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Fixation of hazardous metallurgical sludge containing Cr(VI) in Cementitious binder

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***Abstract*— In India marble dust from gang saw industries is available as wastes in million tonnes and is an environmental hazard due to disposal problems. The marble dust is a filler material having similar properties like limestone and takes part in early hydration reactions due to the presence of high amount of calcium carbonate. In the present study, 40 % of marble dust (CM) blended with Portland cement (C0) has been utilized as filler to immobilize (solidify) hazardous Cr (VI) (1000-3000 mg/l) and the effect on parameters like setting time, compressive strength and leachability of Cr (VI) has been investigated as a function of curing time. It is observed that the initial and final setting times of these cements increase with increase in Cr (VI) concentration. The effect of Cr (VI) addition on the physical, chemical and engineering properties of solidified samples (C0 and CM with Cr (VI)) were studied and the results revealed that the compressive strength reduced with addition of Cr (VI). The samples of C0 and CM containing Cr (VI) were also tested for leachability of Cr (VI) in acidic solution (pH=~3) using Toxicity Characteristics Leaching procedure (TCLP) tests. The leached Cr (VI) concentration was under the allowable limit (5 mg/l) of U.S. EPA at lower initial concentration. The hydration chemistry of the solidified samples has been studied by XRD which shows the formation of various phases like ettringite, Cr-ettringite, tobermorite, monocarboaluminate etc. The morphology of the hydration products was studied by Scanning Electron Microscopy (SEM) which also supports the formation of various hydrations phases as observed during XRD in the solidified Cementitious binders.**

***Index Terms*— Chromium; Compressive strength; Hydration; Leaching; Solidification**

I. INTRODUCTION

Hazardous waste disposal is a major issue confronting the industrialized world because of limited sites, cost, technology and strict environmental standards for land filling. The wide spread use of chromium has resulted in the contamination of soils and water. Chromium contamination is of great concern due to its toxic, mutagenic and carcinogenic nature. The chromium is generated from steel and other alloy's production, chrome plating, pigments and leather tanning industries. Among the various forms of chromium, Cr (VI) is the most important one because of its toxicity, solubility and mobility characteristics [1,10]. Solidification and stabilization (S/S) processes are waste treatments designed to improve the handling and physical characteristics of liquid or semi-solids and decrease the release if hazard to the environment. These processes are based on hydraulic reactions of hydraulic cements or pozzolanic reactions between Portland cement or lime and pozzolanic materials such as pulverized-fuel ash, cement kiln dust and rice husk ash [1-7]. The chemical changes that take place as a result of the interaction between waste components and solidification binders play an important role in controlling the quality of cement based solidified products [8-9]. The limestone filler addition to Portland cement produces several effects on the mechanism and kinetics of cement hydration [12-18]. It has been observed that filler effect imparted by limestone filler causes a hydration acceleration of Portland clinker grains at early ages, provides new nucleation sites for calcium hydroxide and produces the formation of calcium carboaluminates as results of the reaction between calcium carbonate from limestone and tricalcium aluminate from Portland clinker.

In India marble dust from gang saw industries is available as wastes in million tonnes and is an environmental hazard due to disposal problems. The marble dust is a filler material having similar properties like limestone and takes part in early hydration reactions due to the presence of high amount of calcium carbonate. In the present study, high amount of marble dust (40 %) blended with Portland cement has been utilized as filler to fix (solidify) Cr (VI) (1000-3000 mg/l) and the effect on parameters like setting time, compressive strength and leachability of Cr (VI) has been investigated as a function of curing time.

II. EXPERIMENTAL PROGRAM

A. Materials

Marble dust was collected in the form of slurry, dried and ground to a particle size of < 300μm. The physical and chemical analysis of ordinary Portland cement (OPC) cement was carried out as per IS 4031: 1999 and 4032: 1985 respectively. The results of cement analysis are given in Table 1 along with marble dust analysis. The marble dust-blended cement was obtained by mixing 40 % marble dust with OPC using a mixer. A stock solution of 3000 mg/l of Cr (VI) was prepared using potassium dichromate. Table 2 shows the denominations given to each sample during hydration of OPC and blended cement with and without Cr (VI).

B. Determination of setting times

The initial and final setting times of OPC and marble dust blended cement with and without Cr (VI) at different concentration (1000 mg/l to 3000 mg/l) were determined according to IS: 4031 : 1999 using a Vicat needle.

C. Compressive strength

To determine the effect of chromium on the compressive strength of the solidified samples, cubical molds (5cm x 5cm x 5cm) of OPC and marble dust blended cement pastes were cast using water (distilled) to cement ratio of 0.35 as per IS 4031: 1999. The mixing was performed using automatic mortar mixer of ELE, U. K. After initial curing of 1 day, demolded specimens were stored at relative humidity of not

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less than 95% in airtight glass containers at 27±2°C for different periods up to one year. The compressive strengths of these specimens were determined and the average value of three specimens is reported.

Table 1: Physical and chemical analysis of Portland cement and marble dust

Properties	Portland Cement (43 G)	Marble Dust
Specific gravity	3.14	3.35
Insoluble residue (%)	1.13	----
Alkalies	0.35	----
SO_3 (%)	2.10	----
Chloride (%)	0.012	----
LOI (%)	1.51	43.40
Surface area (m^2/kg)	308	310
SiO_2 (%)	20.6	3.01
CaO (%)	64.34	30.80
Magnesia (%)	2.04	19.27
Al_2O_3	4.30	2.70

Table 2: Denominations given to samples during hydration studies

Sample	Denomination
OPC only (control)	C0
OPC + 1000 mg/l of Cr (VI)	C0+1
OPC + 2000 mg/l of Cr (VI)	C0+2
OPC + 3000 mg/l of Cr (VI)	C0+3
OPC + 40 % marble dust	CM40
OPC + Marble dust (40% + 1000 mg/l of Cr (VI)	CM40+1
OPC + Marble dust (40% + 2000 mg/l of Cr (VI)	CM40+2
OPC + Marble dust (40%)+ 3000 mg/l of Cr (VI)	CM40+3

D. Leachability, Scanning Electron Microscopy (SEM) and XRD

Leaching test were carried out on the 28, 90, 180 and 360 day old hydrated pastes using the EPA Standard Toxicity Characteristics Leaching Procedure [12, 19] (TCLP). The sample was ground to a powder with a particle size <0.5 mm and leached in water (distilled) and acetic acid (pH =~3). 200 ml of water or acetic acid solution were added to the 10 g of sample in a high density polyethylene bottle. The bottle and its contents were agitated in a rotary shaker at 30 rpm for 18 h. The leachates were filtered through a 0.45 μm membrane filter to remove suspended solids and the leached solutions were used for determination of Cr (VI) by atomic absorption spectrometer (AAS). Each leachate was analysed in triplicate and average values were reported to ensure the reproducibility of the data.

SEM was carried out using model LEO 438 VP, UK to study micro structural changes in the OPC and blended cement during hydration due to addition of Cr (VI). The hydrated samples were immersed in acetone to stop hydration at definite period of curing. X-ray diffractometry (XRD) was used to study the hydration products of OPC and blended cement paste without and with addition of Cr (VI). The samples were immersed in acetone to stop hydration and grounded to a particle size of <45 μm for XRD. X-ray diffraction patterns were recorded on a Rigaku X-ray Diffractometer equipped with a rotating anode, utilizing CuK_a radiation at 40 kV and 30 mA.

III. RESULTS AND DISCUSSION

The OPC and marble dust blended cement samples containing Cr (VI) were investigated for change in setting time, compressive strength and leachability of Cr (VI). The results are reported and discussed in the following sections:

A. Setting times

The results of initial and final setting times of OPC and marble dust (40 %) blended cement with different concentration of Cr (VI) (1000-3000 mg/l) and without Cr (VI) are shown in Fig. 1. The control cement (C0) reaches initial and final set in 195 and 315 min respectively, while control of blended cement (CM40) reaches initial and final set in 210 and 200 min. It is observed that addition of marble dust (40 %) in cement accelerate the final setting as compared to C0. It is also apparent that the addition of Cr (VI) retards the setting process of OPC (C0+1, C0+2 and C0+3) and blended cement (CM40+1, CM40+2 and CM40+3) and the retardation increases with increasing Cr (VI) concentrations. Further the results show that the initial and final setting times of marble dust blended cement samples (CM40 series) are comparable (± 15-20 min) to OPC samples (C0 series) and comply to the IS: 8112 (1989). The retardation in setting time of cement in presence of Cr (VI) may be due to the reaction between Ca^{2+} from Ca $(OH)_2$ and Cr (VI) to form $CaCrO_4$ which is a low solubility product (5.1 x 10^{-6}) as has been reported earlier [2, 20].

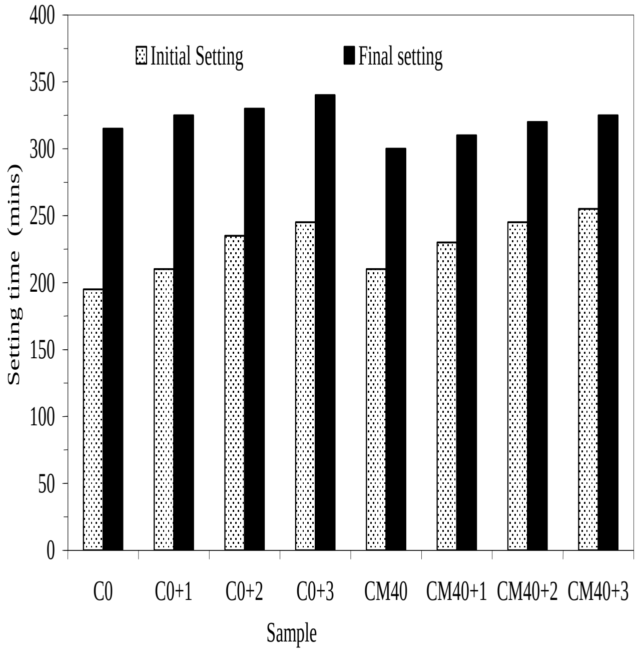


Fig.1: Setting time of OPC (C0 series) and marble dust blended cement (CM40 series) at various Cr (VI) concentrations

B. Compressive strength

Solidified samples with and without Cr (VI) were tested for compressive strength up to 360 days of curing at different time intervals and the results are shown in Fig. 2 and 3 for OPC and blended cement respectively. Samples of OPC (C0) and marble dust blended cement (CM40) without Cr (VI) served as controls for respective binder containing different concentration (1000-3000 mg/l) of Cr (VI). It is observed that in C0 and CM40 series samples containing Cr (VI), the rate of compressive strength development is very fast in early age up to 28 days of curing and decreases in later ages up to 360 days. Further, the compressive strength is a function of Cr (VI) concentration and decreases with increasing Cr (VI) concentrations.

Figure 2 depicts that the average strength of control (C0) is 59 and 73.8 MPa after 28 and 360 days of curing respectively. The samples of C0 series containing Cr (VI) exhibit a loss of compressive strength in the range of about 11-18 % and 8-14 % on 28 and 360 of curing respectively as compared to the control (C0). Figure 3 shows that samples of marble dust blended cement paste (CM40) exhibit a strength of 47.1 and 59.6 MPa after 28 and 360 days of curing respectively and is about 80 % of the strength of C0. The strength of CM40 series samples containing Cr (VI) decreases from 6-16 % and 10-19 % after 28 and 360 days of curing respectively as compared to the control (CM40). The results also depict that the marble dust blended cement samples (CM40 series) exhibit low decrease in the percentage strength at an early age (28 days) as compared to the OPC samples (C0 series) in the presence of Cr (VI). The possible reason for this may be the formation of phases like ettringite and associated phases like Cr-ettringite and Bentorite during hydration as reported earlier (12).

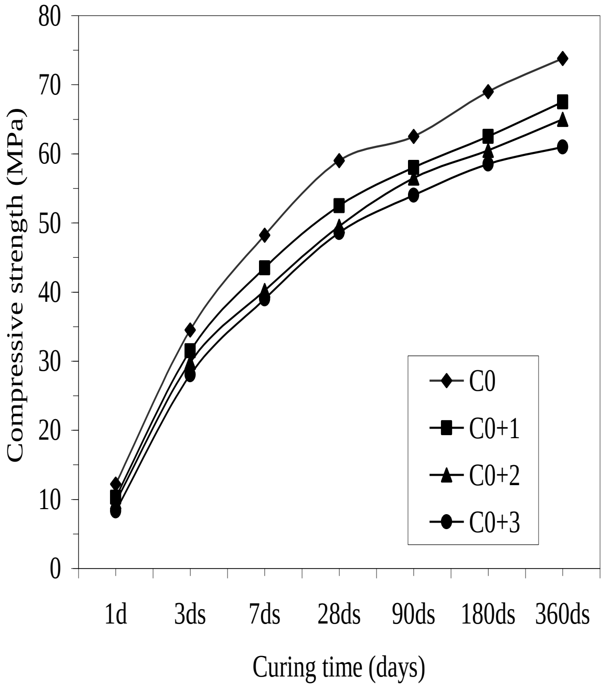


Fig.2: Effect of Cr (VI) concentration on compressive strength of OPC as a function of curing period

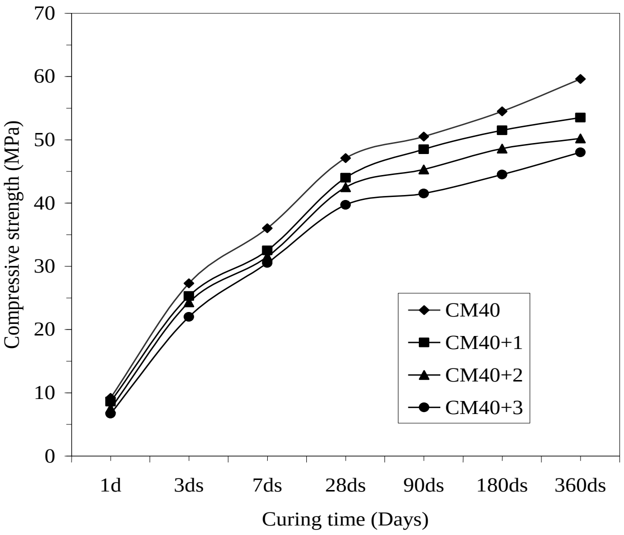


Fig.3: Effect of Cr (VI) concentration on compressive strength of marble dust blended cement

as a function of curing period

C. Leachability, SED and XRD

The results of TCLP leaching tests for the hydrated OPC and blended cement paste samples containing Cr (VI) are depicted in Table 3. The tests were performed at various curing time in water and acid (pH=~3) solution. The leaching of Cr (VI) with curing time decreases in all the samples and it may be due to the increase in compressive strength as a result of more hydration and densification of microstructure [12]. The results also show that the leaching is a function of initial

Cr (VI) concentration and increase in leaching is observed with increase in initial concentration. However the retained percentage of Cr (VI) is independent of initial Cr (VI) concentration and is more than 99 % in acid as well as in water at all curing periods. It is also observed that the percentage Cr (VI) retained is slightly higher in water than in acidic solution. It is evident that the leached Cr (VI) concentration was under the allowable limits (5 mg/l) of US-EPA at 1ower concentration (1000 mg/l) of Cr (VI) for C0 and CM40 samples. The results show the affinity of marble dust to retain Cr (VI) is very high because the quantity of available cement in CM40 is very less as compared to C0 samples.

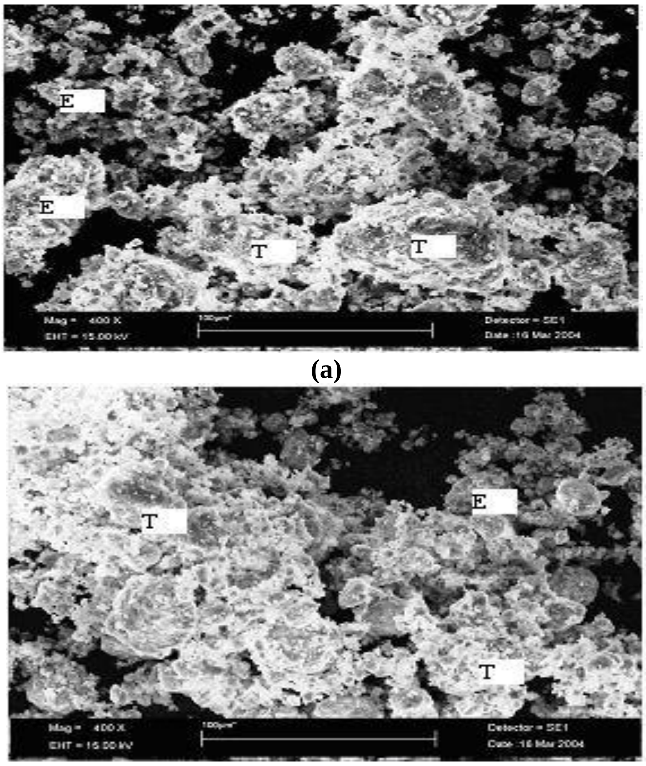
Table 3: Leached values of Cr (VI) from Solidified Samples of C0 and CM40 series

Sample	Medium	Leached Values of Cr (IV) in mg/l			
		28 days	90 days	180 days	360 days
C0+1	Acid	5	3	BDL	BDL
	Water	BDL	BDL	BDL	BDL
C0+2	Acid	22	17	15	12
	Water	15	13	12	8
C0+3	Acid	30	25	23	16
	Water	5	22	17	10
CM40+1	Acid	8	5	3	BDL
	Water	5	3	BDL	BDL
CM40+2	Acid	25	23	17	12
	Water	18	15	13	10
CM40+3	Acid	38	18	21	16
	Water	32	27	20	12

The scanning electron micrographs (SEM) of the hydrated cement samples with and without Cr (VI) are shown in Figs 4-5 for C0 and CM40. After 1 day of hydration of cement, typical hydration products like calcium hydroxide (CH), tobermorite (T) and grain structure appear in the C0 paste together with short acicular and needle like crystals. After 7 days, the microstructure of the cement becomes much denser with pronounced formation of needle like crystals and acicular features. At 28 days, the hydrated grains are interconnected by outgrowth forming a continuous structure as shown in Fig. 4 (a). The micrograph of hydrated OPC samples containing Cr (VI) for 28 days curing are shown in Fig 4 (b) which shows the formation of crystals of ettringite (E) and tobermorite (T).

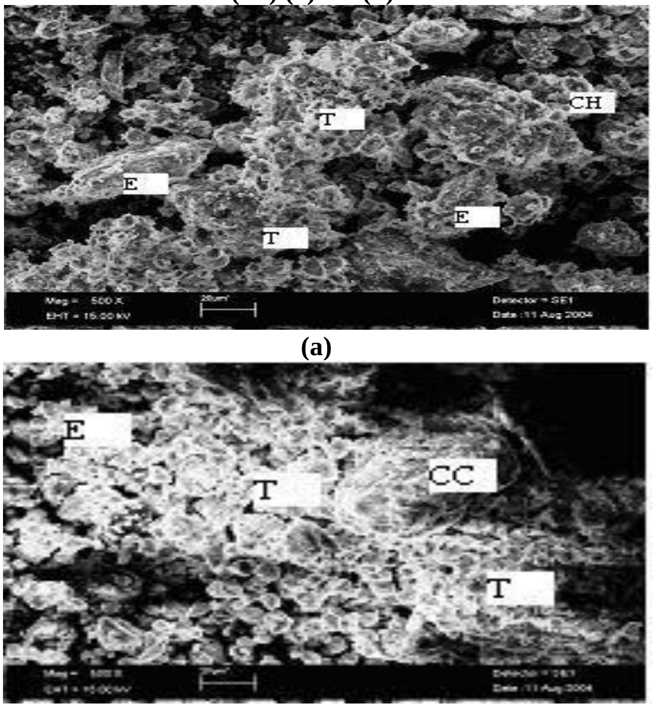
The SEM of blended cement sample (CM40) hydrated for 28 days are shown in Fig. 5(a-b). A perusal of Fig.5 (a) illustrates that at 28 days of hydration, dense structures containing ettringite subhedral to anhedral crystals of CSH agglomerated with cubic calcium hydroxide (CH) as well as prismatic and lath shaped crystals representing various hydration products are formed. Fig. 5 (b) shows the breakdown of the dense hydrated material by carbonation and formation of less crystal of calcium carbonate (CC).

The results of X-ray diffractograms evaluation show the formation of various crystalline phases after 28 days of curing which are more or less same for different Cr (VI) concentrations (1000 to 3000 mg/l). The most prominent peaks in the unhydrated cement were of tricalcium silicate (C_3S) at 29.4^{o}, 32.6^{o}, 34.3^{o}, 41.3^{o}, 51.7^{o}, 56.6^{o} and dicalcium silicate (C_2S) at 26.4^{o} and 32.2^{o} (Fig.6). The peaks of ettringite (E) were also observed at 28.6, 34^{o} and 50.7^{o} and calcium chromate peak was observed at 32.3^{o} along with peak of Calcium ettringite (Ca-E) at 44.9^{o} in samples of OPC with Cr(VI) as shown in Fig. 6.



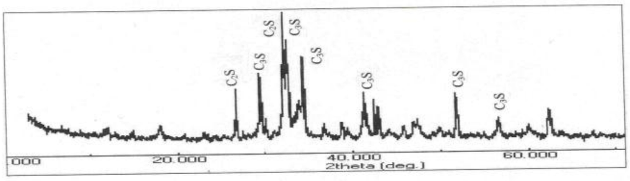
(b)

Fig. 4: SEM of 28 days hydrated OPC without and with Cr (VI) (a) C0 (b) C0+1

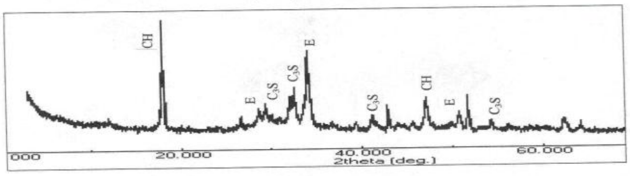


(b)

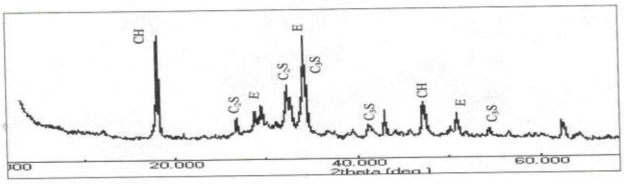
Fig 5: SEM of marble dust blended cement without and with Cr (VI) (a) CM40 (b) CM40+1



(a) Unhydrated Cement

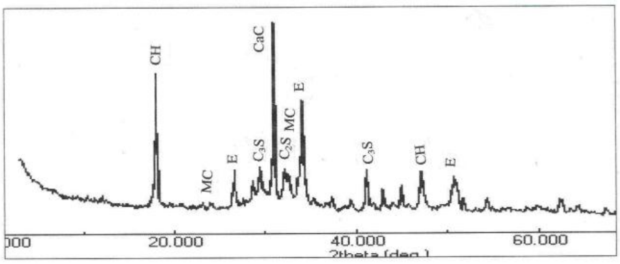


(b) Hydrated OPC Paste

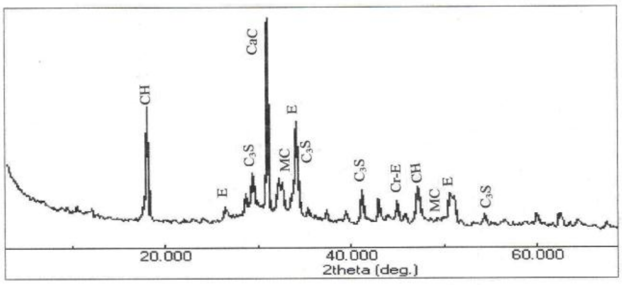


(c) Hydrated OPC Paste with Cr (VI)

Fig.6: XRD of Unhydrated and hydrated cement paste



(a) Hydrated marble dust blended cement



(b) Hydrated marble dust blended cement with Cr (VI)

Fig.7: XRD of hydrated marble dust blended cement without and with Cr (VI) Without and with Cr (VI)

The XRD pattern of marble dust blended cement (CM40) is almost similar to that of C0 at 28 days of hydration (Fig.7). Additionally, the peaks of calcium carbonate (CaC) at 29° and 31.9° and monocarboaluminate peaks at 23.2° and 33.5° were also observed. Addition of marble dust accelerates the formation of ettringite in early ages by the presence of calcium carbonate and also stops or delays the conversion of ettringite to monosulfoaluminate. This phenomenon occurs because some sulphate ions can be interchanged by carbonate ions during hydration of tricalcium aluminate (C_3A). Excess of calcium carbonate accelerates the hydration rate of C_3S in early ages and also responsible for the transformation of monosulfoaluminate to monocarboaluminate because of its low stability. Fig. 7 shows the XRD pattern of CM40+1 after 28 days of curing. The peak of chromium ettringite peak (Cr-E) and bentorite were observed at 44.9° and 34.2° along with other peaks similar to CM40.

IV. CONCLUSIONS

The following conclusions can be advanced based on the experimental study:

(1) Addition of Cr (VI) retards the initial and final setting times of C0 and CM40 pastes and retardation increase with increase in Cr (VI) concentration.
(2) Samples of marbles dust blended cement (CM40 series) exhibit low decrease in the percentage strength at an early age (28 days) as compared to the OPC samples (C0 series) in the presence of Cr (VI). The possible reason for this may be the formation of various Cr-phases at an early age in presence of marble dust. The compressive strengths of all the series) tested were greater than the EPA compressive strength requirement (0.3 MPa) for S/S treatment of hazardous wastes.
(3) TCLP results reveal that OPC (C0) and marble dust blended cement (CM40) are the adequate binders to confine the hazardous Cr (VI) at low concentration for reduction of negative impact on land and ground water quality.
(4) The major hydraulic products like C_3S, C_2S, ettringite, Calcium chromate, Cr-ettringite, bentorite and monocarboaluminate were identified by XRD.

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