

Arsenic stabilization on water treatment residuals by calcium addition

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In memory of Dr. Tim Kramer whose untimely passing is a loss for science and environmental engineering.

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ABSTRACT

A common method of removing arsenic from contaminated water is the co-precipitation or sorption of arsenic onto oxy-hydroxides formed by the addition of metal salts. Arsenic co-precipitation produces solids containing high concentrations of arsenic. The elevated arsenic content poses leaching problems requiring expensive disposal in certified hazardous impoundments. The objective of this research is to determine the effect of calcium addition as a stabilization agent, on arsenic desorption from ferric water treatment residuals. Due to the treatment residual's buffer capacity, desorption experiments in this study did not follow the standard Toxicity Characteristic Leaching procedure (TCLP) test. Arsenate desorption was induced in two ways: controlling solution pH in de-ionized water, and controlling solution pH in a 1.33 mM phosphate solution where phosphate is a competing anion. Desorption from laboratory treatment residuals did not generate any arsenic when calcium was present in solution, especially when excess calcium that did not join the surface of the treatment residual was present. Similarly, arsenic leaching decreased when field treatment residuals were treated with lime as stabilizing agent. Ordinary Portland cement (OPC) was also tested as a stabilizing agent in conjunction with lime since long term lime stabilization can be slowly consumed when directly exposed to atmospheric CO₂. The solidification and stabilization (S/S) technique with lime and OPC was shown to be successfully applied to the immobilization of arsenic tainted water treatment residuals.

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1. Introduction

Arsenic is one of the most toxic environmentally mobile compounds found in water. Due to its high toxicity, arsenic has been used as a pesticide to control insects, fungi, weeds and rodents since the early part of the twentieth century [1]. The effects of drinking arsenic-contaminated water on humans include skin lesions; gangrene; and bladder, kidney, skin, and lung cancer [2].

Sorption of arsenic onto a metal oxy-hydroxide is the most popular and practical treatment method of contaminated waters [3]. The oxy-hydroxide adsorbents are formed by hydrolyzing salts of metals, such as iron and aluminum. Ferric salts have been found to be effective in the removal of arsenic from contaminated waters. During treatment, arsenic is adsorbed on to the ferrihydrite, which is then settled out of solution. The result is solid treatment residuals with high amounts of adsorbed arsenic. Water treatment residuals are typically disposed of in landfills [4]. In natural environments, treatment residuals can come into contact with other dissolved species which can compete for sorption sites causing arsenic leaching. Desorption occurs because more readily adsorbed ions can

displace the adsorbed arsenic species by a competitive process of ligand exchange. In order to prevent arsenic desorption, waste treatment residuals need to be stabilized.

Several factors affect ferrihydrite characteristics and arsenic sorption, and thus the leaching potential. In solution, pH affects the surface charge of ferrihydrite which has a substantial effect on the sorption of arsenic compounds. Another important factor is the presence of other ions in solution which can compete with arsenic for sites in the solids or they can enhance arsenic sorption [5,6]. Whether sorption enhancement or competition occurs depends on the anion/cation ratio. A large excess of anion generally suppresses metal cation sorption, while similar molar concentrations favor sorption by ternary complex formation [7]. Enhancement of phosphate sorption on goethite through the cooperative effect of calcium in seawater has been observed at high pH [8].

It has been reported that calcium inhibits arsenic desorption from water treatment residuals [9] and that phosphate most readily competes with arsenic for sorption sites [3]. The amount of soluble arsenic has been found to be lower in the presence of calcium when treated with ferric oxides. Lime (calcium oxide, CaO) has been used to stabilize arsenic contaminated wastes, residuals, and soils [5,6,9]. Kim et al. [5] studied the stabilization of arsenic in mine tailings using calcium. The results indicated that lower arsenic concentration in the leachate at a pH range of 3–6 was observed when Ca(OH)₂ rather than NaOH was used for pH adjustment.

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The objective of this research was to determine the effect of calcium addition during coagulation as a stabilization agent, on arsenic desorption from iron base water treatment residuals. Due to the treatment residual's buffer capacity, desorption studies did not follow the standard toxicity characteristic leaching protocol (TCLP) test. Arsenic leaching would be underestimated if the standard TCLP test was followed because iron based treatment residuals' buffer capacity can control pH at neutral values. If the standard TCLP test is conducted as prescribed, leaching would not occur at a pH of 4.93, but at a pH around 7.

Ordinary Portland cement (OPC) was also tested as a stabilizing agent since solidified materials treated only by lime are not stable long term because the buffering effects of lime are decreased by dissolution and carbonation when exposed to atmospheric CO₂.

2. Experimental methods

2.1. Laboratory residuals

Residuals of known composition were produced for initial testing. To test the hypothesis that calcium addition may reduce arsenate leaching from iron based treatment residuals, two sets of treatment residuals, with and without calcium, were prepared by changing the pH control chemical during coagulation. A 26.70 mM ferric chloride and 26.7 mM arsenic as As(V) solution was stirred vigorously for 5 min. The pH was monitored and kept between 7 and 8 by adding NaOH, Ca(OH)₂ or HNO₃. The solution was then gently stirred for about 30 min and settled for an additional 30 min. After sedimentation the solution was decanted and filtered through a Buchner funnel lined with filter paper. Standard Method 2540B [10] was used to determine total solids in each residual. Acid digestion of sediments, sludges, and soils, (USEPA method 3050B, USEPA, 1992) was used to establish the initial concentration of arsenate, total iron and calcium in the residual.

2.2. Arsenate desorption from laboratory residuals

Due to the buffer capacity of the treatment residuals, desorption studies did not follow the standard TCLP test. Arsenate desorption was induced in two ways. One method of inducing desorption was by controlling solution pH in de-ionized water. This was accomplished by adjusting the pH of a 50 g/L suspension of the residue, and 10 mM of NaNO₃ solution by adding either NaOH or HNO₃. Sodium nitrate was used as an ionic strength buffer. Another method of inducing desorption was by controlling solution pH in a 1.33 mM phosphate solution where phosphate acts as a competing anion. This was accomplished by adjusting the pH (4, 6, 8 and 10) of a 50 g/L residual, 1.33 mM phosphate as NaH₂PO₄·H₂O and 10 mM of NaNO₃, as an ionic strength buffer, solution was adjusted by adding either NaOH or HNO₃ to achieve a pH of 7. In both cases the residual solutions were mixed in polyethylene bottles by end-over-end rotation. For the experiments where desorption was induced by controlling solution pH in de-ionized water, aliquots of suspension samples were collected at 24 h. For the experiments where desorption was induced by controlling solution pH in a 1.33 mM phosphate solution when phosphate acts as a competing anion, aliquots of suspension samples were collected at intervals for a 24 h period. The collected samples were filtered through 0.2 μm pore size membrane and analyzed for arsenate concentration continuous hydride generation with atomic absorption spectroscopy (HG-AAS) by Standard Method 3114C [10].

2.3. Field treatment samples

Residuals sample from a pilot plant was used as target materials in this study. The treatment residual field sample was composed of sorption media, used during a pilot study at Naval Air Station Fallon (NASF) (Fallon, NV) for arsenic removal from groundwater. Free liquid in residuals was removed by air-drying [11]. Residuals were placed in a clean vinyl-coated paper and dried under laboratory ambient air conditions (20 °C and 1 atm) for 24 h. Air-dried residuals were then crushed, passed through a 2 mm sieve and mixed well to produce homogeneous conditions. Polyethylene bottles were used to contain the residuals. Standard Method 2540B [10] was used to determine total solids in each residual. Acid digestion of sediments, sludges, and soils, (USEPA method 3050B, USEPA, 1992) was used to establish the initial concentration of total arsenic, total iron, aluminum, calcium, and manganese in the residual.

2.4. Arsenic desorption from field treatment residuals stabilized with lime

Quicklime, also known as calcium oxide (CaO), is used for solidification/stabilization (S/S) in field scale application. Mixing calcium oxide and water produces a slurry of hydrated lime or calcium hydroxide (Ca(OH)₂) through an exothermic reaction; a process known as slaking. Great care must be taken when calcium oxide because intense heat is generated [12]. Due to this safety issue, calcium hydroxide was used instead because similar results have been obtained when lime was used instead of calcium oxide for S/S of arsenic in waste [6]. Field samples were stabilized by adding increasing amounts of lime to 10 g of air-dried residuals. The mixtures ranged from 1 g of Ca(OH)₂/10 g of air-dried residual to 10 g of Ca(OH)₂/10 g of air-dried residual with increments of 1 g of lime. The residual and lime combinations were mixed thoroughly by hand with an acid-washed glass bar. The sludge-binder mixtures were placed in acid-washed polyethylene bottles and cured at room temperature for 7 days. After curing, all solidified samples were crushed to the particle size <2 mm (using 2 mm sieve) and kept in polyethylene bottles separately until subjected to extraction tests. All experiments were performed in duplicate. Extraction studies were conducted with 50 g/L residual and 10 mM of NaNO₃, as an ionic strength buffer, solutions at pH of 10. The residual solutions were mixed in polyethylene bottles by end-over-end rotation and aliquots of suspension samples were collected at intervals for a 24 h period. The collected samples were filtered through 0.2 μm pore size membrane and analyzed for arsenic and calcium concentration with atomic absorption spectroscopy (HG-AAS) by Standard Method 3114C [10].

2.5. Arsenic desorption from field treatment residuals stabilized with OPC

OPC is commonly employed as a S/S binder. The OPC used in this study was supplied by the Quikrete Company. Field samples were stabilized by adding increasing amounts of OPC to 10 g of air-dried residuals. The mixtures ranged from 1 g of OPC/10 g of air-dried residual to 5 g of OPC/10 g of air-dried residual with increments of 1 g of OPC. The residual and lime combinations were mixed, cured, crushed and stored using the same method described for the field treatment residuals stabilized with lime. Duplicate extraction studies were conducted with 50 g/L residual and 10 mM of NaNO₃, as an ionic strength buffer, solutions at pH of 10. The residual solutions were mixed in polyethylene bottles by end-over-end rotation and aliquots of suspension samples were collected at intervals for a 24 h period. The collected samples were analyzed using the same

Table 1

Laboratory treatment residuals physical and chemical composition (unit: g/kg dry solids).

Sludge type	Dry solids (%)	As(V)	Iron	Calcium
FeCl ₃ + Ca(OH) ₂	17.4	30.9	500	24.9
FeCl ₃ + NaOH	11.4	26.7	531	–

method described for the field treatment residuals stabilized with lime.

2.6. Arsenic desorption from field treatment residuals stabilized with lime and OPC

Since stabilized materials treated only with lime are not stable long term, arsenic desorption from lime and OPC treated residuals was tested. Based on arsenic desorption from field treatment residuals stabilized with lime and with OPC, two different ratios were selected: 6 g of Ca(OH)₂ and 3 g of OPC per 10 g of air-dried residual; and 6 g of Ca(OH)₂ and 5 g of OPC per 10 g of air-dried residual. The residual, lime and OPC combinations were mixed thoroughly by hand with an acid-washed glass bar. The sludge-binder mixtures were mixed, cured, crushed and stored using the same method described for the field treatment residuals stabilized with lime. Duplicate extraction studies were conducted with 50 g/L residual and 10 mM of NaNO₃, as an ionic strength buffer, solutions at pH of 10. The residual solutions were mixed in polyethylene bottles by end-over-end rotation and aliquots of suspension samples were collected at 24 h. The collected samples were analyzed using the same method described for the field treatment residuals stabilized with lime.

3. Results

3.1. Laboratory residuals

Laboratory residuals were prepared by mixing ferric chloride and arsenate while adjusting pH. Sodium hydroxide (NaOH) was used for pH control during coagulation with no calcium addition, called sodium treatment residuals. Calcium hydroxide (Ca(OH)₂) was used for calcium addition and pH control, called calcium treatment residuals. Both treatment residuals were analyzed for percent dry solids, arsenate, total iron and total calcium (Table 1). Treatment residuals analysis was used to generate desorption plots. As expected, calcium addition during coagulation appears to enhance arsenate sorption since the mass of arsenate per mass of dry solids was higher in the calcium residuals.

3.2. Arsenate desorption from laboratory residuals

Arsenate desorption was induced in two ways: first, by controlling solution pH in de-ionized water; then, by controlling solution pH in a 1.33 mM phosphate solution where phosphate acted as a competing anion. Arsenate desorption with no competing anion was conducted at four pH values. The leached arsenate mass per mass of dry calcium treatment residuals was about half of the arsenate desorbed from sodium treatment residuals (Table 2). At

Table 2

Leached arsenate mass per mass of dry solid after 24 h from laboratory treatment residuals in solid-solution ratio of 1 g/20 mL (unit: mg As/kg dry solids).

Sludge type	pH 4	pH 6	pH 8	pH 10
FeCl ₃ + Ca(OH) ₂	<0.1	<0.1	1.46	45.8
FeCl ₃ + NaOH	<0.1	<0.1	2.95	82.5

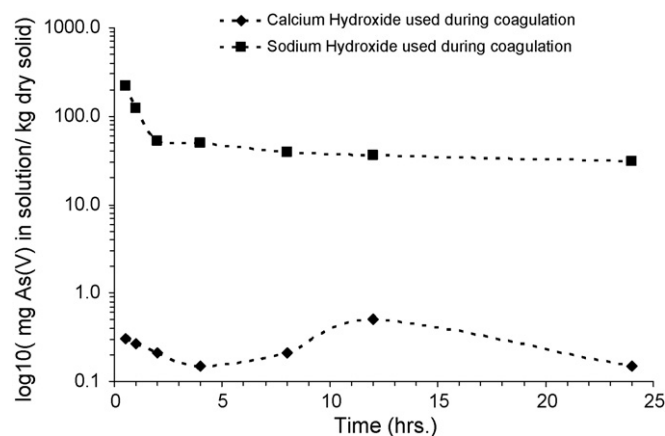


Fig. 1. Percent arsenate mass desorption with time in 1.33 mM phosphate solution at pH 7.

pH 8 soluble arsenate leached from calcium treatment residual was 0.025 mg/L while soluble arsenate leached from sodium treatment residuals was 0.033 g/L. At pH 10 soluble arsenate leached from calcium treatment residual was 0.79 mg/L while soluble arsenate leached from sodium treatment residuals was 0.4 mg/L. Even though leaching from calcium treatment residual was less than leaching from sodium treatment residuals, all soluble arsenate concentrations were above 0.01 mg/L, the maximum contaminant level (MCL) allowed by the Environmental Protection Agency (EPA).

Arsenate desorption at pH 7 with phosphate as the competing anion from calcium treatment residuals was minimal when compared to arsenate desorbed from sodium treatment residuals (Fig. 1). Initially, arsenate leached from the sodium treatment residual to a maximum soluble concentration of 2.5 mg/L at about 0.5 h and was constant at approximately 0.4 mg/L after 20 h. Arsenate leached from the calcium treatment residual to a maximum soluble concentration of 0.008 mg/L at about 8 h which is below the MCL. Calcium addition reduced arsenate leaching from iron based treatment residuals.

3.3. Field treatment samples

The treatment residual field sample was composed of sorption media, used during a pilot study at Naval Air Station Fallon (NASF) (Fallon, NV) for arsenic removal from groundwater. The pilot plant residual from NASF was a granular ferric hydroxide material. The treatment residuals field sample was analyzed for solid content, iron, aluminum, calcium and manganese (Table 3). The percent solids, arsenic mass and iron mass of the field treatment residual were similar to the laboratory treatment residuals. Treatment residuals analysis was used to generate desorption plots.

3.4. Arsenic desorption from field treatment residuals stabilized with lime

Lime as calcium hydroxide was used as a binders for solidification/stabilization and extraction was induced by 0.1 M phosphate

Table 3

Field treatment residuals chemical composition (unit: mg/kg).

Solid content (%)	69.1
Total As	2680
Total Fe	521,000
Total Al	212
Total Ca	1510
Total Mn	741

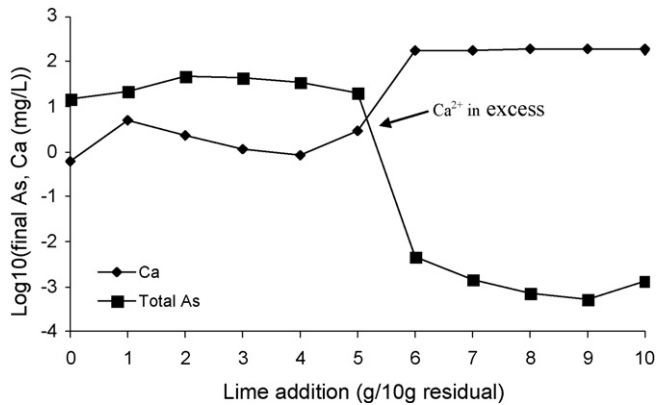


Fig. 2. Soluble total arsenic and total calcium concentrations by 0.1 M phosphate extraction as function of lime addition.

solution at pH 10. Calcium hydroxide was added to the field treatment residual in 1 g increment per 10 g of air-dried treatment residual. Then, the solidified material was cured for 7 days under ambient air laboratory conditions. The effect of calcium addition was determined by phosphate extraction. Leached arsenic concentrations increased when 1–5 g of lime was added. The increase in leached arsenic was expected because the solution pH increased with increasing lime addition since high pH values are favorable for arsenic leaching. However, leached arsenic concentrations decreased when 6 g of lime was added. When more than 6 g of lime was added, soluble calcium was measured. The soluble calcium did not form any bonds with the surface of the ferrihydrite and did not undergo any reaction that would form insoluble solids. In the presence of soluble calcium desorbed arsenic concentrations were not detected (Fig. 2). Therefore, arsenic stabilization was achieved with excess calcium addition.

3.5. Arsenate desorption from field treatment residuals stabilized with OPC

OPC treatment did not immobilize arsenic as effectively as lime treatment. Leached arsenic concentrations after 24 h were higher than arsenic leached from lime treated residuals (Table 4). The results might be explained by the availability of calcium. About 20–25% of $\text{Ca}(\text{OH})_2$ from OPC by weight is normally generated from cement hydration [13]. Therefore, the available amount of calcium was much lower than when compared to the results of lime addition. Even though OPC does not inhibit arsenic leaching, it can be used to improve the handling and the physical characteristics of the residuals [14].

3.6. Arsenic desorption from field treatment residuals stabilized with lime and OPC

Lime and OPC were used as binders for solidification/stabilization and extraction was induced by 0.1 M phosphate solution at pH 10.

Table 4
Leached arsenic after 24 h from field treatment residuals treated with OPC (unit: mg/L).

OPC (g)	As(III)	As(V)	Fe	Ca	Final pH
0	0.150	14.783	3	1	9.17
1	0.199	17.257	<0.05	4	10.10
2	0.226	24.970	<0.05	2	10.83
3	0.325	34.043	<0.05	1	11.71
5	0.297	32.510	<0.05	1	12.65

Table 5

Leached arsenate after 24 h from field treatment residuals treated with lime and OPC (unit: mg/L).

Lime (g)	OPC (g)	As(III)	As(V)	Fe	Ca
6	3	<0.0001	0.018	<0.05	151
6	5	<0.0001	0.024	<0.05	127

Two different lime/OPC/air-dried residual ratios were tested. Desorption from residuals stabilized with lime and OPC (Table 5) was not significantly different from desorption of residuals stabilized with lime results with those for the addition of lime. However, the use of lime as treatment for S/S will not be effective as a long-term solution because calcium–arsenic compounds decompose slowly when exposed to atmospheric CO_2 [15]. Therefore, any barriers which can block contact between the calcium–arsenic compounds and atmospheric CO_2 will be necessary for the management of arsenic immobilization in the residuals for a long period of time.

4. Discussion

There are several possible complexation reactions that can explain the observed results. One is that phosphate in the extraction solution precipitates with the lime [16] or with calcite (CaCO_3) [17]. In wastewater treatment, lime has been used to remove phosphorus. The pK values for phosphate are 2.2, 7.2, and 12.4. At high pH values PO_4^{3-} is the predominant species of phosphate, thus, $\text{Ca}_4\text{H}(\text{PO}_4)_3$ and/or $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ could be precipitated. Another explanation is the formation of calcium–iron complexes. Calcium–iron compounds would maintain a positive surface charge preventing leaching of negatively charged arsenic ions. According to Wilkie and Hering [3], the adsorption of Ca^{2+} onto iron hydroxides results in a positive surface charge of the adsorbents in the high pH range.

The chemistry of phosphate extraction from iron based solids and the adsorption of arsenic onto iron oxides are complex. Chemical modeling is required in order to identify the exact mechanism by which calcium prevents arsenic leaching from iron oxides.

5. Conclusions

Lime addition reduced arsenic leaching from water treatment residuals. However, solidified materials treated only by lime are not stable long term since the buffering effects of lime are decreased by dissolution and carbonation when exposed to atmospheric CO_2 . Barriers that block contact between the calcium–arsenic in the residuals and atmospheric CO_2 will be necessary for the management of arsenic immobilization for a long period of time. Cement can act as a barrier and should be added with lime to prevent and minimize long-term arsenic leaching.

The immobilization of arsenic in treatment residuals may be achieved through the treatment with lime and cement. Therefore, solidification and stabilization (S/S) techniques with lime and cement can be successfully applied to the immobilization of elevated arsenic concentrations in water treatment residuals.

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