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Scoping Candidate Minerals for Stabilization of Arsenic-Bearing Solid Residuals

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Abstract

Arsenic Crystallization Technology (ACT) is a potentially eco-friendly, effective technology for stabilization of arsenic-bearing solid residuals (ABSRs). The strategy is to convert ABSRs generated by water treatment facilities into minerals with a high arsenic capacity and long-term stability in mature, municipal solid waste landfills. Candidate minerals considered in this study include scorodite, arsenate hydroxyapatites, ferrous arsenates (symplesite-type minerals), tooeleite, and arsenated-schwertmannite. These minerals were evaluated as to ease of synthesis, applicability to use of iron-based ABSRs as a starting material, and arsenic leachability. The Toxicity Characteristic Leaching Procedure (TCLP) was used for preliminary assessment of candidate mineral leaching. Minerals that passed the TCLP and whose synthesis route was promising were subjected to a more aggressive leaching test using a simulated landfill leachate (SLL) solution. Scorodite and arsenate hydroxyapatites were not considered further because their synthesis conditions were not found to be favorable for general application. Tooeteite and silica-amended tooeteite showed high TCLP arsenic leaching and were also not investigated further. The synthesis process and leaching of ferrous arsenate and arsenated-schwertmannite were promising and of these, arsenated-schwertmannite was most stable during SLL testing. The latter two candidate minerals warrant synthesis optimization and more extensive testing.

Keywords

Arsenic residuals; landfills; ferrous arsenate; schwertmannite; tooeteite

1. INTRODUCTION

EPA recommended Best Available Technologies (BATs) for arsenic removal from drinking water rely on precipitation/coagulation, adsorption and ion-exchange [1]. All of these technologies generate arsenic-bearing solid residuals (ABSRs) that must be safely disposed [2,3]. The regulatory leaching tests, the Toxicity Characteristic Leaching Procedure (TCLP) and the California Waste Extraction Test (CA-WET), underestimate the leaching of arsenic from the residuals [4], and consequently arsenic leaching from ABSRs disposed in mature Municipal Solid Waste (MSW) landfills. Existing technologies for ABSRs stabilization like

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cement encapsulation or vitrification are expensive and/or ineffective [5–7]. Polymeric encapsulation is promising, both technically and economically, but it is yet to be adopted commercially [5]. The objective of this work is to conduct a scoping analysis of candidate minerals for an eco-friendly, effective Arsenic Crystallization Technology (ACT) for the stabilization of ABSRs under mature landfill conditions. The strategy is to convert ABSRs into minerals with a high arsenic capacity and long-term stability (meaning low arsenic solubility under disposal conditions), particularly those prevailing in MSW landfills. Ideal candidate minerals would be synthesized at ambient temperature and pressure from the original ABSRs, minimize use of expensive or hazardous reagents or complex processing, and exhibit minimal arsenic leaching under disposal conditions.

Five minerals were identified and examined in this study - scorodite, arsenate hydroxyapatite, tooeleite, ferrous arsenate (symplesite-type minerals), and arsenated-schwertmannite. Scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) was considered due to its high arsenic capacity (25–30 % wt/wt) [8,9] and previously known synthesis procedures [10–14]. Hydroxyapatites ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) are a group of minerals with similar crystal structure but varying in exact composition. They are stable over a broad pH range and arsenate may substitute for phosphate in hydroxyapatite to form Johnbaumite ($\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$) [15,16]. Hydroxyapatite minerals have been studied for the immobilization of hazardous compounds containing lead, cadmium, nickel, copper, mercury and arsenic [17–20].

Ferrous Arsenates (symplesite, parasymplesite and ferrisymplesite) belong to the vivianite group with the general formula $\text{Y}_3(\text{XO}_4)_2 \cdot 8\text{H}_2\text{O}$, where Y^{2+} may be Co, Fe, Mg, Ni, or Zn, and X is As or P [21]. Symplesite and parasymplesite both have the chemical formula $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, but differ in physical characteristics. Sadiq et al. [22] determined that the arsenic solubility of Kelly Lake (Ontario) minerals, is controlled by the equilibrium of $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{c})/\text{Fe}_4\text{Fe}_2(\text{OH})_{12} \cdot \text{SO}_4(\text{c})$.

Previous studies have investigated arsenic immobilization by ferrous iron treatment, possibly leading to the formation of ferrous arsenate solids [23,24]. To our knowledge, there are only two studies on the synthesis and stability of ferrous arsenates [25,26]. Despite inconsistency in the solubility products calculated in the studies, the solids showed low arsenic solubility.

In schwertmannite, an iron (III)-oxyhydroxysulfate mineral [$(\text{Fe}_8\text{O}_8(\text{OH})_x(\text{SO}_4)_y \cdot n\text{H}_2\text{O})$, where $8-x=y$ and $1.0 \leq y \leq 1.75$], arsenate can partially (up to 5.6 wt%) exchange for sulfate without significant structural disruption [27,28]. In addition, arsenate can stabilize the schwertmannite and retard its Fe(II)-catalyzed transformation to goethite [27,29]. The transformation would be expected to cause arsenic release due to a decrease in specific surface area between poorly-crystalline schwertmannite and more crystalline goethite. However, Acero et al. [30] reported no substantial decrease in the specific surface area and 99% arsenic retention after transformation of schwertmannite to goethite. Slightly alkaline conditions, such as those present in mature landfills, accelerate the transformation process [31–33]. Burton et al. [34] showed that 1 mM As(III) or As(V) retarded this transformation and was accompanied by negligible arsenic release.

Tooeleite, $\text{Fe}_6(\text{AsO}_3)_4\text{SO}_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$, is an iron arsenite oxyhydroxy-sulfate mineral, recently discovered in gold mines [35,36] and acid mine waters [37–39]. Tooeleite is an attractive candidate ACT mineral because of its high arsenic loading (~20–25% wt/wt). As with other candidates, the objective here was not to conduct a detailed parametric evaluation of tooeleite formation, but to get a first-cut idea of the effectiveness of tooeleite as an arsenic sink. Silica-coating of iron oxides such as magnetite, maghemite and hematite has been

studied to prevent metal leaching [40–42], so this amendment was evaluated for the tooeleite solid.

2. MATERIALS AND METHODS

Water was degassed by heating deionized water to 90 ± 4 °C for 1 hour while bubbling nitrogen. The degassed water was sealed tightly and stored in a Terra Universal Critical Environment Solutions glove box purged with nitrogen.

2.1. Ferrihydrite Preparation

Ferrihydrite was synthesized both without and with arsenic loading to mimic virgin sorbents and ABSRs ready for disposal after drinking water treatment respectively. Synthesis followed a modified procedure by Mukiibi et al. [43]. Briefly, 1.00 M anhydrous ferric chloride solution was titrated with 10 M NaOH to pH 7.0 within 1 hour. The suspension settled and equilibrated for 48 hours, maintaining $\text{pH } 7 \pm 0.3$ by addition of 0.1 M HCl or 0.1 M NaOH as necessary. The pH was monitored for an additional 48 hours to ensure that the pH had stabilized at 7.0. The precipitate was vacuum filtered using 0.22 μm membrane filters to a water content of approximately 75 wt % and rinsed multiple times with deionized water to remove residual salts. The solid was sealed tightly and stored at 4 °C.

Arsenic-loaded ferrihydrite (Fe/As molar ratio = 20:1) was prepared from equal volumes of 1.00 M anhydrous ferric chloride solution and 0.05 M sodium arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, KR Grade, Sigma- Aldrich). The mixture was stirred and titrated with 10 M NaOH to pH 7.0 within 1 hour. All other steps were the same as those for ferrihydrite without arsenic.

2.2. Characterization and Analytical Methods

The iron to arsenic ratio of the arsenic-loaded ferrihydrite was determined as 20.5. Both ferrihydrite solids (Fe/As = 0.0 and 20.5) had water contents of $77.5 \pm 0.2\%$ (wt/wt). Ferrihydrite samples (both Fe/As = 0.0 and 20.5) of 0.500 g were weighed and digested in 14.5 mL of concentrated nitric acid for 20 minutes using a CEM MDS 2100 Microwave Digestion System. Five replicates were run in each case. Digested samples were filtered using 0.22 μm cellulose nitrate filters (Millipore). The filtrate was analyzed for iron using the phenanthroline test [44] and for arsenic by Inductively Coupled Plasma Mass Spectrometer (ICPMS, Agilent 7500a).

Synthesized solids were subjected to the TCLP in accordance with EPA SW-846, Method 1311. The extraction solution consisted of 5.7 mL glacial acetic acid added to 64.3 mL of 1.0 M NaOH solution with the final volume brought to 1 L with DI water. The pH of this solution was adjusted to 4.93 ± 0.05 before use. 5.129 g of size reduced (< 1.4 mm) solid sample was added to 100 mL of leaching solution in a 120 mL bottle and sealed. The sealed bottles were rotated end-over-end shaker (30 rpm) for 18 hours. For all tooeleite cases, the solids were dried and used on a dry weight basis in the TCLP.

A simulated landfill leachate (SLL) solution was used for more aggressive leach testing. This solution was a modified version of SLL solutions used in a previous study on ABSRs [4]. The SLL composition was (mg/L): acetic acid (600.5), sodium citrate dihydrate (58,818), sodium bicarbonate (8,400), hydroquinone (110.1) and hydroxylamine hydrochloride (69.5). SLL pH was adjusted to 8.1 ± 0.1 . The hydroxylamine hydrochloride was added immediately prior to use due its short half life in an oxidizing environment. Similar to the TCLP, 5.129 g of size reduced (< 1.4 mm) sample was added to 100 mL of the leaching solution in a 120 mL sealable bottle. In addition, the headspace of the bottle was

purged vigorously with nitrogen prior to sealing and rotated end-over-end at 30 rpm for 48 hours.

All leaching tests involved three replicate runs. After leaching, the bottles were removed from the shaker, the remaining solids settled, and aqueous samples taken through a 0.22 μm cellulose nitrate filters (Millipore).

Bulk sample crystalline phases were identified by XRD spectra (Bruker D8 ADVANCE diffractometer using $\text{CuK}\alpha$ radiation). Samples were scanned from 5° to 90° for over 285 minutes. Peaks were matched using the International Centre for Diffraction Data (ICDD) database. Schwertmannite samples were analyzed using Synchrotron transmission X-ray diffraction (ST-XRD) collected at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11-3 operating at 12735 eV ($\lambda = 0.976 \text{ \AA}$) with a focused spot size of $150 \mu\text{m}$, using a 345 mm radius Mar detector image plate with a resolution of $100 \mu\text{m}^2$ pixels, and calibrated to a LaB_6 standard. Approximately 50 mg of ground and homogenized sample was dispersed on, and sealed in, matte finish tape (Scotch MagicTM) to obtain a uniform thin layer sample ($<0.5 \text{ mm}$). Laue pattern images were collected while the sample was rastered over a 1 mm^2 area on an x-y stage. Laue ring pattern images were converted into 2-theta diffractograms using the Area Diffraction Machine software [45]. The summed patterns were converted to conventional $\text{Cu K}\alpha$ wavelength for comparison to known reference patterns. A Hitachi S-4800 II Field Emission Scanning Electron Microscope was used to obtain the SEM images and Energy Dispersive X-ray (EDX) spectra were used for elemental composition.

2.3. Scorodite Synthesis

Natural scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), purchased from Caldbeck Fells Mines, UK, and XRD characterized, was used as a reference for scorodite synthesized in this study. Synthesis pH, temperature and Fe/As ratio for scorodite were independent study variables. Synthesis at pH 1.0, 3.0, 5.0 and 7.0 followed a modified Dutrizac and Jambor [11] procedure: 0.300 M $\text{Fe}(\text{NO}_3)_3$ and 0.300 M NaH_2AsO_4 solutions were mixed to attain a Fe/As ratio of 1.0 and autoclaved at 160°C and 8.0 bar for 24 hours. The pH 1.0 experiment required no pH adjustment. For other trials pH was adjusted using 1.0 M NaOH. After 24 hours, the solids were $0.45 \mu\text{m}$ filtered and washed thrice with 500 mL of $80\text{--}90^\circ\text{C}$ water. Solids were dried at 60°C for 4 days and stored at room temperature.

Study on the effect of Fe/As ratio on scorodite synthesis again followed Dutrizac and Jambor [11]. 150 mL of 0.2 M, 0.500 M, or 1.00 M $\text{Fe}(\text{NO}_3)_3$ and 150 mL of 0.10 M NaH_2AsO_4 solutions were mixed in a 400 mL autoclave for Fe/As ratios of 2.0, 5.0, and 10.0, respectively. Initial pH was adjusted to 3.0 using 10.0 M NaOH and incubated for 24 hours at 160°C and 8 bar. Solids were prepared for characterization as above.

Additionally, previously reported scorodite synthesis methods were evaluated with incubation temperatures of 60°C , 95°C , 150°C and 230°C [10,11,46,47]. Synthesis conditions are shown in Table 1. In all cases solutions of 0.11 M $\text{Fe}(\text{NO}_3)_3$ and 0.10 M NaH_2AsO_4 were initially mixed. Following Demopoulos [46] the mixture pH was brought to zero using 10.0 M HNO_3 and heated to 95°C at 1 bar pressure. 10 M NaOH was then added gradually to bring the pH to 1.50. Following Dove and Rimstidt [10], the resulting product was aged at 60°C for 14 days without further pH adjustment. Finally, using a modified Mambote et al. procedure [47], the mixture was maintained for 24 hours at 150°C and 8 bar or at 230°C and 11 bar in an autoclave.

2.4. Arsenate Hydroxyapatite Synthesis

Apatite series compound synthesis followed a modified Mahapatra et al. [15] procedure. For synthesis of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), arsenate phosphate hydroxyapatite, $\text{Ca}_{10}(\text{As}_x\text{P}_y\text{O}_4)_6(\text{OH})_2$, with variable phosphate to arsenate ratios, and Johnbaomite, $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$, calcium, phosphate and arsenate were combined maintaining the Ca:(As +P) molar ratio at 5:3. Solution pH was adjusted to 11.0 using NaOH and the temperature held at 100 °C for 24 hours. Solids were rinsed with deionized water and filtered using a 0.45 μm filter.

To study the effect of iron on synthesis of apatite-like compounds, the As/P ratio was fixed at 1.0, initial pH at 12.0, and different Fe/As ratios from 1 to 10 were studied. All other experimental conditions were the same as above. All synthesized solids were 0.45 μm filtered, washed with deionized water and dried at 100 °C for 24 hours before being characterized.

2.5. Tooeleite Synthesis

Tooeleite, $\text{Fe}_6(\text{AsO}_3)_4\text{SO}_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$, synthesis followed Nishimura and Robins [48] with slight modifications: Equal volumes of 0.04 M ferric sulfate and 0.05 M sodium arsenite solutions were mixed for 2 hours. The pH at this point was 2.6 ± 0.05 . The beaker was incubated at 60 °C for 2 days.

Synthesis of silica-coated tooeleite followed a modified version of the sol-gel coating procedure of Han et al. [40] for Fe_2O_3 nanoparticles. Tooeleite prepared as described was dried and ground into fine particles. 0.45 g of dried and ground tooeleite was mixed vigorously with 20 mL of absolute ethanol for 45 minutes followed by addition of 7 mL of 98% tetraethoxysilane (TEOS). 3 mL of ammonium hydroxide (30%) were then added as a catalyst and mixed for 6 hours to ensure maximum hydrolysis of the TEOS and formation of the monosilicic acid essential for condensation. Finally, the suspension was filtered and dried.

2.6. Ferrous Arsenate Synthesis

Reference ferrous arsenate $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ was synthesized from Fe(II) and As(V) according to Johnston and Singer [26]. Subsequently, ferrous arsenate synthesis started from arsenic-loaded ferrihydrite (Fe/As molar ratio = 20.5) prepared in the laboratory. 1.2028 g of wet ferrihydrite in 250 mL of deoxygenated DI water was combined with zero-valent iron at a ZVI:Fe(III) molar ratio of 10.0 in a N_2 purged glove box. The pH of the mixture was lowered to 1.30. After 3 hours, complete dissolution and reduction of the Fe(III) to Fe(II) was observed. The remaining zero-valent iron was removed and 250 mL of 3.98 mM sodium arsenate heptahydrate, $\text{NaH}_2\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, added. The pH of the solution was raised to 7.50 using NaOH. The resulting dark green precipitate was collected on a 0.22 μm filter and dried inside the glove box. The synthesis procedure was repeated outside the glove box using deoxygenated DI water, although the synthesized solids were dried inside the glove box.

2.7. Schwertmannite Synthesis

Schwertmannite $[(\text{Fe}_8\text{O}_8(\text{OH})_x(\text{SO}_4)_y \cdot n\text{H}_2\text{O})]$, where $8 - x = y$ and $1.0 \leq y \leq 1.75$ was synthesized using the ferrihydrite prepared as previously described. The synthesis procedure was based on Bigham et al. [49]: 7.567 g of wet ferrihydrite solid, equivalent to 20 mmol of Fe(III) was added to 500 mL of 0.25 M HCl solution and mixed for 2 hours. The solution temperature was then raised to 60 °C, sodium sulfate added to yield a 20 mM sulfate solution, and incubated for 12 minutes before cooling to room temperature. The solution was dialyzed using Fisherbrand regenerated cellulose dialysis tubing (Nominal Molecular

Weight Cut-off = 12,000 –14,000 daltons) in ~ 12 L of deionized water. The pH was 2.6 ± 0.05 . The water was exchanged for fresh de-ionized water every day for 18 days. The specific conductance of the dialysis water was continuously $< 5 \mu\text{S}/\text{cm}$ for the last 5 days. Finally, the solids were $0.22 \mu\text{m}$ filtered and dried under flowing nitrogen.

The same procedure was repeated starting with lab-synthesized arsenic-loaded ferrihydrite (Fe/As = 20.5). This procedure was based on the method reported for synthesis of arsenated-schwertmannite starting from ferric, sulfate and arsenate solutions at Fe/As = 22.22 [50]: 7.509 g of wet arsenic-loaded ferrihydrite, equivalent to 20 mmol Fe(III) and 0.96 mmol As(V) was added to 500 mL of 0.25 M HCl solution and mixed for 2 hours, dissolving all ferrihydrite. Subsequently, the solution was held at 60°C and sodium sulfate was added to yield a 22.4 mM sulfate solution. This solution was maintained at 60°C for an additional 12 minutes before being cooled to room temperature and dialyzed following the same steps as described above for the synthesis of schwertmannite from ferrihydrite solid.

3. RESULTS AND DISCUSSION

Scorodite was synthesized at pH 1.0, 3.0, 5.0 and 7.0, at 160°C and Fe/As ratio of 1.0 for 24 hours to evaluate if milder synthesis conditions were feasible than previously reported. The pH 1.0, 3.0, and 5.0 solids showed three primary XRD peaks for scorodite (Figure 1). However, as synthesis pH increased unidentified peaks appeared (marked 1, 4, 5, and 6 in Figure 1) and the intensity of some secondary scorodite peaks (marked 2 and 3 in Figure 1) decreased. The pH 7.0 solid was amorphous with no distinct scorodite peaks. This suggests synthesis at pH 3 leads to mixed solid phases with the crystalline scorodite contribution decreasing with increasing pH.

At pH 1.5 the scorodite synthesized at 95°C , 150°C , and 230°C (Table 1) was crystalline by XRD and SEM analyses (results not shown). The 60°C solid was poorly crystalline scorodite of fine particle size. Particle size increased with increased temperature to 150°C , but not thereafter. Scorodite was synthesized at pH 3.0, 160°C and 8 bar, and an Fe/As ratio of 1.0 yielded only crystalline scorodite, whereas synthesis at a ratio of 2.0 yielded a poorly crystalline scorodite and hematite mixture. Solid synthesized at Fe/As of 5.0 was amorphous and at Fe/As of 10.0 was only crystalline hematite with no scorodite (XRD not shown). Thus, increasing the Fe/As from 1.0 to 10.0 inhibited scorodite formation.

Based on these results, scorodite synthesized at pH 1 and temperatures of 95°C , 160°C and 230°C was selected to evaluate leaching using the TCLP. A Fe/As ratio of 1.1 was used as it was determined to be optimum for the synthesis of crystalline scorodite based on a preliminary parametric testing of Fe/As ratios at these temperatures and pH conditions (not shown here). The arsenic leaching observed was at least an order of magnitude less than the arsenic Toxicity Characteristic (TC) of 5 ppm (Figure 2).

In all phosphate/arsenate hydroxyapatite synthesis trials (100°C and 1 bar), the solids obtained structurally lay along the hydroxyapatite to johnbaumite mineralogic transition (Figure 3). Some weak peaks at 2θ angles of 22° , 26° , 34° and 49° were enhanced for As/P ratios > 1.0 . As also seen in nature, substitution of the phosphate in hydroxyapatite by arsenate to form arsenate hydroxyapatite minerals causes no loss of structural and crystallographic integrity as the phosphate and arsenate tetrahedra readily interchange. Motivated by the ease of synthesis and insensitivity to As/P ratio, the leaching from these arsenate hydroxyapatite minerals was subjected to the TCLP. Only solids synthesized at As/P 0.2 showed As leachate concentrations below the TC (Figure 2).

Coagulation/microfiltration with iron salts and adsorption on ferric (hydr)oxides are EPA recommended Best Available Technologies for arsenic removal from drinking water. Hence,

high iron content typifies ABSRs generated from water treatment facilities. Iron arsenate hydroxyapatite synthesis trials showed iron can have an inhibitory effect on the formation of crystalline apatite minerals (Figure 4). At the lower Fe/As ratios studied (Fe/As = 1.0, 2.0) hematite and hydroxyapatite (both poorly crystalline) were formed. At higher ratios (Fe/As = 5.0, 10.0), only crystalline hematite formed. At these high Fe/As ratios, the iron content combined with high pH and high temperature synthesis (conditions known to favor hematite generation [51]) disposes the system to crystallization of hematite at the expense of hydroxyapatite. Despite some apatite-type structure (at As/P ratio of < 0.2) showing arsenic leaching below the TC, because of the sensitivity of synthesis to low levels of iron, additional work on apatite-type arsenic minerals for arsenic residuals stabilization was not pursued.

Tooeleite synthesis with and without silica coating was confirmed by powder XRD (not shown here). To investigate whether the tooeleite surface was in fact coated with silica, SEM imaging and EDX spectroscopy were employed. Although the images obtained for the two solids using SEM (not shown here) looked different in terms of the surface morphology, this analysis was too crude to confirm that the tooeleite surface was coated with silica. When analyzing a solid sample using EDX, the accelerating voltage is directly proportional to the depth of X-ray penetration into the sample. Hence, at a higher accelerating voltage, the EDX elemental analysis will be influenced more by material deeper in the solid. Thus for one solid phase coated with a second solid of different elemental composition, it may be possible to detect the difference in composition with depth using EDX analysis at different accelerating voltages. For silica-amended tooeleite it was observed that silicon and oxygen were the only elements detected at 5 kV (Table 2). On increasing the accelerating voltage from 5 kV to 30 kV, percent compositions of silicon and oxygen were found to decrease. On the contrary iron and arsenic were not detected below a voltage of 30 kV. The carbon signal, due to the background carbon stub that was used to provide a conductive path for the electrons, became stronger as the accelerating voltage was increased. For tooeleite with no silica coating, iron and arsenic were detected at an accelerating voltage of 5 kV. This indicates that the tooeleite synthesis amended with silica did result in a core coated with silica, however, the technique does not allow for characterization of the coating thickness or uniformity.

The TCLP arsenic leaching from both tooeleite and silica-amended tooeleite was at least an order of magnitude higher than the arsenic TC (Figure 2). The tooeleite and silica-amended tooeleite leached were completely dried prior to leaching. The process of drying often results in increased crystallinity of solid phases, which usually means increased stability of the solid. Hence, tooeleite solids would be expected to show equal or higher leaching if subjected to TCLP without prior drying. Although the silica-coating procedure resulted in an observable reduction in arsenic leaching (Figure 2), neither the pure nor the silica-amended tooeleite were considered for further ACT investigation due to the relatively high concentrations of As in the TCLP leachate.

A parasymphesite reference solid was synthesized from laboratory grade reagents and verified by powder XRD (Figure 5). Other solids synthesized for the ferrous arsenate trials used arsenic-loaded ferrihydrite as the starting material. Synthesis under anoxic conditions was important for the formation and stability of parasymphesite ($\text{Fe(II)}_3(\text{As(V)O}_4)_2 \cdot 8\text{H}_2\text{O}$), because similar synthesis under oxic conditions outside the glove box generated a hydrated ferric arsenate, ferrisymplesite, ($\text{Fe(III)}_3(\text{As(V)O}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$) (Figure 5). It is known that parasymphesite can oxidize to form ferrisymplesite [52]. The use of deoxygenated water for synthesis also seems to be important, since a similar ferrous arsenate synthesis trial performed outside the glove box with deionized but not deoxygenated water yielded an amorphous product.

The ferrous arsenate solids synthesized inside and outside the glove box were acid-digested using 70% nitric acid to determine the iron and arsenic content (Table 3). All Fe/As ratios were higher than the stoichiometric symplectite ratio. We hypothesize that the synthesis process produces another amorphous mineral, such as a ferrous or ferric hydroxide, which results in a higher iron content than that calculated by assuming 100% parasymplectite or ferrisymplectite. Even though strong XRD peaks were detected for parasymplectite and ferrisymplectite, because XRD is semi-quantitative with a minimum detection limit of approximately 5% by weight, it cannot routinely quantify minor phases. If, as hypothesized, an iron hydroxide (ferric or ferrous) is co-precipitated with the symplectite phase, then this could affect the arsenic loading of the solid phase due to the high adsorption capacity of iron hydroxides for arsenic, and also arsenic leaching from the resulting solid mixture.

The arsenic leaching behaviors of parasymplectite and ferrisymplectite were tested using the TCLP. Even though synthesis under oxic and anoxic conditions resulted in different mineral phases, not only was the level of arsenic loading similar (Table 3), but the two solids also displayed similar TCLP arsenic leaching behavior below the TC (Figure 2). Since both parasymplectite and ferrisymplectite passed the TCLP and a low temperature/pressure synthesis route from ferrihydrite-type ABSRs was demonstrated, further investigation of ferrous arsenate was undertaken using the more aggressive SLL test. The SLL conditions are more representative of the conditions in a mature, MSW landfill. Hence, this test should indicate better than the TCLP the suitability of a candidate mineral to act as a sink for long-term arsenic immobilization under landfill conditions. Again the two solids displayed similar leaching behavior (Figure 6), but, as expected, the arsenic concentrations were significantly higher than observed from the TCLP. SLL arsenic leaching was approximately an order of magnitude higher than the arsenic TC.

Solids obtained from schwertmannite synthesis trials starting from ferrihydrite solid (As/Fe molar ratios of 0.0 and 0.05) after 18 days of dialysis were confirmed as schwertmannite by ST-XRD analysis (Figure 7). TCLP leaching of the arsenated-schwertmannite (As/Fe = 0.5) yielded arsenic concentrations below the TC. This solid had the lowest level of arsenic leaching of the candidate minerals studied (Figure 2). Consequently, arsenated-schwertmannite was subjected to leaching using the SLL solution. SLL leaching was lower than that observed for the symplectite-type solids (Figure 6), although still higher than the arsenic TC ($\sim 2X$) and significantly higher than the TCLP leaching results.

Schwertmannite, like other Fe(III) oxides transforms into more crystalline minerals such as goethite and magnetite with time [53–56]. Such transformations can potentially release arsenic. But a recent schwertmannite transformation study by Cutting et al. [56] with arsenic loadings of up to 4% by weight showed that only small quantities of arsenic were released into the aqueous phase ($\sim 120 \mu\text{g L}^{-1}$) due to sequestration in the transformation products.

4. CONCLUSIONS

Five candidate minerals – scorodite, arsenate hydroxyapatite, tooeleite, symplectite-type phases and arsenated-schwertmannite – were considered in this study as candidate phases for arsenic stabilization. The suitability of the candidate phase was judged according to the simplicity of the synthesis route (e.g., temperature, pH, material requirements, duration of process), synthesis route compatibility with iron-based ABSRs starting material, and stability with respect to arsenic leaching under TCLP and SLL conditions (Table 4).

Scorodite synthesis required relatively harsh conditions ($T > 150^\circ\text{C}$, $P \sim 8$ bar, $\text{pH} \sim 1$, $\text{Fe/As} < 2$), but the TCLP arsenic leaching was below the arsenic TC. Apatite-series solids were synthesized under more moderate conditions ($T \sim 100^\circ\text{C}$, $P = 1$ bar, $\text{pH} 12$), but inhibition

of solid formation in the presence of iron precluded use of most ABSRs as a starting material. TCLP leaching was slightly above that of scorodite. Tooeleite was synthesized under modest conditions ($T = 60^{\circ}\text{C}$, $P = 1$ bar, $\text{pH} > 2$), but silica coating required additional time and reagents. Tooeleite leaching was poor and about 10X above the TC, both with and without silica amendment. Symplectite species (ferrous and ferric arsenate) were simple to synthesize (ambient T and P and no pH adjustment) and synthesis was achieved starting with representative iron-based ABSRs. TCLP leaching was lower than the arsenic TC, although SLL leaching was about 10X greater than the TC. Lastly, arsenated-schwertmannite synthesis required an involved and lengthy procedure (HCl dissolution, $T = 60^{\circ}\text{C}$, dialysis, $t = 18$ days), but was amenable to an iron-based ABSRs starting point. The schwertmannite solids demonstrated the best arsenic leaching resistance (in both TCLP and SLL), although SLL was about 2X greater than the arsenic TC.

Based on these scoping results, symplectite-type phases and schwertmannite show the greatest promise for ABSRs stabilization. Although, the combination of synthesis conditions and leaching resistance was not completely satisfactory in both cases, they were both amenable to a ABSRs starting material. Optimization of synthesis route and leaching resistance were beyond the immediate scope of this work. But it is expected that with additional research, one or both of these solids may prove to be a stable, long-term repository for arsenic in ABSRs and might be synthesized through a relatively simple procedure amenable to use at a drinking water utility scale.

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LIST OF ABBREVIATIONS

ACT	Arsenic Crystallization Technology
ABSRs	Arsenic-bearing solid residuals
MSW	Municipal Solid Waste
TCLP	Toxicity Characteristic Leaching Procedure
BAT	best available technology
CA-WET	California Waste Extraction Test
ICPMS	inductively coupled plasma mass spectrometer
EPA	Environmental Protection Agency
DI	deionized
XRD	x-ray diffraction
ICDD	International Centre for Diffraction Data
SSRL	Stanford Synchrotron Radiation Lightsource
SEM	scanning electron microscopy
FA	ferrisymplesite

PS	parasymplesite
SLL	Simulated Landfill Leachate
ST-XRD	Synchrotron transmission X-ray diffraction
EDX spectroscopy	Energy Dispersive X-ray Spectroscopy
TC	Toxicity Characteristic

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Highlight

- Arsenic crystallization technology was explored to stabilize As in minerals before landfill disposal.
- Highly rated candidate minerals had a high arsenic capacity and low arsenic leaching.
- Low-cost, environmentally friendly processes were explored throughout this study.
- Schwertmannite and ferrous arsenate showed the most promise for arsenic stabilization.

Figure 1.

XRD spectra for solids from scorodite synthesis trials at 160 °C for 24 hours, a Fe/As molar ratio of 1.0, and initial pH as indicated. Note: Peaks on the natural scorodite spectrum indicate the positions of characteristic scorodite peaks. Only those scorodite peaks (2 and 3) which decreased in intensity on increasing the synthesis pH and other unidentified peaks (1, 4, 5 and 6) are explicitly marked here.

Figure 2.

Arsenic concentration from TCLP for candidate minerals. FA oxic - Ferrisymplesite synthesized under oxic conditions, Sch - Arsenated-schwertmannite, FA anoxic - Parasymplesite synthesized under anoxic conditions, Sco - Scorodite, Apa - Arsenate Hydroxyapatite (with no Fe and As/P < 0.2), Too - Tooeleite, Si-Too - Silica-amended Tooeleite. Note: Error bars were not obtained for scorodite and arsenate hydroxyapatite.

Figure 3.

XRD spectra of solids generated from arsenate hydroxyapatite synthesis trials using different As/P ratios. All the solids were synthesized at 100 °C, an initial synthesis pH of 11 and reaction time of 24 hours. The positions of characteristic peaks for hydroxyapatite and arsenate hydroxyapatite are indicated by a ● and ▲ respectively.

Figure 4.

XRD spectra for solids obtained from iron arsenate hydroxyapatite synthesis at different Fe/As ratios. Synthesis conditions: 100 °C, Ca/(As+P) ratio of 5/3 and P/As ratio =1, initial pH 12, and reaction time = 24 hours. The positions of characteristic peaks for arsenate hydroxyapatite and hematite are indicated by a ● and a ▲ respectively.

Figure 5.

Solid synthesized from a.) pure Fe(II) and As(V) solutions following the procedure in Johnston and Singer et al. [26]. b.) Fe/As = 20.5, zero-valent iron [Fe(III)/ZVI = 10], at room temperature inside N₂ purged glove box. c.) Fe/As = 20.5 solid, zero-valent iron [Fe(III)/ZVI = 10], at room temperature in ambient air. Note: PS – Parasymplectite, FS – Ferrisymplectite. There were no unidentified peaks. Only major peaks have been labeled in all cases.

Figure 6.

Arsenic leachate concentration from SLL test on FA anoxic - Parasymplesite synthesized inside the glove box, FA oxic - Ferrisymplesite synthesized outside the glove box, and Sch - Arsenated-schwertmannite.

Figure 7.

a.) XRD reference stick pattern for schwertmannite and ST-XRD spectra for solid synthesized after 18 days from b.) lab synthesized arsenic-loaded ferrihydrite (Fe/As molar ratio = 20.5) following a procedure modified from Carlson et al. [50] and c.) ferrihydrite following a procedure modified from Bigham et al. [49].

Table 1

Synthesis parameters for synthesis of scorodite at different temperatures

Temperature (°C)	Pressure (bar)	Initial pH	pH Control	Initial chemical composition			Method Reference
				Fe(NO ₃) ₃ (M)	NaH ₂ AsO ₄ (M)	Fe/As molar ratio	
60	1	1.5	No	0.11	0.1	1.1	[10]
95	1	1.5	Yes	0.11	0.1	1.1	[46]
150	8	1	No	0.11	0.1	1.1	[11]
230	11	1	No	0.11	0.1	1.1	Modified from [47]

Table 2

SEM-EDX results for tooeleite and silica-amended tooeleite

Sample	Accelerating voltage (kV)	Atom	Mean Atomic %*	Error ($\pm\sigma$)
Silica-amended	5	O	78.16	2.89
Tooeleite		Si	21.84	1.3
	10	O	64.2	1.12
		Si	12.72	0.23
		C	23.09	3.65
	15	O	61.18	0.94
		Si	7.38	0.11
	30	O	58.09	1.37
		Si	5.15	0.08
		Fe	0.1	0.01
		As	0.1	0.02
Tooeleite	5	O	56.3	1.48
		Fe	13.37	1.56
		As	10.08	0.27

* Values do not add up to a 100% because contribution from background carbon stub and other trace impurities is not shown here.

Table 3

Characterization of ferrous arsenate synthesized from arsenic-loaded ferrihydrite

Mineral	mmole of Fe/g of wet solid*	mmole of As/g of wet solid*	Experi mental Fe/As molar ratio	Theoretical Fe/As molar ratio (from stoichiometry)
Parasymplesite (anoxic synthesis in glove box)	0.04875	0.00936	5.2	1.5
Ferrisymplesite (oxic synthesis outside glove box)	0.0457	0.00756	6.04	1.5

* Water content was 99.15%.

Table 4
Summary of evaluation results of candidate minerals for Arsenic Crystallization Technology

Candidate mineral	Synthesis Conditions			Maximum expected As loading (wt/wt%) from stoichiometry or literature	% As loading observed in this study (wt/wt%)	Advantages	Drawbacks
	T (°C)	Fe/As ratio	pH <3	Redox conditions			
Scorodite	>95	<2		Oxidizing	~ 32%	NA	TCLP arsenic leaching below TC High temperature, elevated pressure synthesis conditions
Arsenate apatite	4–90	<5	>11	Oxidizing	~ 35%	NA	TCLP arsenic leaching slightly below TC, simple synthesis conditions Presence of Fe interferes with synthesis. Low arsenic capacity. Tendency for hematite co-synthesis
Parasymplectite	25	1.5	7.5	Reducing	~ 25%	8.25%	Favorable synthesis conditions and TCLP arsenic leaching below TC Relatively high arsenic leaching using SLL test
Ferrisymplesite	25	1.5	7.5	Oxidizing	~ 25%	6.67%	Favorable synthesis conditions and TCLP arsenic leaching below TC Relatively high arsenic leaching using SLL test
Arsenated-Schwertmannite	60	20.5	2.6	Oxidizing	5.6	5.4–6.5%	Low arsenic leaching using TCLP and SLL test Long duration of synthesis (at least 18 days)

Candidate mineral	Synthesis Conditions			Maximum expected As loading (wt/wt%) from stoichiometry or literature	% As loading observed in this study (wt/wt%)	Advantages	Drawbacks
	T (°C)	Fe/As ratio	pH <3	Redox conditions			
Tooeleite	60	0.80	2.6	Oxidizing	~20–25%	~ 22%	High arsenic leaching using TCLP
Silica-amended Tooeleite	60	0.80	2.6	Oxidizing	NA	~ 21%	High arsenic leaching using TCLP