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Effect of Immobilization of Cadmium Ions on the Hydration of Ordinary Portland Cement

Minocha AK and Manish Kumar Goyal*

Central Building Research Institute, Roorkee and NIPER, Mohali-Punjab, India

Abstract

The disposal of toxic wastes containing heavy metals may cause a peculiar environmental problem especially when these metals are present in water soluble form. In the present research varying concentration of cadmium ions have been studied for their effect on physical, chemical and engineering properties of 43 grade Ordinary Portland Cement like initial and final setting time, compressive strength, bulk density, leaching studies, microscopic studies etc. our Efforts have been made to establish a quantitative corelation between the different concentrations of cadmium ions used and the intensity of any change in above properties of the cement. Nitrate salt of cadmium has been taken in the concentration range 1000-5000 ppm and the results of these investigations are presented in this paper. The results show that Cd improves the Compressive strength as well as the bulk density of the mortar samples. The leaching studies shows that the concentration of cadmium is almost negligible in the leachate analysed by the Atomic Absorption Spectrophotometer and as the concentration increases in the mortar samples the leaching of cadmium ions decreased it shows all the added cadmium ions gets adsorbed on the surface of cement. Scanning electron microscopic studies shows that the C-S-H gel phases are denser than that of control samples and C-S-H phases are responsible for the improved compressive strength of cement samples.

Keywords: Heavy metals; Cement; Flyash; Setting time; Cadmium; Waste management

Introduction

Cadmium is generally present in a higher concentration in electroplating waste, paper industry waste, Battery waste etc. it is very toxic to human being and environment doses beyond the permissible limit causes Kidney damage, sterility on males, flu-like disorder and high blood pressure. Solidification/Stabilization (S/S) often uses cement and cement like material (and water if necessary) in the treatment of hazardous waste that are in liquid or sludge forms to produce a solid for land disposal in case of heavy metals containing wastes in which metal concentration are too low for economical recovery but high enough to represent a toxicity hazardous. The safe disposal of cadmium waste generating from electroplating, paper industry, paint industry etc. to protect human health and environment is an issue of concern. Cadmium is very interesting metal because of its toxic nature, high solubility and mobility characteristics. In the present work we explored the immobilization of cadmium ions with ordinary Portland cement. This paper also consist the leaching studies using Toxicity Characteristic leaching procedure recommended by USEPA-1311. In recent years there have been increased concern regarding the leaching of hazardous substances from land fill into local surrounding to assess the hazardous of heavy metal containing wastes prior to disposal. The leaching of heavy metal ions from cementitious waste has been extensively investigated by many researchers [1-4]. Solidification/Stabilization technology appears both cost effective and safe since the metals are converted into highly insoluble salts which donot leach into ground water at appreciable rates. Fixation is a technology used to transform potentially hazardous liquid or solid wastes into less hazardous or non hazardous solids before disposal in a landfill, thus preventing the waste from entering the environment [5-6]. The US Environmental Protection Agency also recognizes cementations.

Solidification/stabilization as "The Best Demonstrated Available Technology" (BDAT) for land disposal of most toxic element [7-10]. The solidification/stabilization (S/S) process would be the best practical technology to treat the Cadmium containing waste [11-20] and also found appropriate by other investigators in treating cadmium contaminated wastes [20-28]. Cullinane et al. [3] reported the solidification of hazardous waste. Vipulanandan [18] studied the effect of Chromium (VI) on the ordinary Portland cement. Deja and Ouki [10,28], reported the effect of different metal ions on activated slag and Portland cement. Halim et al. [24], Minocha et al. [25] reported the leaching effect and the effect on setting time of cadmium, chromium and other toxic heavy metal ions. Minocha et al. [26] reported the effect of copper metal ions on the ordinary Portland cement. Sadeghi et al. [29] reported Synthesis, characterization, and experimental investigation of surface activity of SERS substrates using neodymium oxide. Bahniman et al. [30] studied Novel design of combinational and sequential logical structures in quantum dot cellular automata. This paper presents the quantitative correlation between the varying concentrations of cadmium ions and the intensity of effect on physical, chemical and engineering properties of 43 grade Ordinary Portland Cement as there is a very less data reported in the literature about these variables and quantitative relationships are necessary in order to estimate the influence of the amount of metal ions on these properties. Therefore, attempts have been made to fill void in this data.

Materials and Methods

Materials

Nitrate salt of cadmium ($Cd(NO_3)_2.4H_2O$) from loba, India have been used for this study. The metal salt was used as obtained without

***Corresponding author:** Manish Kumar Goyal, Central Building Research Institute, Roorkee (India) and NIPER, Mohali-Punjab, India, Tel: +91-9417867616; E-mail: swetmann@gmail.com

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any further purification. Double distilled water was used to prepare the metal ion solutions throughout the study. Commercial Ordinary Portland cement 43 grade was used. Fly ash is an industrial waste, a byproduct generated from the thermal power plants due to the combustion of the coal at 1350-1650 °C with about 20% excess air in the furnace. Flyash constitutes 80-85% of the total ash produced. Flyash is known as a pozzolanic material which has no cementing properties but in the presence of moisture; chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. Benefit of flyash is the use of a zero-cost raw material. Chemical composition of the cement determined as per IS: 4032-1985 guidelines, presented in Table 1. The physical properties of the cement were tested according to IS: 4031-1996 and the results of these studies are given in Table 2.

Apparatus

Atomic Absorption Spectrophotometer (AAS), from Hitachi model no. Z-7000 has been used to determine the concentration of metal ions present in the leachate as well as in the waste. Hazardous waste filtration system from Millipore model no. YT-30142 HW was used to carry out toxicity characteristic leaching procedure as recommended by United State Environment Protection Agency (USEPA-1311) [7]. UV-Visible spectrophotometer (Aquamate) from Thermo Corporation was used for spectrophotometer studies. Vicat apparatus was used to determine the initial as well as final setting time of the cement. Compressive strength testing machine from central scientific instruments company was used to determine the compressive strength of mortar samples. Scanning electron microscope from LEO 438VP, UK was used for the microstructure visualization of the prepared cement samples.

Methods

Preparation of cement pastes and mortars: The effect of the addition of the varying concentrations of cadmium ions on the initial and final setting time of cement was determined according to IS: 4031-1996 guidelines and compared to the blank sample to know their effect on setting time of the cement. The samples were mixed by hand with a stirring rod. To determine compressive strength of blank mortar samples (cement: fly ash, 1:3) as well as metal ion containing samples were prepared. The mortar pastes were cast in 2.78” cubic iron molds. The samples were demoded next day and were kept dipped in water at constant temperature and humidity for curing. These samples were tested for bulk density, visual changes and compressive strength on 3, 7, 28, 60, 90 and 180 days of curing. Six samples were tested every time and the average values of these results were compared with blank sample values to assess the practical applicability of these compositions.

Constituent	Weight percentage
Silica	20.80
Aluminum oxide	4.40
Iron oxide	3.79
Calcium oxide	66.10
Magnesium oxide	3.30
Anhd. Sulfuric acid	3.00
Sodium oxide	0.20
Potassium oxide	0.70

Table 1: Chemical composition of the cement.

Physical parameter	Results
Loss on ignition	0.7%
Consistency	31.58%
Soundness	1.0 mm
Bulk density	1.421 g/cm^3
Initial setting time	175 min
Final setting time	300 min
Sodium oxide	0.20
Potassium oxide	0.70

Table 2: Physical properties of the cement.

Scanning electron microscopy: In this paper a technique called Scanning electron microscopy and digital image processing is used for obtaining two dimensional images of actual ordinary Portland cement as well as samples containing different concentration of cadmium ions. It is used for the identification of all major phases in OPC and the samples containing varying concentration of cadmium ions. SEM is generally used to know the fractured surface of cement and for the magnification of an image it can magnify an image upto three lakh times. The back scattered rays are used for imaging while secondary and X-rays are used for elemental analysis of the cement samples. Scanning electron microscopy is used for conducting materials. Scanning electron microscope from LEO 438VP, UK was used for the microstructure visualization of the prepared cement samples.

Leaching studies: Leaching experiments of cadmium ions from the solidified sample were conducted in accordance with the USEPA-1311-1996 for 28 days of curing. Metal containing samples were crushed to less than 2.4 mm in diameter was mixed with the distilled water at a liquid to solid (L/S) ratio of 10:1 and trumbled for 18 H at a speed of 30 rpm. The resulting solution (leachate) was filtered through 0.4 micro meter membrane filter to remove suspended solids and was then divided into two portions and the pH was measured. The samples were preserved below 4^{o}C before metal ion analysis. Atomic Absorption Spectrophotometer (Hitachi Z-7000) was used for the determination of heavy metal ion leached out in the solution and the results are presented in Table 5. Leachate was analysed in triplicate and the mean values were reported to ensure the reproducibility of the data. The results were compared with those obtained for blank samples to know the actual enhancement in the concentration of the particular metal in the leachate.

Results and Discussion

Visual observation

Control mortar samples as well as the samples containing different concentrations of cadmium ions were dipped in water for curing and the samples were analysed for visual observations at different intervals of time. It was found that the surface of control samples appeared rough with comparison of samples containing cadmium ions. It was found that as the concentration increases of cadmium ions in the cement samples the surface becomes smoother than the samples containing lower concentration of cadmium ions.

Bulk density

The bulk density values of mortar samples containing different concentrations of cadmium ions are reported in Table 3. The results shows that the bulk density values for one day curing is 2.303 ± 0.001

Binder system	No. of days	Average bulk density (+ 0.001 g/cm3) Cadmium			
		Control	1000 ppm	2000 ppm	5000 ppm
Cement + fly ash	1	2.303	2.303	2.303	2.303
	28	2.303	2.345	2.380	2.395

Table 3: Average bulk density values of solidified products on 1 and 28 days of Curing.

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g/cm^3 which is similar than that of control samples. But the result of the 28^{th} day of curing is quite improved than that of control samples. The bulk density values for 1000, 2000, 5000 ppm cadmium containing samples are 2.345, 2.380, 2.395 ± 0.001 g/cm^3. The result shows that the bulk density values increased with the increasing concentrations of cadmium ions in the mortar samples (Figure 1).

Compressive strength

The result of the compressive strength of cadmium ions with cement based system are presented in Table 4. Four samples have been taken and the average values are reported for the compressive strength. The result of the compressive strength of cadmium containing samples shows that the addition of cadmium ions improved the strength of the mortar samples. The compressive strength values for the blank mortar samples are according to the IS: 8112-1989 for 43 grade ordinary Portland cement, should be at least 230 kg/cm^2, 330 kg/cm^2 and 430 kg/cm^2 for 3, 7 and 28 days of curing. The addition of 1000, 2000, 5000 ppm of cadmium shows improved compressive strength for all the concentration added. Figure 2 for 1000 ppm cadmium containing samples 3 day CS is 352.5, for 7 day is 382.5 and for 28 day it was observed 510.0 kg/cm^2 for the concentration 2000 ppm 3,7, 28 day CS is 380.0, 486.6, 556.0 kg/cm^2 for 5000 ppm the CS values are 380.0, 484.0, 620.0 kg/cm^2. The percent change in compressive strength for 1000 ppm is 108.9, 87.7, 104.9, 96.8, 105.3, 111.6 for 3, 7, 28, 60, 90, 180 days of testing. For 2000 ppm 117.5, 111.6, 114.4, 97.5, 105.2, 113.8 and for 5000 ppm it was found 117.5, 111.0, 128.0, 13.7, 117.8, 116.1 Figure 3 It is clear from Table 4 that there is a significant increase in compressive strength for the Cadmium containing samples in comparison with controls and the intensity of the effect is directly proportional to the concentration of cadmium added.

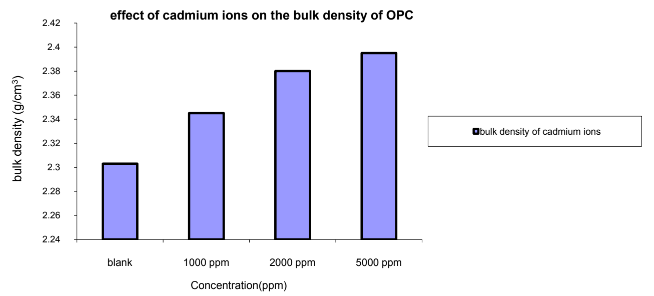

Figure 1: Bulk density of control and Cadmium on 28 day of curing.

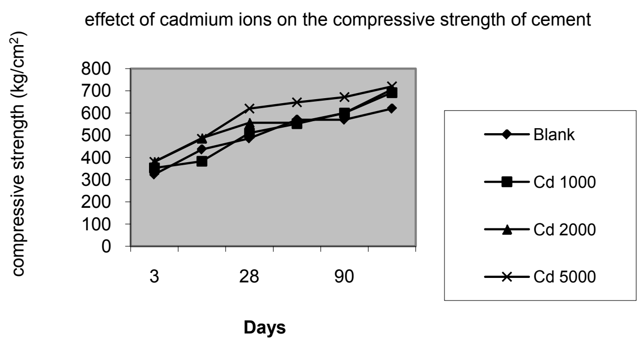

Figure 2: Effect of addition of cadmium ions on the compressive strength of cement.

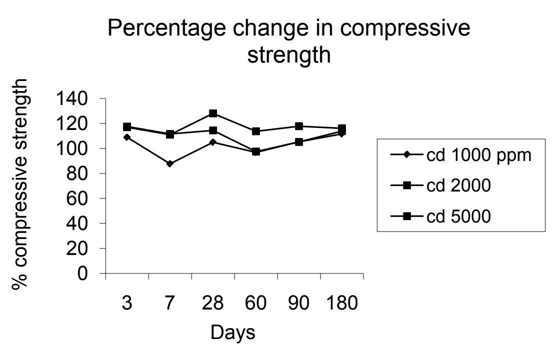

Figure 3: Percentage change in compressive strength of cadmium containing samples in comparison with control.

Microscopic analysis of the cement paste

The added cadmium salts have rather minor effect on cement hydration. When Cadmium Nitrate salt added with ordinary Portland cement cadmium ions begins to precipitated in the form of $Cd(OH)_2$. As clinker begins to be dissolved and hydroxide ion concentration increases. Apart from the rather minor acceleration of C-S-H hydration. The Cd salts have a little effect on the cement matrix. There are minor differences in the cement matrix at 28 days of curing specially an increase in the proportion of the C-S-H gel phase (Figures 4-7) as the C-S-H gel phase is responsible for strength development in the C-S-H gel phase very little free Cd^{2+} is available in solution so cadmium can not be readily leached because it is neither very accessible to water nor in a very soluble chemical form. Cadmium was assumed to be dispersed in the C-S-H matrix as it trapped with in the C-S-H pores. Interactions of cadmium salt with C-S-H were governing with the following Equation.

C-S-H+ metal metal-C-S-H

C-S-H+ metal metal –C-S-H+ Ca^{2+}

In C-S-H gel the addition of cadmium salts precipitated during solidification may accelerate or retard the hydration process. However when metal waste species are present as hydroxide or silicate salts they are more compatible with ordinary Portland cement because they from low solubility precipitate whose leachability reduced during solidification process. Cd formed a double compound $CdCa(OH)_4$ and it formed a precipitate present on the surface C-S-H matrix and inside the cement pores.

Leaching studies

The results of the leaching studies of the samples containing cadmium ions are reported in the Table 5. The data shows that the concentration leached out in the leachate are very very small and almost negligible. The concentration leached out in the samples containing 1000 ppm of cadmium ions are 2.5 ppm while the leaching concentration for the samples containing concentration 2000 ppm cadmium ions is 3.0 ppm and for 5000 ppm it is found only 5.0 ppm analysed by the Atomic Absorption Spectrophotometer. So almost all the concentration of added cadmium ions get adsorbed at the surface of cement. And as the concentration increases in the cement samples the concentration leached out becomes lower. So concentration

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Added metal concn. (ppm)	No. of days	% change in compressive strength in comparison of control					% change in compressive strength in comparison of control					
	3	7	28	60	90	180	3	7	28	60	90	180
Control	323.4	436.0	486.0	570.0	570.0	620.0	-----	-----	-----	-----	-----	-----
Cd (1000)	352.5	382.5	510.0	552.0	600.0	692.0	108.9	87.7	104.9	96.8	105.3	111.6
Cd (2000)	380.0	486.6	556.0	556.0	600.0	706.0	117.5	111.6	114.4	97.5	105.2	113.8
Cd (5000)	380.0	484.0	620.0	648.0	672.0	720.0	117.5	111.0	128.0	113.7	117.8	116.1

Table 4: Compressive strength (kg/cm^2) of mortar samples.

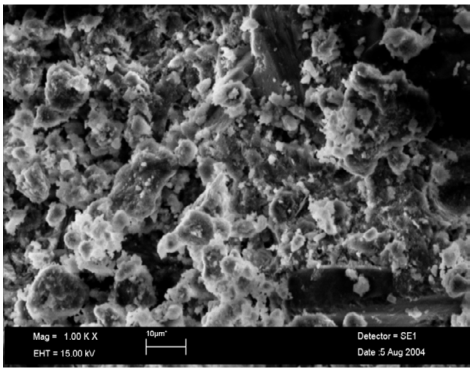

Figure 4: Sem image of control at 28 day of curing.

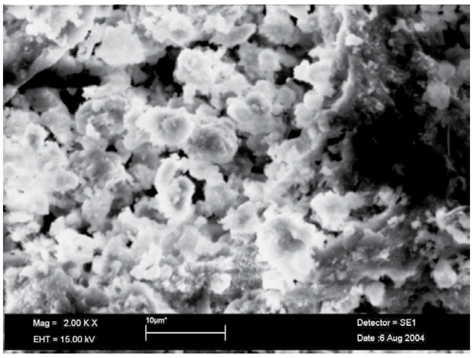

Figure 5: Sem image of Cadmium 1000 ppm at 28 day of curing.

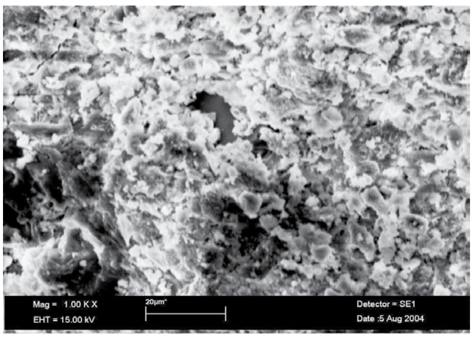

Figure 6: Sem image of cadmium 2000 ppm at 28 day of curing.

Cadmium ions	Results
Conc. Added (ppm)	Conc. Leached out (ppm)
1000.0	2.5
2000.0	3.0
5000.0	5.0

Table 5: Leaching Studies of cadmium ions with TCLP.

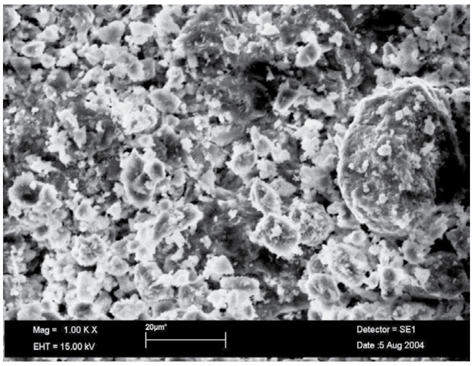

Figure 7: Sem image of cadmium 5000 ppm at 28 day of curing.

leached out of added cadmium ions is inversely proportional to the added cadmium ions.

Conclusions

On the basis of the above experimental study the following conclusions can be drawn:

1. Cadmium increased the compressive strength at different intervals of time to an appreciable extent as the concentration increased.

2. Different concentration of added cadmium ions increased the bulk density values and it is found the directly proportional to the added cadmium ions.

3. Leaching behaviuor of cadmium ions from the solidified mortar samples are negligible which shows that all the cadmium ions gets adsorbed on the surface of cement.

4. Scanning electron microscopic studies states that the C-S-H gel phases are denser of the cadmium containing samples than that of the control samples and C-S-H phases are responsible for the strength development of cement mortar samples.

So according to the following studies it is confirmed that the cadmium improved the above physical properties of the ordinary Portland cement so the industrial waste containing cadmium ions can be used as a material for the improvement of physico-chemical properties of ordinary Portland cement.

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