology were used for comparison between two different Cr(VI) determination method. The calculated t and f values were compared with test value at a proper degree of freedom, the results showed that both methods are reliable up to 15 mg/L solution. As a result, Percentage of recovery were found slightly higher which means that the DPC method suffers from the presence of interfering metal species (such as Mo(VI), Cu(II), Fe(III), Hg(II), and V(V)) which can react with DPC giving positive interference [109].

Table 4.10: Validation test

	Proposed Method (VB)					Reference method (DPC)					
Sample	Cr(VI) added (ppm)	Cr(VI) found (ppm)	RSD* (%)	Relative error (%)	Recovery (%)	Cr(VI) found (ppm)	RSD (%)	Relative error (%)	Recovery (%)	T^a test	F^b Test
OPC NIST	5	4.55± 1.2	9.87	-9	91	4.93± 1.2	14.59	-1.4	98.6	0.13	0.33
	10	9.78± 0.5	8.87	-2.2	97.8	10.0± 0.9	10.59	0.2	100.2	0.39	0.64
	15	15.01± 1.1	4.43	0.07	100.06	15.05± 1.4	10.65	0.33	100.33	0.85	0.10

*Relative standard deviation , Mean ± standard deviation (n = 5). [a] Tabulated t-value for 8 degrees of freedom at 5% level of significance is 2.306. [b] Tabulated F-value for (4,4) degrees of freedom at P (0.95) is 6.39.

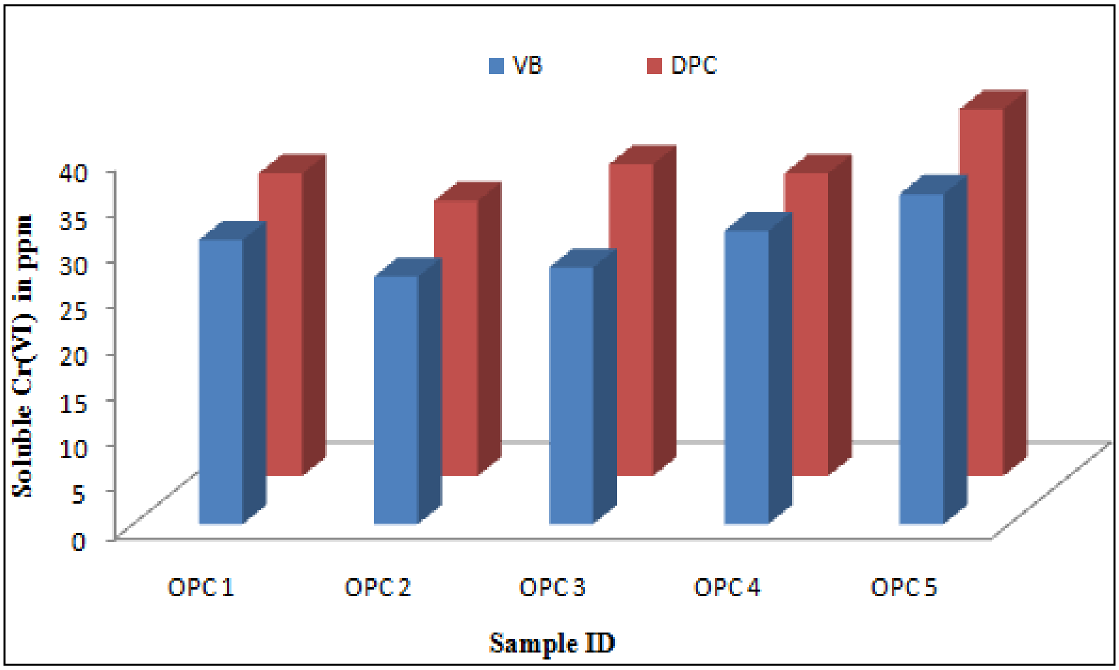


Figure 4.6: Variation in soluble Cr(VI) results in OPC samples by DPC and VB method

Variation in Cr(VI) concentration amongst in five OPC samples can be due to geological condition of raw materials or cement manufacturing conditions [55]. Water soluble Cr(VI) concentration in samples (**O1-O5**) ranges from 27-36 ppm (by VB method) and 30-40 ppm (by DPC method). Lower value of soluble Cr (VI) concentration was found in **O2** samples and higher concentration was found in **O5** sample. The concentration of water soluble Cr(VI) in OPC samples was slightly higher than the PPC samples due to the partial replacement of OPC by fly ash as an additives [55]. This difference showed that the main source of chromium in cement is lime. Therefore there is a need of a screening test for lime content in cement before cement manufacturing.

Chapter-5

Inluence of Hexavalent Chromium Reduing Agents

5.1 Reduction of water soluble Cr(VI) from $FeSO_4.7H_2O$ and $SnCl_2.2H_2O$

Toxic hexavalent chromium can be reduced to non toxic Cr(III) by using various reducing agents. Industries generally used salt of iron and tin because they are more effective and economic. Both these salts were added during manufacturing of cement and it has been observed that efficiency of reducing agent decreases if delayed in consumption (after 3-4 months) which raises need of more amount of reducing agent for effective reduction of Cr(VI). Use of excess of reducing agents can affect cement properties [55]. Thus $FeSO_4.7H_2O$ and $SnCl_2.2H_2O$ in different proportion were added in OPC cement samples (**S2-S7**) during consumption of cement and the samples were tested for Cr(VI) concentration. Reducing agents were added both crystalline as well as powder form. The process of reduction of Cr(VI) by reducing agents is given in Scheme 4. The detection of water soluble Cr(VI) was done by DPC method and result has given in Table 5.1.

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

$$2CrO_4^{-2} + 3Sn^{+2} + 2OH^- + 8H_2O \longrightarrow 2Cr(OH)_3\downarrow + \{3Sn(OH)_6\}^{-2}$$

Scheme 4

Table 5.1: Soluble Cr(VI) concentration in OPC with various amount of reducing agents

Reducing Agent	Dosage in % w/w (crystalline form)	Cr(VI) (ppm)	Dosage in % w/w (powder form)	Cr(VI) (ppm)
OPC	-	25	-	25
$FeSO_4.7H_2O$	0.1	15	0.1	13
$FeSO_4.7H_2O$	0.5	10	0.5	4
$FeSO_4.7H_2O$	1.0	4	1.0	Nd
$SnCl_2.2H_2O$	0.1	6	0.1	1.5
$SnCl_2.2H_2O$	0.5	3	0.5	Nd
$SnCl_2.2H_2O$	1.0	Nd	1.0	Nd

From the result obtained, it has been observed that powder form is more effective in decreasing Cr(VI) content as compare to crystalline form probably due to greater surface area in powder form. A comparing of reducing efficiency of both reducing agent in different proportion is represented graphically in Figure 5.1.

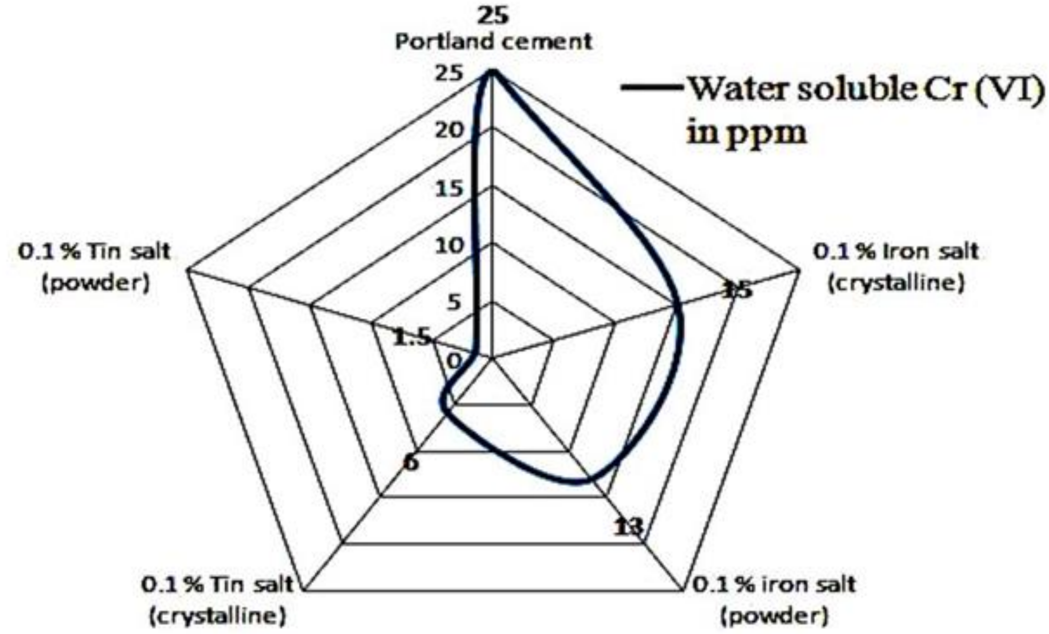


Figure 5.1: The comparison in reduction efficiency of $FeSO_4.7H_2O$ and $SnCl_2.2H_2O$.

It has also been observed that $SnCl_2.2H_2O$ show better reducing efficiency even at low (0.1%) amount. The decrease in Cr(VI) concentration after addition of reducing agent was observed by taking UV-Visible spectrum of extract (Figure 5.2). The maximum reduction has been observed by $SnCl_2.2H_2O$ (1.0%). These results are in agreement with analytical data.

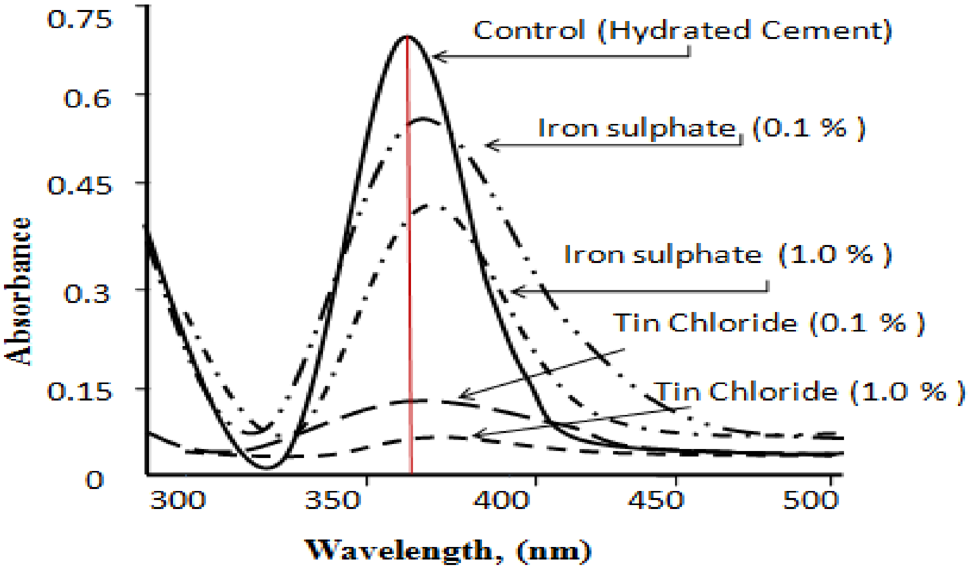


Figure 5.2: UV-Visible spectrum showing decreasing concentration of Cr(VI)

5.2 Physical and mechanical properties

The effect of addition of reducing agents ($FeSO_4 .7H_2O$ and $SnCl_2.2H_2O$) on the consistency, setting times and compressive strength of cement mortar has been determined at 3, 7 and 28 days. The results are given in Table 5.2. Incorporation of reducing agent in different proportion retarded the initial hydration process thus lower its compressive strength but after 28 days no effect on compressive strength of cement mortar has been observed except for cement samples containing 1.0% ferrous sulfate (**S4**) as per IS: 8112-1989. In the case of $FeSO_4.7H_2O$, the cement mortars with 1% reducing agent are lower in compressive strength. However, at 1% dosage of $SnCl_2$ in the cement mortar, the compressive strength increases after 7 days curing as well as at later age. Large size of sulfate ion (from iron sulfate) may retard the hydration process therefore lowered the cement strength, whereas small size of chloride ion (from tin chloride) like enhanced the hydration process as well as strength of cement mortar. Apart from this soluble salt like $SiOCl_2$ might have been produced and crystallization of these salts might have been taken place in the pores. Another reason for retardation in initial hydration process may be the size of metal ions (tin and iron) involved in crystallization of ettringite leading to increase in voids [239, 240].

Table 5.2: Physical and mechanical test report of cement samples with $FeSO_4 .7H_2O$ and $SnCl_2.2H_2O$

Sample ID	Standard water consistency	Initial setting time	Final setting time	Compressive strength (MPa)		
	%	Min	Min	3 days	7 days	28 days
Cement (**S1**)	27	80	120	29.20	38.13	49.53
Cement with 0.1% FSHH (**S2**)	28.5	123	179	22.56	34.56	44.54
Cement with 0.5% FSHH (**S3**)	29	133	198	20.23	32	45.67
Cement with 1.0% FSHH (**S4**)	29.5	143	202	17.58	20.56	39.94
Cement with 0.1% SCDH (**S5**)	28.2	128	172	24.67	34.46	49.93
Cement with 0.5% SCDH (**S6**)	29.5	130	167	23.89	33.76	50.80
Cement with 1.0% SCDH (**S7**)	30.5	121	165	25.67	36.46	53.93

FSHH (Ferrous sulphate hepta hydrate) and SCDH (Stannous chloride dihydrate)

5.3 Hydration study

Microstructural changes that resulted into good reduction efficiency of $SnCl_2.2H_2O$ and good compressive strength of cement mortar at 28 days (**S7**) was investigated using TGA, SEM and XRD techniques were carried out in order to understand phase alterations during hydration of cement with and without additives.

5.3.1 FTIR (Fourier Transform Infrared Spectroscopy)

Hydration of cement samples and formation of polymerization of silica (C-S-H) can also be observed through FTIR studies. IR spectrum of un-hydrated cement samples (Figure 5.3) the peaks of calcium silicate or aluminum silicate, due to Si-O stretching appeared in the range 935-1100 cm^{-1}. The carbonate peak appeared in the range 875-1426 cm^{-1} [275-277]. Peak due to Cr(VI) get merged with carbonate peak [81. 276]. A week band at 3789

cm^{-1} due to O-H stretching of free lime, $Ca(OH)_2$ also appeared in un-hydrated cement samples (Table 5.3). Hydration of cement samples **S1, S2, S4, S5** and **S7** was insured by appearance of broad peak of O-H stretching (water of crystallization) in the range 3425-3488 cm^{-1} (Figures 5.4-5.8). During hydration reactive silica had converted in C-S-H gel form (polymerized form), formation of this form was confirmed by disappearance of Si-O peak in the range, 935-1100 cm^{-1} in the hydrated sample.

Table 5.3: FTIR results shows frequencies shift (cm^{-1}) of different phases in Samples

Important Peaks	**Sample ID**					
	OPC (Un-hydrated)	**S1** (Hydrated OPC)	**S2** (0.1% FSHH)	**S4** (1.0% FSHH)	**S5** (0.1% SCDH)	**S7** (1.0% SCDH)
O-H stretching from $Ca(OH)_2$ **(3600-3800 cm^{-1})**	3789	-	-	-	-	-
O-H stretching from crystallize water **(3250-3580 cm^{-1})**	-	3488	3450	3435.5	3480.6	3425.7
Silicate peak (Si-O stretching) **(919-1200 cm^{-1})**	935 1002.1 1100.4	- - -	- - -	- - -	- - -	- - -

FSHH ($FeSO_4.7H_2O$), SCDH ($SnCl_2.2H_2O$)

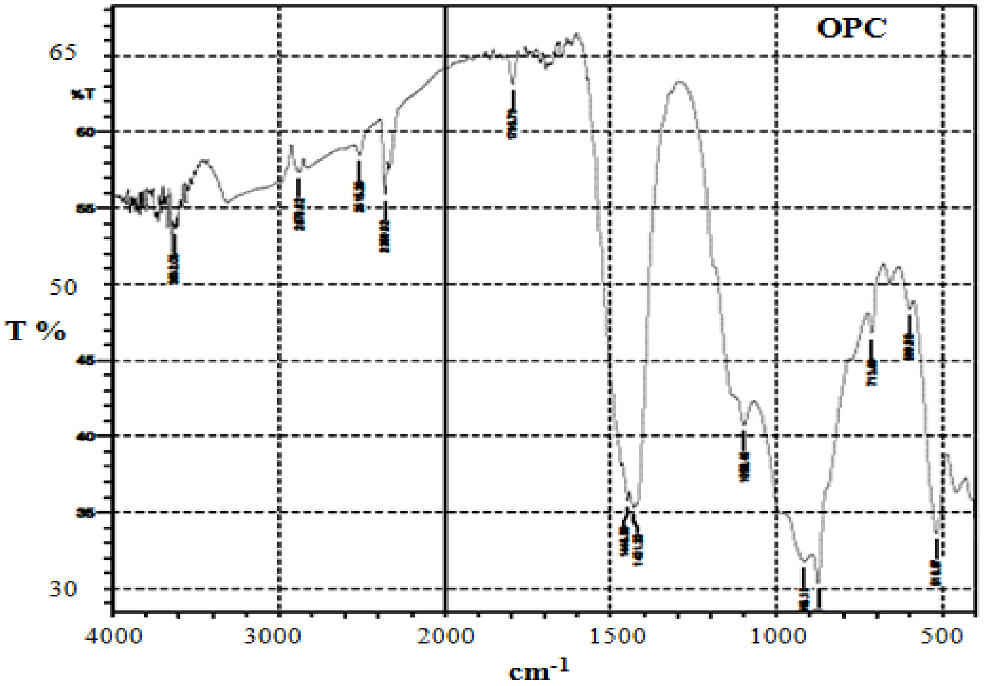


Figure 5.3: FTIR spectra of unhydrated **OPC** sample without reducing agents

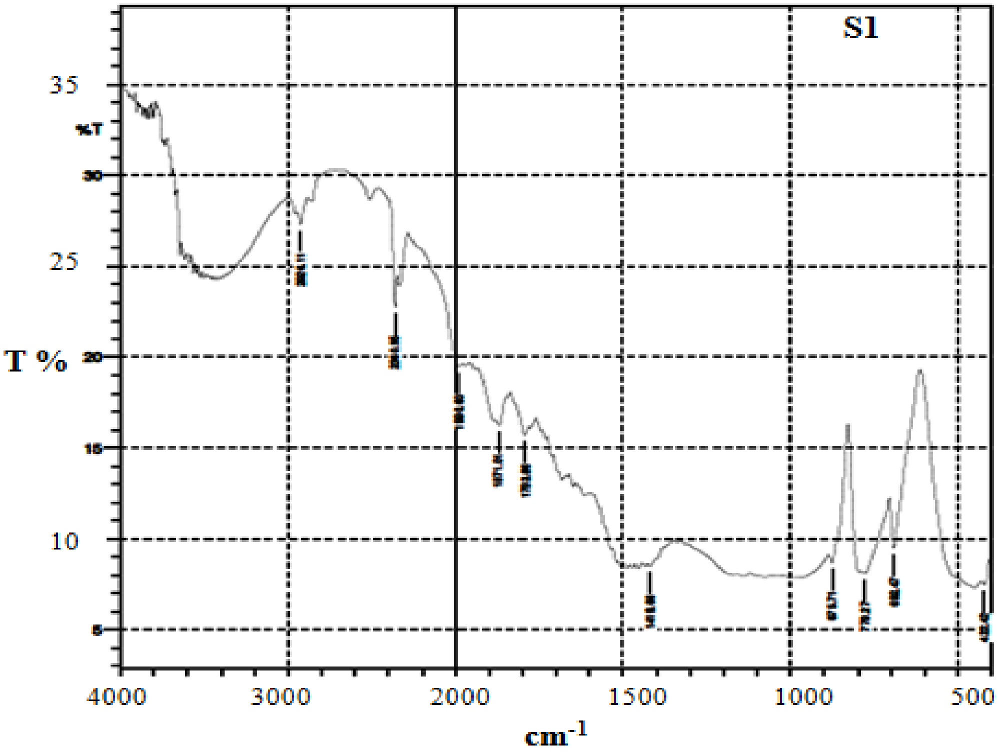


Figure 5.4: FTIR spectra of hydrated OPC (**S1**)

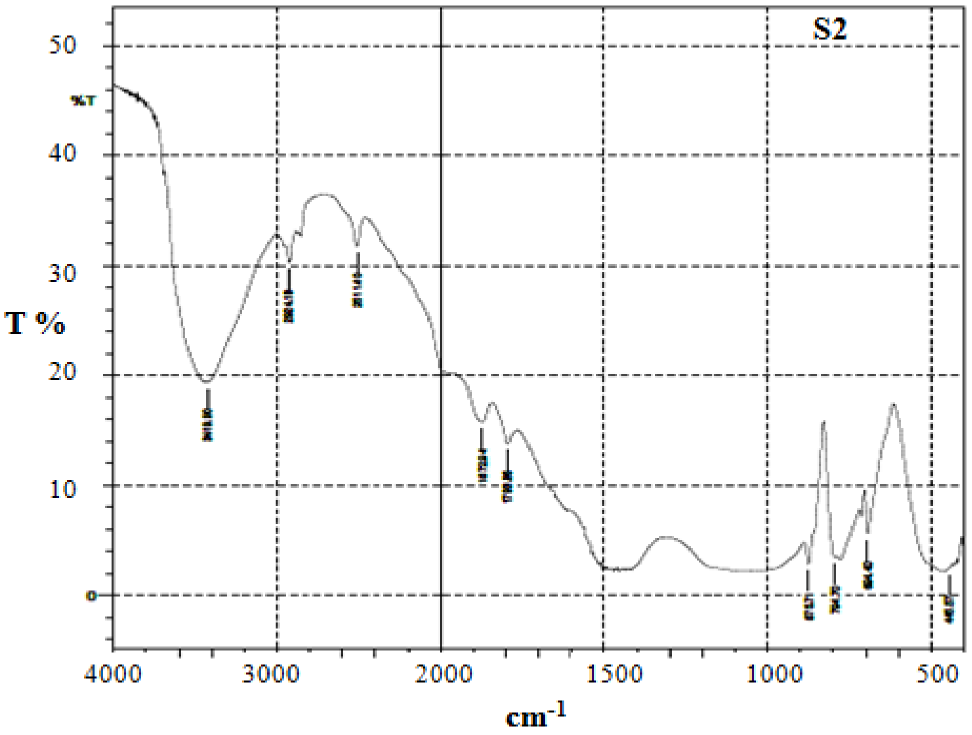


Figure 5.5: FTIR spectra of hydrated OPC with 0.1% $FeSO_4.7H_2O$ (**S2**)

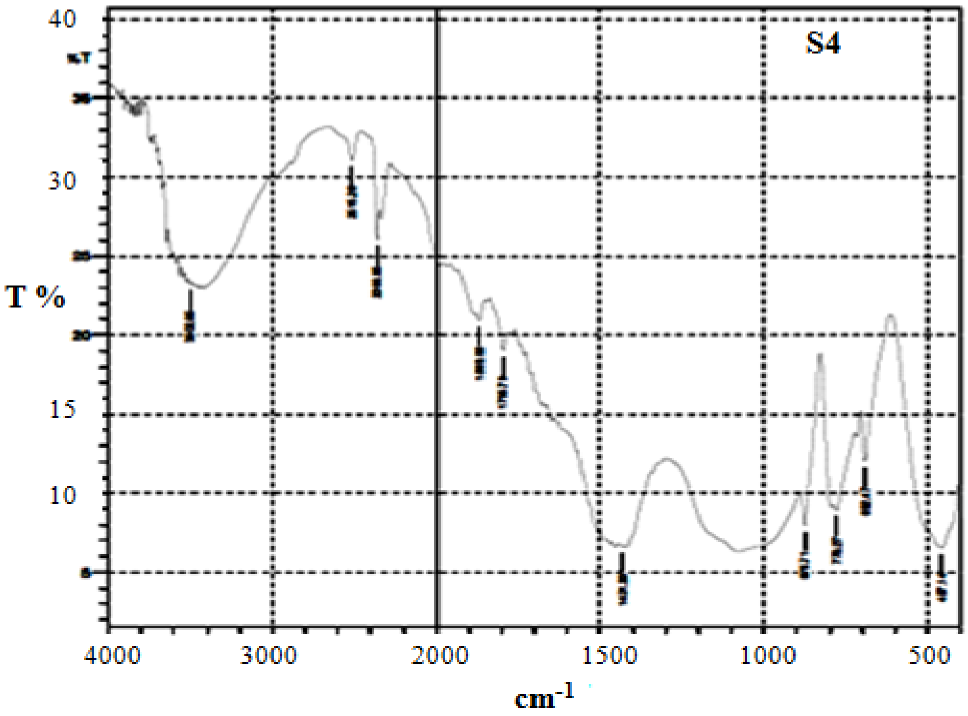


Figure 5.6: FTIR spectra of hydrated OPC with 1.0% $FeSO_4.7H_2O$ (**S4**)

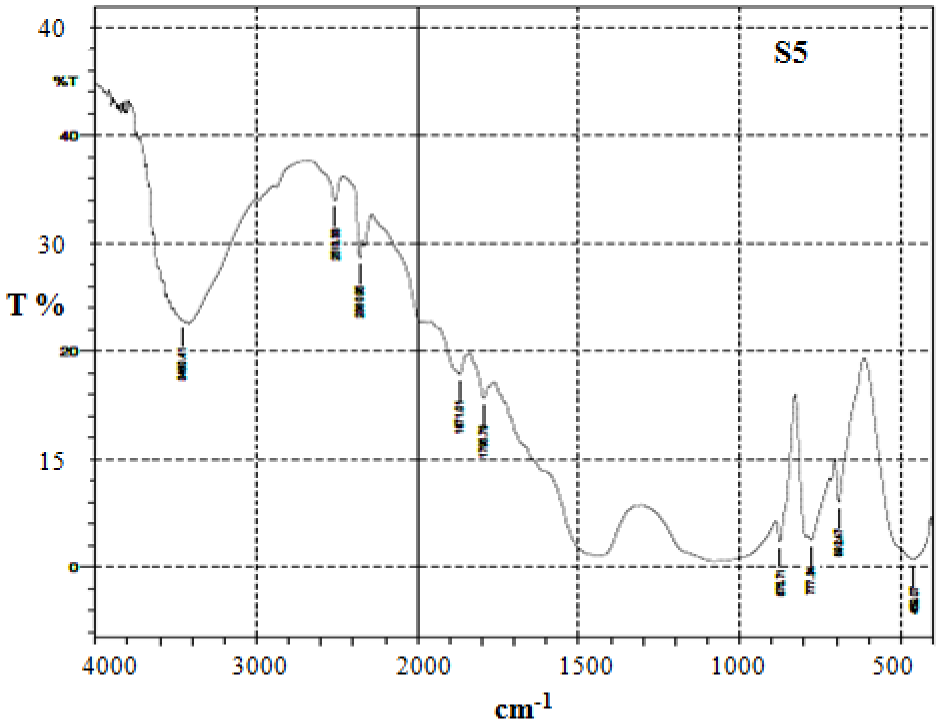


Figure 5.7: FTIR spectra of hydrated OPC with 0.1% $SnCl_2.2H_2O$ (**S5**)

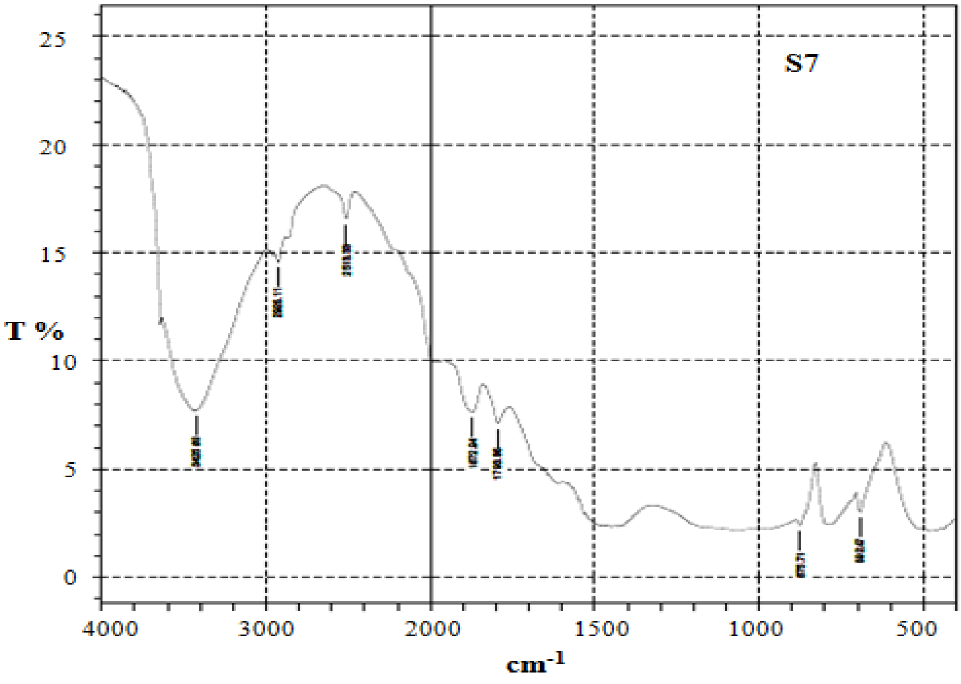


Figure 5.8: FTIR spectra of hydrated OPC with 1.0% $SnCl_2.2H_2O$ (**S7**)

5.3.2 Thermo-gravimetric (TGA) studies

The Calcium hydroxide content of the cement mortars was determined by the thermo gravimetric analysis (TGA). In hydrated samples (**S2**, **S4**, **S5** and **S7**), the peak corresponding to $Ca(OH)_2$ was observed in cement samples (**S1**), where no reducing agent was added (Figure 5.9), three peaks in TGA has been observed which are due to i) dehydration (removal of water from hydrated phases like C-S-H), ii) dehydroxylation (thermal dehydration of calcium hydroxide), iii) decarbonation (thermal decomposition of calcium carbonate). We are mainly interested in second peak dehydroxylation due to $Ca(OH)_2$ (formation of $Ca(OH)_2$ indicates about the thermal decomposition of tricalsium silicates, it means hydration is on progress, which is in hydrated cement samples (**S2**, **S4**, **S5** and **S7**) appeared in the range 420 to 431˚C [53] as shown in Figure 5.10-5.13.The percentage of $Ca(OH)_2$ (w/w) was calculated using formula: $CH\% = (M_T - M_i)100 / M_i$. where M_T = mass loss at perticlate temperature T, M_i = Intial mass of sample and its percentage is given in Table 5.4.

In pure cement sample **S1** weight of $Ca(OH)_2$ was found to be 17.42% (w/w) (Figure 5.9). In **S2** and **S4** decrease in $Ca(OH)_2$ concentration was observed (Figure 5.10 and 5.11), where as $Ca(OH)_2$ content in **S5** and **S7** (Figure 5.12 and 5.13) is more close to pure cement sample **S1**. This indicates that $FeSO_4.7H_2O$ has effected the concentration of $Ca(OH)_2$ therefore effected the compressive strength of cement sample, where as $SnCl_2.2H_2O$ has little effect on compressive strength of cement samples. These results suggest that $SnCl_2.2H_2O$ is a better reducing agent as compare $FeSO_4.7H_2O$ in all three compositions.

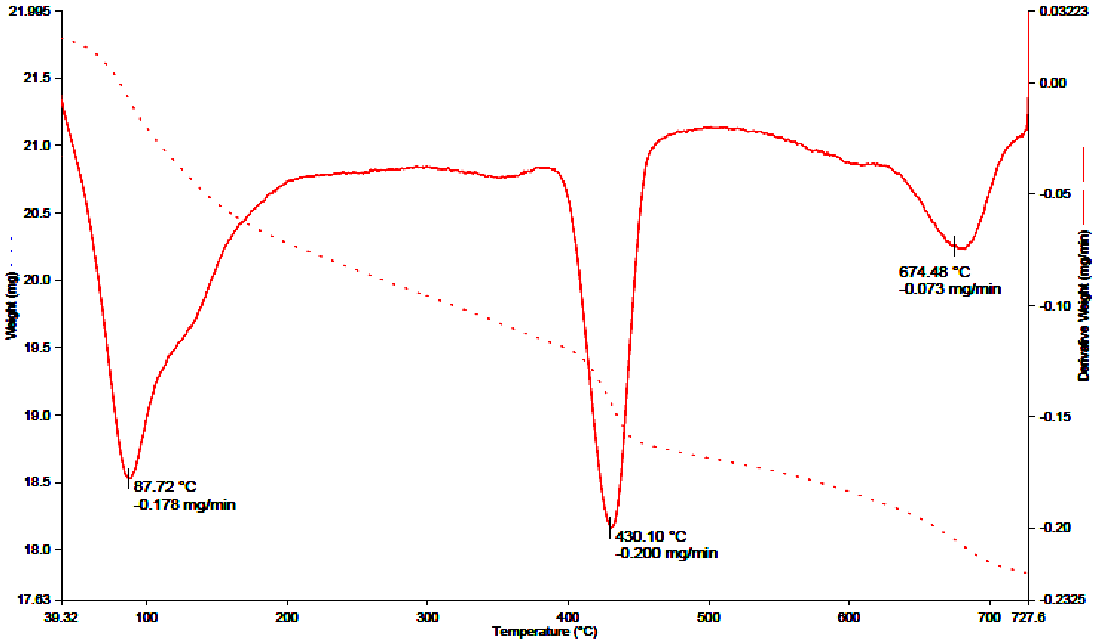


Figure 5.9: TGA curve of hydrated cement OPC (**S1**)

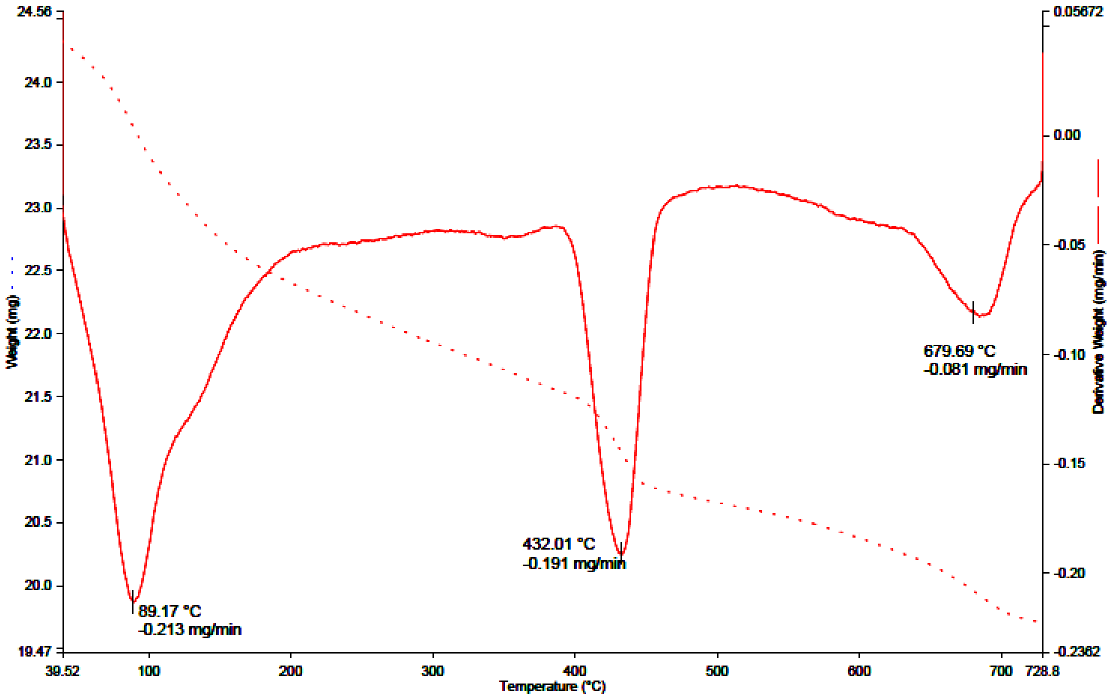


Figure 5.10: TGA curve of hydrated cement with 0.1% $FeSO_4.7H_2O$ (**S2**)

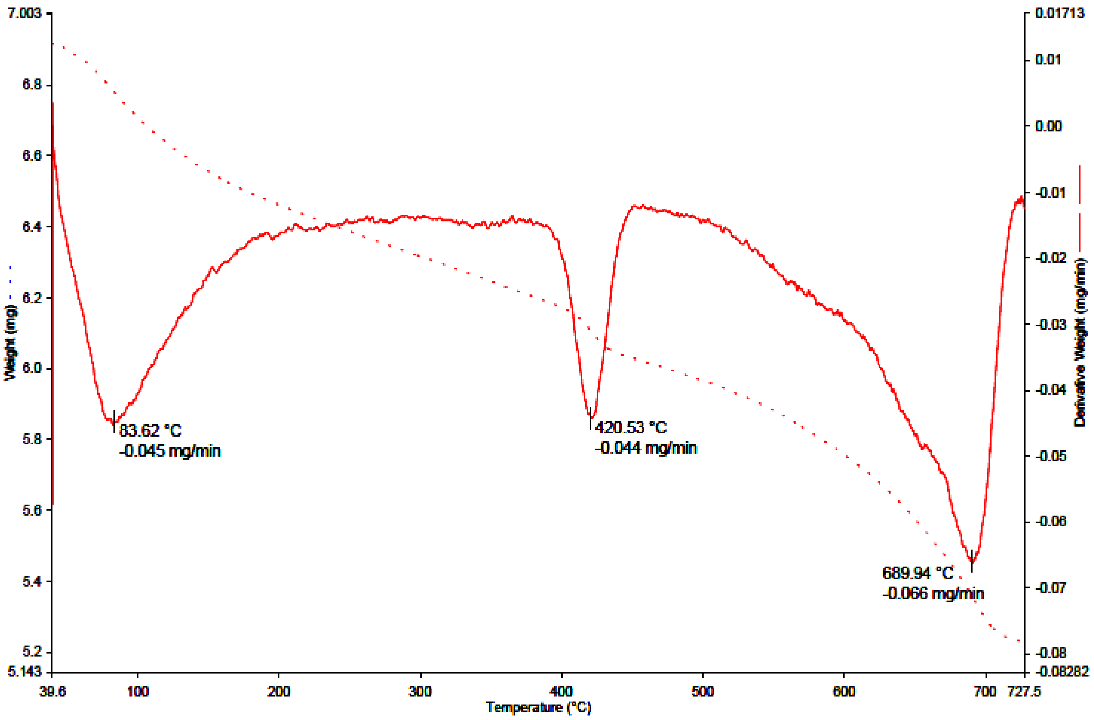


Figure 5.11: TGA curve of hydrated cement with 1.0% $FeSO_4.7H_2O$ (**S4**)

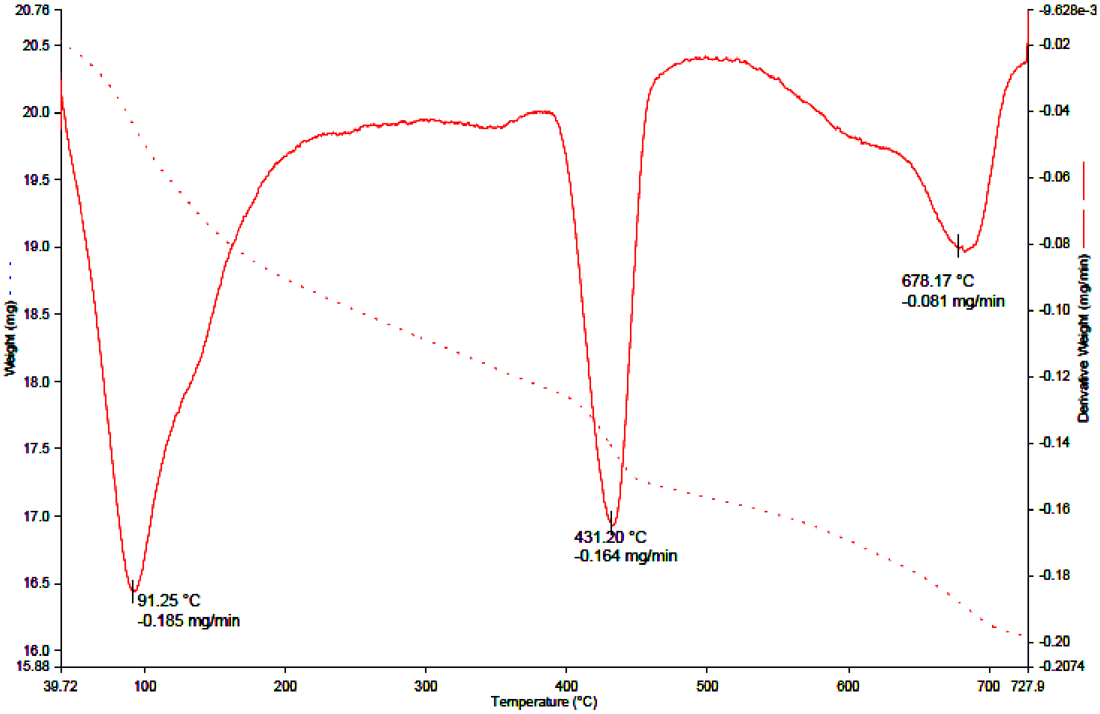


Figure 5.12: TGA curve of hydrated cement with 0.1% $SnCl_2.2H_2O$ (**S5**)

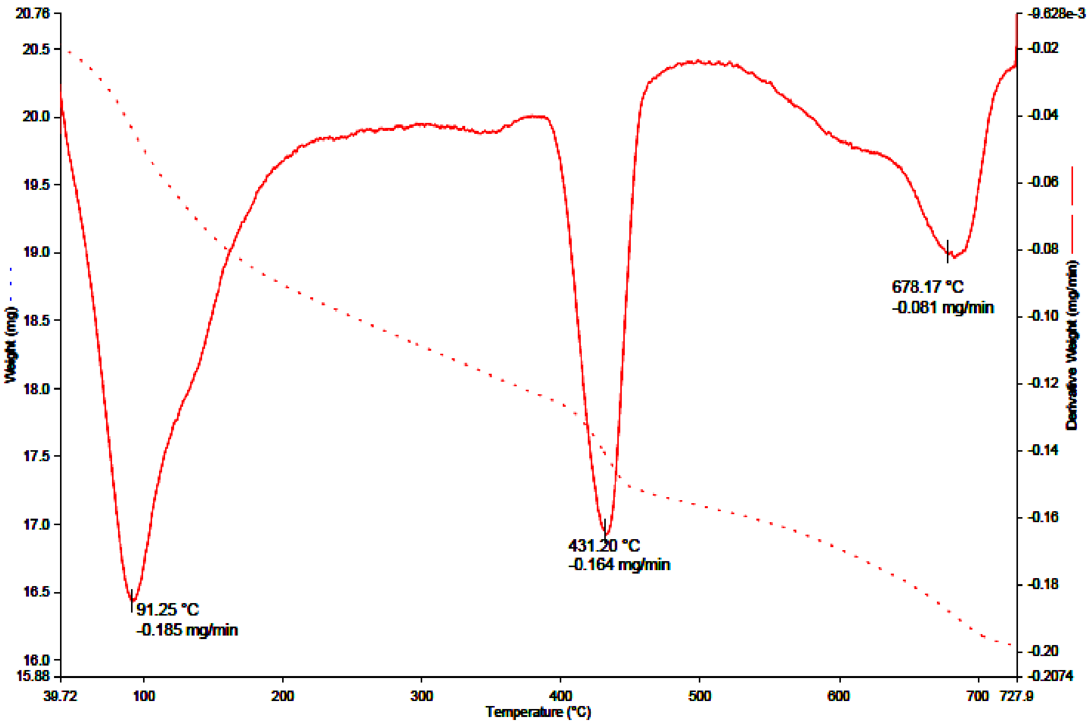


Figure 5.13: TGA curve of hydrated cement with 1.0 % $SnCl_2.2H_2O$ (**S7**)

Table 5.4: The percentage of $Ca(OH)_2$ formation during of cement samples

Sample ID	**Temperature (°C)**	**$Ca(OH)_2$ % (w/w)**
OPC (**S1**)	430.10	17.42
0.1% $FeSO_4.7H_2O$ (**S2**)	432.01	13.38
1.0% $FeSO_4.7H_2O$ (**S4**)	420.53	11.69
0.1% $SnCl_2.2H_2O$ (**S5**)	431.20	14.66
1.0% $SnCl_2.2H_2O$ (**S7**)	431.68	15.14

5.3.3 Microscopic studies (Scanning electron microscopy, SEM)

The hydration of the two mineral compounds (C_3S and C_2S) produces calcium silicate hydrate (C-S-H) or hydrosilicates having gel structure (like tobermorite) which developed the strength of cement materials [272]. Therefore C-S-H information is essential to know. Qualitative information on (Calcium silicate hydrate) CSH gels was obtained from SEM-EDS morphology of hydrated samples (Figure 5.14-5.23) with and without additives at 28 days hydration. Generally amorphous C-S-H gel (light color), which is the main hydration product, was observed in hydrated cement samples, dicalcium silicate hydrate phases are in spherically small size and tricalcium silicate hydrate phases are in large rectangular size [53, 281].

In 28 days hydrated OPC sample (**S1**), tobermorite (a gel like form of C-S-H) was seen as solid rigid surface (Figure 5.14). On the surface of **S1** light colour crystals of different shapes were observed in spherical and rectangular form which support formation of C-S-H phase whereas light colour grains gave indication about the presence of un-hydrated C_3S and C_2S as mineral phase due to uncured hydration. Appearance of cracks in **S1** sample can be due to high percentage of lime in OPC resulted from exothermal hydration reactions. High mass percentage of calcium in EDS spectra (Figure 5.15) was also seen. The SEM image are given in different resolution forms (1µm, 5 µm and 10 µm), to understand the image. Thus we can conclude that during consumption of OPC cement in constraction proper curing is required.

SEM image of hydrated sample (**S2**) having 0.1% $FeSO_4.7H_2O$, showed crystal formation of different shape as rectangular, rounded and hexagonal form (Figure 5.16) due to delayed in silicate polymerization [284]. Some new types of unshaped crystal were observed which indicate that iron salt may affect the shape and colour of the crystals or it may be participated in hydration [282]. This has been confirmed in XRD spectra. Portlandite (or calcium hydroxide) can be identified in its characteristic hexagonal shape.

In hydrated sample (**S4**) having 1.0% $FeSO_4.7H_2O$, light grains and rounded crystal of dicalsium silicate hydrate phase are more as compare to tricalsium silicate hydrate phase, indicating retardation of intial hydration (Figure 5.18). Irregular crystals of hydrated calcium sulphate were also observed. This was confirmed by the EDS spectra (Figure 5.19) which showed Sulphur element (1.84% by mass) in hydrated phase due to presence of 1.0% $FeSO_4.7H_2O$ as reducing agent in cement. In EDS spectra carbon (7.46% by mass) was observed indicates carbonation (Figure 5.18). Thus the use higher percentage of $FeSO_4.7H_2O$ in cement is required to avoid carbonation and hydrated calcium sulfate formation [**55**].

SEM image of **S5** (0.1% $SnCl_2.2H_2O$) indicate formation of higher amount of calcium silicate phase at 28 days hydration along with hexagonal crystals of calcium hydroxide and calcium carbonate (Figure 5.20). The same was also confirmed by it EDS spectra (Figure 5.21). SEM image showed many polymerized silicate phase. However in case of 1% $SnCl_2.2H_2O$ (Figure 5.22 and 5.23) good solid rigid surfaces found it ensure that maximum reactive silica gets polymerized into gel and rigid surface.

From the above discussion, it can be concluded that on increasing the percentage of reducing agents (iron sulfate and tin chloride) in cement sample having 1% $SnCl_2.2H_2O$. Initial hydration gets delayed but 28 days hydration gets improved.

Formation of less hydrated phases has been observed in **S4** (1% $FeSO_4.7H_2O$) sample (Figure 5.18 and 5.19). A delay in hydration has been observed in **S4**, which may be due to lower concentration of $Ca(OH)_2$ formation as hexagonal plate like structure of Portlandite or uncured hydration. From the above discussion it can be concluded lack of amorphous silica in OPC sample can be the possible reasons for delay in hydration in **S4** sample [48]. Cement sample **S7** (1% $SnCl_2.2H_2O$) showed more compressive strength due to formation of rigid surface and hydrated tricalcium silicate phase [158] (Figure 5.22 and 5.23

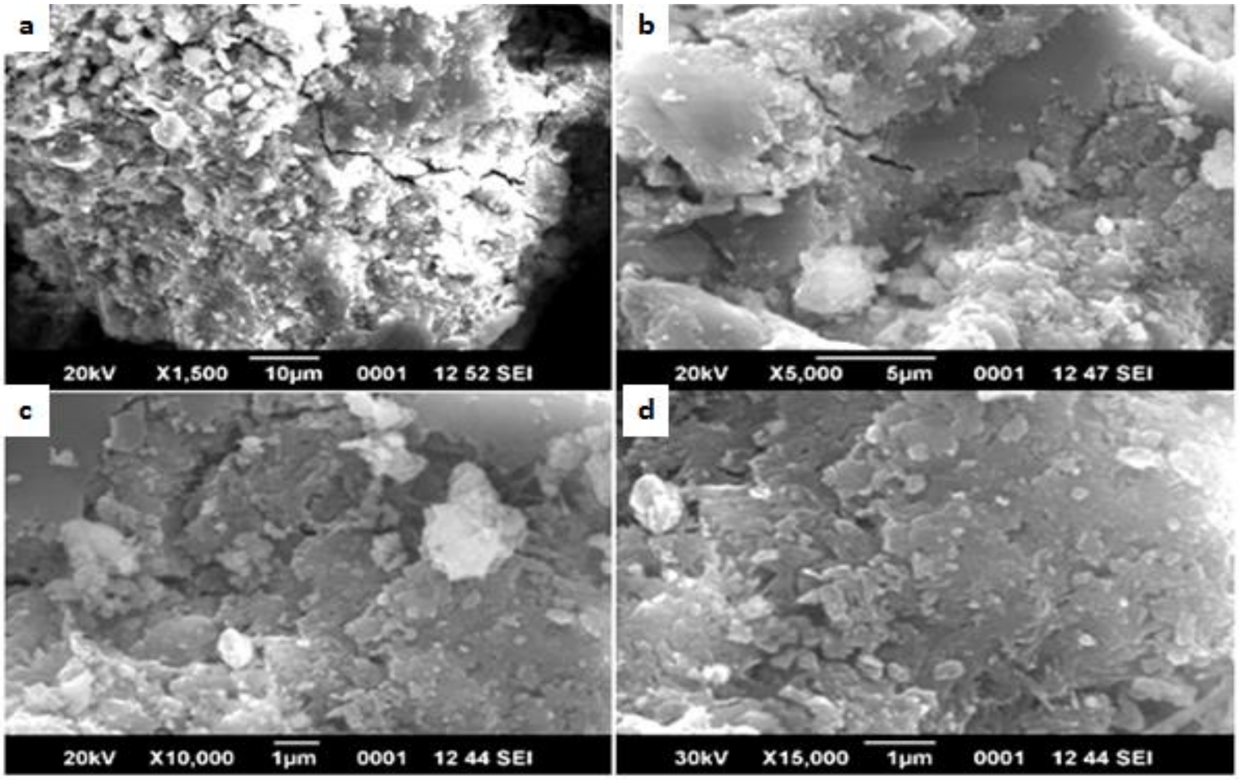
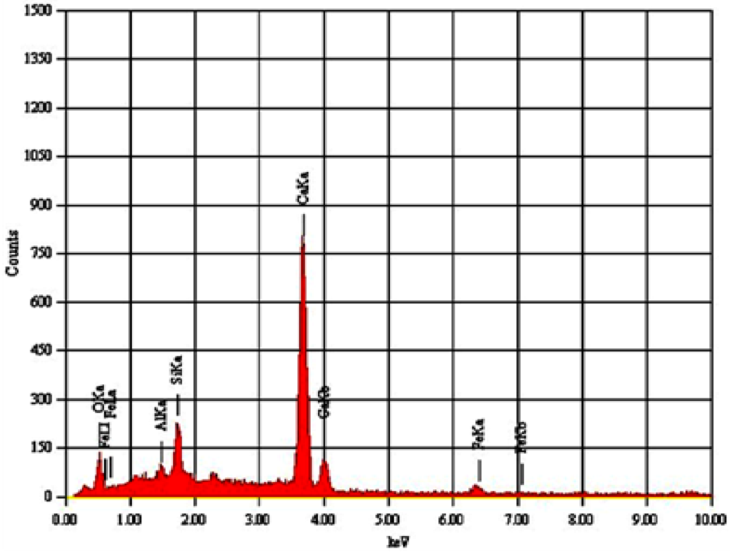


Figure 5.14: SEM of hydrated OPC sample (**S1**) at different resolution parameters



Element	(keV)	Mass%	Atom%	K
O K	0.525	7.72	16.69	0.9633
Al K	1.486	2.59	3.31	0.6923
Si K	1.739	10	12.31	0.6945
Ca K	3.69	75.34	64.99	1
Fe K	6.398	4.35	2.69	1.7499
Total		100	100	

Figure 5.15: EDS of hydrated OPC sample (**S1**)

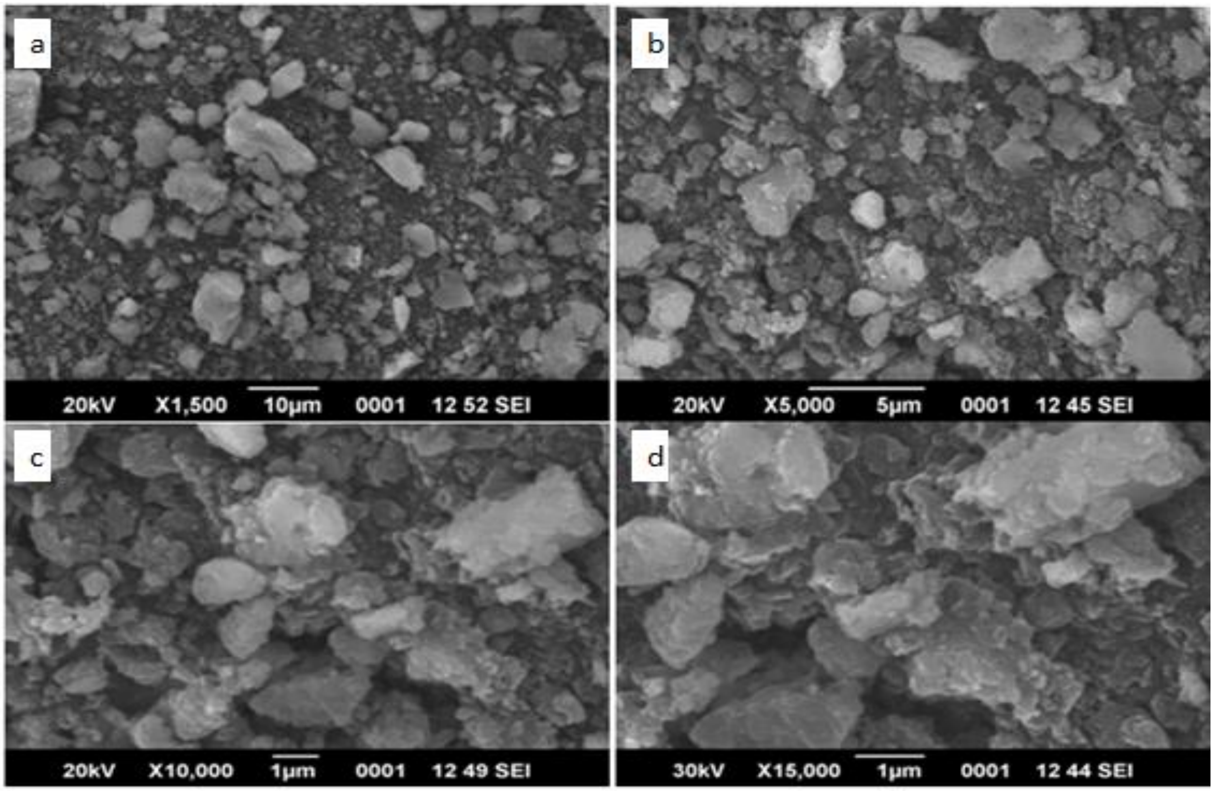
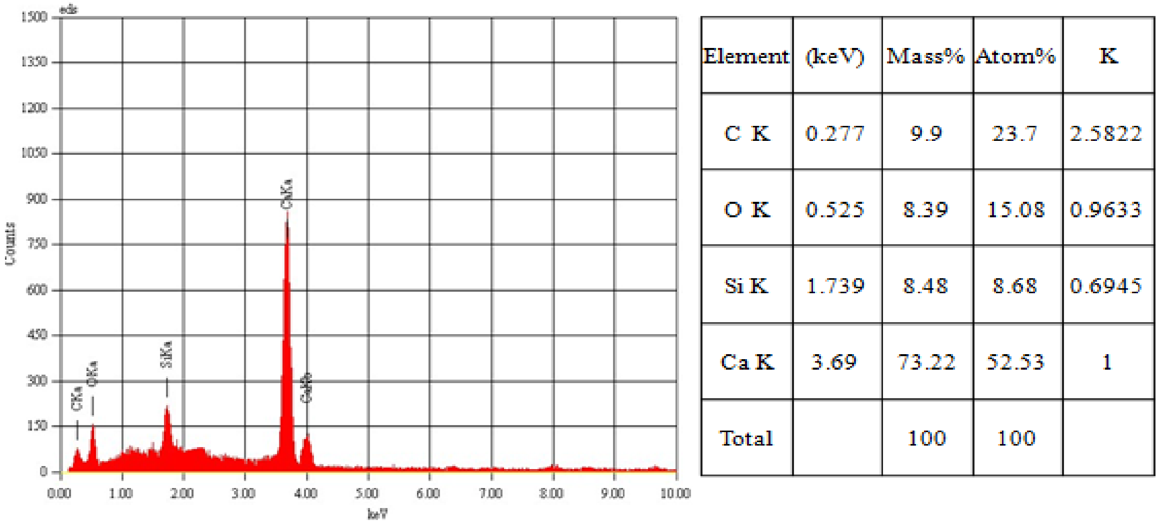


Figure 5.16: SEM of hydrated 0.1% $FeSO_4.7H_2O$ sample (**S2**) at different resolution parameters



Element	(keV)	Mass%	Atom%	K
C K	0.277	9.9	23.7	2.5822
O K	0.525	8.39	15.08	0.9633
Si K	1.739	8.48	8.68	0.6945
Ca K	3.69	73.22	52.53	1
Total		100	100	

Figure 5.17: EDS of hydrated 0.1% $FeSO_4.7H_2O$ sample (**S2**) at different resolution parameters

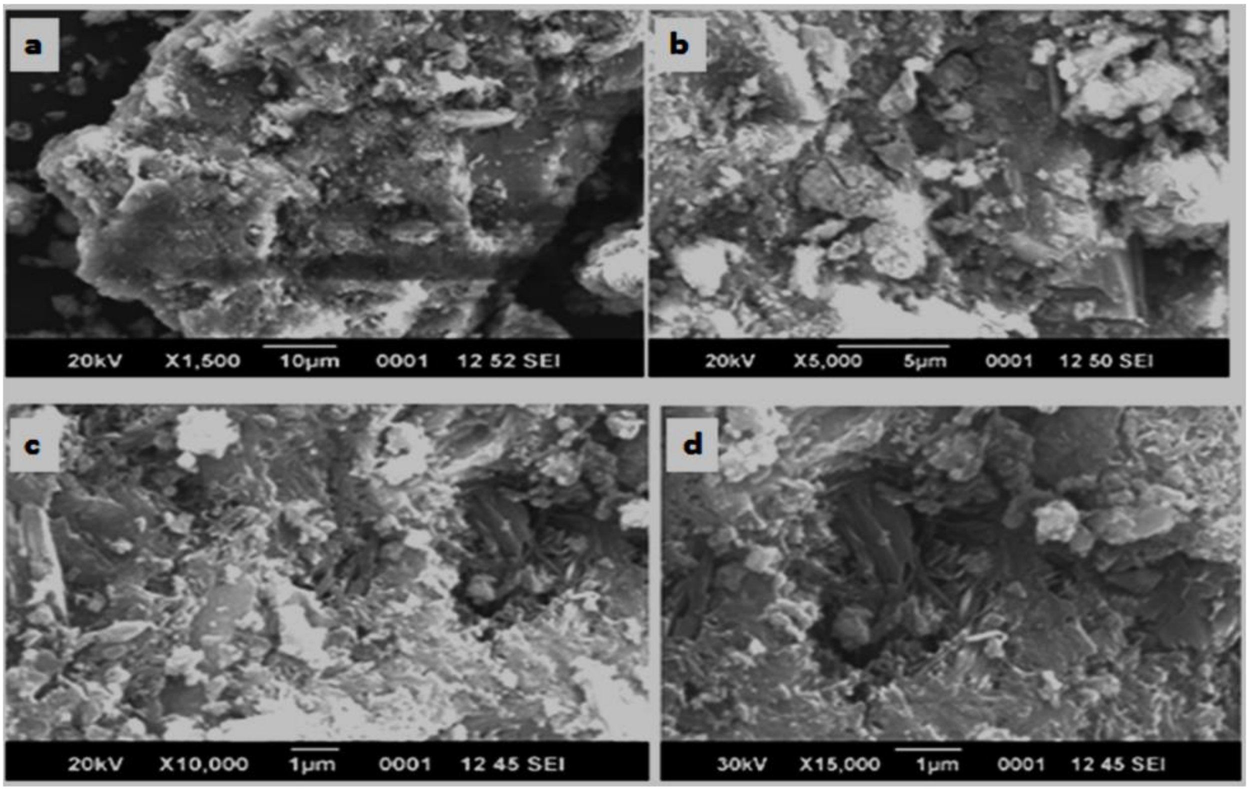
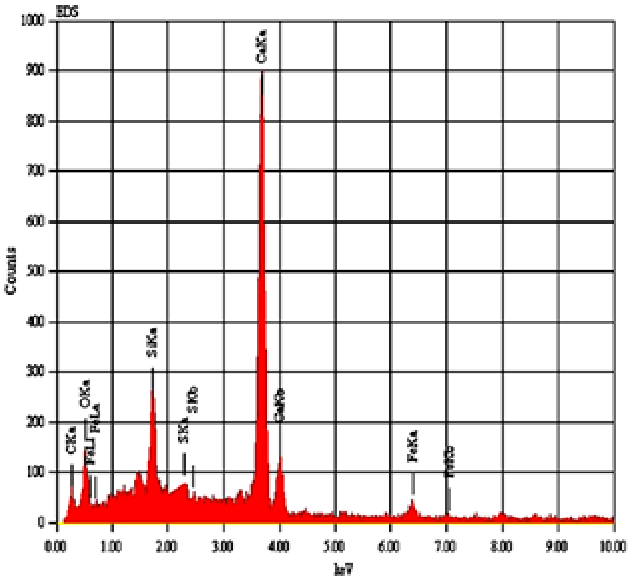


Figure 5.18: SEM of hydrated 1.0% $FeSO_4.7H_2O$ sample (**S4**) at different resolution parameters



Element	(keV)	Mass%	Atom%	K
C K	0.277	7.46	18.94	2.5822
O K	0.525	7.13	13.58	0.9633
Si K	1.739	9.67	10.49	0.6945
S K	2.307	1.84	1.75	0.8313
Ca K	3.69	69.3	52.72	1
Fe K	6.398	4.6	2.51	1.7499
Total		100	100	

Figure 5.19: EDS of hydrated 1.0% $FeSO_4.7H_2O$ sample (**S4**)

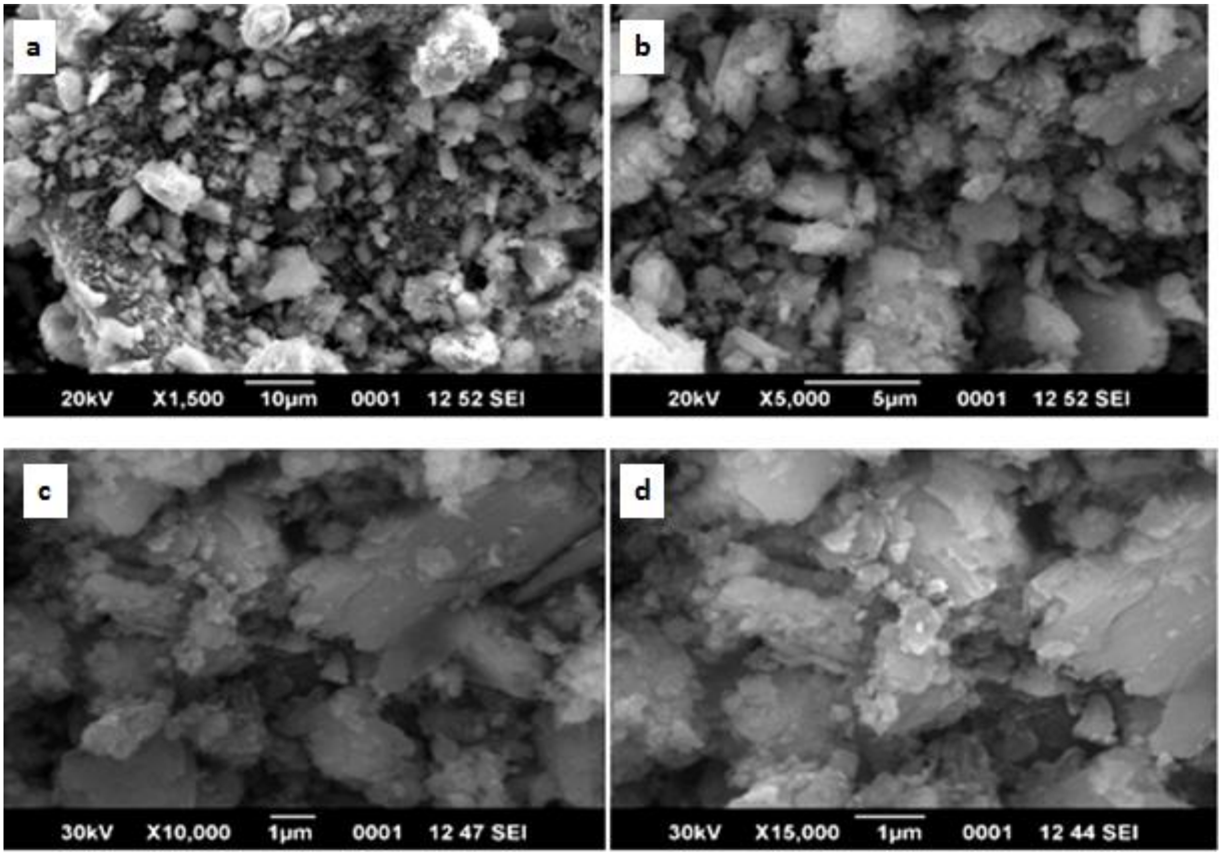
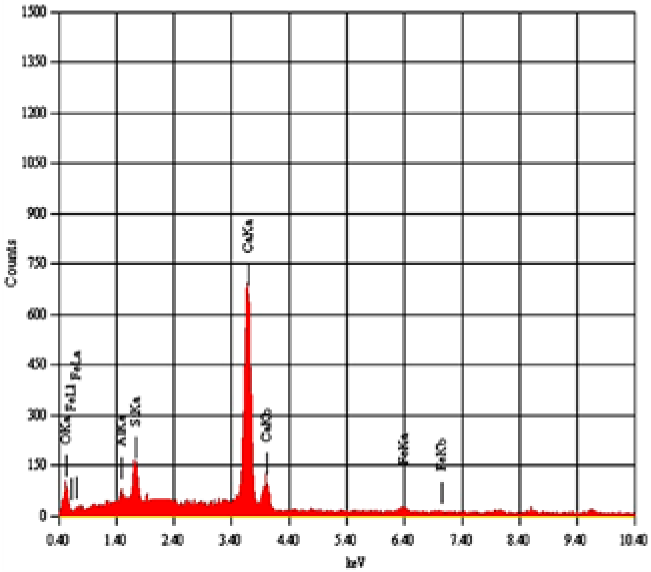


Figure 5.20: SEM of hydrated 0.1% $SnCl_2.2H_2O$ sample (**S5**) at different resolution parameters



Element	(keV)	Mass%	Atom%	K
C K	0.277	6.52	16.87	2.5822
O K	0.525	7.15	13.88	0.9633
Al K	1.486	2.14	2.47	0.6923
Si K	1.739	7.06	7.81	0.6945
Ca K	3.69	73.24	56.8	1
Fe K	6.398	3.9	2.17	1.7499
Total		100	100	

Figure 5.21: EDS of hydrated 0.1% $SnCl_2.2H_2O$ sample (**S5**)

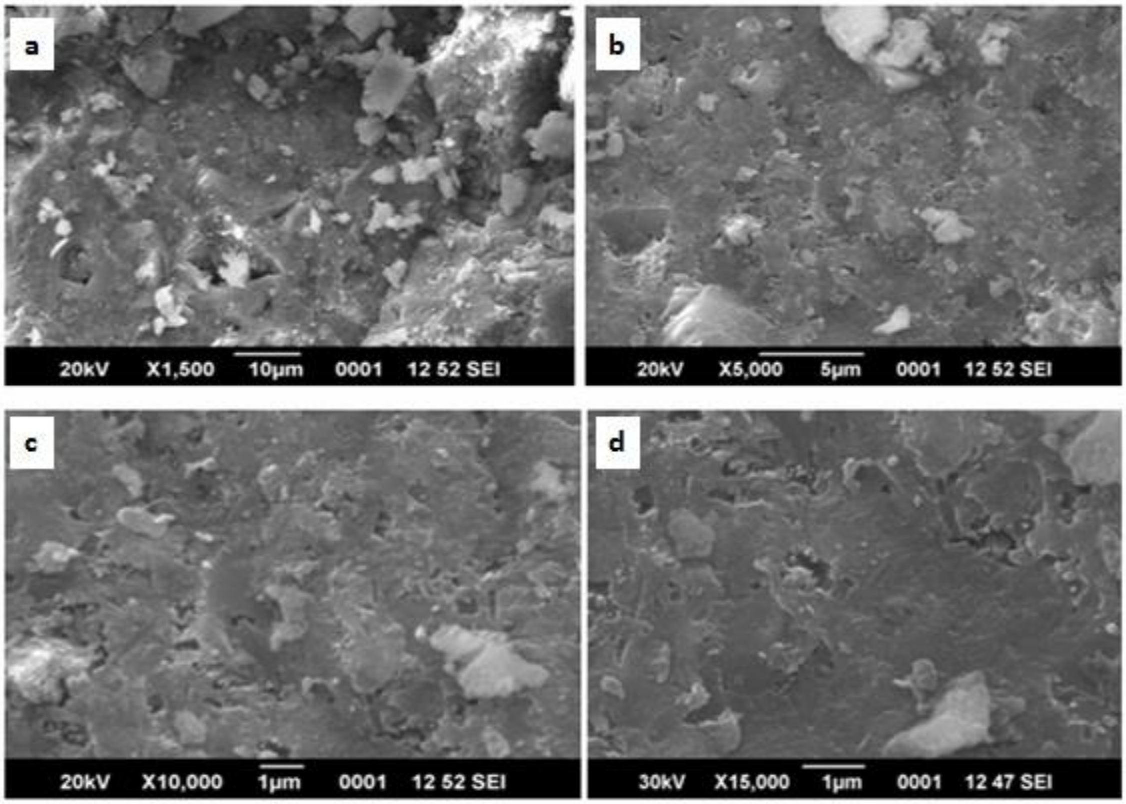
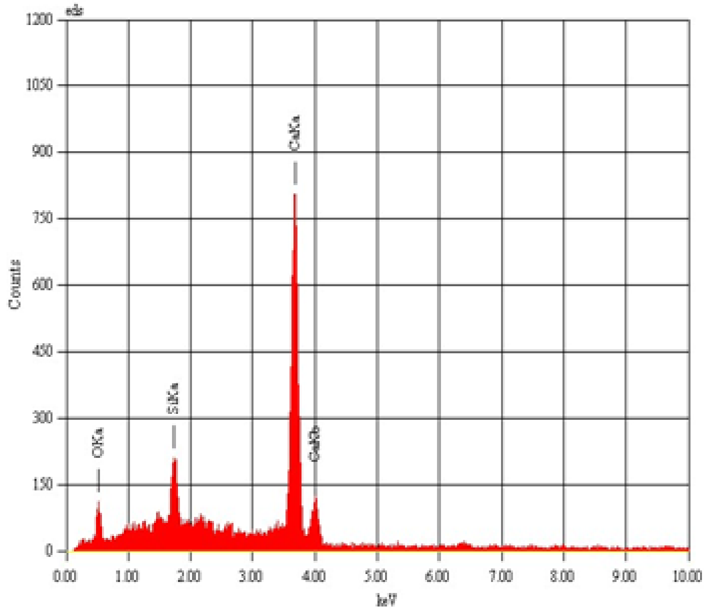


Figure 5.22: SEM of hydrated 1.0% $SnCl_2.2H_2O$ sample (**S7**) at different resolution parameters



Element	(keV)	Mass%	Atom%	K
O K	0.525	33.06	78.51	34.325
Si K	1.739	6.08	4.46	3.3723
Ca K	3.69	60.87	17.02	23.5743
Total		100	100	

Figure 5.23: EDS of hydrated 1.0% $SnCl_2.2H_2O$ sample (**S7**)

5.3.3 X-ray diffraction (XRD) studies

The XRD patterns of hydrated OPC with and without additives are presented in Figure 5.24. The main peaks of Calcium hydroxide (CH) at (2θ = 18.2˚, 34.2˚and 47.32˚), Tricalcium silicate (C_3S) at (2θ = 29.6˚), dicalcium-silicate (C_2S) at (2θ = 32.32˚) and ettringite phase at (2θ = 9.35˚) are observed in spectrum. If we look in XRD spectra, the total intensity of CH formation in **S1, S2, S4, S5** and **S7** samples are 3845, 3032, 2918, 2834 and 3093 counts. Calcium hydroxide content is more in pure OPC sample and decreases on addition of reducing agent which indicates less hydration in **S2, S4, S5** and **S7** (Figure 5.25-5.28). An extra peak observed in XRD spectrum of **S7** at 2θ = 11.5 (Figure 5.28). This peak is due to monocarbonate as well as Friedal's salt ($Ca_3Al_2O_6.CaCl_2.10H_2O$) formation and thus support increases in hydration. Monocarbonate phase decreases the porosity of cement thus helped in enhancing the strength of cement materials after 28 days [282] Monocarbonate phase get destabilized to monosulphate and calcite at above 47˚C, which resulted into higher coarse porosity and reduces the compressive strength of cement samples [283]. Due to release of energy during hydration in **S1** and **S4** may be one reason for absence of monocarbonate phase in XRD spectra of **S1** and **S4** (Figure 5.24 and 5.26). Extra peak in the range of 0-11.5 (2θ angle) in **S4** and **S7** indicated participation of metal salts in hydration process (Figure 5.26 and 5.28) [282-284].

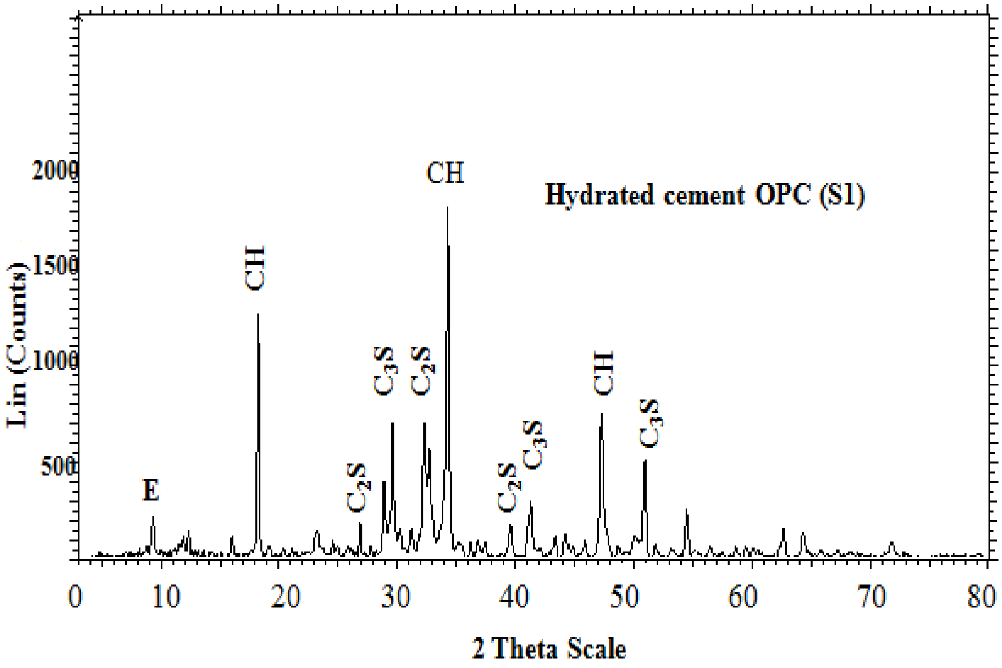


Figure 5.24: XRD spectra of hydrated cement OPC (**S1**)

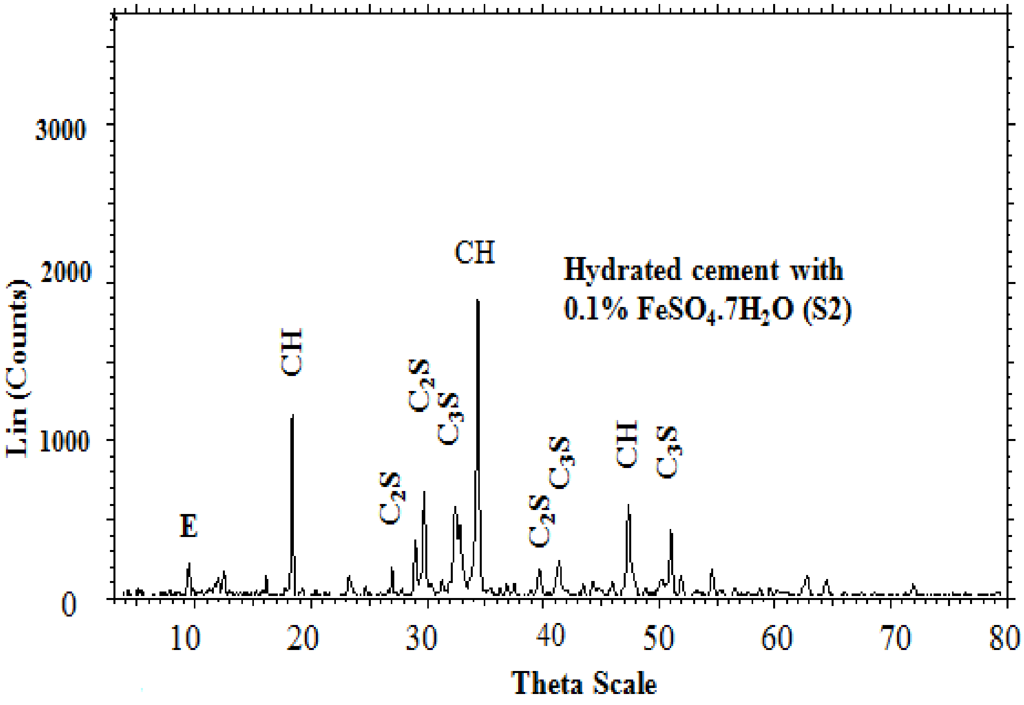


Figure 5.25: XRD spectra of hydrated cement with 0.1% $FeSO_4.7H_2O$ sample (**S2**)

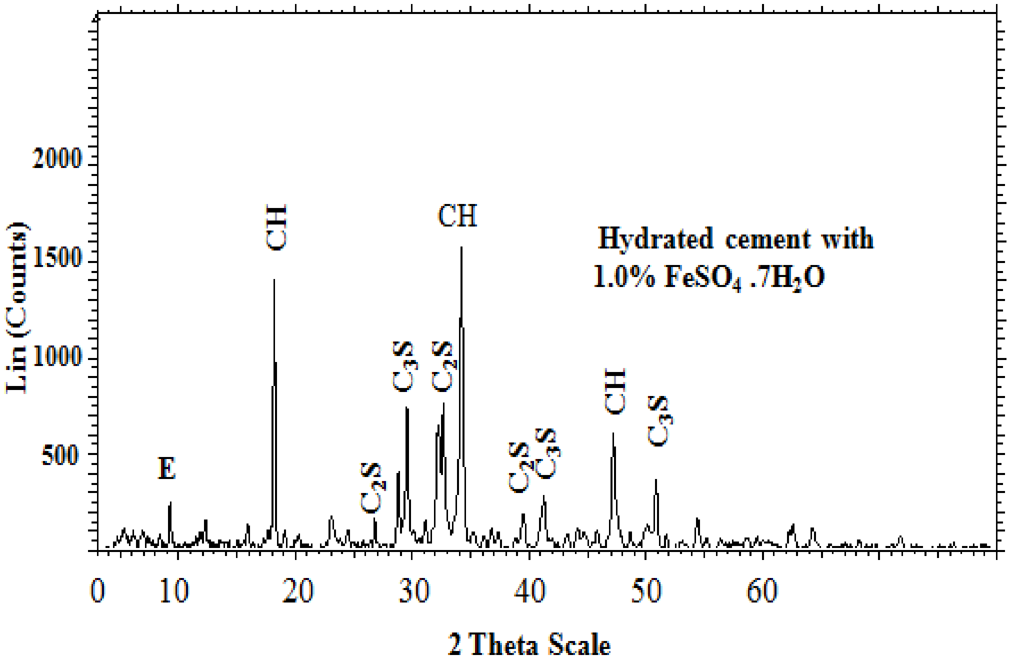


Figure 5.26: XRD spectra of hydrated cement with 1% $FeSO_4.7H_2O$ sample (**S4**)

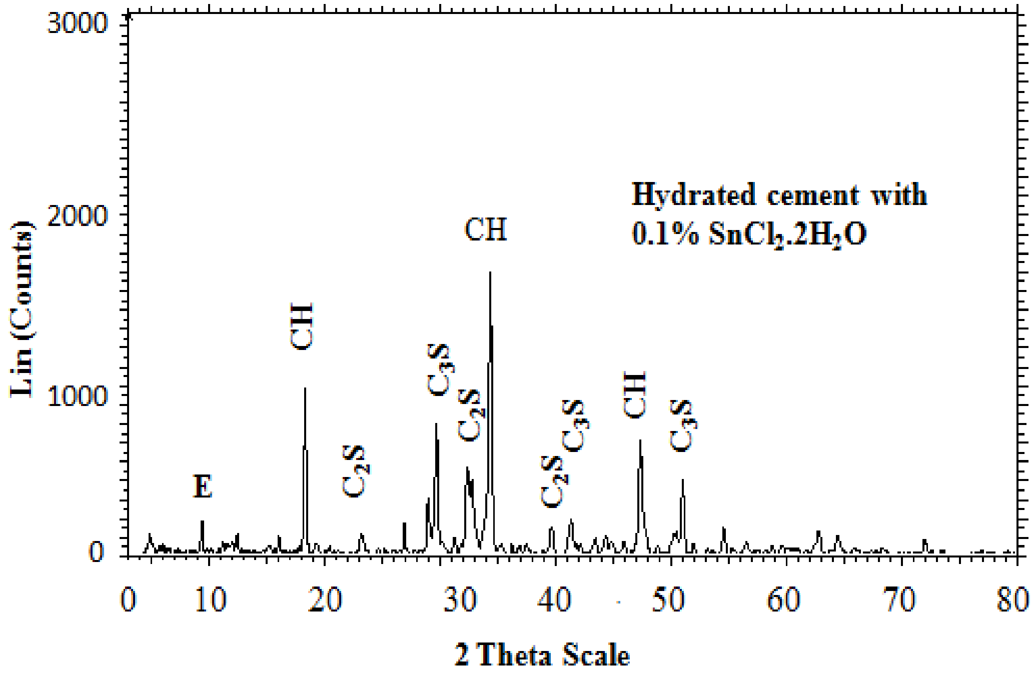


Figure 5.27: XRD spectra of hydrated cement with 0.1% $SnCl_2.2H_2O$ sample (**S5**)

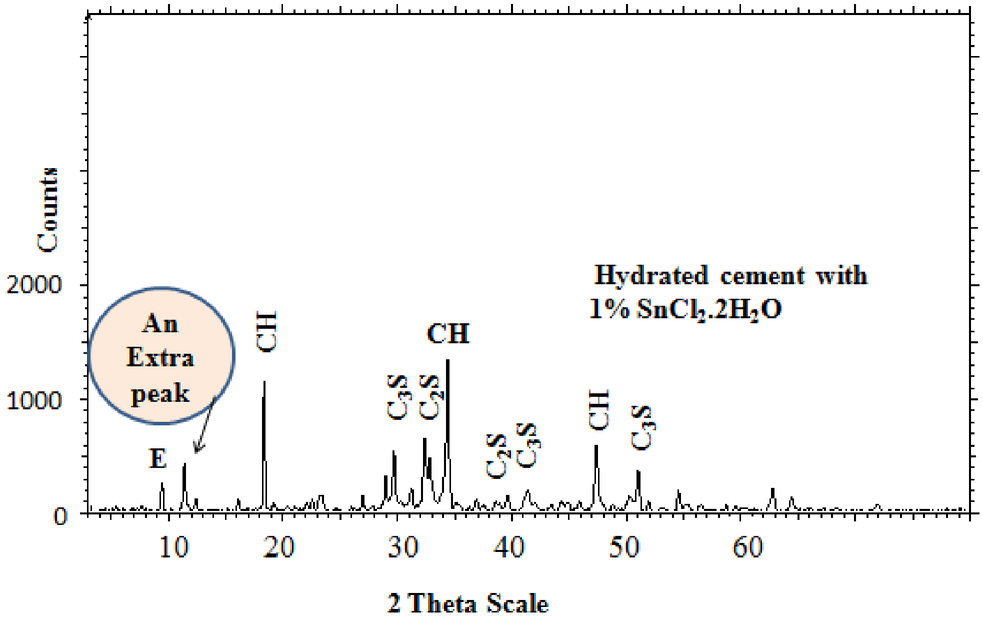


Figure 5.28: XRD spectra of hydrated cement with 1.0% $SnCl_2.2H_2O$ sample (**S7**)

As per above discussion, it is cleared that economical reducing agent such as $FeSO_4.7H_2O$ has a dosing problems due to unstability in cement so they demanded over dosages which delay the further reaction of free lime and silica to make strengthen phase (calcium silicate hydrate phase) [163, 164]. However it has been observed that very less amount of reducing agent is required, if we add this reducing agent during consumption. If it will allowed, kept in mind in that cases industries will not provide these reducing agent along with cement and consumers has to bear extra cost therefore it is better that industries adopt some alternatives to enhance the storage stability of reducing agent with minimum effect. Other problem comes as per TGA and SEM results. According to TGA lower amount of Calcium hydroxide was found in cement sample having 1% $FeSO_4.7H_2O$ but according to SEM morphology, it showed that higher mass of $Ca(OH)_2$ formed during hydration but these calcium hydroxide had not reacted with silica. It means requirement of more amorphous (reactive) silica for reaction with free lime in ordinary Portland cement samples specially in case of cement having reducing agent (iron salt). Therefore this research designed two types of modified reducing agent for above said problems. These methods (types) are as follows. First method: Coating of reducing agent by liquid detergent. Second method: Adding agricultural waste with reducing agent in cement, Details of these methods are given in Chapter 6 and 7.

Chapter-6

Effect of Modified Reducing Agent

(With liquid detergent)

Reducing agents were mixed with liquid detergent (EZEE brand, manufactured by Godrej Company) in different proportions to make paste. This paste was dried at 45°C for 15 min. On solidification, liquid detergent form a layer on reducing agent, which protect the reducing agent from air, moisture etc. These modified reducing agents were then mixed with cement samples and the effect of these modified reducing agents on their reducing efficiency, storage stability and various properties of cement was studied and discussed below

6.1 Storage stability

The water soluble Cr(VI) concentration was determined upto 90 days for samples having reducing agents with or without liquid detergent. The results obtained are given in Table 6.1.

Table 6.1: Determination Cr(VI) concentration of samples having reducing agent with or without reducing agent

Sample ID*	**Concentration of Cr (VI) in ppm**					
	0 day	8 days	15 days	30 days	60 days	90 days
Only Cement sample (S1)	25	25.5	25	25.3	25.4	25
Cement with 0.1% FSHH (S2)	15	19	20	21	24	24.5
Cement with 0.1% LDFSHH (S8)	10	11.3	12.4	15	17	19
Cement with 0.5% FSHH (S3)	4	14	15	17	22	24.5
Cement with 0.5% LDFSHH (S9)	6	9	12	14	18	20.2
Cement with 1.0% FSHH (S4)	3	6	9	10	15	23.2
Cement with 1.0% LDFSHH (S10)	ND	ND	ND	1.2	1.8	18.4
Cement with 0.1% SCDH (S5)	6	5.8	10.3	15	19.6	23.8
Cement with 0.1% LDSCDH (S11)	4.5	5.0	7	10	13	15.3
Cement with 0.5% SCDH (S6)	3	6	8.8	9	10.7	12
Cement with 0.5% LDSCDH (S12)	ND	1.4	3	5.5	6.7	8.3
Cement with 1.0% SCDH (S7)	ND	4.4	6	7.6	8.2	9
Cement with 1.0% LDSCDH (S13)	ND	ND	ND	ND	1	1.8

*LDSCDH (Liquid detergent blended $SnCl_2.2H_2O$), LDFSHH (Liquid detergent blended $FeSO_4.7H_2O$), SCDH ($SnCl_2.2H_2O$), FSHH ($FeSO_4.7H_2O$)

From Table 6.1, it has been observed the reducing efficiency of reducing agents. It decreases day by days in samples (**S2, S3, S4** and **S5**), became negligible after 90 days, thus storage stability of reducing agent decreasing. Addition of liquid detergent with reducing agents has enhanced the storage stability upto 90 days. Specially in **S13** sample. It also has been observed that storage stability of cement containing $FeSO_4.7H_2O$ is less as compare to $SnCl_2.2H_2O$.

6.2 Physical and mechanical properties

The result of consistency and setting times for various cement samples having modified reducing additives are indicated in Table 6.2. In ordinary Portland cement sample (**S1**) the consistency was found 27% and the initial and final setting time values are 80 and 120 min respectively. In case of liquid detergent blended cement, consistency increased up to 31.5% and delayed the initial and final setting time up to 187 and 254 min respectively. It means, use of liquid detergent with reducing agent may be delayed the setting time and increases the water demand (it means higher consistency). Increasing the percentage of reducing agent (more than 0.5%) alone or with liquid detergent in cement influenced the physical properties.

The effect of liquid detergent blended reducing agents on the compressive strength of 1:3 blended cement-sand mortars has been determined at 3, 7 and 28 days (IS: 8112-1989). The results are given in Table 6.2. Incorporation of blended additives with different dosages were retarded the initial hydration process, thus lower compressive strength initially (3 days) but latter on (with 28 days) strength of cement mortar improved.

Table 6.2: Standard consistency, setting times and compressive strength of samples

Sample ID*	Standard water consistency	Initial setting time	Final setting time	Compressive strength (MPa)		
	%	min	Min	3 days	7 days	28 days
Only Cement Sample (**S1**)	27	80	120	29.20	38.13	49.53
Cement with 0.1% LDFSHH (**S8**)	27.5	111	143	25.4	33.34	45
Cement with 0.5% LDFSHH (**S9**)	28.6	130	189	22.59	29.50	44.54
Cement with 1.0% LDFSHH (**S10**)	29	139	218	19.65	21.74	38.86
Cement with 0.1% LDSCDH (**S11**)	28	122	153	25	30.56	48.67
Cement with 0.5% LDSCDH (**S12**)	29	144	179	20.45	27.43	51.32
Cement with 1.0% LDSCDH (**S13**)	31.5	187	254	17.56	22.56	52.43

*LDSCDH (Liquid detergent blended $SnCl_2.2H_2O$), LDFSHH (Liquid detergent blended $FeSO_4.7H_2O$), SCDH ($SnCl_2.2H_2O$), FSHH ($FeSO_4.7H_2O$)

6.3. Hydration study

This study was done to understand and verify the effect of modified reducing agent on cement properties such as setting time and compressive strength. Therefore any phase alteration due to use of liquid detergent was investigated by TGA, SEM, XRD and FTIR.

6.3.1 Thermo gravimetric (TGA) studies

The weight loss in different events is given in Table 6.3 and Figures 6.1-6.5, first weight loss occurred through dehydration, which increased in blended samples (**S7, S10** and **S13**) except sample **S4**. The second weight loss through dehydroxylation in blended cement samples (**S4, S7** and **S10**) showed decrease and this loss was not observed in **S13** (as per Figure 6.6). In **S13**, one extra peak was observed at 272.47˚C. Third weight loss peak due to carbonation increased in two samples (**S4** and **S7**) whereas it decreased in samples (**S13**). This peak was absent in **S7**.

Table 6.3: Peaks identified in TGA results and their calculated content in the samples

About Peaks	**Mass loss (%) in Samples**#				
	OPC Cement (**S1**)	Cement with 1% FSHH (**S4**)	Cement with 1% LDFSHH (**S10**)	Cement with 1% SCDH (**S7**)	Cement with 1% LDSCDH (**S13**)
Dehydration* (Up to 300˚C)	2.09 (87.72˚C)	1.98 (83.62˚C)	4.43 (96.37˚C)	2.6 (93.63˚C)	2.4 (89.21˚C) 6.8 (272.47˚C)
Dehydroxylation (420-460˚C)	17.42 (430.1˚C)	11.69 (420.5˚C)	15.89 (456˚C)	12.7 (431.7˚C)	-
Decarbonation (660-700˚C)	17.06 (674.5˚C)	22.52 (689.9˚C)	-	21.01 (697.5˚C)	14.19 (676.29˚C)

***** Removal of water from hydrated phases (like C-S-H and ettringite phases), capillary pore water, interlayer water and adsorbed water, # LDSCDH (Liquid detergent blended $SnCl_2.2H_2O$), LDFSHH (Liquid detergent blended $FeSO_4.7H_2O$), SCDH ($SnCl_2.2H_2O$), FSHH ($FeSO_4.7H_2O$)

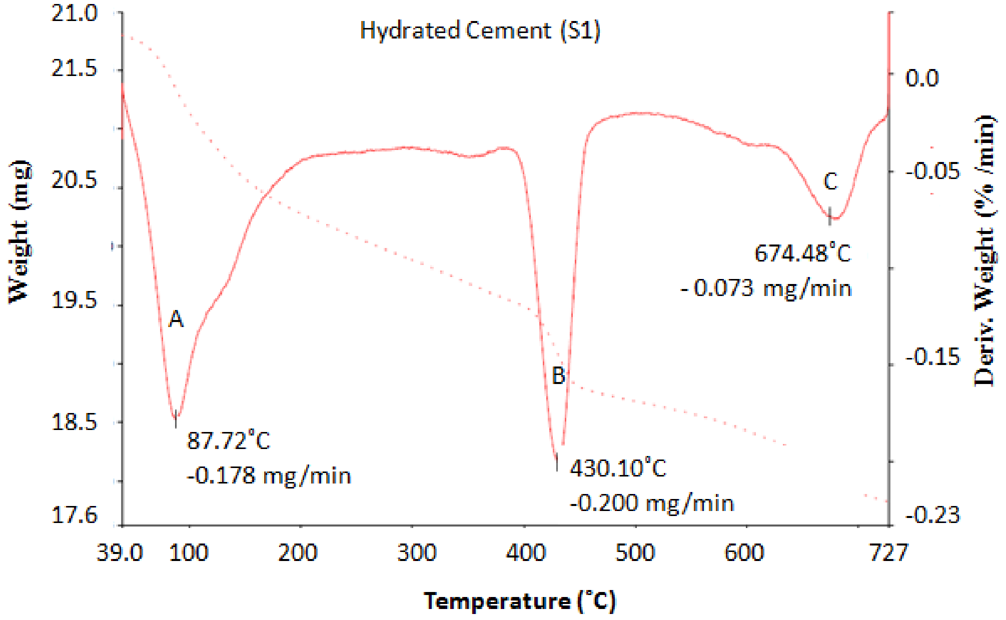


Figure 6.1: TGA curve of hydrated OPC cement sample (**S1**, as control)

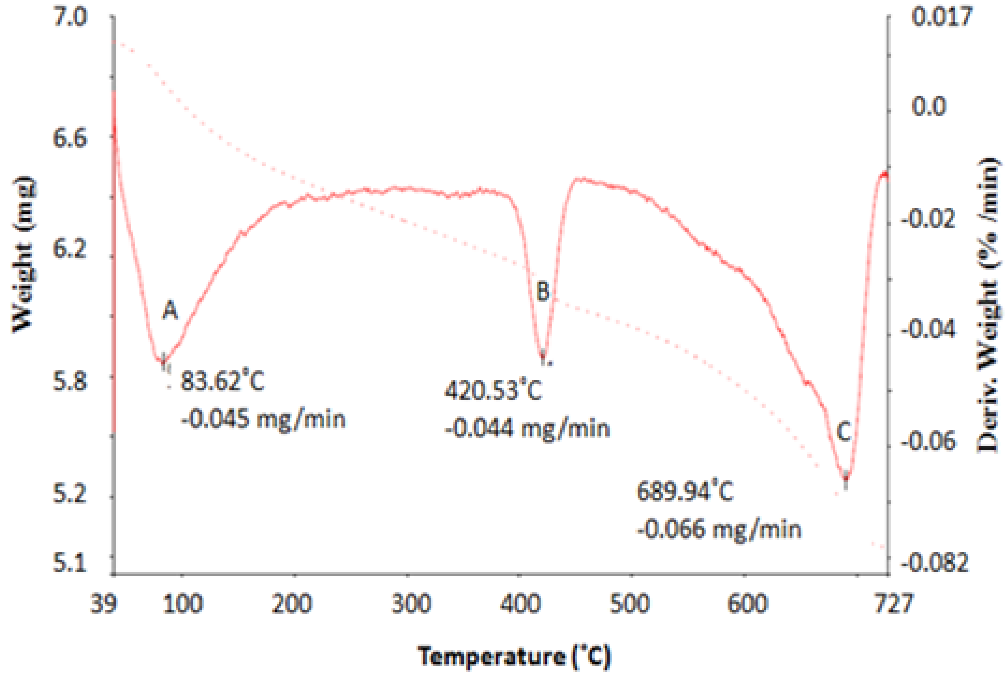


Figure 6.2: TGA curve of hydrated cement with 1% $FeSO_4.7H_2O$ (**S4**)

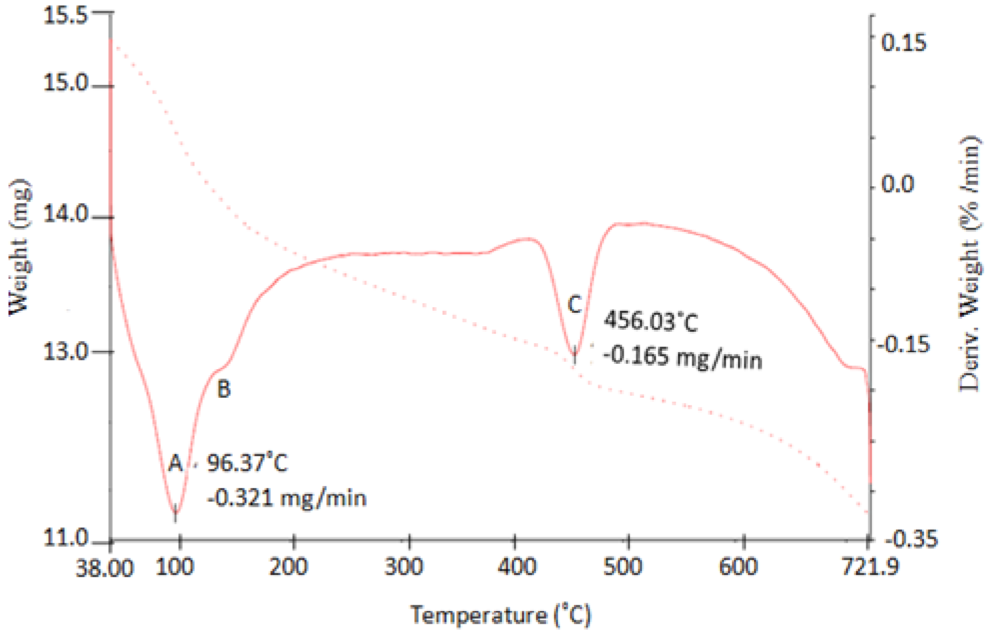


Figure 6.3: TGA curve of hydrated cement with 1% Liquid detergent blended $FeSO_4.7H_2O$ (**S10**)

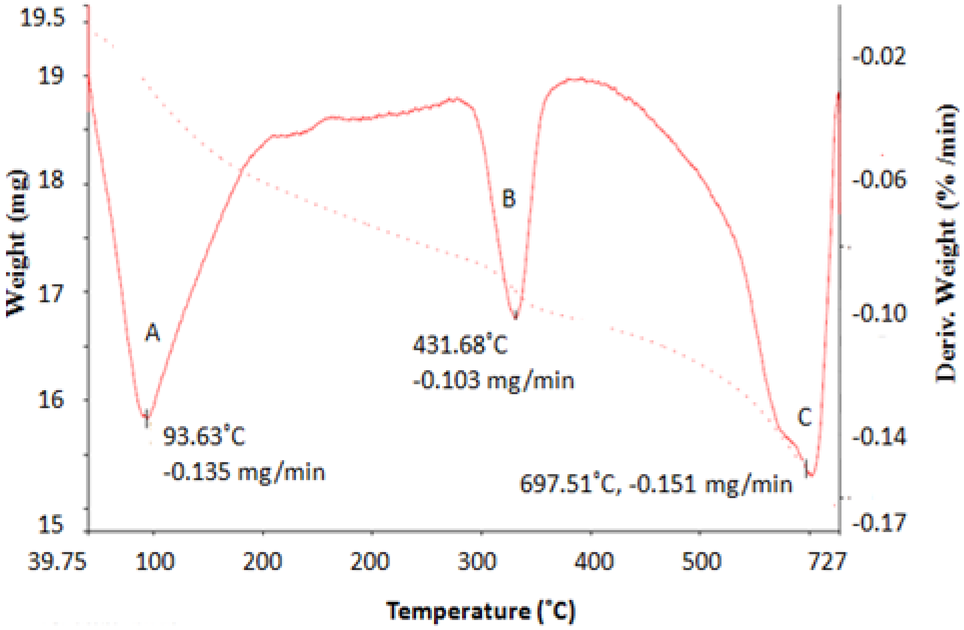


Figure 6.4: TGA curve of hydrated cement with 1% $SnCl_2.2H_2O$ (**S7**)

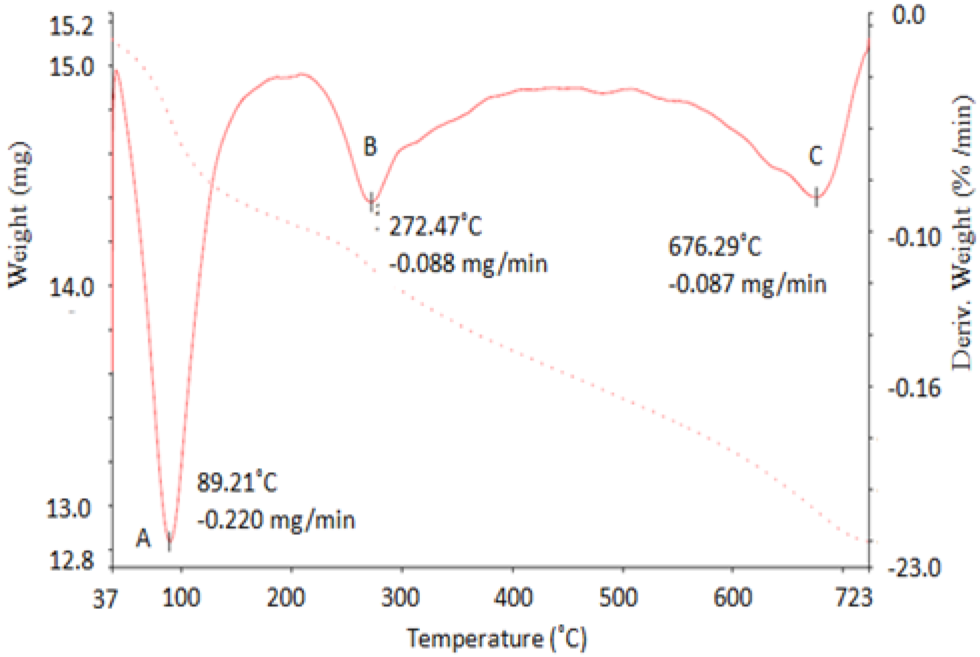


Figure 6.5: TGA curve of hydrated cement with 1% Liquid detergent blended $SnCl_2.2H_2O$ (**S13**)

6.3.2 Scanning electron microscopy (SEM) studies

Microscopic studies were carried out with five 28 days hydrated samples (**S1, S6, S7, S12** and **S13**). The SEM images of three samples (**S1, S4** and **S7**) are already described in chapter 5. SEM images of **S10** and **S13** is given in Figure 6.6 and 6.7 respectively. Calcium silicate hydrate (C-S-H), Ettringite phases and Calcium hydroxide (CH) were found in SEM images which are responsible for cement's hardening. Amorphous C-S-H phase was observed as light color which is the main product of cement hydration [285-286]. Needle or fibers formation has been seen in sample **S7** and **S13**. Well hydrated solid surface was seen in samples **S1, S4** and **S7**. But the samples **S10** and **S13** showed immaturity of hydration at 28 days. In the image of sample **S13**, some cylindrical crystals were also seen, which are not found in other samples at all. It means reducing agent $SnCl_2.2H_2O$ might be reacted with librated lime during hydration and formed cylindrical structure. Whereas in samples **S1, S4, S7** and **S10**, hexagonal plates were observed, due to calcium hydroxide, it indicates which was not consumed by reducing agent ($FeSO_4.7H_2O$). Above mentioned views agrees with the TGA results.

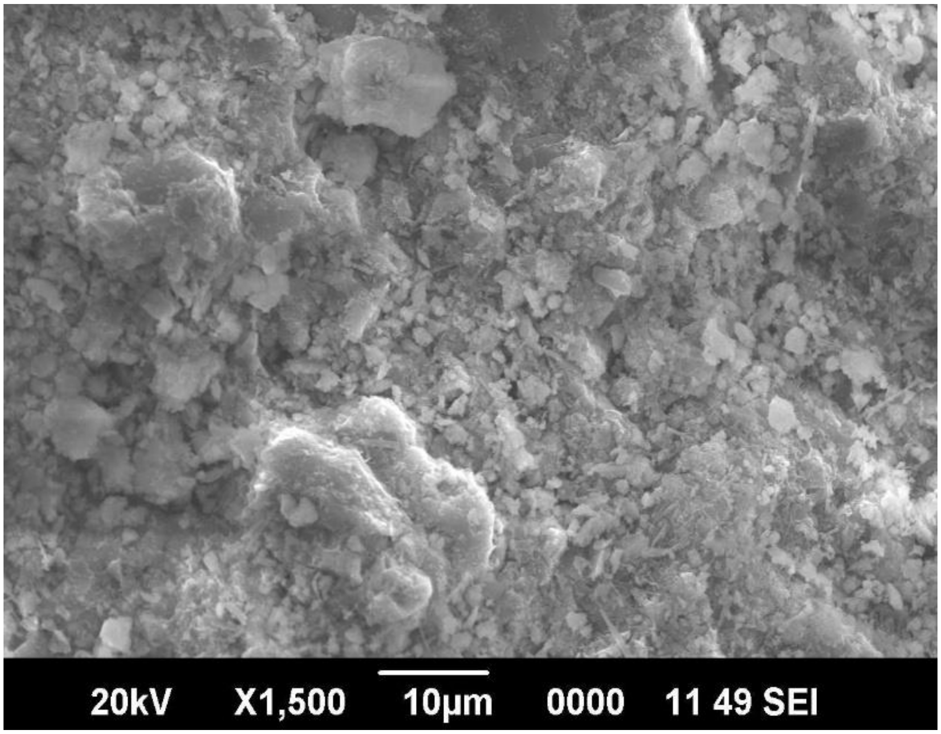


Figure 6.6: SEM morphology of hydrated cement with 1% Liquid detergent blended $FeSO_4.7H_2O$ (**S10**)

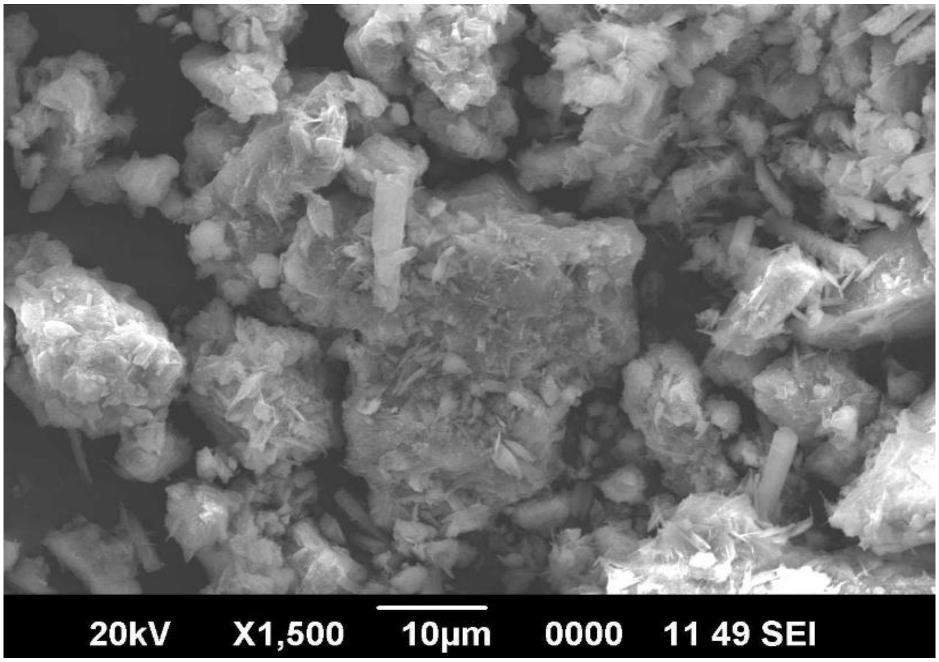


Figure 6.7: SEM morphology of hydrated cement with 1% Liquid detergent blended $SnCl_2.2H_2O$ (**S13**)

6.3.3 X-Ray Diffraction studies

Figure 6.8-6.9 and 5.24, 5.26 and 5.28 (from above chapter) show the XRD image of these 28 days hydrated cement samples of **S10, S13 and S1, S4** and **S7**. The important peaks such as calcium hydroxide (CH), Ettringite (E) and mineral phases (C_3S, C_2S etc) with their intensity are given in Table 6.4. The Peaks of mineral phases indicate not only alite and belite phase but it shows about the progress of C-S-H phase [281-282]. The total intensity of calcium hydroxide (CH) in OPC sample (**S1**) is higher than another reducing additive blended cement samples. Low intensity of calcium hydroxide formation in additive blended samples indicates about retardation in hydration process yet few blended samples showed slightly higher compressive strength. The possible reasons for this might be the formation of new phase (as ettringite form) or acceleration of C-S-H phase formation [1]. The intensity of Portland cement without additives showed more hydration results which is conformity with TGA and SEM. An ettringite phases (from E1 to E4) were seen in blended cement samples also. Hydrated cement samples show an ettringite phase (at $2\theta = 9.5^\circ$), this phase indicating about participation of iron during cement hydration [4]. Unreacted silica (at $2\theta = 22.5^\circ$) was found in cement sample (**S13**) having 1% liquid detergent blended $SnCl_2.2H_2O$. Decreasing order of librated calcium hydroxide (CH) during hydration is as **S1>S4>S7>S10>S13**. The sample **S13** showed very less amount of calcium hydroxide. The possible reasons for this can be (i) Liquid detergent blended tin chloride was lowered the decomposition of tri calcium silicate into dicalsium silicate and calcium hydroxide. (ii) Second reason could be, lime was consumed completely by reducing agent. Towards of mineral phase (C_3S/C_2S), the decreasing order of unreacted calcium silicate is given as: **S4>S1>S13>S7>S10**. Thus the sample **S7** and **S10** has very less quantity of mineral phases (alite and belite) which supports about better hydration it means maximum quantity of minerals phase would be converted into hydrated phases. Hence, it is not cleared from above XRD results that high amount of calcium hydroxide formation is an effective reason for better hydration.

Table 6.4: XRD results shows intensity of different phases in Samples

Phases Identity	**Two Theta**	**Intensity (Counts)**				
		S1	**S4**	**S10**	**S7**	**S13**
Calcium Hydroxide (CH)	18.3	1260	1400	310	1160	85
	34.6	1860	1560	625	1500	440
	47.5	775	650	240	600	175
Total CH	-	**3895**	**3610**	**1175**	**3260**	**700**
C_3S	29.7	710	750	438	500	655
C_2S	32.4	700	750	355	700	605
Total unhydrated CS		**1410**	**1500**	**793**	**1200**	**1250**
Quartz (Q)	22.0	-	-	-	-	110
Etringite, E1	9.5	200	250	95	200	384
E2	11.5	-	-	65	400	118
E3	16.5	-	-	86	-	172
E4	23.5	-	-	101	-	134
Total E		**200**	**250**	**347**	**600**	**808**

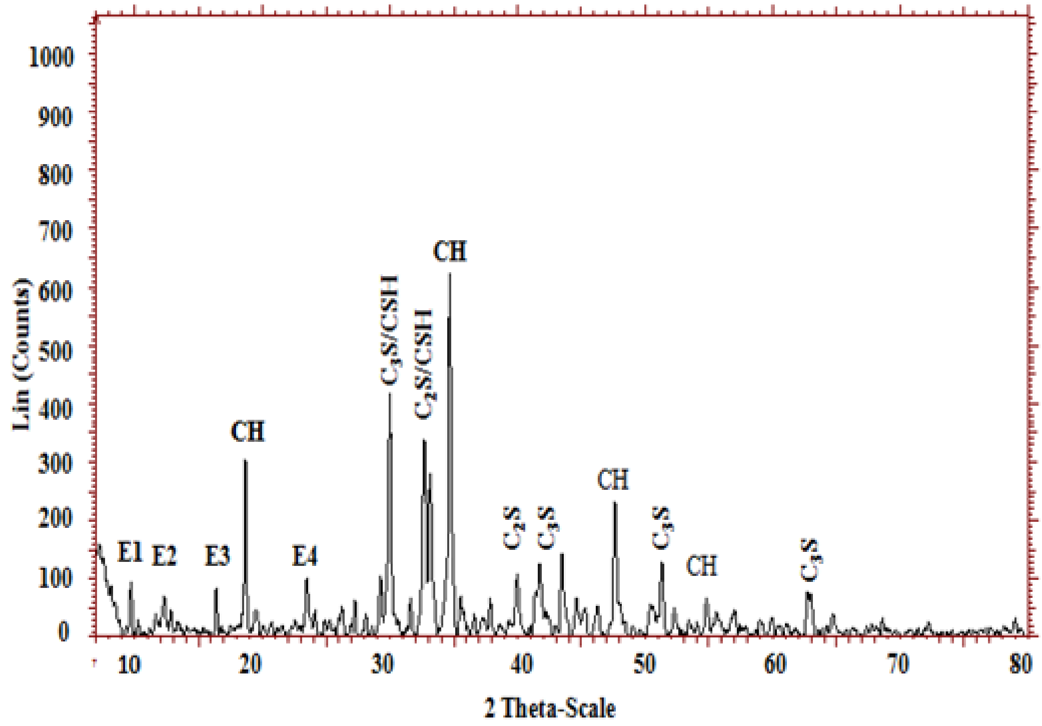


Figure 6.8: XRD spectra of hydrated cement with 1% Liquid detergent blended $FeSO_4.7H_2O$ (**S10**)

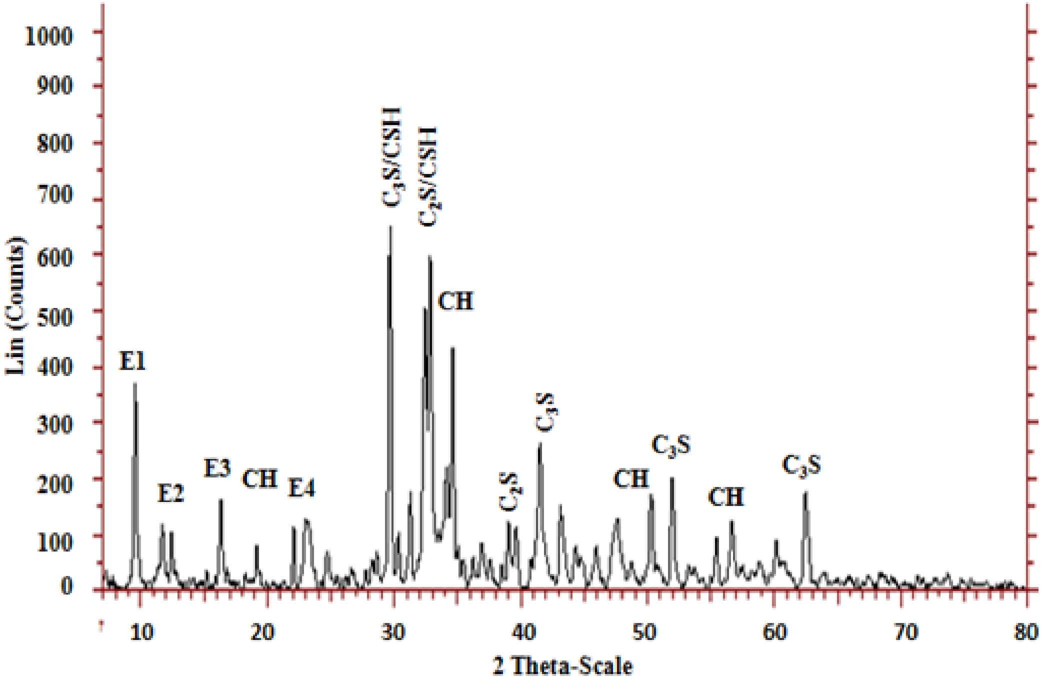


Figure 6.9: XRD spectra of hydrated cement with 1% Liquid detergent blended $SnCl_2.2H_2O$ (**S13**)

6.3.4 Fourier-transform infrared spectroscopy (FTIR study)

Silicate and hydrate linkage (Si-O and O-H) in cement samples can be predicted with the help of FTIR spectroscopy. As per Figure 5.3, Anhydrate OPC showed a sharp peak at 3789 cm^{-1} due to O-H stretching (from $Ca(OH)_2$) and carbonate peak appeared at 1426.4 cm^{-1}, 716.6 cm^{-1} and 875.7 cm^{-1} [275-277]. The presence of Cr(VI) in anhydrous OPC sample is also appeared at carbonate peak, both peaks are merged to each other therefore they are appeared at 875.7 [81, 276]. The week band at 654.8 cm^{-1} are due to the presence of SO_4^{-2} ion. The bands at 935, 1002.1 and 1100.4 cm^{-1} are appeared due to Si-O asymmetric stretching vibration of calcium silicate and bending vibration of aluminates silicates is also observed at 518 cm^{-1}. According to Figures 5.4, 5.6 and 5.8 and 6.10, 6.11 and Table 6.5, the infrared spectrum of hydrated samples shows wave number shifting in the silicate region from 935 to 1100 cm^{-1} as well as hydrated crystalline water region is shifting from 3425 to 3488 cm^{-1}. Shifting in both regions (Si-O and O-H) is confirming about hydration. As per Table 6.5, the silicates polymerization (Si-O-Si) and crystalline water (O-H) formation in hydrated samples do not correlate to each other, it means besides silicate polymerization few extra crystalline phases might be formed which makes differences in peak's wave numbers. Free lime was consumed completely in samples S10 and S13; it means additives might be reacted with free lime. Hydration of cement samples **S1, S4, S10, S7** and **S13** was insured by appearance of broad peak of O-H stretching (water of crystallization) in the range 3425-3488 cm^{-1}. During hydration reactive silica get converted in C-S-H gel form (polymerized form), formation of this form was confirmed by disappearance of Si-O peak in the range, 935-1100 cm^{-1} in the hydrated sample except sample **S13**.

Table 6.5: FTIR results shows frequencies shift (cm^{-1}) of different phases in Samples

Important Peaks	Sample ID					
	OPC	S1	S4	S10	S7	S13
O-H stretching from $Ca(OH)_2$ **(3600-3800 cm^{-1})**	3789	-	-	-	-	-
O-H stretching from crystallize water **(3250-3580 cm^{-1})**	-	3488	3435.5	3439.19	3480.6	3434.37
Silicate peak (Si-O stretching) **(919-1200 cm^{-1})**	935 1002.1 1100.4	950 - -	985 - 1100	970.23 - 1112.96	992 - -	928.76 1007.84 1100.43

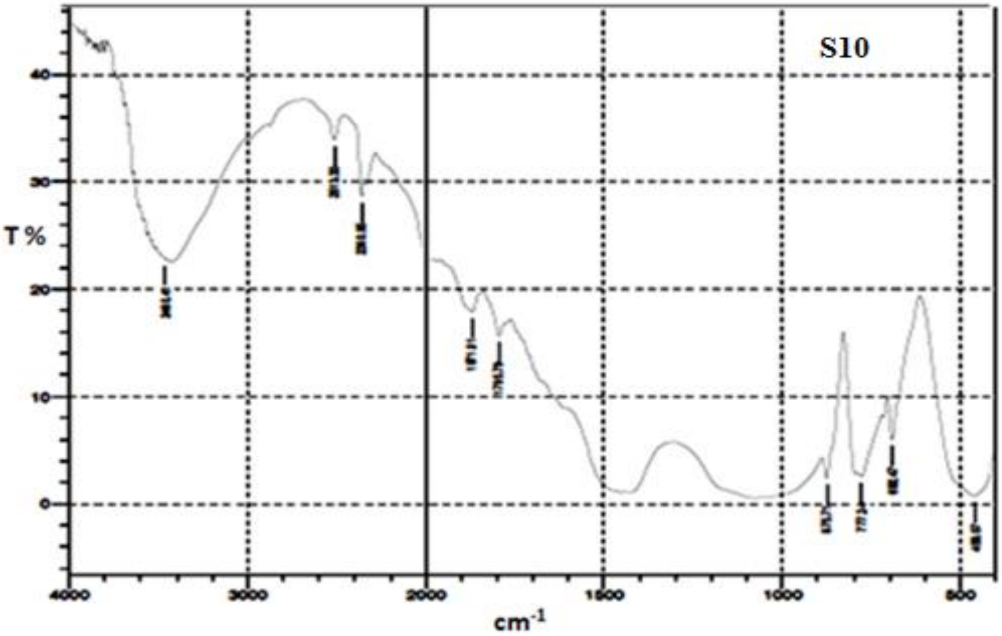


Figure 6.10: FTIR spectra of hydrated cement with 1% Liquid detergent blended $FeSO_4.7H_2O$ (**S10**)

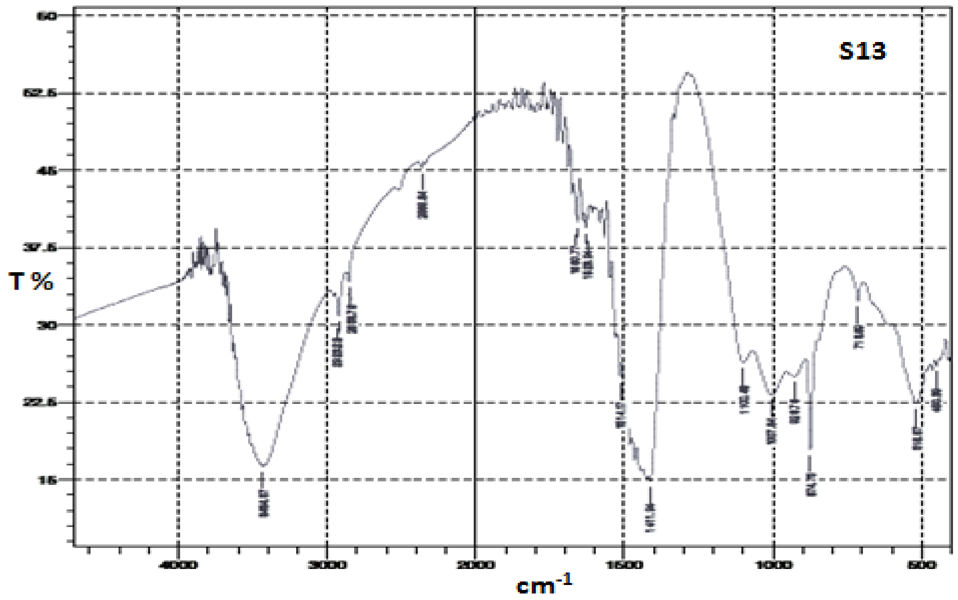


Figure 6.11: FTIR spectra of hydrated cement with 1% Liquid detergent blended $SnCl_2.2H_2O$ (**S13**)

From the above discussion, it has been concluded that reducing agent along with liquid detergent can be used to enhance the storage stability as well as reduction efficacy of agents. However, in case of hydration, both reducing agent and liquid detergent can be used as best retarding agent and workability enhancing agent. Out of these, reducing agent along with liquid detergent was good easy to handle. Thus enhance workability was good. Such types of agent can be suitable in hot condition as hydration started earlier. Therefore use of these reducing agents along with liquid detergent would be better choice for hot weather conditions. This limitation can be eliminated by adding amorphous silica to cement

In next chapter we will study about new reducing composition along with RHA and RTA. This new composition will be beneficial for industries and consumers. Use of RHA and RTA ash in cement can enhance the silicate polymerization (C-S-H), decreases the cost of cement by utilization of agricultural waste product, decreases the air dust pollution on stormy air, enhance the storage stability and reduction efficacy of reducing agent because it consumed the lime. If free lime is available them lime reacted with reducing agent specially stannous chloride and was converted into stannic form so reduction efficacy was lost.

Chapter-7

Effect of RHA-RTA along with reducing agents

To overcome the problems of storage stability, hydration process and compressibility, six new cement compositions (blended cement) of Ordinary Portland Cement (OPC) with agricultural wastes (RHA/RTA) and chromate reducing additives ($FeSO_4.2H_2O$ or $SnCl_2.2H_2O$) have been prepared and effect of these compositions on leachability of toxic Cr(VI) content, standard water consistency, setting time, compressive strength and hydration process has been carried out and compared with samples **S1-S7**. The hydration of these compositions has been ensured by FTIR, TGA/DTA, XRD and SEM.

7.1 Leachability

Leaching of Cr(VI) was tested by standard method as well as in-house developed method for nineteen samples (**S1-S7** and **S14-S25**) and then results are presented in Table 7.1 and 7.2 respectively. It has been observed that leaching of Cr(VI) decreases with increase in curing time. This decrease in hexavalent chromium concentration may be due to more hydration and densification of microstructure, which results in an increase in compressive strength [287]. In pure OPC cement (**S1**) concentration of Cr(VI) in leachate is maximum. The addition of reducing agents ($FeSO_4.7H_2O$ and $SnCl_2.2H_2O$), decreases the concentration of Cr(VI) in leachate considerably, but still not able to remove hexavalent chromium completely due to the instability of ferrous and stannous ion in aqueous medium. It has also been reported that leaching of immobilized Cr(VI) from cement phases takes more time [133]. The concentration of hexavalent chromium is found to be more in samples (**S1, S2, S3** and **S5**) at 28 days where only reducing agents are added except sample **S1** as compare to other samples (**S14-S25**), where either RHA or RHT or both are added.

Amorphous silica (from rice husk ash and rice tiller ash) in Samples (**S14-S25**) replaced the chromate from cement phases (as calcium chromate etc., $CaCrO_4 + SiO_3^{-2} \rightarrow CaSiO_3 + CrO4^{-2}$ and $CrO_4^{-2} + Fe^{+2}/Sn^{+2} \rightarrow Cr^{+3}$) which may reduce Cr(VI) during initial hydration. It is also possible that amorphous silica reacts with lime and produce hardened cement phases (C-S-H), which leads to the densification of microstructure ($Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3.H_2O$) capable of stabilizing the Cr(VI) [17].

Table 7.1: Leached values of Cr (VI) from Solidified Samples at 28 days (standard method)

Sample ID	Leachate Cr(VI)	Sample ID	Leachate Cr(VI)	Sample ID	Leachate Cr(VI)
Only Cement sample (**S1**)	3.0	Cement with 0.1% FSHH+ 10%RHA (**S14**)	ND	Cement with 0.5% FSHH+5 %RHA+5%RTA (**S21**)	ND
Cement with 0.1% FSHH (**S2**)	2.5	Cement with 0.5% FSHH+ 10%RHA (**S15**)	ND	Cement with 1.0% FSHH+ %RHA+5%RTA (**S22**)	ND
Cement with 0.5% FSHH (**S3**)	2.0	Cement with 1.0% FSHH+ 10%RHA (**S16**)	ND	Cement with 0.1% SCDH+5%RHA+5%RTA (**S23**)	ND
Cement with 1.0% FSHH (**S4**)	ND	Cement with 0.1% SCDH+10%RHA (**S17**)	ND	Cement with 0.5% SCDH+5%RHA+5%RTA (**S24**)	ND
Cement with 0.1% SCDH	2.0	Cement with 0.5% SCDH+10%RHA (**S18**)	ND	Cement with 1.0% SCDH+5%RHA+5%RTA (**S25**)	ND

(**S5**)					
Cement with 0.5% SCDH (**S6**)	ND	Cement with 1.0% SCDH+10%RHA (**S19**)	ND		
Cement with 1.0% SCDH (**S7**)	ND	Cement with 0.1% FSHH+ 5%RHA+5%RTA (S**20**)	ND		

Table 7.2: Leached values of Cr (VI) from Solidified Samples (In-house developed method)

Sample Details	**Sample ID**	**Leachate concentration (in ppm)**				
		3 days	7 days	28 days	60 days	90 days
Only Cement sample	**S1**	12	4	6	ND	ND
Cement with 0.1% FSHH	**S2**	7	3.5	2	ND	ND
Cement with 0.5% FSHH	**S3**	5.2	3	ND	ND	ND
Cement with 1.0% FSHH	**S4**	4	2	ND	ND	ND
Cement with 0.1% SCDH	**S5**	4	2.3	ND	ND	ND

Cement with 0.5% SCDH	**S6**	3.1	1.5	ND	ND	ND
Cement with 1.0% SCDH	**S7**	2	ND	ND	ND	ND
Cement with 0.1% FSHH+ 10%RHA	**S14**	4.7	2.4	ND	ND	ND
Cement with 0.5% FSHH+ 10%RHA	**S15**	3.5	2	ND	ND	ND
Cement with 1.0% FSHH+ 10%RHA	**S16**	3	2	ND	ND	ND
Cement with 0.1% SCDH+10%RHA	**S17**	3.2	2.5	ND	ND	ND
Cement with 0.5% SCDH+10%RHA	**S18**	2.3	1.8	ND	ND	ND
Cement with 1.0% SCDH+10%RHA	**S19**	2	ND	ND	ND	ND
Cement with 0.1% FSHH+ 5%RHA+5%RTA	**S20**	4	3	ND	ND	ND
Cement with 0.5% FSHH+5 %RHA+5%RTA	**S21**	2.4	1.6	ND	ND	ND
Cement with 1.0% FSHH+ %RHA+5%RTA	**S22**	2	2	ND	ND	ND
Cement with 0.1% SCDH+5%RHA+5%RTA	**S23**	4.2	3	ND	ND	ND
Cement with 0.5% SCDH+5%RHA+5%RTA	**S24**	3.2	nd	ND	ND	ND
Cement with 1.0% SCDH+5%RHA+5%RTA	**S25**	3	ND	ND	ND	ND

7.2 Standard consistency, Setting time and Compressive strength

The effects of agricultural wastes (RHA and RTA) along with reducing agent on standard water consistency and setting times of OPC cement in Table 7.3. Standard consistency of pure OPC cement was found to be 27% with initial and final setting time of 80 min and 120 min respectively (Table 5.2). In all the blended samples (**S14-S25**) an increase in standard consistency and initial and final setting time has been observed. Use of rice husk ash along with reducing additives in cement samples enhance the compressive strength as well as improved the initial and final setting time as compare to use of only reducing additives. The compressive strength of cement samples depends on amount of $Ca(OH)_2$ or calcium silicate hydrate phase and was effected by the use of reducing agents and agricultural waste rich in amorphous silica. The compressive strength of **S16** (with 1% $FeSO_4.7H_2O$ and 10% RHA) is found to be higher than other samples. In **S18** and **S20**, initial strength is less, but increased up to 28 days. Increase in strength up to 28 days is due to the formation of monocarbonate; Ettringite phases as well as amorphous silica (from RHA and RTA) might be reacted with free lime of liberated calcium hydroxide during hydration and formed C-S-H phases [17]. From Table 7.3, it can be concluded that addition of rice husk ash and rice tiller ash has improved the initial hydration and the compressive strength of cement.

Table 7.3: Standard consistency, setting times and compressive strength of samples

Sample ID	Standard water consistency	Initial setting time	Final setting time	Compressive strength		
	%	Min	Min	3 days	7 days	28 days
Cement with 0.1% FSHH+ 10%RHA (**S14**)	29	129	175	24.50	32.34	50.23
Cement with 0.5% FSHH+ 10%RHA (**S15**)	29.5	130	178	24	33.43	49.25

Cement with 1.0% FSHH+ 10%RHA (**S16**)	30	132	189	25.33	33.20	54.03
Cement with 0.1% SCDH+10%RHA (**S17**)	31	150	198	22.34	30.5	51.73
Cement with 0.5% SCDH+10%RHA (**S18**)	31.4	175	234	20.30	30	50.45
Cement with 1.0% SCDH+10%RHA (**S19**)	32	145	255	21.59	29.57	49.94
Cement with 0.1% FSHH+ 5%RHA+5%RTA (**S20**)	29	110	160	20.43	29.44	47.45
Cement with 0.5% FSHH+ 5 %RHA+5%RTA (**S21**)	30	118	161	21.49	32.65	50.32
Cement with 1.0% FSHH+ %RHA+5%RTA (**S22**)	30.5	121	165	25.67	36.46	53.93
Cement with 0.1% SCDH+5%RHA+5%RTA (**S23**)	29.5	160	210	26.34	37.45	49.67
Cement with 0.5% SCDH+5%RHA+5%RTA (**S24**)	30.2	169	245	25.98	33.67	50
Cement with 1.0% SCDH+5%RHA+5%RTA (**S25**)	31	175	305	24.89	34.76	50.80

7.3 Hydration studies

From the leachability test, setting time and compressive strength studies, it has been observed that addition of reducing agents alone or in combination with RHA and RTA has affected the microstructure of cement thus effected its physical properties. The details of phase alteration during hydration of cement samples are studied using TGA, XRD and SEM.

7.3.1 Thermo gravimetric Analysis (TGA)

TGA curves of seven uncured hydrated cement samples (**S1, S4, S7, S16, S19, S22** and **S25**) are given in Figure 5.9, 5.11, 5.13 and 7.1-7.4. The three events has been recognized in TGA curves: i) initial weight loss due to dehydration of capillary pore water, interlayer water and adsorbed water in the temperature range 70-93˚C, which generally appear near 100˚C [288]. The shift in the curve indicated phase change, a higher shift for crystalline phase's formation and lower shift for amorphous phase's formation [289]. ii) Weight loss in the temperature range 420-462˚C due to dehydration of $Ca(OH)_2$ and iii) some weight loss due to decomposition of $CaCO_3$ in the range of 670 to 700˚C. All the three events are endothermic [288, 289].

Strength of OPC cement is mainly due to $Ca(OH)_2$ and calcium silicate hydrate. The amount of $Ca(OH)_2$ in a given sample can be estimated from weight loss in TG curve. The weight loss of the samples during various events in TGA is given in Table 7.4. It has been observed from above experiment that weight loss from the calcium hydroxide decomposition (at 420-462˚C) is less in **S4** and **S7**, which indicated the lower content of $Ca(OH)_2$. Reducing agents 1.0% $FeSO_4.7H_2O$ (**S4**) and 1.0% $SnCl_2.2H_2O$ (**S7**) might be reacted with $Ca(OH)_2$ to form ettringite phases, thus reduce $Ca(OH)_2$ content and resulted into a delay in the hydration process. To enhance the initial hydration process, along with reducing agents, RHA and RTA have been added in samples (**S16, S19, S22** and **S25**). Amorphous silica of RHA and RTA reacted with $Ca(OH)_2$ to form calcium silicate (C_2S and C_3S), which on hydration produced $Ca(OH)_2$ and calcium silicate hydrate phase [53, 288, 289]. Increase in weight loss of $Ca(OH)_2$ content in samples (**S16, S19, S22** and **S25**) in TGA studies supports an increase in hydration as compare to **S4** and **S7**.

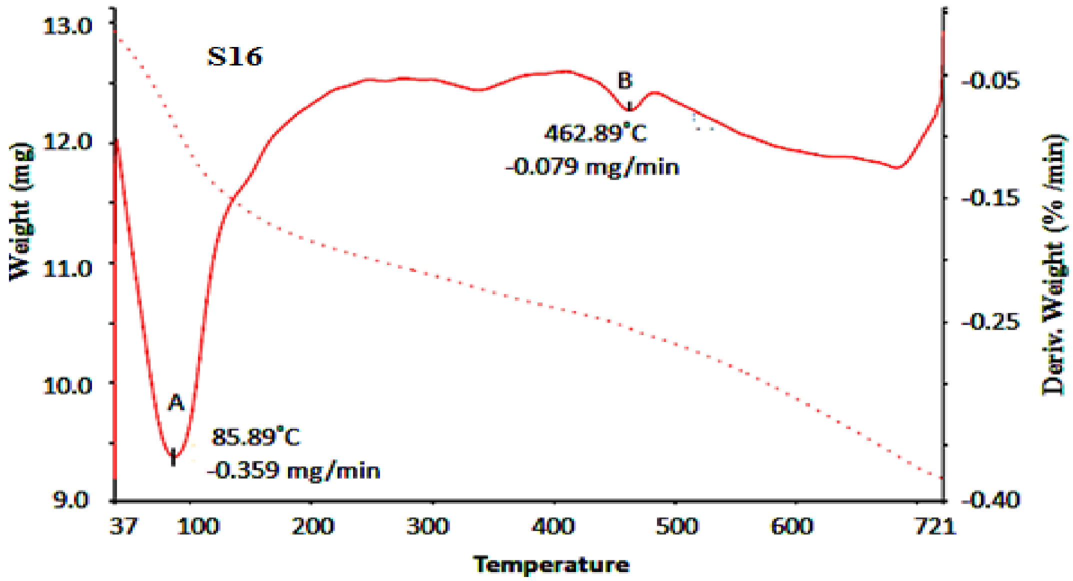


Figure 7.1: TGA curve of hydrated cement with 1.0% FSHH+ 10%RHA (**S16**)

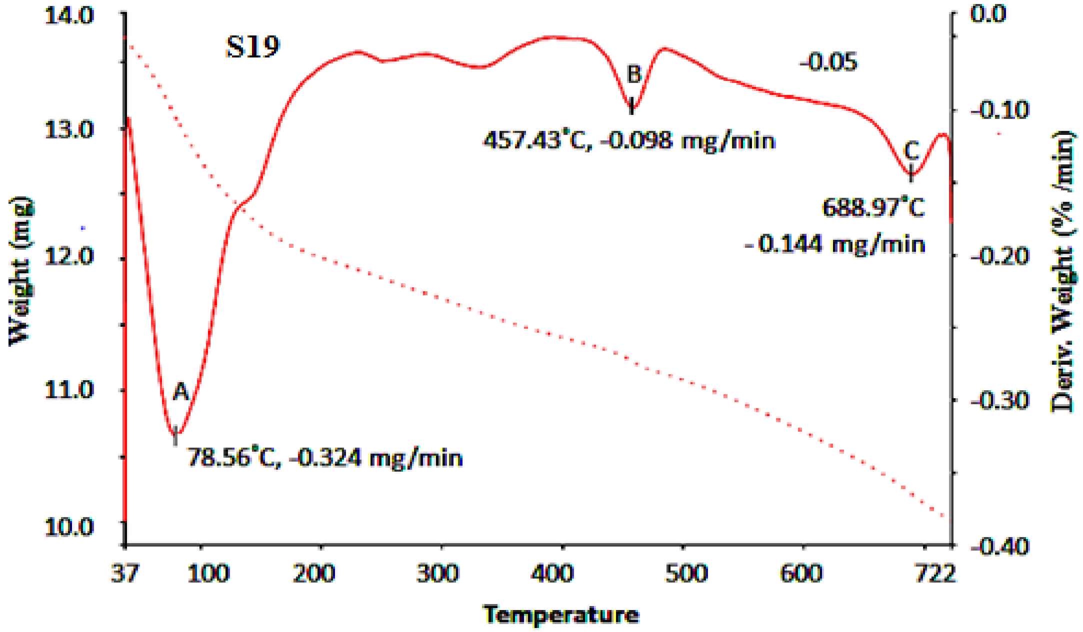


Figure 7.2: TGA curve of hydrated cement with 1.0% SCDH+10%RHA (**S19**)

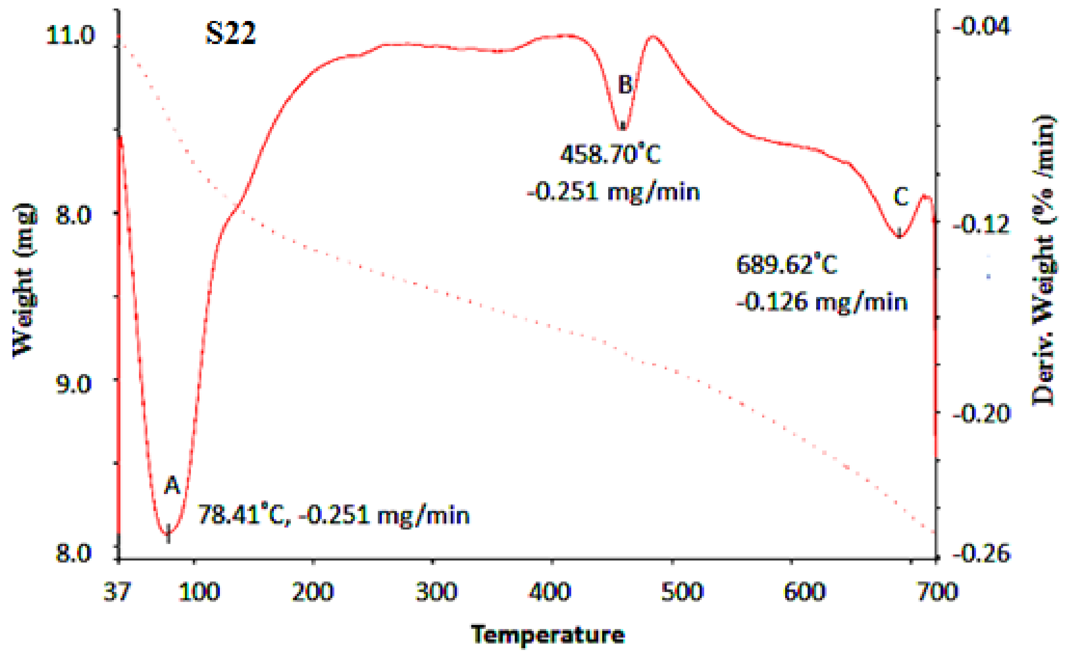


Figure 7.3: TGA curve of hydrated cement with 1.0% FSHH+ %RHA+5%RTA (**S22**)

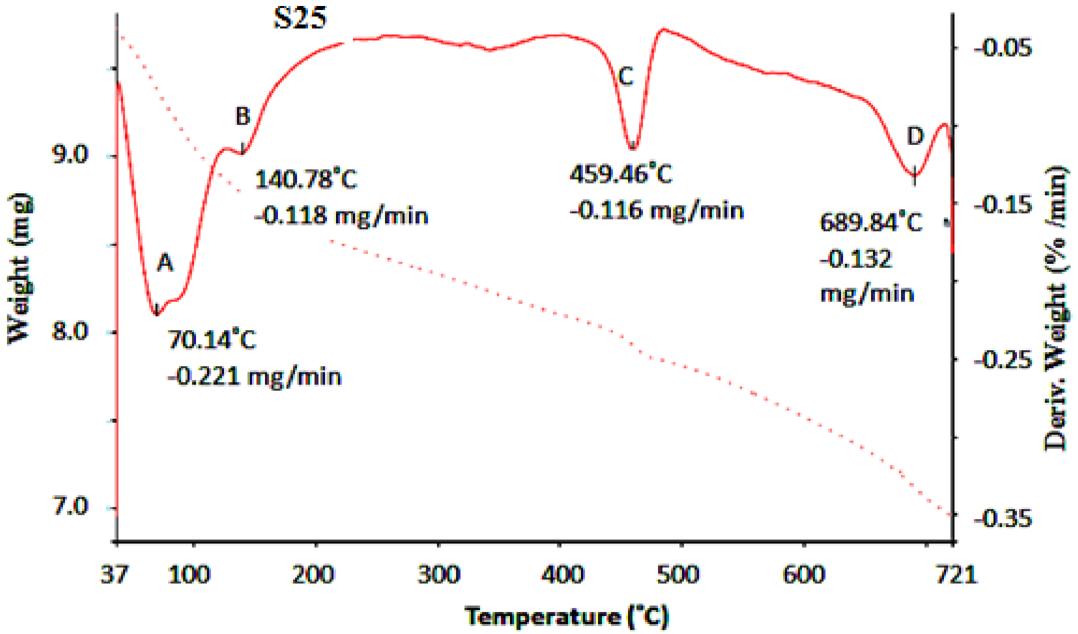


Figure 7.4: TGA curve of hydrated cement with 1.0% SCDH+5%RHA+5%RTA (**S25**)

Table 7.4: Peaks identified in TGA results and their calculated content in the samples

Peak	**Temp (˚C)**	**Mass loss (%)**						
		S1	**S4**	**S7**	**S16**	**S19**	**S22**	**S25**
Dehydration*	Up to 300	2.09 (87.72˚C)	1.98 (83.62˚C)	2.6 (93.63˚C)	5.87 (85.89˚C)	4.4 (78.56˚C)	4.4 (78.4˚C)	3.6 (70.14˚C)
		-	-	-	11.2 (140.2˚C)	9.9 (140.3˚C)	9.4 (140.7˚C)	9.8 (140.8˚C)
Dehydroxylation	420-460	17.42 (430.1˚C)	11.69 (420.5˚C)	12.7 (431.7˚C)	19.19 (462.9˚C)	17.99 (457.4˚C)	17.14 (458.7˚C)	18.5 (459.5˚C)
Decarbonation	660-700	17.06 (674.5˚C)	22.52 (689.9˚C)	21.01 (697.5˚C)	27.65 (689.6˚C)	25.38 (688.9˚C)	25.43 (689.6˚C)	26.8 (689.8˚C)
Total loss		36.57	36.19	36.31	63.91	57.67	56.37	58.7

* Removal of water from hydrated phases (like C-S-H and ettringite phases), capillary pore water, interlayer water and adsorbed water

7.3.2 Scanning Electron microscopy (SEM)

The changes in microstructure of 28 days hydrated cement samples prepared by adding either reducing agents only (**S4** and **S7**) or reducing agents in combination with RHA and RTA (**S16, S19, S22** and **S25**) has been observed using scanning electron microscopy (SEM) techniques. The strength of cement depends on the formation of calcium silicate hydrate (C-S-H), ettringite phase and calcium hydroxide [284, 290]. Amongst these, amorphous C-S-H gel (light color) is the main hydration product. SEM image of pure OPC (**S1**) showed high amounts of amorphous C-S-H gel, but the lack of curing had produced cracks on its surface. High lime content in **S1** was also confirmed by the SEM image (Figure 5.14) and EDX image (Figure 5.15) and, where the ratio of calcium to silica is 7.534. A decrease in formation of C-S-H gel phase has been observed in **S4** and **S7** (Figures 5.18 and 5.22), indicating less hydration product formation. High % age of C supports carbonation in **S4** (Figure 5.19), which is in conformity with TGA studies however hydrated rigid surface could be seen in **S7** (Figure 5.22). In **S4** the decomposition of C_3S into C_2S and $Ca(OH)_2$ take place which stopped the further reaction of librated $Ca(OH)_2$ with available silica. Thus librated $Ca(OH)_2$ promotes the carbonation and delyed the C-S-H formation. Available silica in cement become crystalline due to high temp condition in cement manufacturing. Therefore such samples demanded reactive silica i.e amorphous silica formed by burning rice husk ash and tiller ash at below 700°C.

Increase in C-S-H gel phase has been observed in **S16, S19, S22** and **S25** (Figure 7.5 – 7.8), where RHA and RTA have been added along with reducing agents. Needle or fiber formation has been observed in sample **S16** and **S19** (Figure 7.5 and 7.6); however, three dimensional honeycomb structures are present in **S22** (Figure 7.7). SEM image of **S25** (Figure 7.8) indicates decomposition of tricalcium silicate phases into dicalcium silicate and a hexagonal plate of portlandite (Calcium hydroxide).

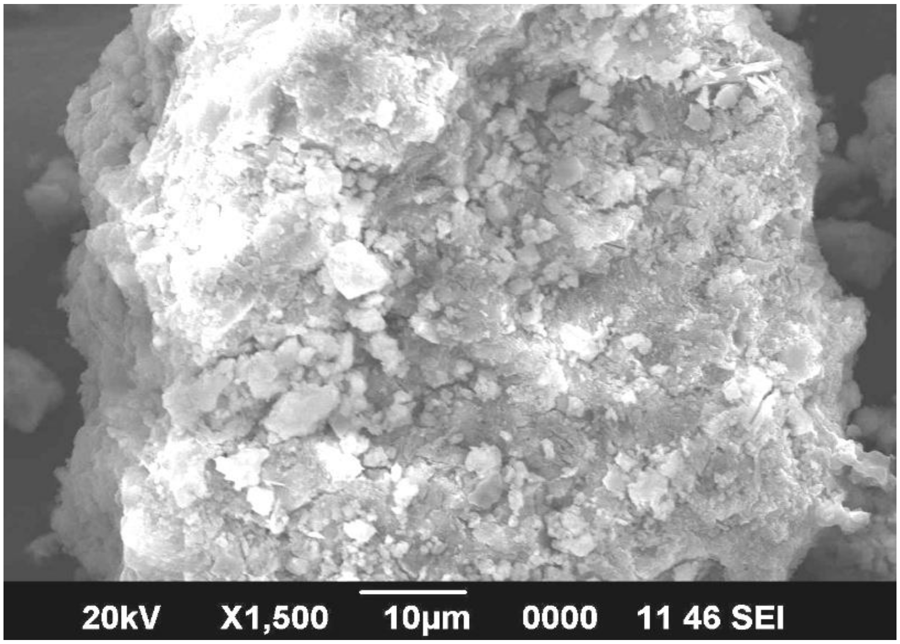


Figure 7.5: SEM morphology of hydrated cement with 1.0% FSHH+ 10%RHA (**S16**)

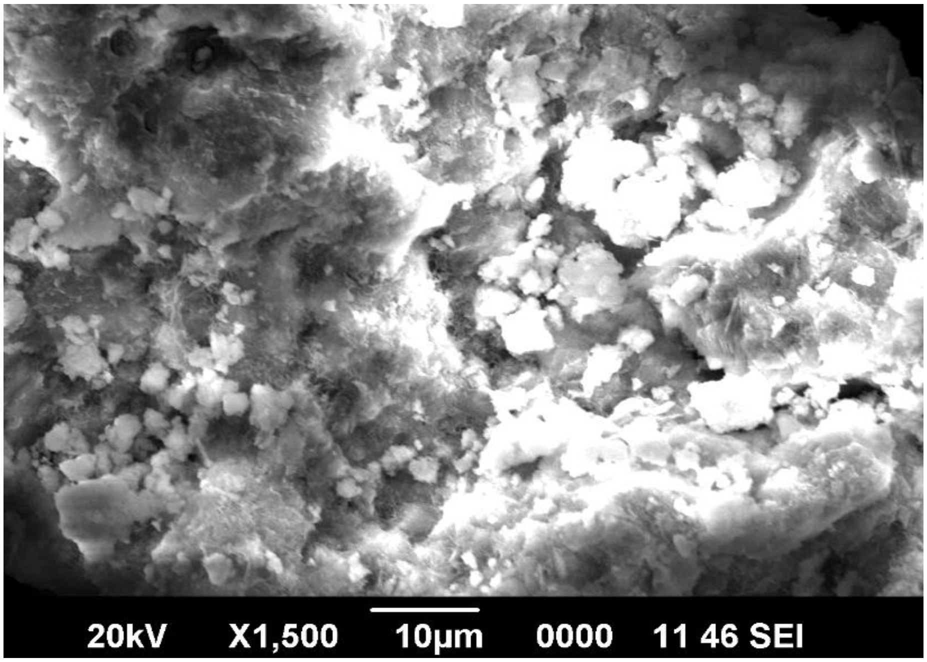


Figure 7.6: SEM morphology of hydrated cement with 1.0% SCDH+10%RHA (**S19**)

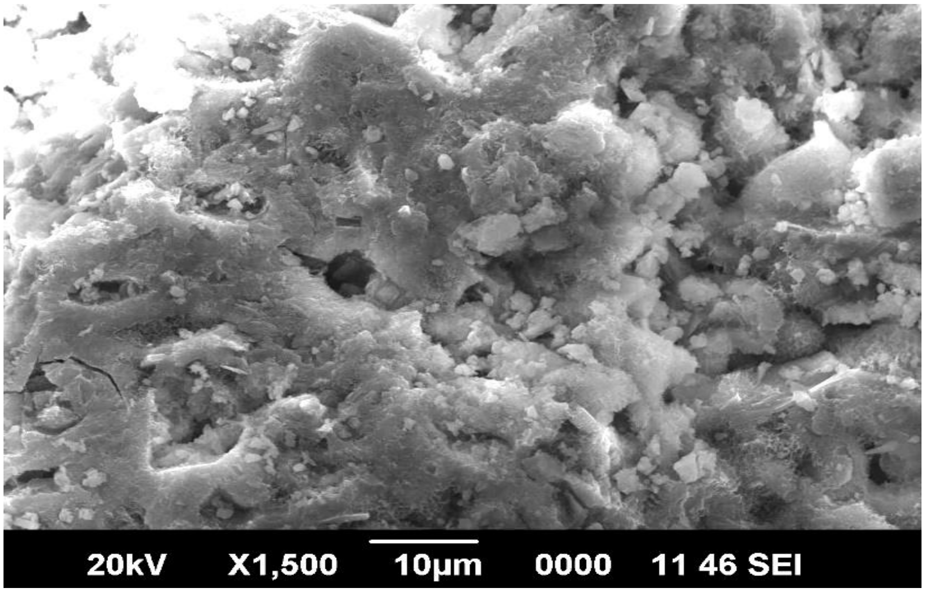


Figure 7.7: SEM morphology of hydrated cement with 1.0% FSHH+ 5%RHA+5%RTA (**S22**)

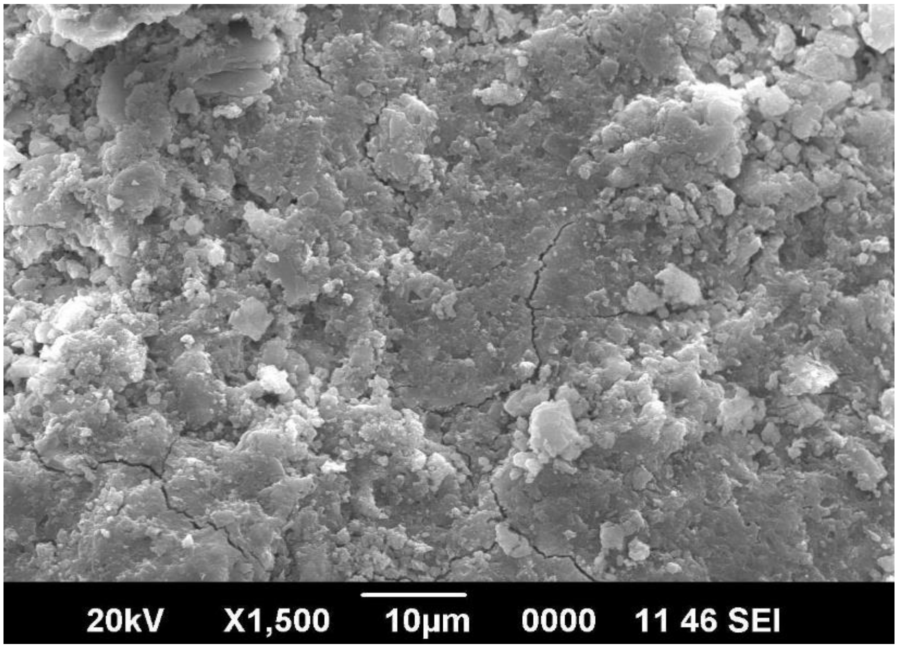


Figure 7.8: SEM morphology of hydrated cement with 1.0% SCDH+5%RHA+5%RTA (**S25**)

7.3.3 XRD results

XRD of samples (**S1, S4, S7, S16, S19, S22** and **S25**) after 28 days of hydration without curing is given in Figures 5.24, 5.26, 5.28 and Figures 7.9-7.12. Unhydrated OPC sample gave peaks at 29.4˚, 32.6˚, 34.3˚, 41.3˚, 51.7˚and 56.6˚ due to tricalcium silicate (C_3S) and at 26.4˚ and 32.2˚ due to dicalcium silicate (C_2S) in X-ray diffractogram [17, 291]. XRD peaks of hydrated OPC (**S1**) and its blend forms samples (**S4, S7, S16, S19, S22** and **S25**) are mentioned in Table 7.5. In all these hydrated samples calcium hydroxide (CH) appeared at 18.3˚, 34.6˚ and 47.5˚ along with Ettringite phases (E1-E5) at 9.5˚, 11.5˚, 16.5˚, 23.5˚ and 19.5˚. Appearance of unreacted alite (C_3S) and belite (C_2S) phases at 29.7˚ and 32.4˚ respectively, suggested that the samples were not completely hydrated due to uncured hydration. The amount of CH formed in **S1** and **S4** (more intense peak) is higher than that of **S7** indicated that reducing agents $SnCl_2.2H_2O$ (**S7**) might have reacted with calcium hydroxide and these results are in agreement with SEM studies. Formation of Friedal's salt ($Ca_3Al_2O_6.CaCl_2.10H_2O$) and monocarbonate phase can be observed at 11.5° in S7 [282-292]. Monocarbonate phase decreases the porosity of cement materials thus helped in enhancing the strength after 28 days [282-284]. The greater reduction in

CH has been observed in samples **S16, S19, S22** and **S25** due to the reaction of $Ca(OH)_2$ with amorphous silica and reducing agents to form C_2S, C_3S and number of Ettringite phases, respectively (Table 7.5), which can be seen in SEM images of **S16, S19, S22** and **S25** either in the form of needles, fibers, honeycomb structures and small rod-like crystals. An ettringite phase at 9.5˚ indicates participation of iron during cement hydration in the form of Aft (alumina ferric oxide Tri sulphate).

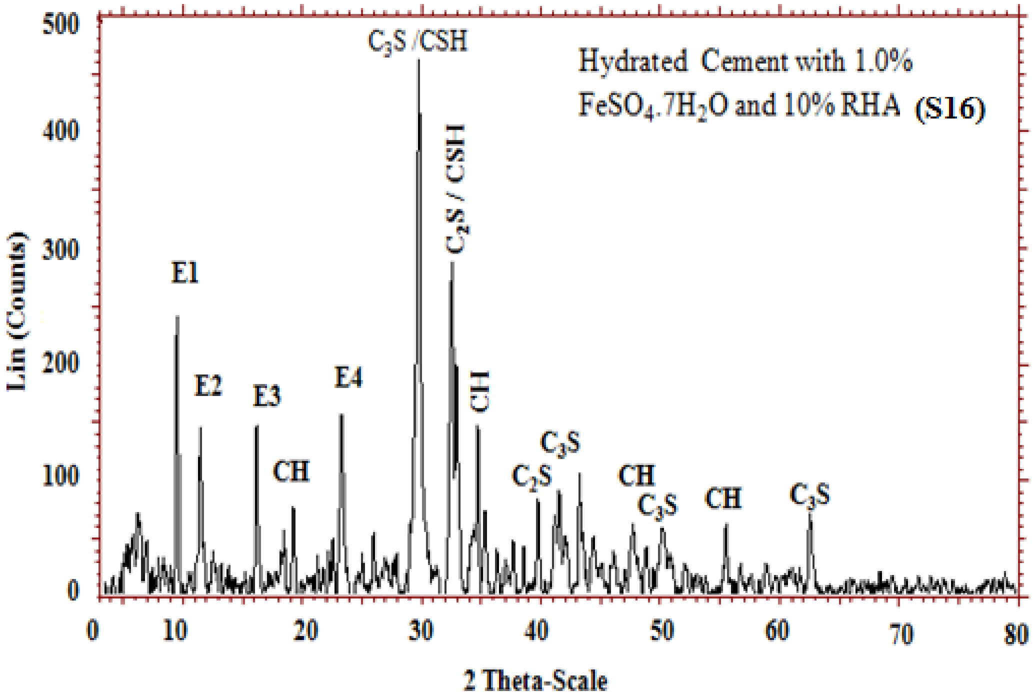


Figure 7.9: XRD spectra of hydrated cement with 1.0% FSHH+ 10%RHA (**S16**)

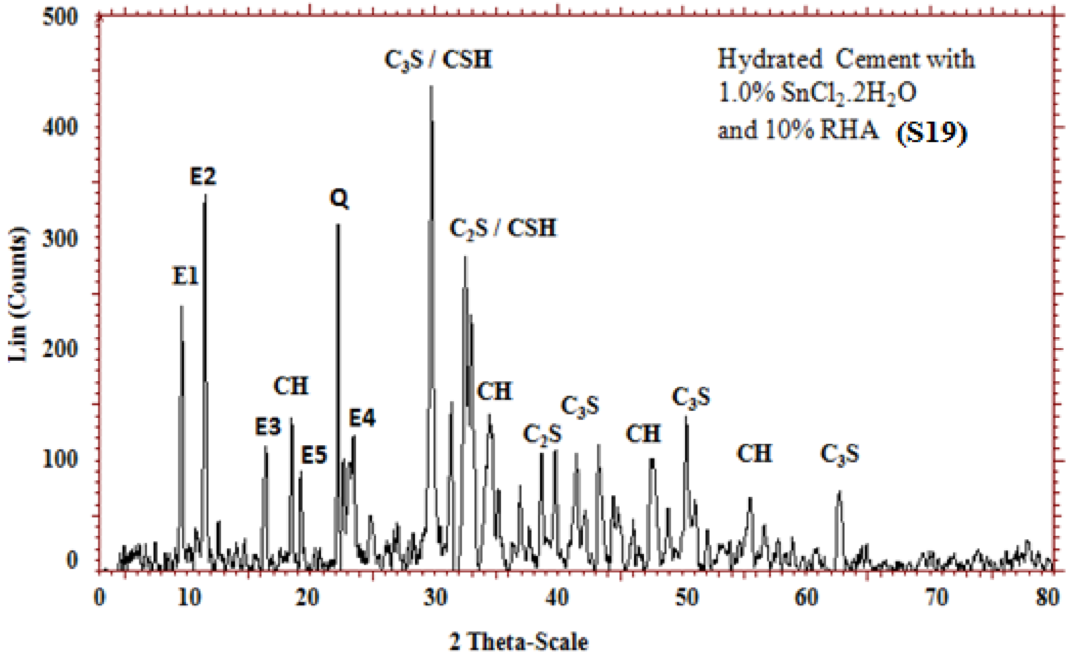


Figure 7.10: XRD spectra of hydrated cement with 1.0% SCDH+10%RHA (**S19**)

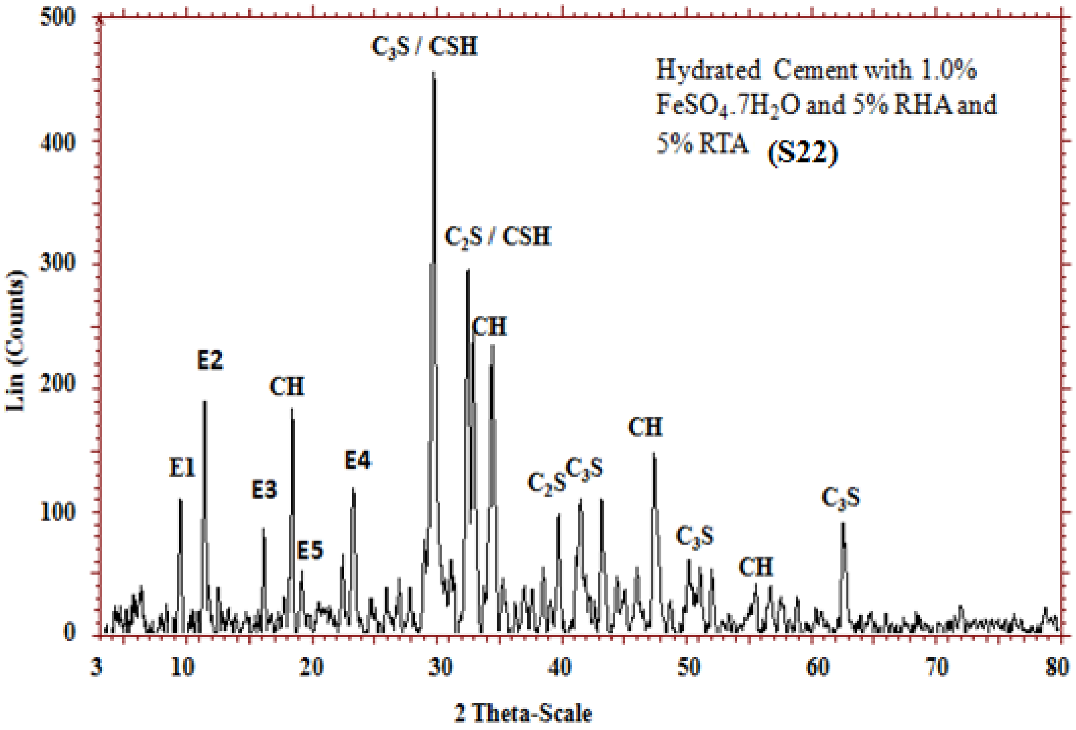


Figure 7.11: XRD spectra of hydrated cement with 1.0% FSHH+ 5%RHA+5%RTA (**S22**)

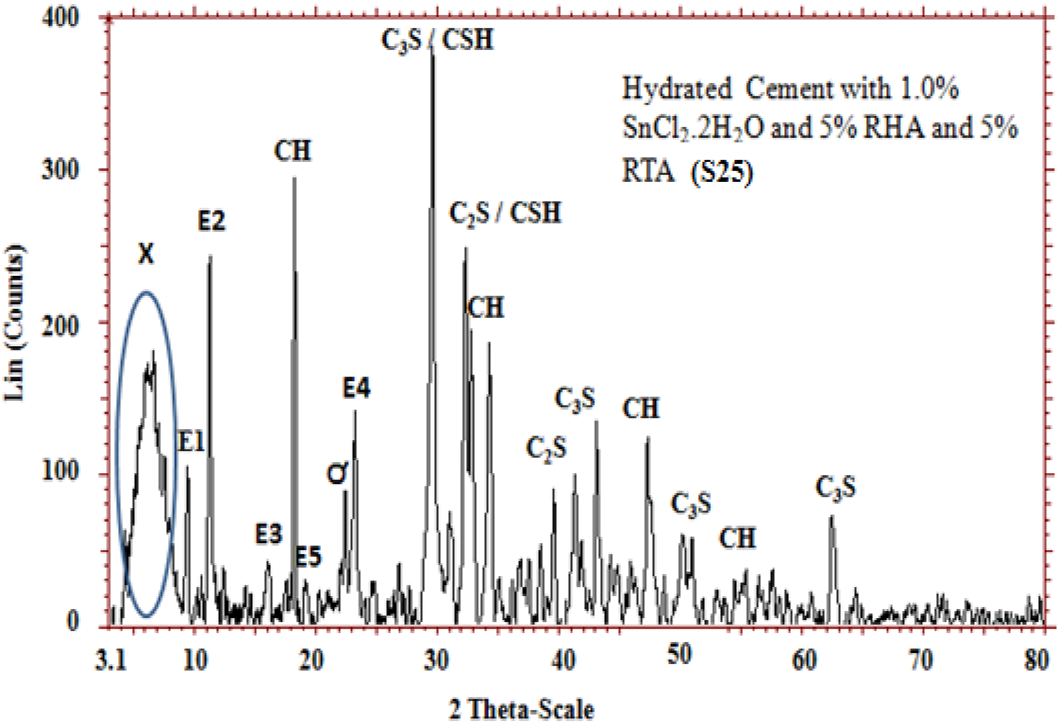


Figure 7.12: XRD spectra of hydrated cement with 1.0% SCDH+5%RHA+5%RTA (S25)

7.3.4 Fourier-transform infrared spectroscopy (FTIR)

The infrared spectrum of hydrated samples **S16, S19, S22** and **S25** (Figure 7.13-7.16) shows lower wave number shift in the silicate region as compare to samples **S1, S4** and **S7** (given in Figure 5.4, 5.6 and 5.8) whereas in hydrated crystalline water region, shifting in O-H regions was observed. These results confirmed that other crystalline phases were formed besides calcium silicate hydrated phases. The possible reason for lower silicate polymerization which appered in FTIR, use of amorphous silica in excess which suppressed the silicate polymerization wide peaks and appered itself as a silicate peaks. The liberated calcium hydroxide from hydrated samples (**S1, S4** and **S7**) appeared as O-H stretching of lime from 3600 to 3800 cm^{-1} which were consumed completely after use of RHA and RTA in those cement, samples in the form of **S16, S19, S22** and **S25**. These samples were not appeared as O-H stretching of calcium hydroxide (from 3600 to 3800 cm^{-1}).

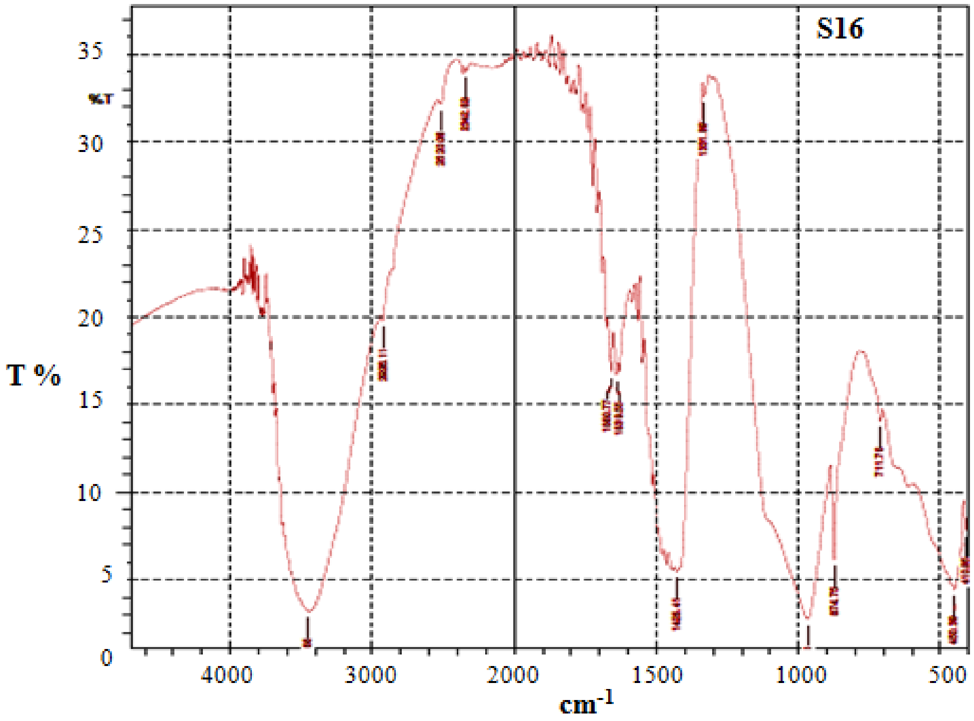


Figure 7.13: FTIR spectra of hydrated cement with 1.0% FSHH+ 10%RHA (**S16**)

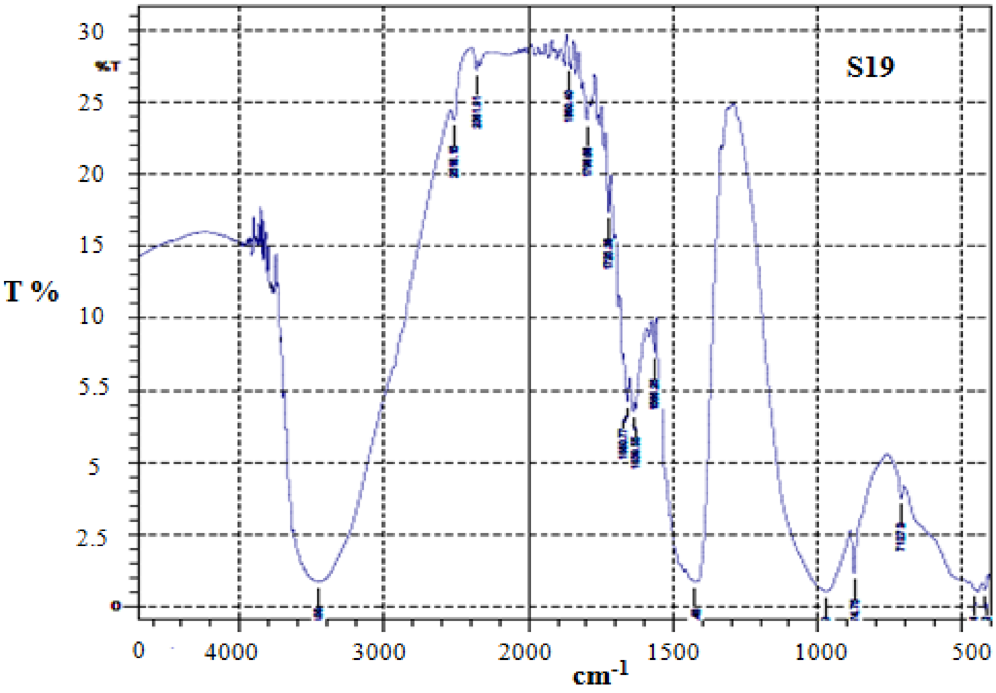


Figure 7.14: FTIR spectra of hydrated cement with 1.0% SCDH+10%RHA (**S19**)

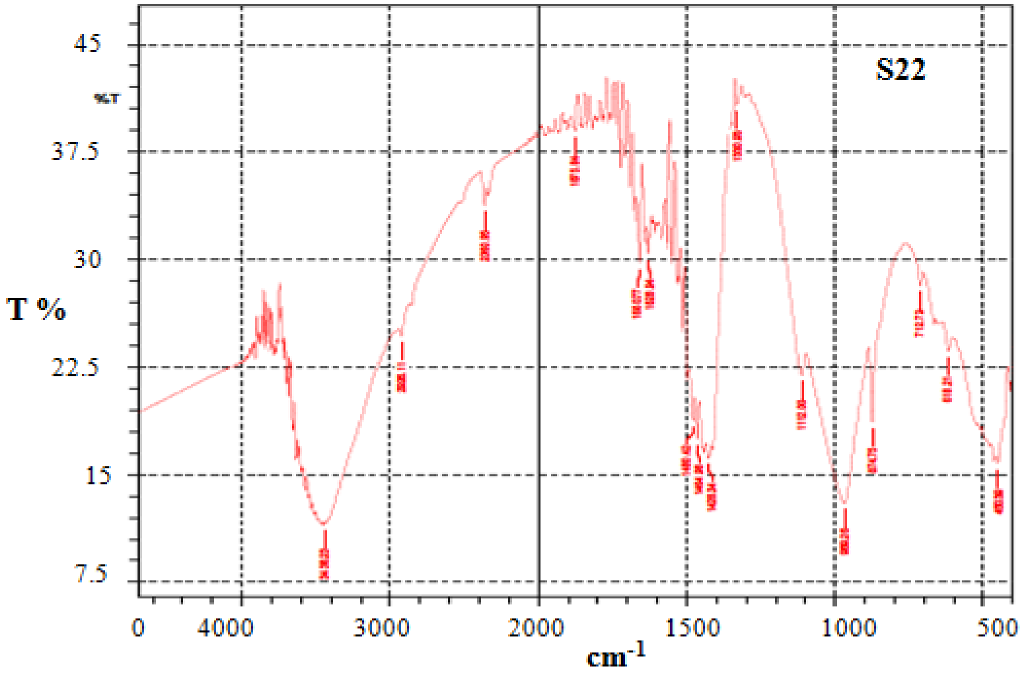


Figure 7.15: FTIR spectra of hydrated cement with 1.0% FSHH+ 5%RHA+5%RTA (**S22**)

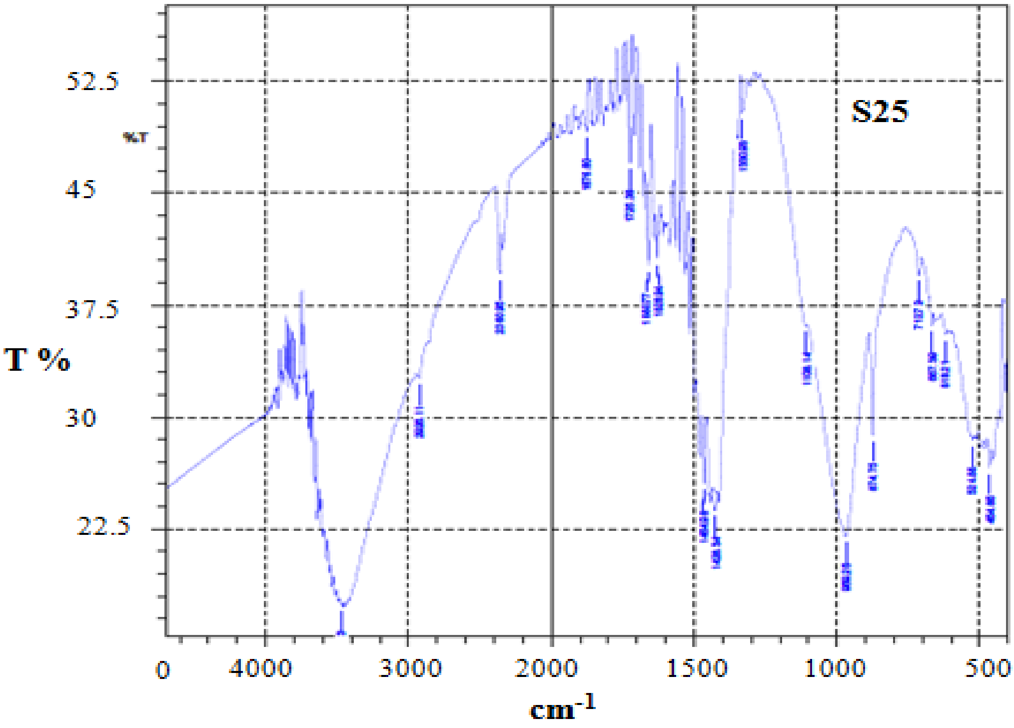


Figure 7.16: FTIR spectra of hydrated cement with 1.0% SCDH+5%RHA+5%RTA (**S25**)

Chapter-8

Conclusion

Objective wise conclusions are given below

(i) The concentration of water soluble Cr(VI) and total Chromium in PPC samples was found to be in range from 8.55 to 32.68 ppm and 85 to 165 ppm respectively, whereas in OPC samples, it ranges from 13.65 to 34.98 and 130 to 184 ppm respectively. Thus the concentration of Cr(VI) and total chromium in OPC samples was found to be more than PPC samples. Results obtained from five days extraction process (In-house developed method) are in good agreement with standard methods (European method, Danish method and German method). The percentage of water soluble, partially soluble and insoluble Cr(VI) in PPC samples has been found to be 54-55%, 30% and 10% respectively.

(ii) The chromium concentration estimated by DPC method was found to be more than variamine blue method. Comparatively high concentration of chromium in DPC method may be attributed to interference caused by various ions because of high colour sensitivity of DPC. Since, the interference by these ions is less in VB method, this method can be used for accurate detection of Cr(VI) in cement sample. High colour stability of Variamine blue dye added an additional feature to this reagent.

(iii) Reducing agents ($FeSO_4.7H_2O$ and $SnCl_2.2H_2O$) are more effective in powder form than crystalline form and $SnCl_2.2H_2O$ was found to be the better reducing agent at 0.1% (w/w) than $FeSO_4.7H_2O$.

(iv) Storage stability of reducing agents can be enhanced by applying a protective covering of liquid detergent on the surface of reducing agents

(v) Addition of reducing agents only delayed the initial hydration process. To improve the initial as well later age hydration, rice husk ash or rice tiller ash was added along with reducing agents. RHA–RTA blended cement samples with 1% stannous chloride are more effective in reducing Cr(VI) content to Cr(III) than RHA-RTA blended cement samples with 1% ferrous sulphate. Amorphous silica of RHA and RTA reacted with $Ca(OH)_2$ to form calcium silicate hydrate which provides strength to the cement and improve the hydration which was confirmed by TGA, SEM and XRD studies.

(vi) Microstructural changes during hydration (28 days) and their effect on standard consistency and compressive strength were observed by XRD, TGA and SEM. The less amount of leaching of Cr(VI) from RHA-RTA blended cement mortar indicates densification of microstructure capable of stabilizing the Cr(VI).

Chapter-9

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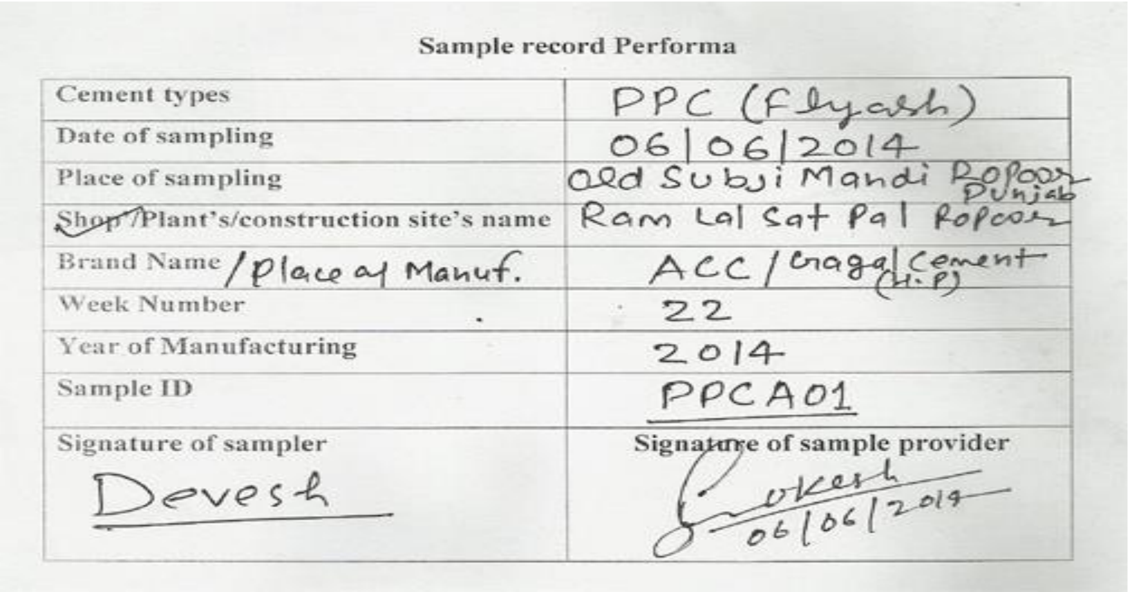
Appendix–I



Sample record Performa

Cement types	PPC (Flyash)
Date of sampling	06/06/2014
Place of sampling	Old Subji Mandi Ropoor Punjab
~~Shop~~ /Plant's/construction site's name	Ram Lal Sat Pal Ropoor
Brand Name /Place of Manuf.	ACC / Gagal Cement (H.P)
Week Number	22
Year of Manufacturing	2014
Sample ID	PPCA01
Signature of sampler Devesh	Signature of sample provider Lokesh 06/06/2014

Figure 1: Sampling record Performa

Figure 2: At sampling Site

Figure 3: A worker without safety precaution

Figure 3: Cement paste (Low workability) **Figure 4: Cement paste (high workability)**

Figure 5: Cement mortar preparation **Figure 6: Vibrating the Cement Mortar**

Figure 7: Molding of cement mortar **Figure 8: Compressive strength testing machine**

Appendix-II

Calibration data of proposed method (Varamine Blue method)

DR/2010 User Experiment Report: Hexavalent chromium

High Limit: 12 mg/L of Cr(VI)

Low Limit: 0.05 mg/L of Cr(VI)

Monochromator Wavelength: 556 nm

Table 1: Calibration data (Varamine Blue method)

S.No	Standard Concentration	Absorbance (Optical density)
1	0.05	0.003
2	0.1	0.006
3	0.2	0.010
4	0.4	0.023
5	0.8	0.049
6	1	0.062

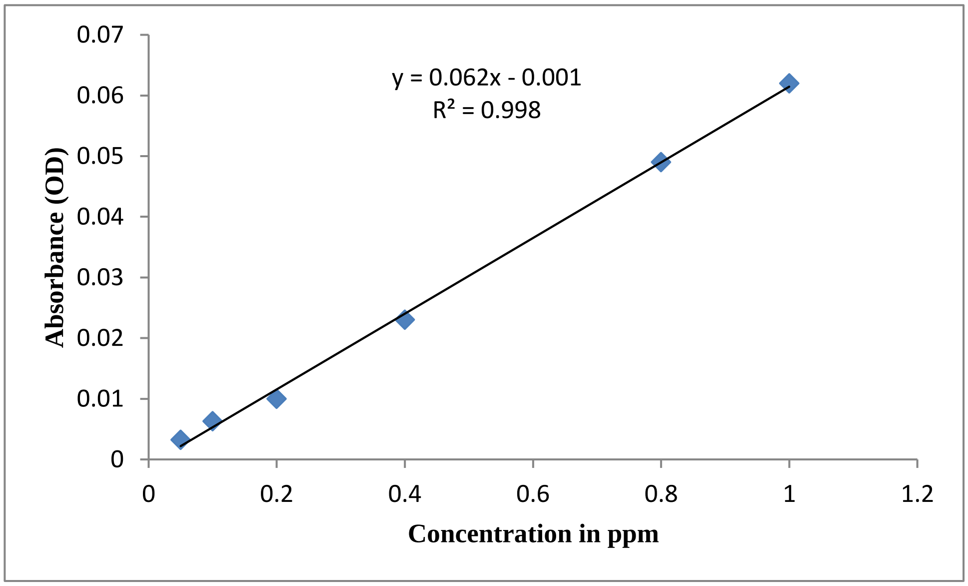


Figure 1: Calibration curve (Varamine Blue method)

Calibration data of Reference method (Diphenycarbazide)

DR/2010 User Experiment Report: Hexavalent chromium

High Limit: 2.0 mg/L of Cr(VI)

Low Limit: 0.001 mg/L of Cr(VI)

Monochromator Wavelength: 540 nm

Table 2: Calibration data (DPC method)

S.No	Standard Concentration	Absorbance (Optical density)
1	0.05	0.010
2	0.1	0.041
3	0.2	0.090
4	0.4	0.220
5	0.6	0.290
6	0.8	0.422
7	1	0.520

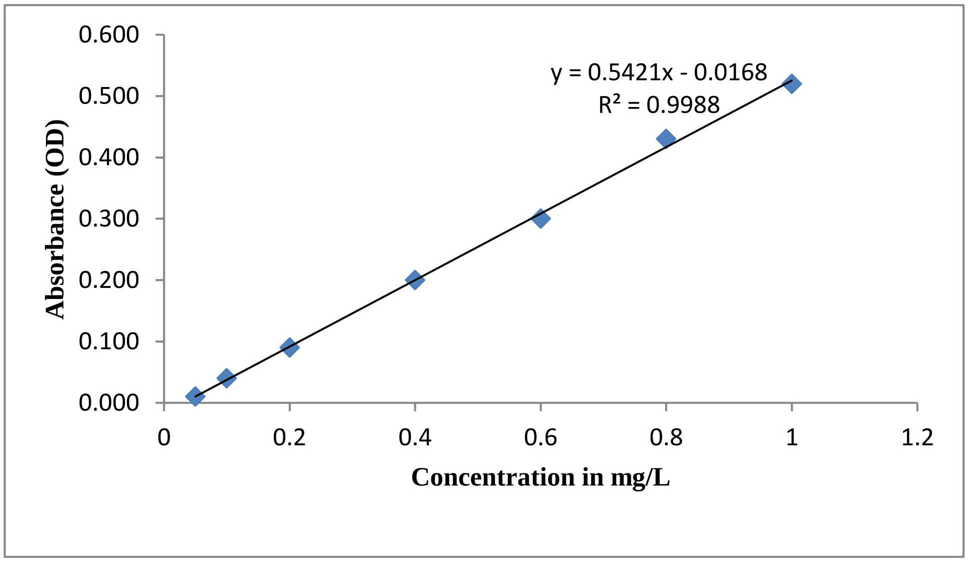


Figure 2: Calibration curve (DPC method)

Appendix–III

Table 1: Optimization of in-house method for water soluble Cr(VI) determination

About Sample	**Water soluble Cr(VI) in ppm**					
	By Reference method (DS1020)	By In-house developed method (Values with respect to different cement/water ratio)				
		2g/25ml	2 g/50ml	2g/75ml	2g/100ml	2g/125 ml
OPC43J22	29.45	29.98	30.11	30.71	30.88	30.53
PPCJ03	11.52	11.05	11.45	12.12	12.56	12.50