

STABILIZATION OF ARSENIC-BEARING IRON HYDROXIDE SOLID WASTES IN POLYMERIC MATRICES

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ABSTRACT

This work explores the use of an aqueous-based emulsion process to create an epoxy/rubber matrix for separating and encapsulating waste components from salt-laden, arsenic-contaminated, amorphous iron hydrate sludges. Such sludges are generated from conventional water purification precipitation/adsorption processes, used to convert aqueous brine streams to semi-solid waste streams, such as ion exchange/membrane separations, and from other precipitative heavy metal removal operations. In this study, epoxy resin and polystyrene butadiene (PSB) rubber emulsions are mixed together, combined with residual sludge, and cured and dried at 80°C to remove water. The microstructure of the resulting waste form is characterized by scanning electron microscopy (SEM), which confirms that the epoxy/PSB matrix surrounds and encapsulates the arsenic-laden amorphous iron hydrate phase, while allowing the salt to migrate to internal and external surfaces of the sample. Soluble salts leach from the sample at a rate given by diffusion coefficients of the order of 10^{-8} cm²/s. Long-term leaching studies reveal no evidence of iron migration and, by inference, arsenic migration, and demonstrate that diffusivities of the unextracted salt yield leachability indices within regulations for non-hazardous landfill disposal.

INTRODUCTION

Efforts to implement new water quality standards, increase water reuse and reclamation, and reduce the cost of waste storage motivate the development of new processes for stabilizing wastewater residuals that minimize waste volume, water content and the long-term environmental risk from related by-products. Processes to remove toxic heavy metals from drinking water and other aqueous streams are not new, but a number of recent trends have both greatly increased the frequency of their use and drawn critical attention to the nature of their by-products.¹ The Environmental Protection Agency (EPA) has recently passed more strict standards for the allowable concentrations of many heavy metals in drinking water. The recently revised arsenic standard and the currently debated lead and copper rules are examples of this tightening of water quality standards.^{2,3} As the readily available sources of new potable water diminish, there is an increasing emphasis on reuse and reclamation of water to augment supplies. Furthermore, as the available space for solid waste disposal becomes scarcer and the potential

negative impacts of such disposal are better realized, the scrutiny and cost of by-product disposal has greatly increased. As a consequence of these trends, there is a rapidly increasing volume of by-products requiring disposal at the same time as there is a need to minimize the volume, water content and long-term environmental risk of the by-products.

Since heavy metals are elemental, removal processes do not destroy them, but merely transfer them from the primary water stream to an alternative fluid or solid stream which constitutes the by-products (or as is often termed, residuals) of the process. Toxic heavy metal removal generates a metal-laden solid waste stream or, more commonly, a concentrated brine stream of the toxic components mixed with various nontoxic salts. Large-volume, troublesome examples include the ion exchange/membrane separation concentrated streams generated from the use of arsenic removal technologies by water treatment utilities and the aluminum and iron sludges emanating from precipitative, heavy metal removal operations utilized by semiconductor, pulp and paper and metal plating industries. The emphasis of the research is on treating the sludges generated from conventional precipitation/adsorption technologies that are used to convert aqueous brine streams to semi-solid waste streams. Even though precipitation/adsorption greatly reduces the waste volume, the sludges generated are still prone to toxics release unless disposed in hazardous waste sites. The only competing technologies to the proposed polyceram technology for stabilization of such wastes are grout/cement based, which are inapplicable to high salt wastes (as salt interferes with the calcination reactions necessary for cement curing) and cannot remove the added waste volume composed of benign salts.^{4,5} To the authors' knowledge, the combination of a stabilization technology for toxic waste and controlled release for nontoxic, soluble salts has not been successfully attempted before.

The work described here uses an arsenic-laden sludge as the residual of interest. Arsenic sludges were chosen because in 2001, drinking water standards were enacted that reduced the allowable levels of arsenic from 50 ppb to 10 ppb.² These new standards will affect thousands of small utilities and cause production of an estimated six million pounds of solid residuals every year.^{2,3} Options expected to be used for arsenic removal from drinking water are: modified lime softening, modified coagulation/filtration, and ion exchange. These technologies will produce arsenic-bearing brine streams, which in turn will be treated to generate a final, arsenic-laden residual of amorphous ferric hydroxide (AFH) sludge. These residuals typically will not pass the Toxicity Characteristic Leaching Procedure (TCLP) specified by EPA to discriminate between hazardous and non-hazardous wastes and, consequently, must be disposed of in controlled, hazardous waste landfills.⁶ Hazardous waste disposal costs are a factor of 5 to 10 higher than non-hazardous disposal costs. Thus, considering that implementation of the new arsenic rule will cost an estimated \$180-206 million per year,² it will cost water providers approximately \$9-19/lb more to dispose of a hazardous treatment residual, as opposed to a non-hazardous one. In order to place the sludge in a non-hazardous landfill, toxic components have to be stabilized so they do not leach significantly into the environment. At the same time, reducing the total volume of residuals will minimize landfill costs; hence there is an incentive to separate benign components from wastes prior to disposal. Consequently, this work focuses on an overall program objective to develop a separation/fixation technology for arsenic-laden AFH sludges that is simple, cost effective, safe, efficient, and durable. The development effort is based on application of polyceram waste-form technology as a means of meeting the proposed objectives.

The sludge used in this study was modeled after an AFH sludge that represents the solid residuals expected from an ion exchange (IX) operation used for removal of arsenic from drinking water. To treat water by IX, contaminated water containing arsenic passes through an

IX column filled with an anion exchange resin containing free chloride ions. As the water passes through, the chloride ions in the resin are exchanged with the arsenic ions in the water and the treated arsenic-free water exits the system. After about one thousand bed volumes of contaminated water have passed through the column, the resin is exhausted and must then be regenerated. At this point, four bed volumes of a regenerating solution containing 3% sodium chloride (NaCl) are passed through the column to return chloride ions to the resin and remove the arsenic ions. This process concentrates the contaminated water down to four bed volumes as opposed to one thousand bed volumes. The resulting brine, containing 2% NaCl and arsenic, then exits the column and enters a settling tank. Sodium hydroxide (NaOH) is added to the brine to precipitate ferrihydrite ($\text{Fe}(\text{OH})_3$) to adsorb the arsenic. Enough ferric chloride (FeCl_3) is added to bring the iron to arsenic mass ratio to 10 to reduce the arsenic concentration below the drinking water standard of 10 ppb. The supernatant liquid in the settling tank contains a toxic-free brine solution of 2% NaCl which is extracted and recycled. The sludge that is deposited on the bottom of the settling tank consists of solid $\text{Fe}(\text{OH})_3$, arsenic (both sorbed/coprecipitated with the AFH and as free species in the sludge-associated water), NaCl, and water. It is this sludge that requires the fixation of the iron and arsenic components while simultaneously separating the salt in order to reduce the volume to minimize the cost of disposal.

Polycerams, a hybrid of organic and inorganic components, have been known to be mechanically stable, chemically durable, to have low processing temperatures (under 100°C), and are easily fabricated, which make them feasible materials for fixating $\text{Fe}(\text{OH})_3$. However, one disadvantage of polycerams involved the use of flammable and volatile solvents.⁷ This disadvantage is mitigated in this work by the application of an aqueous processing route in which an emulsion was created by mixing two polymers throughout a continuous water phase.⁸ When cured, the water evaporates and the emulsion undergoes a phase inversion causing the polymer to become the continuous phase with the salt and solid residuals distributed throughout. In previous work by our group, it was found that soluble salts were successfully encapsulated in the polymer matrix using this water-based route,⁹ and the salt diffused at a slow rate yielding leachability indices well within the minimum requirements for land disposal. Microstructural characterization revealed that some portion of the dissolved salt was carried to the outer regions of the waste form as water evaporated during the curing process. This migration of salt can be further exploited as a separation and fixation technology that would separate the salt from the toxic components in a brine stream and fix those toxic components in a durable waste form matrix.

MATERIALS AND METHODS

A representative sludge was created to mimic the end residual of an IX operation for arsenic removal. All the chemicals used to make the sludge were reagent grade or better. Sodium hydrogenarsenate heptahydrate was first added to deionized water. Ferric chloride, FeCl_3 , was then added and completely dissolved in solution. While the solution was being mixed, NaOH was added to precipitate $\text{Fe}(\text{OH})_3$. Once the mixture was stirred to homogeneity, the batch was allowed to settle for 24 hours, during which time the arsenate adsorbed onto the $\text{Fe}(\text{OH})_3$. After the 24-hour period, free liquid was decanted from the settled sludge layer and more NaCl was added to bring the chloride concentration up to that typical of an AFH sludge from IX. Sodium nitrate (NaNO_3) was also added because it typically coexists in the brine stream with the arsenate. The pH was adjusted to neutral with NaOH, the batch was mixed, and then allowed to settle to facilitate liquid decanting when needed.

Sludge of varying water content was used in sample fabrication to cover the range of sludge

produced by industries. Changing the liquid content in the wet sludge affects the salt content of the dry sludge. At low liquid content (~70% w/w), the sludge is mud-like and, when dried, contains 33 wt% salt. At high liquid content (~95% w/w), the sludge is a fine particulate slurry and dries to contain 75 wt% salt (the remainder is the AFH phase). X-ray powder diffraction reveals that the AFH in the sludge is structurally amorphous. The final sludge composition (dry basis by weight) is NaCl: 29.6%; NaNO₃: 1.9%; Fe(OH)₃: 64.5%; HAsO₄: 4.0 %.

All waste forms were prepared in order to obtain equal parts, by weight, of polystyrene-butadiene (PSB) rubber and epoxy resin in the final cured sample. To fabricate the waste forms, PSB latex (Styronal ND 656, BASF) and the surfactant sorbitan monooleate (Span-80, Aldrich) were mixed for 10 minutes in a narrow, round-bottom mixing vessel to create an emulsion. While continually mixing, the arsenic-containing sludge was added. Then, epoxy resin (Epo-Kwick Resin, Buehler) was added drop-wise with a syringe while stirring. Next, a cross-linking agent, diethylenetriamine (DETA, Aldrich), was added to the mixture. The emulsion was mixed for 10 additional minutes to ensure uniformity and then cast in shallow aluminum dishes and placed in an oven to dry and cure at 80°C until no further weight loss was detected (approximately 3 days). Cured samples were flat “cookie” shapes with diameters of about 4 cm and ranging between 0.15 and 0.4 cm in thickness. In some cases, cylindrical monoliths of about 2 cm in diameter and 3.5 cm long were cast. Samples with various iron loadings, salt loading, and initial water content were fabricated.

Scanning Electron Microscopy (SEM) was used to analyze sample microstructure. Energy-Dispersive X-Ray Spectrometry (EDS) was used to obtain qualitative compositional analyses. An initial analysis of the polymeric matrix of which the waste forms are composed was performed. Microstructural features were revealed using the modified osmium tetroxide (OsO₄, Aldrich) staining method for rubber-toughened epoxies.¹⁰ Salt leaching and extraction were conducted to calculate the diffusivity of salt through the polymeric matrix. Iron leaching was also performed. Arsenic leaching is assumed to be identical to the behavior of iron; however, leaching experiments will be conducted in the future to confirm this hypothesis.

To study the leaching behavior, portions of each sample were cut and suspended in a beaker of well-stirred water of known volume. A conductivity probe was placed in the beaker to measure the changes in the conductivity of the liquid as the salt leached out of the sample. The measurements were correlated to salt concentration and a mathematical model based on Fick’s law of diffusion was fit to the data. The model equations are presented elsewhere.⁹ Assuming that the samples leach to completion, the percent salt retention of the material is calculated using the following equation:

$$\% \text{ Salt Retention} = (\text{Total salt in sample} - \text{Salt Concentration}) / \text{Total salt in sample} \times 100\% \quad (1)$$

The model yields the effective diffusivity of the salt in the waste form, which is then used to calculate the leachability index for each sample.⁹ Figure 1 shows an example of the model fit to actual experimental data. The model only starts correlating with the data after approximately one hour of initial extraction of salt from the outside of the sample. During the first part of the leaching experiment, solid salt close to the surface of the sample dissolves rapidly without participating in diffusion-limited transport. After this initial hour, all of the unincorporated salt has dissolved, and the remainder of the curve represents the diffusive mechanism of the leaching process.

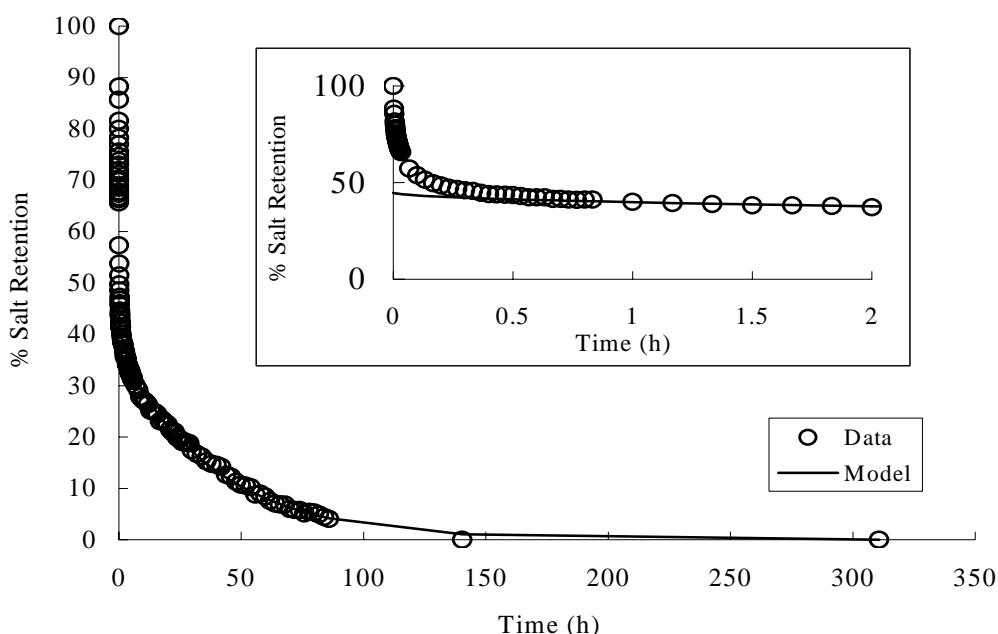


Figure 1. Example of experimental data fit to diffusion model⁹ with an inset of the first two hours of leaching for sample 3.08 (Table I).

RESULTS AND DISCUSSION

An initial study of the sample microstructure of the polymeric matrix alone revealed that it is not homogeneous but in effect is composed of dispersed epoxy droplets in a continuous PSB phase. This was determined by the osmium tetroxide staining procedure, which provides contrast for SEM viewing, as the electron-dense OsO_4 binds preferentially to unsaturated bonds present in the PSB molecule.¹⁰ The rubber components appear as brighter regions in a SEM micrograph and epoxy components appear darker. The epoxy droplets have a large size distribution ranging between 0.1 and 5 μm . Usually, addition of rubber to epoxy resins is associated with a dispersed rubber phase to reduce the stiffness of the epoxy matrix.¹¹ In our case, the relatively high rubber to epoxy ratio leads to a continuous rubber phase, whose hydrophobicity represents, in principle, an advantage for the encapsulation process. SEM analysis showed that the phase distribution of the polymeric matrix is not influenced by the presence of the arsenic-containing iron sludge and salt.

Table I. Sample numbers and overall compositions based on dry weight.

Sample ID	Dry wt% $\text{Fe}(\text{OH})_3$	Dry wt% HAsO_4	Dry wt% NaCl	Dry wt% NaNO_3
3.08	12.5	0.8	35.7	2.3
3.12	16.3	1.0	22.3	1.5
3.13	12.5	0.8	35.9	2.3
3.17	10.0	0.6	4.6	0.3
3.18	10.0	0.6	4.6	0.3

Table I lists the compositions of the waste form samples investigated in this study. Microstructural analysis by SEM reveals that AFH incorporation is similar in all waste forms but

that salt features in the microstructure vary with the relative salt loading. For example, Figure 2a shows the microstructure of a waste form containing a low salt loading, sample 3.17. While Figure 2a shows only a portion of the sample, it is representative of the entire cross-section. Because the elements in the salt and AFH phase scatter electrons more strongly than the carbon and hydrogen atoms in the polymer, these phases appear lighter in the micrographs, even though the samples have not been stained with OsO₄. The dark region is the polymeric matrix. As seen in the figure, the AFH phase forms dense, elongated particles with aspect ratios around 1/5 and lengths along the largest dimension in the range of 20-150 μm. The imaging done at a higher magnification and shown in Figure 2b shows that, at this low level of salt loading, the salt appears as cubic crystals about 5 μm in size embedded in the polymeric matrix. EDS analysis was conducted on the region containing the ferrihydrite particle circled in the magnified image of Figure 2a and shown in more detail in Figure 3a. Figures 3b-e show the elemental maps that correspond to this region. Lighter regions in these maps indicate the presence of the element indicated. The dark area surrounding the AFH particle is composed mainly of carbon as shown by the elemental carbon map (Figure 3b). Most of the light regions in the micrograph correspond to the iron containing phase, as shown in Figure 3d. The arsenic map (Figure 3c) shows that arsenic is strongly associated with the AFH phase. Finally, the maps indicate that the groups of crystals seen on either end of the AFH particle are composed of both sodium (Figure 3e) and chlorine (Figure 3f).

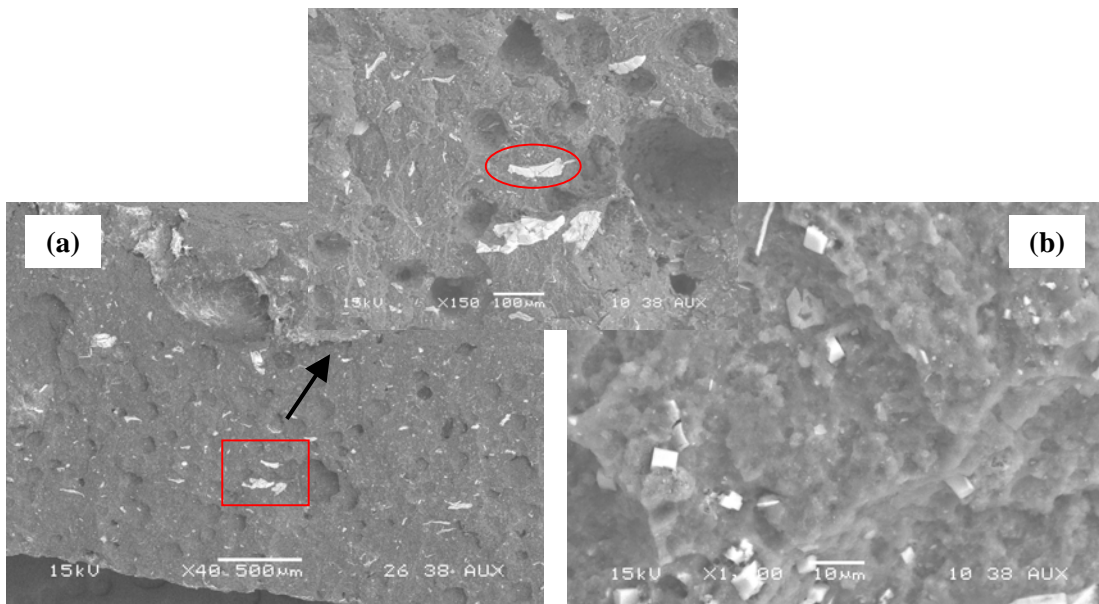


Figure 2. SEM micrographs of a sample with a low salt loading (sample 3.17) showing (a) a cross-section of cookie where the upper boundary of the image indicates the top of the cross-section and the lower boundary indicates the bottom; (b) the matrix of the cookie at high magnification; the image directed by the arrow is a magnified image of the region shown in the rectangular box in (a). Dry salt content of sample is 4.9%.

While the matrix phase does contain small salt crystals, EDS analyses of several samples indicate that the salt also concentrates as crystals in the cracks and interfacial regions of the AFH phase. The salt crystals seen on the ferrihydrite surface in Figure 3a originally lay inside cracks

that ran parallel to the plane of EDS analysis. They were exposed for analysis when the sample was fractured for viewing.

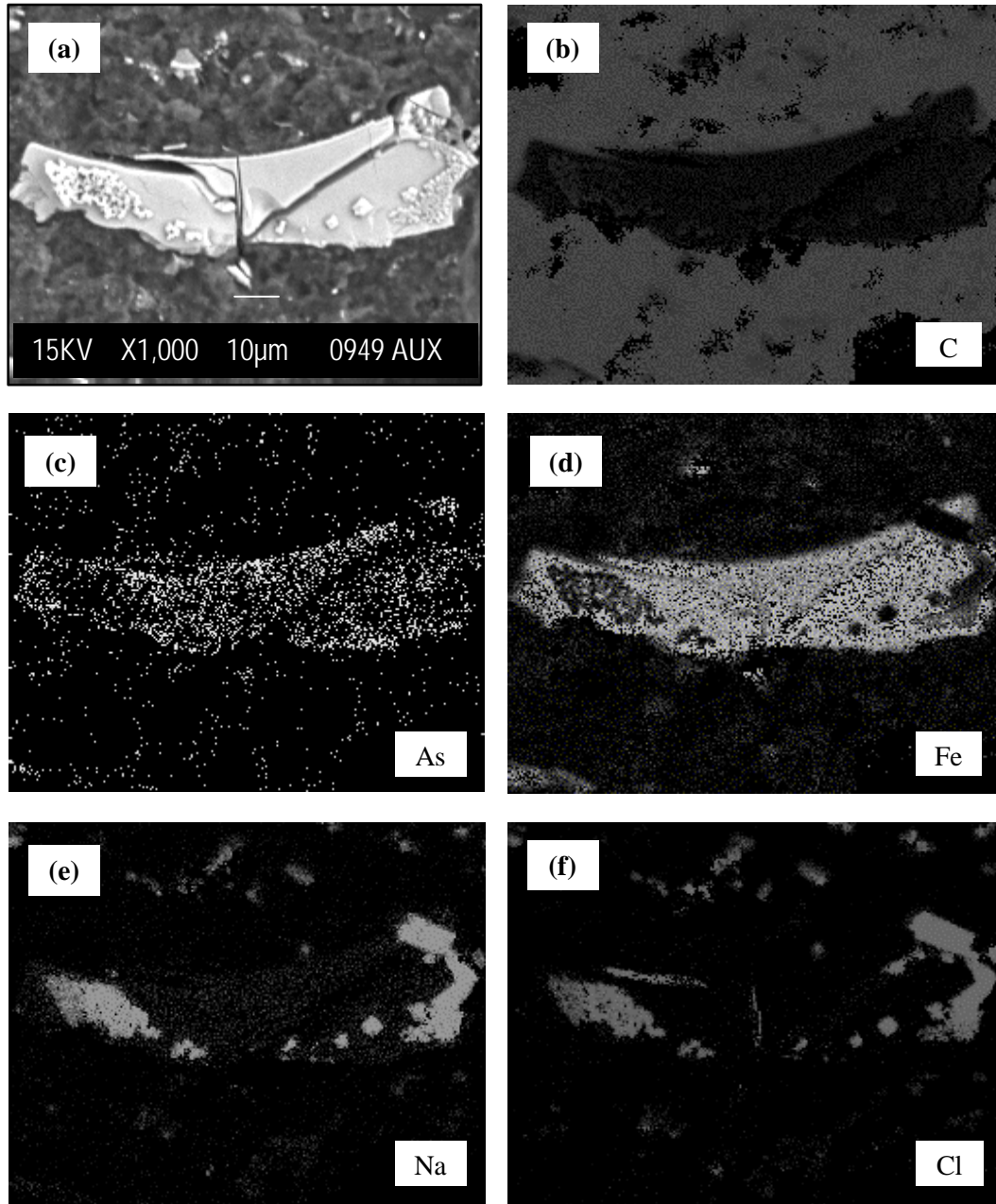


Figure 3. (a) SEM micrograph of sludge particle found in sample 3.17; maps of compositional elements: (b) carbon, (c) arsenic, (d) iron, (e) sodium, and (f) chlorine. Light areas indicate presence of specified element.

The microstructural features of a waste form containing a high salt loading are shown in Figure 4. The image in Figure 4a illustrates sample 3.08 at the middle of the monolith, which is representative of the majority of the sample. In contrast to sample 3.17, the polymeric matrix of sample 3.08 contains large amounts of salt in the form of agglomerated regions distributed uniformly throughout the waste form and high concentrations of salt at the outer edges (Figure

4b). In particular, the bottom of sample 3.08 includes a well-defined salt crust approximately 100 μm in thickness. Additionally, the matrix near the bottom contains a number of pores around 400 μm in diameter whose inner surfaces are coated with a thick layer of salt.

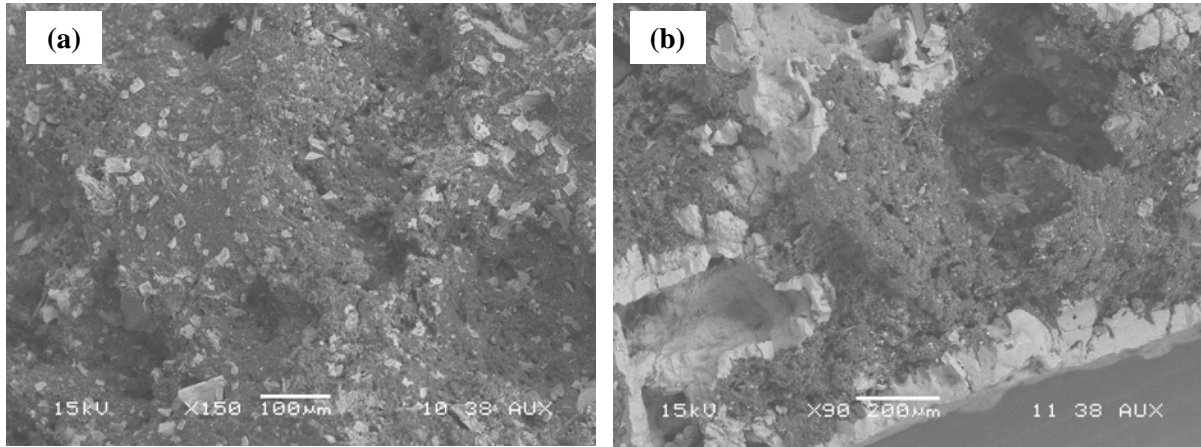


Figure 4. SEM micrographs showing microstructure of a sample with a high salt loading (sample 3.08) at (a) middle of monolith, and (b) bottom of monolith. Dry salt content of sample is 38%.

The high salt loading of sample 3.08 limited its structural integrity and caused it to be somewhat crumbly when cured, which may limit its applicability as a viable waste form. However, the fact that the waste form retains a large amount of salt in regions that are accessible by a very open network of pores suggests that the underlying process has great potential as a technology for extracting or separating the salt to minimize the amount of waste for disposal. A significant reduction in the quantity of waste would be achieved if this salt were separated or extracted from the waste form before disposal and storage.

To test the capabilities of the manufacturing processes for salt separation, salt extraction experiments were performed on a variety of samples containing varying amounts of AFH and salt. As seen in Table II, most of the salt (60 to 90%) in the sample was removed in the first hour of extraction. These results demonstrate that for a higher initial salt loading, a larger fraction of the salt is successfully removed.

Table II. Amount of salt dissolved after one hour of initial salt extraction for samples of various sludge loadings.

Sample ID	Dry wt% Fe(OH) ₃	Dry wt% Salt	% Salt Extracted
3.12C	16.3	23.8	86.1
3.13A	13.9	31.4	91.3
3.13D	13.9	31.4	85.7
3.17A	10.0	4.9	59.2
3.17E	10.0	4.9	61.0

To be an effective separation medium, the waste form must allow the rapid removal of salt while still retaining the arsenic-containing AFH phase. Separate iron leaching tests were performed, which indicated that no appreciable iron existed in the leachates after 300 hours of

extraction. It is inferred that iron is therefore not extracted in 1 hour, and because arsenic adsorbs to the iron species in the waste form, it is also assumed that no arsenic is removed. This shows that the waste form can be used to separate the salts from toxic components from water treatment sludges. Upon contact with water, an important fraction of the salt will leach out of the waste form while keeping the AFH and associated arsenic still encapsulated.

The salt extraction experiments measure the behavior of the salt that is easily removed by immersion in water. When the salt leaching experiments are continued beyond the first hour of extraction, the rate of leaching of the salt that does not have ready access to internal or external surfaces of the waste form (e.g. the salt that is embedded in the polymeric matrix) can be determined. The diffusion rate of the salt in this period should be representative in magnitude of the rate at which arsenic or iron will diffuse from the waste form. It is important to recall that driving forces for diffusion of iron or arsenic species are drastically lower than those of salt because of their low solubility (iron) and their strong adsorption to AFH (arsenic).

Table III shows the diffusivities and their corresponding leachability indices for samples of different relative salt loadings, high and low. The minimum required leachability index for land disposal is 6. Both waste forms present leachability indices well within the required limit. The diffusion model used is amenable to calculating the diffusivity coefficient of the most mobile species in the waste form, i.e. the salt, and these results, compared to those shown in Table II, show that at various salt loadings, the majority of the salt can be separated using this waste form while indicating that the remaining salt, and thus the toxic, least mobile species, will be encapsulated well within leachability limits for non-hazardous land disposal.

Table III. Diffusivities and leachability indices of unextracted salt in samples of different salt contents.

Sample ID	Relative Salt Content	Diffusivity (cm ² /s)	Leachability Index
3.08	High	6.00×10 ⁻⁸	7.22
3.17	Low	3.50×10 ⁻⁸	7.46

CONCLUSIONS

The important step in making a waste form for the encapsulation of toxic residuals occurs at the phase inversion during the curing process. The evaporation of water causes the material to transform from a continuous water phase to a continuous polymeric phase. The evaporation of water also drives the salt to the outer surface of the polymer, while the arsenic-laden AFH particles remain in the host material. Subsequent water immersion successfully extracts a high percentage of salt from the host material by dissolution and transport through interconnected porosity, which thereby promotes a reduction in waste volume and ultimately reduces disposal costs. Most importantly, based on leaching studies of the unextracted salt, the diffusion coefficients of both a high and low salt loaded sample yielded leachability indices within regulations for non-hazardous landfill disposal. Because salt is the most mobile species, it is inferred that arsenic leaches from the host material at an even slower rate, making the waste forms amenable to unregulated land disposal options.

The environmentally-benign, water-based emulsion processing of epoxy/PSB polymeric hosts show great promise as a separation and fixation technology for treating brine streams from wastewater treatment facilities. Future work should address the explicit measurement of arsenic leaching rates, the increase in residual loading, and the waste form volume consolidation by post cure heat treatment of extracted host material. A sensitivity study determining the impact of

processing variations should be performed before the waste form fabrication is scaled-up for marketing.

ACKNOWLEDGEMENTS

The authors wish to thank the United States Department of Energy, the National Science Foundation, and Pacific Northwest National Laboratory for providing the opportunity to participate in the Faculty and Student Teams program. The research team also thanks Rod Quinn and the Environmental Technology Directorate, the Advanced Process and Application Group, especially Evan Jones, Bradley R. Johnson, Gordon Xia, Michael Schweiger and Jim Davis, and the Process Science and Engineering Division at PNNL. Finally, the team thanks William Velez and the CSEMS for facilitating the organization of the FaST appointment at UA.

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