

Research Article

Solidification and Leachability of Cr (VI) in Rice Husk Ash-Blended Cement

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Received 15 March 2011; Accepted 26 April 2011

Academic Editor: M. Maslehuddin

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Investigations carried out to study the effect of Cr (VI) (1000–3000 mg/l) on solidification and hydration behavior of Ordinary Portland cement (OPC) and rice husk ash (RHA) blended (10%, 20%, and 30%) cement show that addition of RHA accelerates final setting as compared to control samples (OPC) and retardation in setting time has been observed on increase in rice husk ash concentration (10%–30%). Solidification studies show that the compressive strength of controls and rice husk ash blended samples increases with increase in the curing period and maximum strength was observed with 20% RHA blended samples. With the increase in Cr (VI) concentrations, the strength of OPC and RHA blended samples decreases as compared to controls (without chromium). The results of Toxicity Characteristics Leaching Procedure (TCLP) test, ($\text{pH} \approx 3$), show that the retention capacity of OPC and RHA blended samples was in the range of 92% to 99% and the leached Cr (VI) concentration was under the allowable limit (5 mg/l) of U.S. EPA. The chemistry of influence of Cr (VI) on hydration of cement was examined by X-ray diffraction which shows the formation of various crystalline phases during solidification in rice husk ash blended cement.

1. Introduction

Solidification and stabilization (S/S) processes are waste treatments designed to improve the handling and physical characteristics of liquid or semisolids and decrease the release of 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 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].

Many investigators have analyzed the effect of chromium on the different Portland cement phases [11–13] and its solidification in cementitious matrix [14–16]. The solidification of the stabilized zinc-cyanide plating sludge was carried out using OPC and pulverized fuel ash (PFA) as solidification binders. Experimental results showed that a significant reduction is observed when plating sludge was added to both OPC and OPC/PFA binders, but the negative effect was minimized when PFA was used as part substitute for OPC [2]. Pera et al. [15] reported that the immobilization of Cr (VI) by hydraulic binders occurs by one or a combination of the following mechanism at the same time: addition, substitution, (Cr-CSH, Cr-ettringite), or precipitation of new components. The results obtained show that OPC is the most efficient binder. The limestone filler has been used to solidify Cr (VI) with Portland cement [16, 17], and it is observed that limestone caused a hydration acceleration of Portland cement at early ages. In this reaction, formation of calcium carboaluminate as results of the reaction between CaCO_3 from limestone and C_3A from cement have been reported. The incorporation of limestone in calcium silicates hydrates (CSH) and the acceleration of C_3S hydration has

also been proposed [16, 18, 19]. X-ray diffraction (XRD) has been found to be useful application to characterize the crystalline phases of the solidified wastes [1, 12–16]. XRD patterns of OPC and limestone-blended cement containing Cr (VI) have revealed the formation of similar crystalline structures like ettringite, Cr-ettringite, and betornite during hydration of C_3A [12, 13, 16]. Leaching characteristics of the Cr (VI) has been studied by TCLP in different pH conditions and binder systems [1, 12, 13, 15, 16]. It is observed that factors such as waste form, binder system, curing time, and cement-to-waste ratio affect the leachability of a waste after an S/S treatment.

Rice husk is an external covering of rice, which is generated during dehusking of paddy rice. The rice husk accounts for 20 wt% of the paddy produced. The husk is bulky in characteristics and, therefore, causes problems during its handling and disposal. In developing countries, rice husk is normally used as bulking agents for composting of animal manure or as biomass fuel. The high silicon content of rice husk also makes it more favorable to be used as part substitute for ordinary Portland cement (OPC) in low-cost concrete for rural housing [20, 21]. Several research works have been conducted on the use of rice husk ash as mineral additive to improve the performance of concrete [22–24]. However, its application in hazardous waste treatment is relatively new and is under investigations. Recently, the role of rice husk ash-blended cement has been studied in stabilizing metal containing wastes [25]. The results reveal that the interfering effect of synthetic zinc hydroxide and plating sludge have been reduced using cement blended with 10 wt% reactive rice husk ash.

In the present study, rice husk ash was partly used to replace OPC for solidification of synthetic Cr (VI) solution, and the effect on setting time, strength development, XRD behavior, and leachability of Cr (VI) has been investigated.

2. Experimental Program

2.1. Materials. The ordinary portland cement (OPC) and rice husk ash (10%–30% w/w) mixed with OPC were taken as solidification binders. The physical and chemical analysis of OPC and rice husk ash is given in Table 1. A stock solution of 3000 mg/L of Cr (VI) was prepared using potassium dichromate to represent chrome plating industry effluent. The synthetic Cr (VI) solution was added to the solidification binders at a concentration of 1000, 2000, and 3000 mg/l. In the controls, distilled water was added in place of Cr (VI) solution.

2.2. Setting Time. The initial and final setting times of solidification binders 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. The penetration of the needle into the samples was observed for every 5 min, and the average values were reported.

2.3. Compressive Strength. To determine the effect of Cr (VI) on the compressive strength of the solidified samples,

TABLE 1: Physical and chemical analysis of Portland cement and rice husk ash.

Properties	Portland cement (43 G)	Rice husk ash
Specific gravity (kg/cm^3)	3.14	2.04
Insoluble residue (%)	1.3	—
Alkalies (%)	0.35	2.64
SO_3 (%)	2.10	—
Chloride (%)	0.012	—
LOI (%)	1.51	1.20
Surface area (m^2/kg)	308	22,000
Silica content (%)	20.6	90.52
CaO (%)	60.2	2.0
Magnesia (%)	1.4	0.7
Fe_2O_3	—	0.80
Al_2O_3	—	1.90

TABLE 2: Mix designs of the solidified wastes.

Identity	W/S ratio	Identity	W/S ratio
R0	0.27	R20	0.35
R0+1	0.27	R20+1	0.35
R0+2	0.27	R20+1	0.35
R0+3	0.27	R20+1	0.35
R10	0.30	R30	0.40
R10+1	0.30	R30+1	0.40
R10+2	0.30	R30+1	0.40
R10+3	0.30	R30+1	0.40

R = only RHA; R10 = 10% RHA; R20 = 20% RHA; R30 = 30% RHA

1 = 1000 mg/L Cr (VI); 2 = 2000 mg/L Cr (VI); 3 = 3000 mg/L Cr (VI).

cubical molds ($2.5\text{ cm} \times 2.5\text{ cm} \times 2.5\text{ cm}$) of OPC and rice husk ash-blended cement pastes were prepared. The mix designs and optimum water to solid (W/S) ratio are given in Table 2. The consistency was the same in all the cases. After initial curing of 1 day, demolded specimens were stored at relative humidity of not less than 95% in airtight glass containers at $27 \pm 2^\circ\text{C}$ for different periods up to one year. The compressive strength of the solidified samples was determined after curing for 1, 3, 7, 28, 90, 180, and 360 days. The compressive strength was determined as per IS: 4031 (1999) and the average value of three specimens were reported.

2.4. XRD and Leachability. X-ray diffractometry (XRD) was used to study the hydration process of OPC and rice husk ash-blended cement paste without and with addition of Cr (VI) at 28 days of curing. The samples were immersed in acetone to stop hydration and grounded to a particle size of $<45\text{ }\mu\text{m}$ for XRD. X-ray diffraction patterns were recorded on a Rigaku X-ray Diffractometer equipped with a rotating anode, utilizing CuK_α radiation at 40 kV and 30 mA.

The leaching tests were conducted for 28-, 90-, 180-, and 360-days-old hydrated samples using the EPA standard toxicity characteristics leaching procedure (TCLP) [13, 26]. Leaching test were carried out in distilled water as well as in

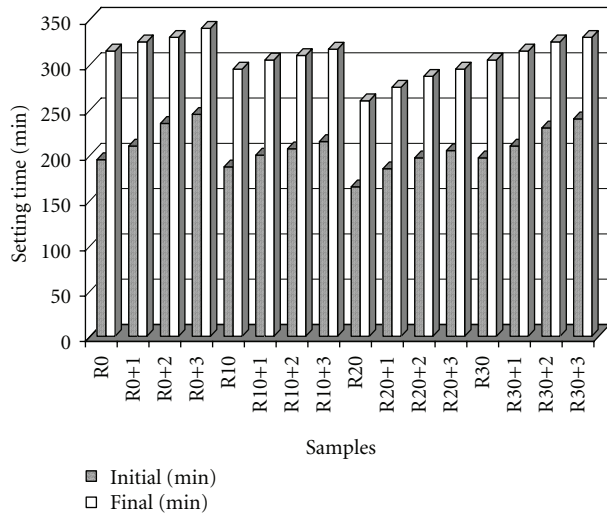


FIGURE 1: Effect of Cr (VI) on setting time of OPC and rice husk ash-blended cement.

acidic medium at a pH of about 3.0. Samples were ground to powder with a particle size <0.5 mm and leached (10 g) in 200 mL of water as well as in acetic acid ($\text{pH} \approx 3$) 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 $0.45 \mu\text{m}$ 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.

3. Results and Discussion

The effect of various Cr (VI) concentrations on the setting time, compressive strength, and leachability in OPC and rice husk ash-blended cement was investigated. The results are reported and discussed in the following sections.

3.1. Setting Time. The initial and final setting time of OPC and rice husk ash (10%–30%) blended cement without and with Cr (VI) (1000–3000 mg/L) were reported and are shown in Figure 1. The control cement (OPC) reaches initial and final set in 195 and 315 min, respectively. Addition of rice husk ash accelerates final setting as compared to control samples. Retardation in setting time was observed on increase in rice husk ash concentration (10%–30%), and this may be due the negative effects on silicate hydration responsible for longer setting [25]. It is also apparent (Figure 1) that the addition of Cr (VI) retards the setting process of control as well as rice husk-blended samples and the retardation is the function of Cr (VI) concentrations. The retardation in setting time of cement in presence of Cr (VI) may be due to the reaction between Ca^{2+} from $\text{Ca}(\text{OH})_2$ and Cr (VI) to form CaCrO_4 which is a low-solubility product (5.1×10^{-6}) as has been reported earlier [1, 27]. Further, the results show that mixes containing Cr (VI) have setting times within the range of IS: 8112 (1989).

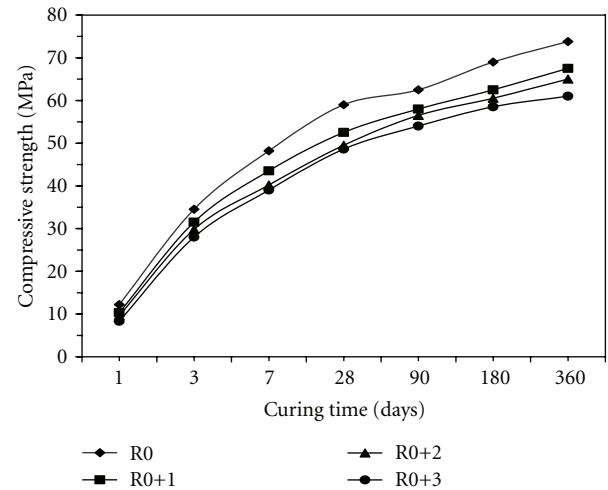


FIGURE 2: Effect of Cr (VI) concentration on compressive strength of OPC as a function of time in days.

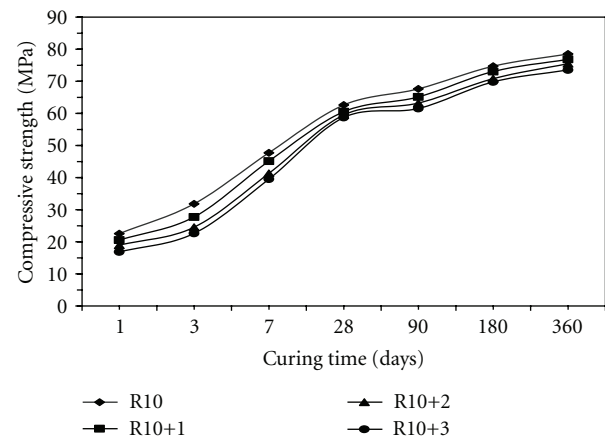


FIGURE 3: Effect of Cr (VI) concentration on compressive strength of OPC and rice husk ash- (10%) blended cement as a function of time in days.

3.2. Compressive Strength. The results of compressive strength of solidified samples of OPC and rice husk ash-blended cement paste are shown in Figures 2, 3, 4, and 5. It can be seen that the compressive strength of controls (R0 series) and rice husk ash-blended samples (R10, R20, and R30 series) with and without Cr (VI) increases with increase in the curing period up to 360 days. It is also observed that with the increase in Cr (VI) concentrations, the strength of all the mixes containing OPC and RHA blended samples decreases as compared to controls. The strength of samples ranges from 61 to 79 MPa for OPC as well as RHA-blended samples. However the strength in each case was more than the minimum strength required (0.3 MPa) as per EPA guidelines. Figure 2 shows that at 28 days, the strength of samples R0+1, R0+2 and R0+3 exhibits a loss of about 11%–18% as compared to the control (R0) at an early age of 28 days, while the loss in strength is 3%–8% (Figures 3–5) for the RHA-blended samples containing Cr (VI) as

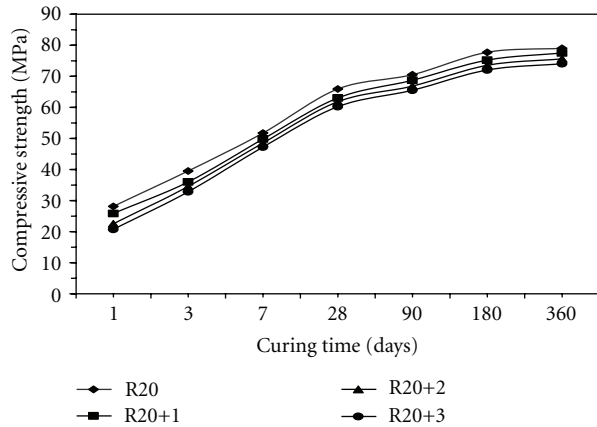


FIGURE 4: Effect of Cr (VI) concentration on compressive strength of OPC and rice husk ash- (20%) blended cement as a function of time in days.

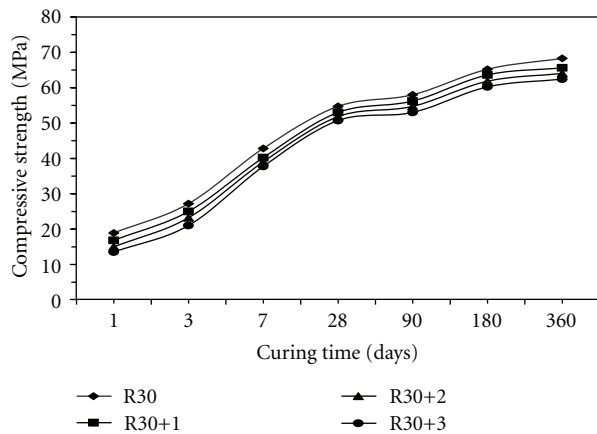
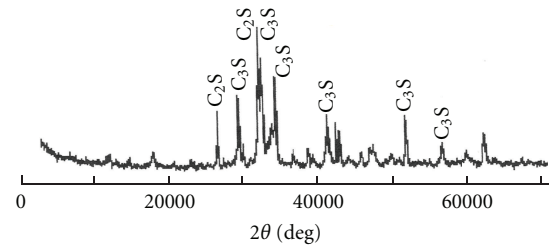


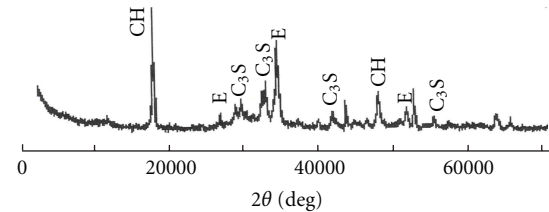
FIGURE 5: Effect of Cr (VI) concentration on compressive strength of OPC and rice husk ash- (20%) blended cement as a function of time in days.

compared to RHA blended samples without Cr (VI). It is evident from the results that the samples of RHA blended cement containing Cr (VI) show less reduction in strength as compared to OPC samples (R0 series). It confirms that the addition of rice husk ash in OPC minimizes the negative effect of Cr (VI) and the possible reason for this may be the formation of various crystalline phases containing Cr at an early age (28 days). It is also observed that with the increase in Cr (VI) concentrations, the strength of decreases as compared to controls (without chromium).

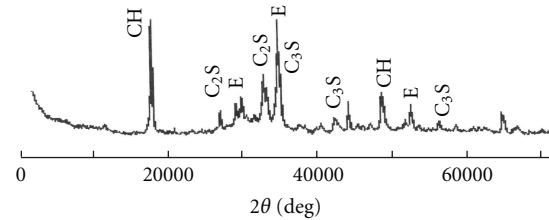
3.3. XRD and Leachability. The results of X-ray diffractograms evaluation show the formation of various crystalline phases after 28 days of curing which are more or less same for different Cr (VI) concentrations (1000 to 3000 mg/L). The X-ray diffractogram of R0+3, R20+3 of solidified samples after 28 days of curing are shown in Figures 6 and 7 along with X-ray diffractograms of unhydrated cement, R0 and R20.



(a) Unhydrated Cement



(b) Hydrated OPC paste



(c) Hydrated OPC paste with Cr (VI)

FIGURE 6: XRD of Unhydrated and hydrated cement paste without and with Cr (VI).

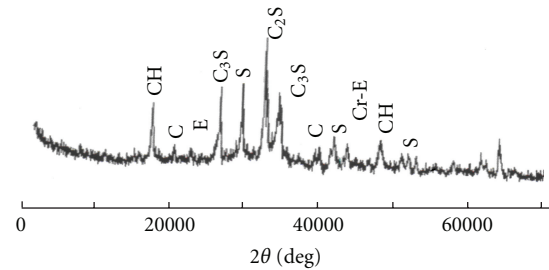


FIGURE 7: XRD of RHA-blended (20%) cement paste with Cr (VI) (S: sylvite).

The most prominent peaks in the unhydrated cement (Figure 6(a)) are of tricalcium silicate (C_3S) at 29.4°, 32.6°, 34.3°, 41.3°, 51.7°, and 56.6° and dicalcium silicate (C_2S) at 26.4° and 32.2°. Figures 6(b) and 6(c) show the XRD patterns of R0 and R0+3 samples after 28 days of hydration. The intensity of peaks of C_3S and C_2S reduces in hydrated OPC (R0) due to formation of calcium silicate gel (CSH). Calcium hydroxide (CH) was identified at 2θ of 18.1° and 47.3°. The peaks of ettringite (E) are also observed at 28.6°, 34°, and 50.7°. X-ray diffraction of rice husk ash shows that the ash mainly contains amorphous materials with small quantity of crystalline phases such as cristobalite (SiO_2) and sylvite. Figure 7 shows the XRD pattern of R20+3 after 28

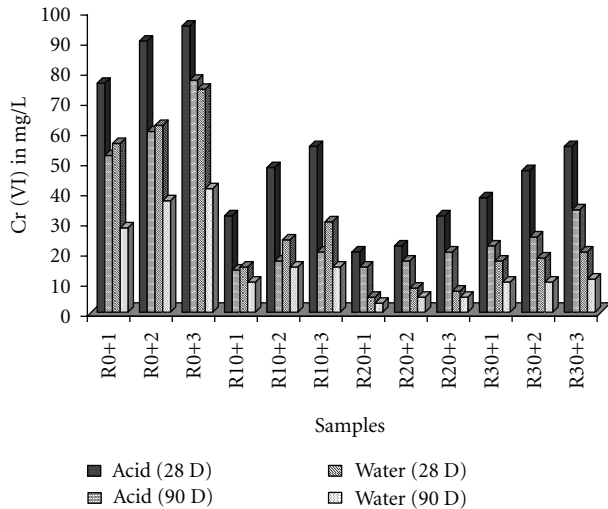


FIGURE 8: Leaching of Cr (VI) from solidified OPC and rice husk ash-blended cement.

days of curing, which shows chromium ettringite peak (Cr-E) at 44.9° along with other crystalline phases of CH, C_2S , C_3S , cristobalite (C), sylvite (S) similar to rice husk ash. The Cr-ettringite phase is a low-solubility product which restricts Cr (VI) leaching in acidic medium and solidification of Cr (VI) in R0 and R20 may be due to addition, substitution (Cr-CSH, Cr-ettringite) or precipitation of new components as is observed by earlier workers [17].

TCLP leaching tests for the hydrated OPC and blended cement samples containing Cr (VI) are carried out at various curing time (28 and 90 days) in water and acid ($pH \approx 3$), and results are shown plotted in Figure 8. It is observed that leaching was less in water in all cases as compared to acidic medium. The Cr (VI) concentration in the leachate of OPC samples was less as compared to leachate of RHA blended samples. This may be due to binding of Cr (VI) by the cement which is available in more quantity as compared to RHA-blended samples. Figure 8 shows that maximum leaching of Cr (VI) in acidic medium for OPC samples R0+1, R0+2 and R0+3 which decreases from 76 to 52, 90 to 60, and 95 to 77 mg/L, respectively, with increase in curing time from 28 to 90 days in acidic environment. The leached Cr (VI) concentration reduced from 55, 20, and 22 mg/L to 20, 15, and 17 mg/L for RHA-blended cement samples R20+1, R20+2, and R20+3, respectively, (Figure 8). The results also show that the leaching of Cr (VI) is a function of initial concentration and increases with the increase in initial concentration. The retained percentage of Cr (VI) in OPC and blended cement samples was observed in the range of 92% to 99% and was independent of initial Cr (VI) concentration. However, the percentage of Cr (VI) retained in water is higher for R0 and R20 series samples (about 99%). It is evident that the difference in percentage retention of Cr (VI) between R0 and R20 samples is very less, while the quantity of available cement in R20 is smaller. It shows that R20 samples have higher efficiency of Cr (VI) retention as compared to the R0 samples. However, the

leached concentration of Cr (VI) was more as per US-EPA allowable limit (5 mg/L) in RHA-blended samples (10%) containing 1000 mg/L of Cr (VI).

4. Conclusions

The following conclusions can be drawn based on the experimental study.

- (1) Addition of Cr (VI) retards the initial and final setting times of R0 and RHA-blended cement and retardation increases with increase in Cr (VI) concentration.
- (2) Samples of R20 series containing Cr (VI) exhibit low decrease in the percentage strength at an early age (28 days) as compared to the R0 series, and the possible reason for this may be the formation of various Cr phases at an early age in R20 series samples. The compressive strength of R0 and R20 series observed were greater than the EPA compressive strength (0.3 MPa) requirement for S/S treatment of hazardous wastes.
- (3) During TCLP tests, RHA-blended samples (R20) show high retention capacity for Cr (VI) as compared to R0 samples in acidic $pH \approx 3$. This shows that rice husk ash-blended cement are the adequate binders to confine the high concentration of hazardous Cr (VI) for reduction of negative impact on land and ground water quality.
- (4) The reaction products and various crystalline phases were identified by XRD for R0 and R20 samples with and without addition of Cr (VI). The retention of Cr (VI) by solidification in cementitious matrix in OPC may be due to addition, substitution (Cr-CSH, Cr-ettringite), or precipitation of new components.

Acknowledgment

Author is grateful to the Director, CSIR-CBRI, Roorkee for his permission to publish the present work.

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