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Influence of rice husk ash and rice tiller ash along with chromate reducing agents on strength and hydration properties of Ordinary Portland Cement

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HIGHLIGHTS

- Blended cement samples of stannous chloride are more effective in reducing Cr(VI) than 1% ferrous sulphate.
- Delay in initial hydration process can be overcome by adding rice husk ash or rice tiller ash.
- Amorphous silica of RHA and RTA provides strength to the cement.
- Formation of calcium silicate hydrate was confirmed by TGA SEM and XRD studies.

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ABSTRACT

Six blended cement samples were prepared by adding either reducing agents (1% $SnCl_2{\cdot}2H_2O$ and $FeSO_4{\cdot}2H_2O$) only or reducing agents along with agricultural waste (rice husk ash, RHA and rice tiller ash, RTA). Cr (VI) leachability of pure Ordinary Portland Cement, OPC (S1) and blended samples (S2–S7) was checked using the standard diphenylcarbazide (DPC) method. It has been observed that blended cement samples with 1% stannous chloride (S3, S5 and S7) are more effective in reducing Cr(VI) content than cement samples with 1% ferrous sulfate (S2, S4 and S6). Addition of reducing agents only (S2 and S3) delayed the initial hydration process, as reducing agents might be reacted 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 (S4–S7). 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 thermo gravimetric analysis (TGA), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

1. Introduction

Leaching of hexavalent chromium from the cement sample leads to serious health hazards in the people working with cement [1]. Inhalation and direct contact of Cr(VI) may cause asthma and skin cancer, respectively [2,3]. Thus, the reduction of Cr(VI) to Cr (III) (less toxic) is an area of prime concern and need special attention. Addition of reducing agents likes salts of iron and tin during the grinding and packaging in the industry is already in practice [4–6]. The presence of free lime and other oxides in Portland cement affect the reduction efficiency and storage stability of these reducing agent and to overcome this problem high dose of these agents is required [7,8]. But high doses not only affect the cost of cement, but also retard the hydration process and compressive strength of cement materials [9,10]. Overdosing of reducing agent can be minimized by the used of reducing agent at the time of construction, but it retards the initial hydration processes [7,9]. Presently, industries using rice husk ash and rice tiller ash for improving the hydration process. The non-crystalline silica of RHA posses high specific surface area and pozzolanic reactivity, thus the use of RHA with cement enhances its workability and stability, decreases heat evolution, thermal cracking and plastic shrinkage. It also provides a solution to dispose of this byproduct [11–17].

Thus, there is a need of new composition which can take care of storage stability, hydration process, compressibility and utilization of agricultural waste. Keeping these points in mind, in present

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Table 1
Particle size analysis of OPC, RHA and RTA.

S. No	Particle size (μ)	Sample OPC (%)	Sample RHA (%)	Sample RTA (%)
1	>212	Nil	14.857	33.873
2	>150 < 212	Nil	12.995	22.444
3	>125 < 150	Nil	10.305	9.621
4	>106 < 125	0.463	11.910	8.906
5	>90 < 106	0.280	9.637	3.492
6	>75 < 90	0.632	10.224	5.021
7	>63 < 75	1.184	6.312	4.625
8	>53 < 63	1.109	5.166	2.114
9	>45 < 53	1.750	3.808	1.779
10	>38 < 45	3.446	3.422	1.660
11	>25 < 38	10.802	2.314	1.633
12	>15 < 25	27.130	2.691	0.832
13	>8 < 15	33.855	2.401	Nil
14	<8	19.349	2.958	Nil

Table 2
Chemical composition of OPC, RHA and RTA.

Sample ID	Constituents%								
	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	LOI
OPC 43G	63.5	21.70	5.84	3.50	2.00	1.10	0.35	0.10	0.5
RHA	1.5	88.5	1	0.5	–	0.4	0.2	0.4	3
RTA	0.5	45.2	2.5	1.5	–	5.5	1.2	0.9	–

Table 3
Sample Information.

Sample ID	Composition of Samples
S1	Only OPC cement
S2	Cement with 1.0% $FeSO_4{\cdot}7H_2O$
S3	Cement with 1.0% $SnCl_2{\cdot}2H_2O$
S4	Cement with 1.0% $FeSO_4{\cdot}7H_2O$ + 10% RHA
S5	Cement with 1.0% $SnCl_2{\cdot}2H_2O$ + 10% RHA
S6	Cement with 1.0% $FeSO_4{\cdot}7H_2O$ + 5% RHA + 5% RTA
S7	Cement with 1.0% $SnCl_2{\cdot}2H_2O$ + 5% RHA + 5% RTA

research, six new cement compositions (blended cement) of Ordinary Portland Cement (OPC) with agricultural wastes (RHA/RTA) and chromate reducing additives ($FeSO_4{\cdot}2H_2O$ or $SnCl_2{\cdot}2H_2O$) 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. The hydration of these compositions has been ensured by FTIR, TGA/DTA, XRD and SEM.

2. Materials and experimental techniques

2.1. Materials

The Ordinary Portland Cement (OPC, 43-Grade of ACC brand) was supplied by Oriental Structural Engineers Pvt. Ltd. Rice husk ash (RHA) was collected from the local rice mill in district Etawah (U.P) and rice tiller ash (RTA) was obtained from agricultural land. Ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$), stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$), 1,5 diphenylcarbazide (DPC), H_2SO_4 and $K_2Cr_2O_7$ were procured from Mark India and are of analytical grade.

Chemical and particle size analysis of OPC, RHA and RTA has been carried out in the Shankar Laboratory (Table 1). TG studies were recorded with Perkin Elmer, Diamond at a heating rate of 10 °C/min. Cement samples with and without additive were tested for standard consistency as well as an Initial and final setting time using Vicat apparatus. Scanning electron microscopy (SEM) images of hydrated Portland cement were recorded with the help of JEOL Model JSM-6390LV scanning electron microscope. FAXS D8 advance diffractometer equipped with a Si(Li)PSD detector includ-

Table 4
Leached values of Cr(VI) from solidified samples (S1–S7).

Sample ID	Leachate concentration (in ppm)				
	3 days	7 days	28 days	60 days	90 days
S1	12	4	6	ND	ND
S2	4	2	ND	ND	ND
S3	2	ND	ND	ND	ND
S4	3	2	ND	ND	ND
S5	2	ND	ND	ND	ND
S6	2	2	ND	ND	ND
S7	3	ND	ND	ND	ND