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Immobilization of Arsenate (As^{5+}) Ions in Ordinary Portland Cement: Influence on the Setting Time and Compressive Strength of Cement

A.K. Minocha and Amit Bhatnagar
Environmental Science and Technology (EST) Division,
Central Building Research Institute (CBRI) Roorkee-247 667, India

Abstract: In this study, the results of the studies exhibiting the effect of addition of varying concentrations of arsenic (V) on the initial and final setting time and compressive strength of 43 grade ordinary Portland cement have been presented. Efforts have been made to establish a quantitative correlation between the concentrations of As (V) used and the intensity of any change in above properties of the cement. Arsenic is present in ground water in a wide area of West Bengal (India) in lower concentrations and we have tried these concentrations also for this study. Sodium hydrogen arsenate ($Na_2HAsO_4.7H_2O$) has been taken in the concentration range 0.1-500 ppm and the results of these investigations are reported in this study. The results show that As (V) is bearable up to 500 pm concentration, without any considerable change in any characteristics of the cement.

Key words: Fixation, arsenic (V), cement, setting time, compressive strength, waste management

Introduction

Arsenic is a toxic element, which can be found in the natural environment as well as in various industrial wastes. It has widespread applications in agriculture and industry to control a variety of insect and fungal pests. In nature arsenic occurs in different oxidation states such as -3 (arsine), +3 (arsenite), +5 (arsenate), 0 (elemental arsenic) and organic matter mixed with arsine. The arsenic valence state primarily depends on type and source of arsenic pollutant, environmental pH, oxidation-reduction potential, ligand exchange, the presence of iron oxides and other sulfur-containing compounds, as well as microbial activities (Ferguson and Gavis, 1972; Matera and Hecho, 2001). In general, As (III) is the most toxic form of arsenic, followed by As (V) and to a lesser extent, methylated arsenic, e.g., $CH_3H_2AsO_3$. Arsenic is classified in the US Environmental Protection Agency (EPA) priority pollutant list with a carcinogenicity classification (human carcinogen). The LD50 (lethal dose) is estimated to be 1-4 mg As/kg for adult (Pontius *et al*., 1994). The US EPA has established a maximum contaminant level for arsenic in drinking water (0.01 mg L^{-1}) by 2006. The demand for arsenic trioxide in the manufacture of wood preservatives has increased noticeably over the last 20 years, increasing from 970 tones in 1971 to 9100 tones in 1981 and 14,300 tones in 1991. The only other area that has seen an increase in the use of arsenic is the electronics industry. High purity arsenic metal of 99.9999% or higher purity is used in the manufacture of crystalline gallium arsenide, a semi-conducting material used in optoelectronic circuitry, high speed computers and other electronic devices. As arsenic is a carcinogen, the management of hazardous wastes containing arsenic is of major public concern. Therefore, environmental regulators are adopting a more stringent attitude to arsenic exposure.

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

Corresponding Author: A.K. Minocha, Environmental Science and Technology (EST) Division,
Central Building Research Institute (CBRI) Roorkee-247 667, India Tel: 0091-1332-283317

the environment. The US Environmental Protection Agency also recognizes cementations solidification/stabilization as The Best Demonstrated Available Technology (BDAT) for land disposal of most toxic elements (Landrett, 1986). The solidification/stabilization (S/S) process would be the best practical technology to treat the arsenic waste and also found appropriate by other investigators in treating arsenic contaminated wastes (Artiola *et al*., 1990; Dutre and Vandecasteele, 1995; Akhter *et al*., 2000; Voigt *et al*., 1996; Miller *et al*., 2000; Fuessle and Taylor, 2000; Kameswari *et al*., 2001; Sanchez *et al*., 2002; Shih *et al*., 2003; Vandecasteele *et al*., 2002; Leist *et al*., 2003). Many reports exist where fixation of arsenic or arsenic containing wastes has been investigated by various researchers.

The present study describes the quantitative correlation between the concentrations of arsenic (V) and the intensity of effect on physical, chemical and engineering properties of 43 grade Ordinary Portland Cement as there is a very less data available in literature about these variables and quantitative relationships which are necessary in order to estimate the influence of amount of metal ions on these properties of cement. Therefore, attempts have been made to fill void in this data.

Materials and Methods

Materials

Sodium hydrogen arsenate ($Na_2HAsO_4.7H_2O$) was procured from Merck and was used as the arsenic (V) source in the present studies. Double distilled water was used to prepare the solutions throughout the study. All experiments were conducted in 500 mL polyethylene bottles. All other chemicals used were of analytical grade. Commercial Ordinary Portland cement 43 grade was used. 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 arsenic. Vicat apparatus was used to determine the 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.

Table 1: Chemical composition of the cement

Constituent	Weight (%)
Silica	20.80
Aluminum oxide	4.40
Iron oxide	3.79
Calcium oxide	66.10
Magnesium oxide	3.30
Sodium oxide	0.20
Potassium oxide	0.70

Table 2: Physical properties of the cement

Physical parameter	Results
Loss on ignition	0.7 (%)
Consistency	31.58 (%)
Soundness	1.0 mm
Initial setting time	175.0 min
Final setting time	300.0 min

Methods

Preparation of Cement Pastes and Mortars

The effect of different concentrations of arsenic (V) 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. To determine the compressive strength of blank samples as well as arsenic containing samples, the mortar pastes were cast in 2.78″ cubic iron molds. The samples were demolded next day and were kept dipped in water at constant temperature and humidity for curing. These samples were tested for compressive strength on 3, 7, 28, 60 and 90 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.

Results and Discussion

Initial and Final Setting Time

Cement exists in a fluid like state when suitable quantity of water is mixed into it. There is a period time of several hours in which the paste is fluid or viscous. Generally speaking, setting refers to a change from a fluid to rigid state. According to Indian standard IS: 8112-1989, initial setting time of 43 grade Ordinary Portland cement is at least 30 min while the final setting time is less than 600 min Both these parameters were determined for the blank samples as well as after the addition of varying concentrations of the arsenic (V). Vicat apparatus was used to determine the initial and final setting time of the cement as per IS: 4031-1996. All the experiments were carried out in triplicate to assure accuracy and reproducibility. The results of these studies are compiled in Table 3. It is clear from the data that As (V) showed little change up to 1 ppm concentration either in initial or final setting time of cement in comparison with blank samples. When the concentration of As (V) is increased beyond this limit, the setting time reduces sharply. It was observed that for the addition of 100 ppm As (V), initial setting time reduced by 20 min and final setting time reduced by 40 min while for the addition of 500 ppm As (V), initial setting time reduced by 25 min and final setting time reduced by 60 min. It seems that retardation of setting time of cement (due to presence of arsenic) occurs due to the formation of a protective layer that inhibits the normal hydration of cement grains. This layer does not allow the transport of water to C_3S phase therefore, retarding the setting time of cement.

Visual Observations

The molded specimens were observed for any change prior to compressive strength testing. Negligible change was observed between the controls and the As (V) containing samples. No significant change was observed in colour and shape also. The only change observed was that the surface of As (V) containing sample was slightly smoother than that of the controls.

Table 3: Effect of fixation of As (V) ions on initial and final setting time of cement

S. No.	Concentration of As (V) ion (ppm)	IST	FST
1	-	175	300
2	0.1	180	290
3	0.5	185	305
4	1.0	185	305
5	5.0	170	295
6	10.0	165	290
7	50.0	160	280
8	100.0	155	260
9	500.0	150	240

IST- Initial setting time in min. FST- Final setting time in min

Table 4: Compressive strength (kg cm^{-2}) of prepared samples

Added metal concentration (ppm)	No. of days					Change in compressive strength in comparison of control (%)				
	3	7	28	60	90	3	7	28	60	90
Blank	323.4	436.0	486.0	570.0	570.0	-	-	-	-	-
As (0.5)	330.0	428.0	492.0	605.0	622.0	102.0	98.1	101.2	106.1	109.1
As (1.0)	335.0	480.0	525.0	627.0	635.0	103.5	110.1	108.0	110.0	111.4
As (10.0)	337.0	488.0	545.0	628.5	635.0	104.3	111.9	112.1	110.3	111.4
As (100)	340.0	493.0	555.0	630.0	635.0	105.1	113.0	114.1	110.5	111.4
As (500)	348.0	495.0	584.0	632.0	635.0	107.6	113.5	120.0	110.8	111.4

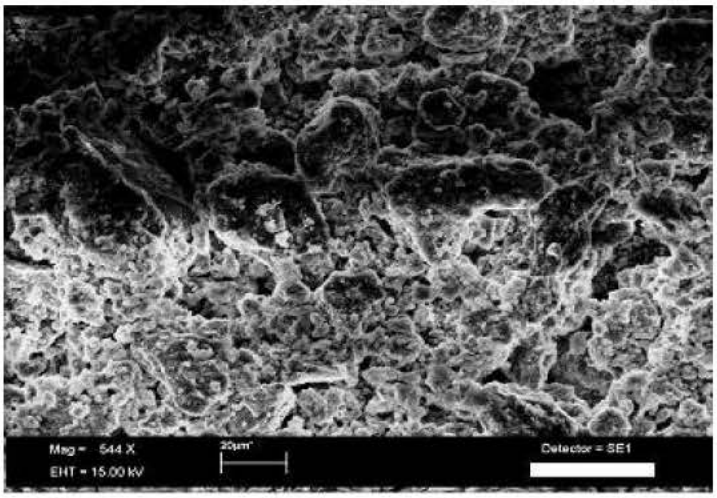

Fig. 1: SEM image of pure cement samples after 28 days of curing

Compressive Strength

The compressive strength values of blank sample as well as of the samples containing As (V) in varying concentrations are presented in Table 4. The results of compressive strength on 3, 7, 28, 60 and 90 days of curing are reported here. According to the IS: 8112-1989 for 43 grade Ordinary Portland cement, the compressive strength of cement should be at least 230, 330 and 430 kg cm^{-2} for 3, 7 and 28 days of curing. The addition of 0.1, 0.5 and 1.0, 10, 100 and 500 ppm As (V) ions exhibit considerable effect on the rate of strength attainment as well as on the compressive strength of the binding system. Great care was taken to reduce variability associated with batch preparation steps and reagent addition to avoid any substantial variability within a specific batch. It is clear from Table 4 that there is a significant increase in compressive strength for the arsenic (V) containing samples in comparison with controls and the intensity of the effect is directly proportional to the concentration of arsenic added. The compressive strength of the cement improves to 120% on 28 day of curing for 500 ppm of As (V) ions. In arsenic containing samples, higher amounts of C-S-H gel like phase was detected in SEM photographs which may be well correlated with the increased compressive strength of arsenic containing sample in comparison with controls.

Microscopic and Spectroscopic Analysis of the Cement Paste

The microstructures of hardened cement paste (control as well as arsenic added samples) were investigated by scanning electron microscopy (Fig. 1 and 2). All the samples were very compact, with gel like C-S-H phase as a main component. The significant difference between the samples doped with arsenic and reference sample were not observed. In the arsenic doped sample, higher amount of dense gel like product was detected.

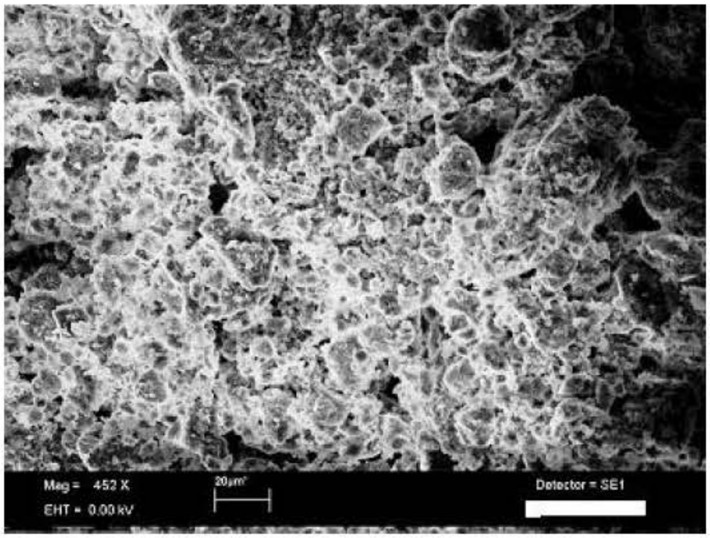

Fig. 2: SEM image of As (V) 500 ppm containing cement samples after 28 days of curing

Conclusions

In this study, the effect of fixation of arsenic (V) ions was studied on physical, chemical and engineering properties of 43 grade Ordinary Portland cement. As (V) has been taken in the concentration range 0.1-500 ppm for these investigations which also include the concentration range (0.1-4.0 ppm) in which as it is present in ground water in a wide area of West Bengal, India. It is evident from the results obtained that arsenic addition improves some of the characteristics of the cement. The compressive strength of the cement improves to 120% on 28 day of curing for 500 ppm of As (V) ions. In arsenic containing samples, higher amounts of C-S-H gel like phase was detected which may be well correlated with the increased compressive strength of arsenic containing sample in comparison with controls. Therefore, it may be concluded from the obtained results that arsenic (V) ions show no adverse effects on either of these parameters when added up to 500 ppm concentration.

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