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Feasibility and Environmental Compatibility of Concrete using Chromium Bearing Wastewater

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The effluents of chrome plating industry seepage contain toxic hexavalent chromium generally in the range of 100 to 300 mg/L. The said values of chromium are not advisable to dispose to surface water bodies or land and the treatment process of this wastewater is quite expensive. Herein, we found a course of action to reuse the wastewater in cement matrix in manufacturing concrete work. The M-30 grade concrete samples were casted with portland slag cement (PSC) at wastewater to binder ratio of 0.45. The technical compatibility of concrete specimen *i.e.* the chromium immobilization and other properties are well satisfied nevertheless a small decrease in hardened concrete values also observed. XRD study revealed that the hydration product $Ca(OH)_2$ is replaced by more insoluble $CaCrO_4$. Scanning electron microscopy study (SEM) with energy dispersive spectrum (EDS) study exhibited the immobilization of chromium and quantification of chromium content. The mortar samples from concrete after 56 days of air curing were subjected to toxicity characteristic leaching procedure (TCLP) test at pH 2.88. In addition, two days' short tank leaching test was conducted with the concrete samples as a whole. The leachability of toxic Cr^{6+} found in the range 0.03-0.09 mg/L and the total chromium (TCr) values in the range 0.12 -0.17 mg/L, which are less than discharge standard as per EP Act (1986), India. All these leaching test results comply with the discharge norms to land and inland surface water, respectively. Thus, the concrete specimens using aforesaid wastewater satisfy the technical aspects and fulfil the environmental requirement.

Keywords: Chromium, Leaching, Immobilization, Concrete, Water treatment.

INTRODUCTION

Hexavalent chromium (Cr^{6+}) is carcinogenic in nature and one of the fatal contaminants in chrome plating industry widespread to the water bodies without stabilization [1,2]. It is a serious environmental issue as Cr^{6+} is very toxic and the majority of movable chromium form in water systems are lethal to biological system [3]. Unlike insoluble Cr(III) salts, Cr(VI) are soluble and they leach out when used in cement matrix. It has been reported that Portland cements blended with blast furnace slag were effectively reduced to Cr(III) and were immobilized in cement matrix [4-8]. Furthermore, there is immobilization of [Cr^{6+}] by cement-based S/S owing to the creation of a low soluble calcium chromate ($CaCrO_4$) complex [9]. Slag based Portland cements provide effective immobilization matrix and the same is increased with decreasing water to cement ratio [10]. The mechanism behind the reduction of Cr^{6+} to Cr^{3+} was accomplished by ferrous salts in iron bearing waste slag. Reports are there for the immobilization of Cr(III) by the cement matrix and the reduction rate of Cr^{6+} improved by lowering pH or increasing slag dosage [11,12]. According to Zhang *et al*. [13], sulphide ions play a crucial role in the reduction of hexavalent chromium followed by immobilization in alkali-activated fly ash matrices. Though ferrochrome slag has approximately 12% chromium, still it was reported that the chromium was intrinsically immobilized [14]. Bae *et al*. [15] reported the reduction of Cr^{6+} to Cr^{3+} and resultant immobilization was accomplished by the use of Sb_2O_3 with the oxidation of Sb(III) to Sb(VI). In addition, reduction in slump value in the range of 25-50% has been reported with the use of treated wastewater in concrete work, thus necessitating use of super plasticizers to improve workability. Strength aspects of concrete by and large is reported to be almost unchanged [16]. In general, based on the results of different tests, indicated that leachability of chromium extensively dependent on the amount of chromium present in the mortar. Increasing water-to-cement ratio (W/C) slightly decreased the leaching of chromium and also, both increasing the amount of Cr^{6+} and W/C affect the microstructure of cement mortar. Furthermore, result shows that stabilization/solidification (S/S) efficiency of Cr^{6+} in cement mortar is very low [17].

The effluents from chrome plating industry mainly contain Cr^{6+} in their wastewater in the range of 100 to 300 mg/L. With this mentioned value of chromium, it cannot be disposed to surface water or inland water bodies. In this study, we used Cr^{6+} contaminated wastewater in manufacturing of concrete for civil work. In order to optimize chromium immobilization, different blended cement pastes were attempted. Slag based Portland cement was found to be optimized slag for the immobilization of Cr^{6+}. Thus, Portland slag cement (PSC) was selected for experimental work in concrete. Concrete specimens were cast with PSC and chromium bearing wastewater and further cured for 28 and 56 days. Various fresh and hardened properties of concrete were evaluated to analyze the technical suitability of the concrete for various applications. The mortar samples from concrete after 56 days of air curing were subjected to toxicity characteristic leaching procedure (TCLP) test at pH 2.88. Chromium(VI) and total chromium (TCr) leachate was found to be less than 2.0 mg/L in each sample, which is very less than the TCLP limit (5.0 mg/L) to be used for concrete manufacturing. Furthermore, two days' short tank leaching test was conducted with whole concrete samples. The amount of Cr^{6+} and total chromium content (TCr) leached out was less than 0.1 mg/L and 2.0 mg/L, respectively. Aspiration of this study was to make a process that optimizes the quantity of stabilization and solidification agents and to resolve whether concrete concentrated the quantity of chromium in the TCLP leachate. The above studies bring the technical compatibility and environmental compliance of concrete specimen with respect to chromium pollution.

EXPERIMENTAL

Chromium bearing wastewater with the chromium(VI) concentration of 100, 200, 300, 500 and 1000 mg/L were prepared by dissolving analytical grade potassium dichromate. The standard Portland slag cement (PSC) was selected as per the specification (Table-1). Concrete mixture proportionate was prepared with natural crushed stone as coarse aggregate, natural river sand as fine aggregate with the chromium bearing wastewater in the mix ratio of 1:1.53:2.88 at wastewater to binder cement ratio of 0.45.

TABLE-1
PROPERTIES OF PORTLAND SLAG CEMENT (PSC) IN CONCRETE

Properties	PSC [IS 455: 2000]
Specific gravity	3.10
Initial setting time (min)	30
Final setting time (min)	600
Blast furnace slag (%)	55-58
Insoluble residue (%)	2.5
MgO (%)	6
SO_3 (%)	2.75
Loss of ignition (%)	5
Specific surface (cm^2/g)	3000
Compressive strength (28 days) (MPa)	31

Properties of cement, coarse and fine aggregate: As specified the properties of materials PSC, coarse aggregate and find aggregate in Tables 1-3, respectively were all meeting the IS specification.

TABLE-2
PROPERTIES OF NATURAL STONE AS COARSE AGGREGATE IN CONCRETE

Properties	Natural stone	IS specification
Specific gravity	2.72	
Abrasion resistance (%)	27.1	< 50%
Crushing strength (%)	31.9	< 45%
Impact strength (%)	26.5	< 45%
Size mm	6 to 20	
Water absorption (%)	0.32	

TABLE-3
PROPERTIES OF NATURAL SAND AS FINE AGGREGATE IN CONCRETE

Properties	Natural sand IS specification
Specific gravity	2.67
Fineness modulus	4.00
Grading	Zone III
Fineness modulus	4.0%

Properties of ground granulates blast furnace slag: Ground granulates blast furnace slag (GGBFS) chemical composition as obtained from National slag association data base are compared with IS 12089-2004 and the same is given in Table-4.

TABLE-4
CHEMICAL COMPOSITION OF BLAST FURNACE SLAG

Constituent	Percentage by mass	As per IS 12089-2004
Calcium oxide CaO	34-43	Manganese oxide 5.5% maximum
Silicon dioxide SiO_2	27-38	Magnesium oxide 17.0% maximum
Aluminium oxide Al_2O_3	10.7-12	Sulphide sulphur 2.0% maximum
Magnesium oxide MgO	12.7-15	Insoluble residue 5.0% maximum
Iron FeO or Fe_2O_3	0.5-1.6	Glass content 85% minimum
Manganese oxide MnO	0.44-0.76	$(CaO + MgO + Al_2O_3)/SiO_2 >= 1.0$
Sulfur	1.4-1.9	$(CaO + CaS + 1/2MgO + Al_2O_3)/(SiO_2 + MnO) >= 1.0$

Fresh and hardened concrete test: Fresh concrete tests like slump value, compaction ratios and fresh density values were measured. The M-30 grade concrete cubes were cast and curing with water at normal temperature for 28 and 56 days were carried out. After requisite days of curing the values of hardened concrete tests like compressive strength, split tensile strength and flexural strength values were measured.

XRD and SEM analyses: The mortar portions from the concrete specimens were carefully removed crushed and subjected to X-ray diffraction (XRD) make Rigaku-Ultima IV of Japan. Different minerals were characterized by comparing with ASTM data cards. The SEM characterization studies were conducted using instrument, Model-FEI-Quanta 250 with Oxford EDS detector to determine the chemical composition of different phases in the mortar portion of the concrete.

Leaching study: Regulatory leaching studies were undertaken to evaluate the performance of concrete specimens with respect to the elution of chromium from each of the concrete specimen. The mortar portion of the concrete samples were removed and powdered to size < 9.5 mm. TCLP test standardized by US EPA Method 1311 [US EPA 2003] was used for characterizing a waste as hazardous or non-hazardous.

Extraction liquid 1 was prepared by diluting a mixture of glacial acetic acid (11.4 mL) and of 1 N NaOH (128.6 mL) to 2 L using distilled water and the pH of the solution maintained to 4.93 ± 0.05. Extraction liquid 2 was prepared by adding 5.7 mL glacial CH_3COOH with 1 L of distilled water. The pH of this extraction liquid 2 was maintained to 2.88 ± 0.05. In this case, the extraction liquid 2 was added to 50 g of mortar at liquid-to-solid ratio of 20:1 and the mixture was agitated for 18 ± 2 h. After rotation, the final pH was measured and the slurry was filtered using a 0.45 μm Whatman filter paper. The leachate samples were then analyzed as per the procedures laid down in standard methods of water and wastewater analysis (APHA 2005), for the estimation of hexavalent chromium and the total chromium.

Two day's short tank leaching test: In order to determine the nature and properties of the material matrix under investigation, NEN 7375, the Dutch tank leaching test was used. The leaching characteristics of concrete sample under aerobic condition with two days' short tank leaching under similar conditions were investigated. The concrete blocks after 56 days air curing was placed in a leaching fluid (demineralized, pH neutral water) and reloaded the eluate at specified times. Cubes of 5 cm size were kept in contact with deionized water using a liquid to surface area ratio of 5 mL of deionized water for every exposed solid surface area. The concentrations of chromium leached in the successive eluate fractions were measured and the appropriate pH value at which leaching takes place was determined by the material itself. The chromium release values after two days were reported to be higher than 64 days' average concentration. Hexavalent chromium and total chromium were determined as per the procedures laid down in standard methods of water and wastewater analysis (APHA). These values are compared with that of Indian standard discharge norms [EP rules 1986].

RESULTS AND DISCUSSION

Fresh concrete tests like average results of slump value, compaction factor and fresh density values of the concrete specimens were determined and shown in Table-5. From the results, it has been found that with increase in chromium concentration values, there was marginal decrease in slump value (maximum decrease of 7 mm for Cr5) and similarly, the compaction factor with respect to conventional concrete sample was in the medium range *i.e.* from 0.87 to 0.81 (Table-5) with normal water curing. Nevertheless, fresh concrete properties by and large remained unaffected by the use of chromium containing wastewater. This could be attributed for the presence of lower concentration of chromium in the wastewater. As shown in Table-6, the average hardened concrete test properties such as compressive strength of cast cubes, split tensile strength of cast cylinders and flexural strengths of cast prisms after 28 and 56 days of curing were determined and the same was compared with conventional concrete to assess the variation of these properties. It was observed that the compressive strength showed a gradual marginal decline with increase in chromium(VI). The similar kinds of trend in case of split tensile strength and flexural strength were observed. As the concentration of chromium in wastewater remains at lower value and they are not likely to affect the hydration reactions and thus the strength properties. To observe the chromium immobilization behaviour in the different hydration products, The XRD analysis of the mortar portion of concrete specimen consisting of PSC and natural river sand were carried out after curing of 56 days. As shown in Fig. 1, no peak had been observed in the hydration product without addition of hexavalent chromium. One of the important products of hydration is Portlandite has the tendency to interact with any addition of chromium and form relatively insoluble calcium chromate.

TABLE-5
FRESH CONCRETE TESTS

Concrete specimens	Slump value (mm)	Compaction factor	Fresh density (kg/m^3)
C1-control sample with no chromium	67	0.89	2360
Cr1 with 100 mg/L	65	0.87	2384
Cr2with 200 mg/L	65	0.82	2390
Cr3 with 300 mg/L	64	0.81	2421
Cr4 with 500 mg/L	62	0.81	2422
Cr5 with 1000 mg/L	60	0.81	2424

TABLE-6
HARDENED PROPERTIES OF CONCRETE SPECIMEN

Specimens	Compressive strength		Split tensile strength		Flexural strength	
	28 days	56 days	28 days	56 days	28 days	56 days
C1	57.2	69.6	3.92	4.88	12.2	13.5
Cr1	56.8	63.1	3.89	4.95	12.3	13.7
Cr2	55.5	63.0	3.85	4.92	12.0	13.5
Cr3	50.2	58.8	3.78	4.81	11.9	13.5
Cr4	48.1	58.4	3.77	4.76	11.9	13.5
Cr5	48.1	58.4	3.76	4.98	12.1	13.6

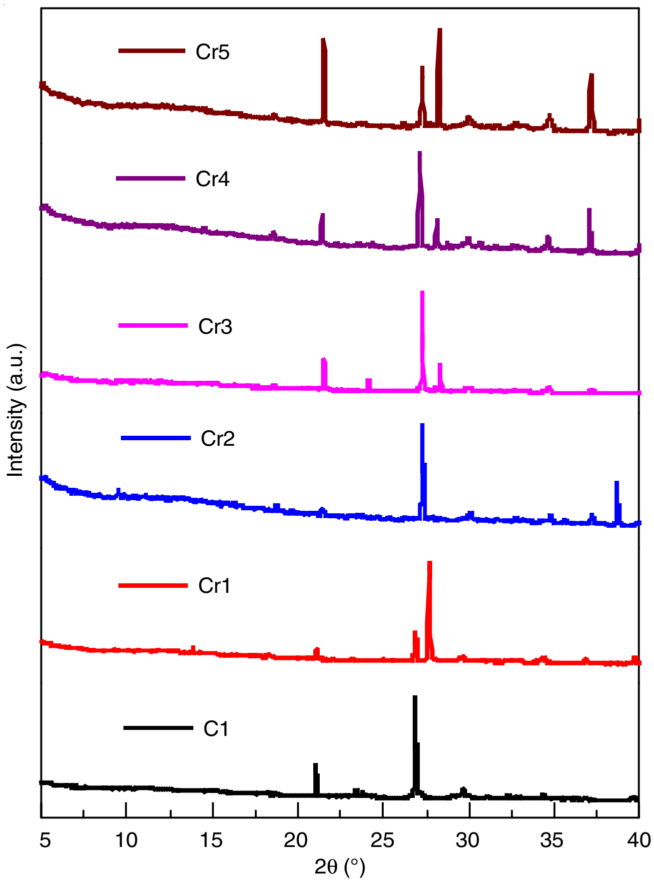

Fig. 1. XRD study of the mortar portion of the concrete specimen after 56 days of curing

At a higher pH of 12, hexavalent chromium converted largely to the insoluble calcium chromate and was immobilized in cement matrix at 2θ angle 32.3° and 35.2° in XRD (Fig. 1) [9,18]. Thus, the immobilization of Cr^{6+} by cement matrix was attained due to the formation of this low solubility salt of calcium chromate. As the concentration of Cr(VI) in wastewater remains at lower value and they are not likely to affect the hydration reactions and thus the strength properties.

SEM-EDS studies: Scanning electron microscopy and energy dispersive spectrum (EDS) study was carried out for samples cured for 56 days. Fig. 2 shows the chromium traces in different samples and the corresponding chromium quantifications for each sample are shown in Table-7. As observed, the chromium is present in traced as the small chromium peaks were observed in the SEM morphology. The chromium values ranging from 0.01 to 0.07 mg/L (Table-7) observed in EDS figures and are expected as the chromium concentration in the wastewater varies from 100 to 1000 mg/L.

TABLE-7
QUANTIFICATION OF CHROMIUM IN EDS

Sample code	[Cr^{6+}] conc. in samples	Weight % of chromium in EDS
C1	Nil	0.00
Cr1	100 mg/L	0.01
Cr2	200 mg/L	0.01
Cr3	300 mg/L	0.02
Cr4	500 mg/L	0.05
Cr5	1000 mg/L	0.07

Short tank leaching study: After successful immobilization of chromium in the cement matrix, the leaching studies were performed to find out the amount of chromium leached out from the concrete sample. The 2 day's short tank leaching test results (Table-8) [19] indicated that the leached out chromium(IV) values found were in the range 0.03-0.09 mg/L and the total chromium (TCr) values in the range 0.12 -0.17 mg/L, which are less than the 0.1 mg/L (Cr^{6+}) and 2.0 mg/L (TCr), respectively. Thus, the low-level release of chromium complying the government of India discharge standard as per EP Act (1986).

Toxicity characteristic leaching procedure (TCLP) leaching test: Table-8 shows the amount of leachate chromium extracted from the mortar samples of crushed concrete samples using the TCLP test. The regulatory TCLP leaching studies were carried out to find out the elution of chromium. The leached Cr^{6+} and TCr were in the range 0.21-1.56 mg/L and 0.23-1.74

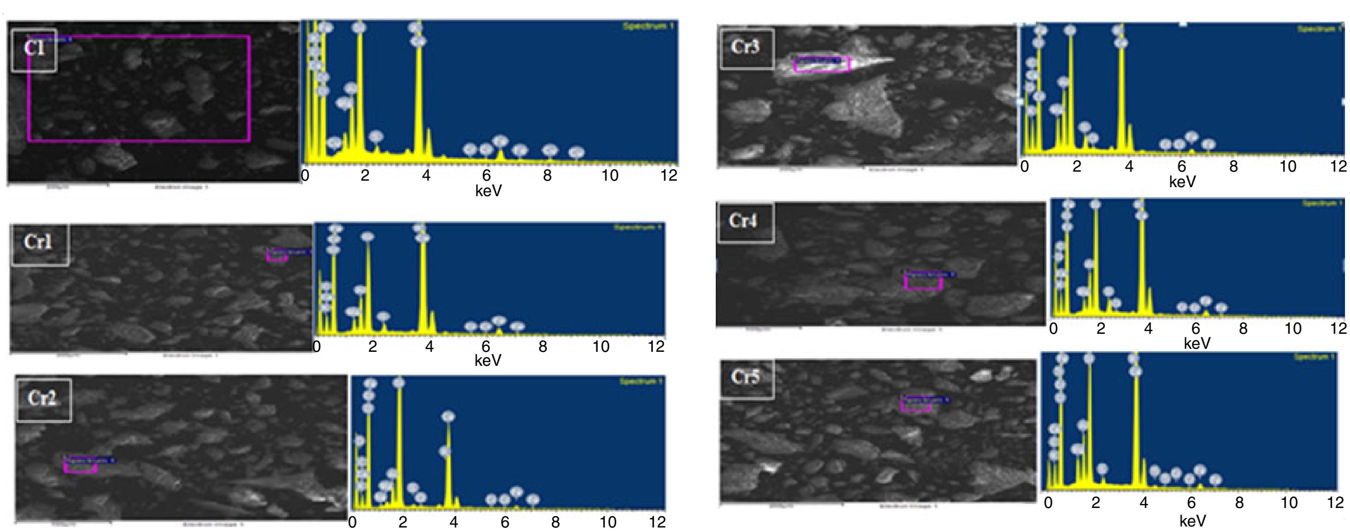

Fig. 2. SEM and EDS study of samples C1 and Cr1-Cr5 after curing for 56 days

TABLE-8
CHROMIUM LEACHATE IN SHOT TANK LEACHING TEST

Sample code	Cr(VI) in leachate (mg/L)	TCr leachate (mg/L)	EP Act (1986) India
C1	0.02	0.08	
Cr1	0.03	0.12	
Cr2	0.04	0.13	Cr^{6+} = 0.1 mg/L
Cr3	0.05	0.14	TCr = 2.0 mg/L
Cr4	0.07	0.16	
Cr5	0.09	0.17	

mg/L, respectively (Table-8) and are in compliance with the chromium limits of 5 mg/L prescribed by TCLP standard. That means the wastewater coming out of concrete samples can be safely disposed to land.

Conclusion

The adverse effect of the chromium mobilization in the chromium contaminated wastewater could be minimized by reusing chromium bearing wastewater in concrete preparation without any significant effect in its hardening properties. Fresh concrete test values are reported slightly less than the control sample with no chromium and are by large in acceptable range. The hardened test results for the said chromium(IV) containing concrete samples revealed that the decrease in compressive strength, split tensile strength and flexural strength are very less and in the acceptable range to satisfy the mechanical strength requirements. The immobilization of chromium(IV) in calcium chromate phase has been investigated through the XRD studies. The quantification of chromium(IV) in concrete specimens made in chromium contaminated water revealed from SEM and EDS studies. The leaching studies investigated through toxicity characteristic leaching procedure (TCLP) study and short tank leaching tests were complied the regulatory requirements. Thus, the chromium plating industry wastewater with chromium(VI) concentration in the range of 100-300 mg/L may be safely used in preparation of concrete for general purpose civil work.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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