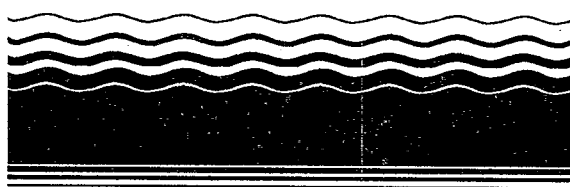**♻EPA**

SITE

SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Emerging Technology Summary

Metals Treatment at Superfund Sites by Adsorptive Filtration

This project evaluated an innovative approach for removing inorganic contaminants from the liquid phase at Superfund sites. In the process, called adsorptive filtration, metals are collected by attachment to a thin layer of ferrihydrite (iron oxide) that has been immobilized on the surface of sand grains. The modification of the sand surface allows the grains to simultaneously adsorb soluble heavy metals and remove particulate metals by filtration from a wastewater.

The metals studied were Cd, Cu, and Pb, present at concentrations of 0.5 or 5 mg/L each, in synthetic solutions. A few preliminary tests were also conducted to evaluate removal of the toxic oxyanions of As and Se. The effects on process performance of solution pH, the empty bed detention time (EBDT), and the presence of complexing agents, oil, surfactant, and biodegradable substances were evaluated. In addition, the potential to regenerate the media after a run was investigated, including both the kinetics and overall efficiency of the regeneration process. Finally, a model waste solution from a Superfund site was treated by adsorptive filtration in a small-scale test.

In general, adsorptive filtration proved to be an efficient and effective treatment process. Soluble and particulate forms of all the metals tested could be removed from the water stream at both concentrations tested. The contact time required for treatment was minimal (<5 min), and treatment was successful at moderate pH values (near 9). Removal efficiencies ranged from about 70% to >99%, depending on treatment conditions. Regeneration was also fairly rapid and efficient, metal concentrations in the regenerant solutions reached several hundred times those that were in the influent. Over the duration of the tests, there was no indication that the media were deteriorating. Finally, the process was shown to be applicable for removing Zn from a waste stream generated at a Superfund site. Overall, the project adequately demonstrated the potential applicability of the process, and it appears that the process is appropriate for testing on a larger scale.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate

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report of the same title (see Project Report ordering Information at back).

Introduction

Adsorption is the binding of chemical species on the surface of suspended particles. If the adsorbent (solid surface) is chosen carefully and the solution chemistry is adjusted appropriately, adsorption-based processes are capable of removing metals over a wider pH range and to much lower levels than can processes based on precipitation. Additionally, sorption may remove some metals in systems where precipitation will simply not work at all. For instance, adsorption can often remove inorganically- and organically-complexed metals that would not be removed by conventional treatment methodology. Adsorption can also be very effective for removing anionic metals such as oxyanions of Se, Cr, and As. These capabilities make adsorption an effective process for remediation at sites where a wide variety of cationic, anionic, and complexed metals co-exist.

One adsorbent that is commonly present in metal treatment processes is amorphous iron oxide, or ferrihydrite, which forms when iron salts precipitate in neutral to slightly alkaline solutions. Since adsorption processes are most effective when large quantities of adsorbent are present, a higher coagulant dose will improve treatment efficiency in most cases. However, increasing the ferrihydrite concentration leads to a corresponding increase in sludge mass. Thus, while optimization of the metal removal efficiency requires that large amounts of ferrihydrite be used, optimization of the sludge processing step requires that minimal amounts of this material be disposed. This trade-off can be dealt with successfully by first adsorbing contaminant metals onto ferrihydrite and then separating the metals from the adsorbent, so that the adsorbent can be retained and reused to treat subsequent batches of waste.

One efficient way to retain ferrihydrite in a system is to use it as the media in a packed-bed treatment process. Unfortunately, this approach is not practical, since ferrihydrite is a bulky, flocculant material with extremely low hydraulic conductivity. To overcome this problem, a means was developed by which the ferrihydrite could be coated onto the surface of sand. A photograph of some coated sand grains used in the current study is shown in Figure 1.

After treatment has proceeded for a period of time, either the coating reaches its maximum capacity to remove metals or the filter requires backwashing. At this time,

the column can be backwashed to recover particulate metals from the column, and an acidic solution can be used to recover the adsorbed metals, thereby regenerating the column. Because the ferrihydrite is trapped on the sand particles, only the contaminant metals and not the ferrihydrite are released. Thus, the need to dispose of large amounts of iron oxide with the metal sludge, one of the main drawbacks of a conventional treatment process, is eliminated.

In sum, there are six essential aspects of adsorptive filtration that combine to make it a potentially valuable and widely applicable technology:

- Ferrihydrite is a strong metal adsorbent that can be regenerated by changing pH.
- Ferrihydrite can be coated onto sand, retaining much of its adsorbent activity.
- Ferrihydrite can adsorb some metal complexes that are not removed from solution by conventional precipitation.
- Many metal oxyanions that cannot be treated by conventional precipitation can adsorb onto ferrihydrite.
- A column of coated sand acts as a filter as well as an adsorbent.
- The technology appears to be applicable over a wide range of contaminant concentrations.

Methodology

The project consisted primarily of pilot-scale testing of the ferrihydrite-coated sand. The experiments addressed the kinetics of adsorption and regeneration, the adsorption capacity of the media for both soluble and particulate metals, the effects of various organic contaminants on metals removal by the media, the long-term stability of the adsorbent, and the metal concentrations achievable in the regenerant solution. In addition, although model influents were studied during most of the project, a few tests were conducted with a metal-containing solution from a Superfund site.

The coating was applied by heating a solution containing an iron salt to dryness, under controlled conditions and in the presence of Ottawa sand with an average diameter of 400μm. Some relevant features of the plain sand and the two batches of coated sand used in the project are presented in Table 1.

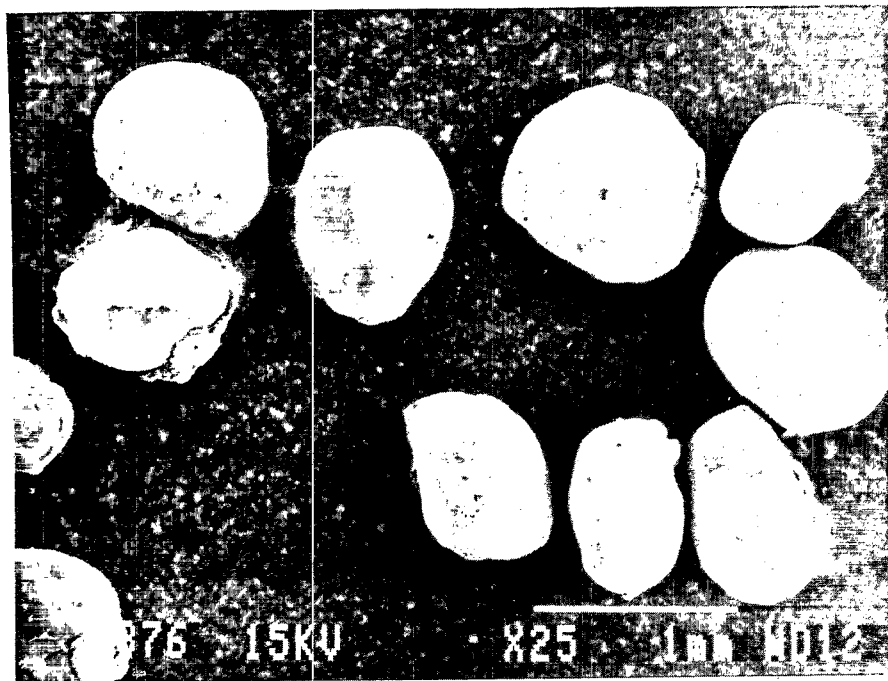The runs were conducted using a packed bed containing 250 mL (bulk vol-

Figure 1. *Electron micrograph of the coated sand magnified 25x. Large areas of the grains are completely coated with a skin-like layer of iron oxide, which appears to be about ten μm thick.*

Table 1. *Characteristics of Plain Ottawa Sand and Iron-oxide-coated Sand Used in Adsorptive Filtration Study (All Sands Were 20-30 Mesh Size)*

	Plain Sand	Media I	Media II
Fe salt used for coating	none	$Fe(NO_3)_3$	$FeCl_3$
% iron by weight	0	2.1	3.2
surface area by BET, m²/g	0.04	2.4	9.1
pH of the PZC	0.7	9.2	9.8

ume) of the coated sand. The rest of the setup consisted of automated instruments for maintaining pH of the influent water, pumping water through the column, and regenerating the column at fixed intervals. Samples were collected automatically and were analyzed for metal content. Headloss across the bed was also monitored. Once a predetermined criterion was met (related to either the duration of the run or the headloss), the bed was cleaned by backwashing and/or acid regeneration, and the cleaning solutions were analyzed. A solution adjusted to and maintained at pH near 2.0 was generally used for regeneration.

Model influent solutions contained 0.5 or 5.0 mg/L of Cu, Cd, and Pb, sometimes individually and sometimes in combination. The pH of the test solutions ranged from 7.0 to 9.5, with most tests conducted at pH 9.0. Test solutions also contained 0.01 M $NaNO_3$. Also, several tests were conducted in which an additional substance was added to the influent solution to assess its effect on metal behavior in the column. The substances tested in this way included ammonia (as a complexing agent), EDTA (as a chelating agent), sodium dodecyl sulfonate (a surfactant), motor oil, and antifreeze. In addition, some tests were conducted using a column containing biogrowth. Finally, as noted above, a few tests were run with a solution collected from a Superfund site where conventional treatment is currently being applied.

Results

Systems with 0.5 mg/L Cu, Cd, and Pb in the Influent

The effluent concentrations of the metals for a run with 0.5 mg/L each of Cu, Cd, and Pb in the influent at pH 9.0, using a 2-min EBDT and a hydraulic loading rate of about 11 gal/min-ft² , are shown in Figure 2. Initially, concentrations of all three metals in the effluent were less than 0.1 mg/L and were gradually increased to around 0.1 to 0.2 mg/L after 7000 bed

volumes of influent had been treated. Headloss was usually under 5 psi at the beginning of a run and increased gradually thereafter. When the headloss reached around 10 to 13 psi, the column was backwashed to remove particulate matter that had been trapped. This process was successful in that the pressure drop through the column was reduced after backwashing and the metal removal efficiency was at least as good, and often better, after backwashing.

Systems with 5 mg/L Cu, Cd, and Pb in the Influent

In the runs with 5 mg/L of each metal in the influent, most of the metal load was particulate; soluble influent concentrations were typically around 1.5 mg Cd/L, 0.8 mg Pb/L, and 0.2 mg Cu/L. Under these conditions, for the process to be successful, filtration must be at least as significant a mechanism of metal removal in the columns as adsorption.

During each run, effluent was sampled until the pressure drop across the column reached a predetermined value, usually either 20 or 25 psi. At that point, an automatic shut-off switch was activated, and flow to the column was terminated. The column was then backwashed with pH 9.0 water, and flow was reinitiated. Influent to the column at that point was identified as "Batch 2." A similar sequence occurred when the pressure reached the target value again, and Batch 3 was treated. When the pressure reached the maximum allowable value after treatment of Batch 3, the column was backwashed and then regenerated with water adjusted to pH 2.0. Data for a typical run under these conditions are shown in Figure 3. Batch 2 began at Bed Volume 260, and Batch 3 at Bed Volume 500.

The total concentrations of all the metals in the effluent were well below 0.1 mg/L until a few hundred bed volumes had been treated (a 6- to 12-hr period), at which point particulate metals began breaking through the column. Backwashing of the media allowed additional influent to

be treated effectively. Removal of soluble metal was substantial throughout these runs, with typical removal efficiencies of 80% for Cu, 90% for Pb, and 98% for Cd, and typical overall removal efficiencies (comparing total effluent and total influent) of 99% or greater for all three metals.

Backwashing

The metal concentration in the backwash water was on the order of a few hundred mg/L for each metal. Interestingly, the amount of metal recovered by backwashing was consistently and substantially less than the computed particulate load that had been applied to the column. Most of the difference between the amount of particulate metal removed and the amount recovered by backwashing was recovered during the acid regeneration step: overall recovery efficiencies (backwash plus regeneration) were almost always greater than 80% and were often 100% ± 10%.

Regeneration

The regeneration protocol was typically to circulate two bed volumes of water adjusted to pH 2.0 through the column for 2 hr, although in some cases a larger volume of solution was used. After 2 hr, another, equal volume of acidified water was passed through the column and was not recirculated. The metal concentration in the recirculation fluid increased rapidly at first and then only slowly thereafter (Figure 4). Based on these results, it appears that a recirculating period as short as 10 min. would release a large fraction of the available metal. Metal concentrations in the first and second regenerant solutions were as high as 3000 and 500 mg/L after the 5 mg/L runs.

Anion Removal

Five runs were conducted to evaluate the removal of As and Se from model solutions by the coated sand. In this case, the influent was adjusted to pH 3.5, but conditions were otherwise similar to those for removal of cationic metals. Significant amounts of Se or As began appearing in the effluent after about 200 to 300 bed volumes of solution had been treated (Figure 5). The removal pattern was remarkably consistent, regardless of the metal (As or Se) being treated or its oxidation state (+3 or +5 for As; +4 or +6 for Se). The latter result was particularly surprising, since selenate (SeO_4^{2-}) is generally much more difficult to remove from solution than is selenite (SeO_3^{2-}).
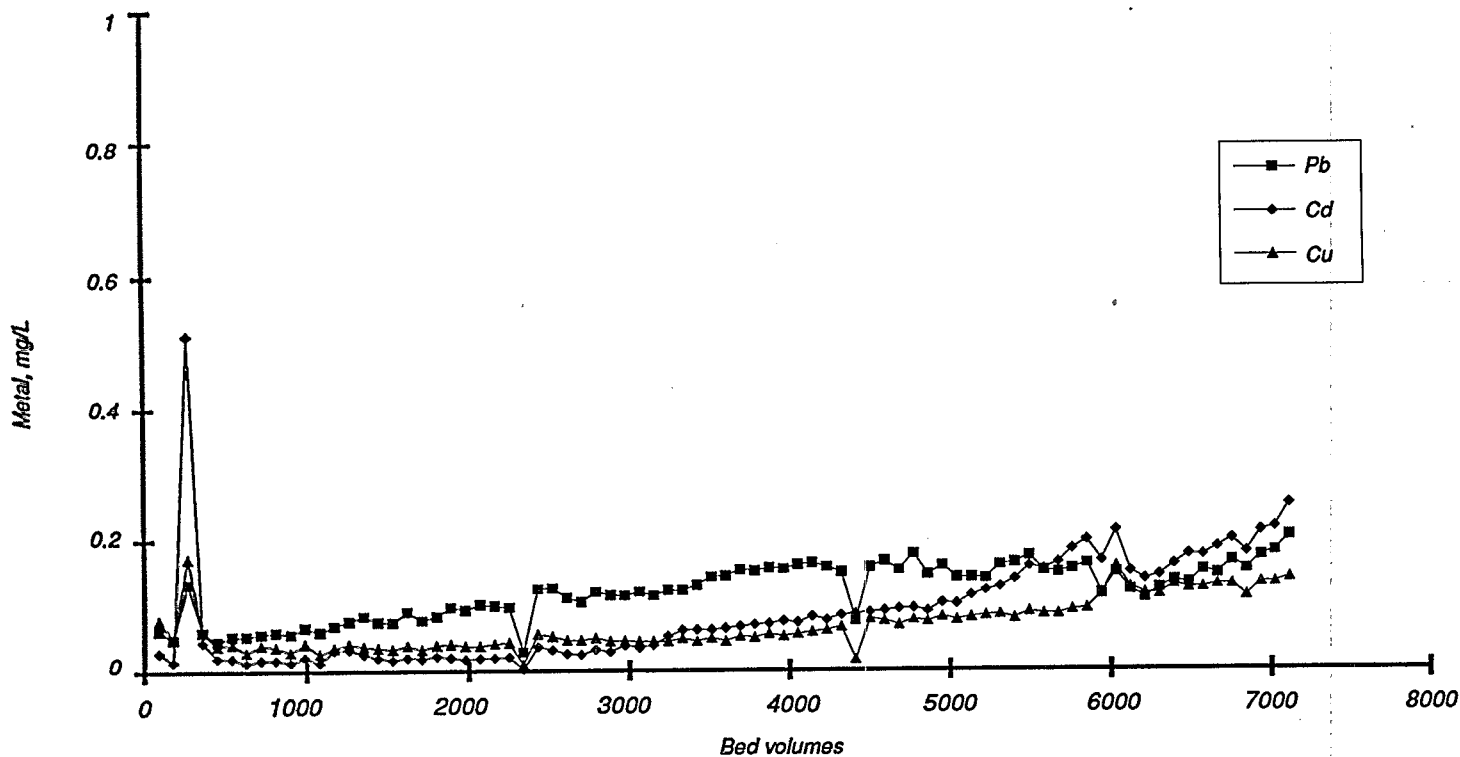
Figure 2. Breakthrough curves for Pb, Cd, and Cu for an influent containing 0.5 mg/L of each metal. EBDT = 2 min, pH = 9.0.
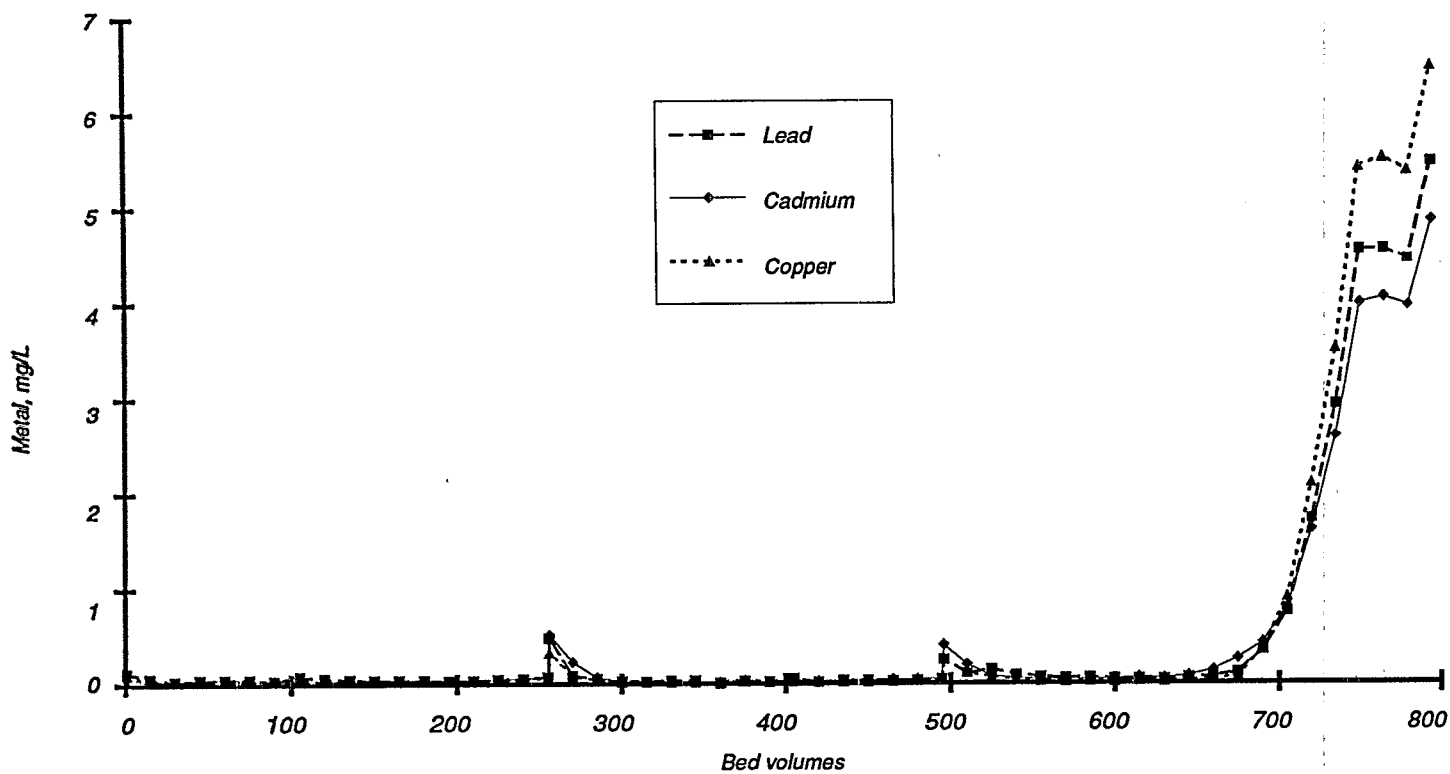

Figure 3. Breakthrough curve for Run 14. Influent contained Cd, Cu, and Pb at 5 mg/L each. EBDT = 2 min, pH = 9.0.
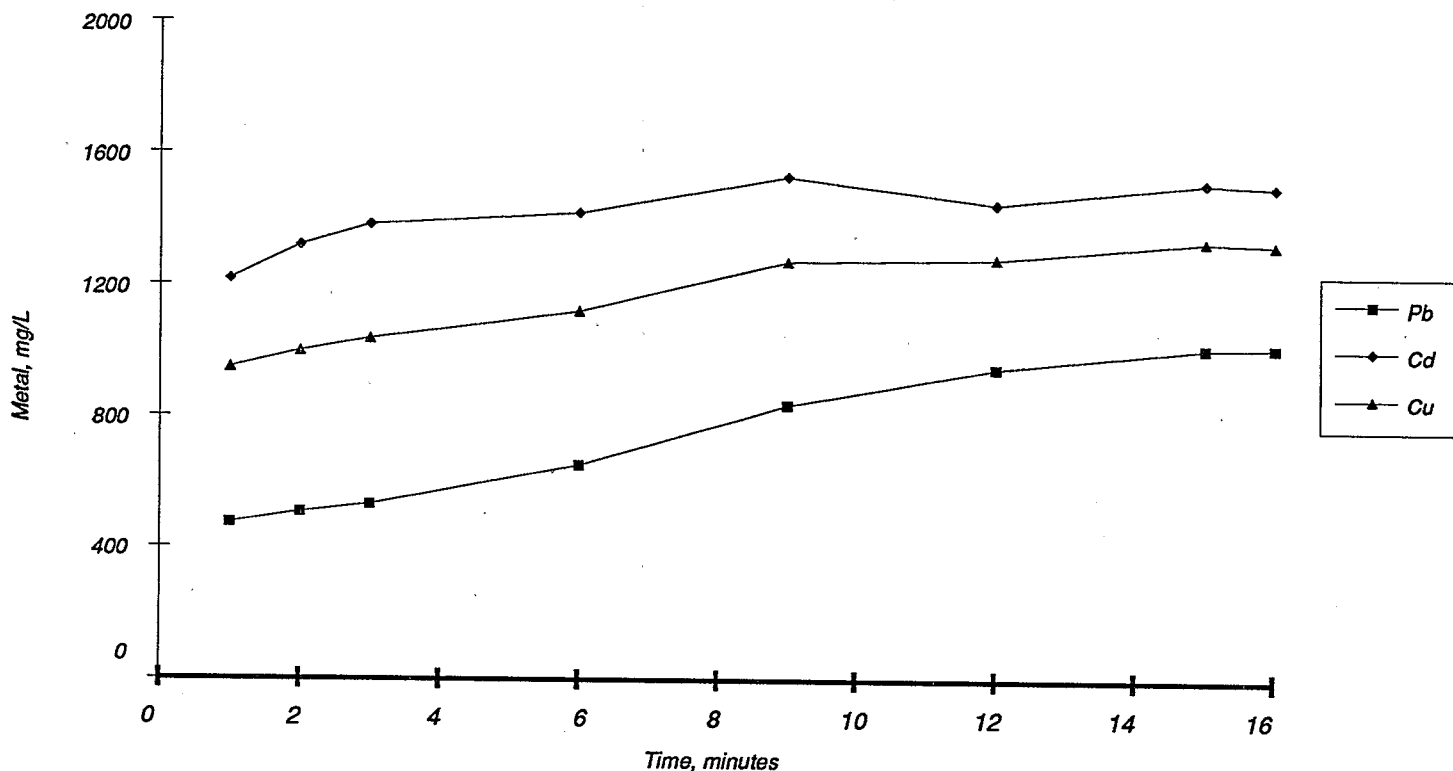
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Figure 4. Column regeneration data for Run 15. The graph shows metal concentrations in the first regeneration solution, which was maintained at pH = 2 and continuously recycled through the column.

Effects of Other Contaminants on Removal of Cu, Pb, and Cd

Tests were also conducted in which the metals in the influent solution were complexed by ammonia or EDTA. Only Cd and Cu were tested with ammonia present as a complexing agent, since the ammonia did not maintain Pb in a soluble form. All three metals were present in the influent when EDTA was used as the chelating agent.

Substantial amounts of ammonia-complexed metal were sorbed by the iron-coated sand: about 1500 mg of each metal sorbed per liter of media before the effluent concentration exceeded a few tenths of a mg/L, and about 4000 mg of each metal sorbed per liter of bed before the effluent concentration reached 4mg/L. Regeneration of this column at pH 2.0 recovered 93% of the sorbed Cd and 100% of the Cu.

When the metals were complexed with EDTA, they broke through the column almost immediately. The capacity of the media to remove metals under these conditions is not significant either at pH 10.0 or at pH 4.5, and the adsorptive filtration process would not be applicable for treat-

ment of waters containing EDTA-complexed metals.

Sodium lauryl sulfonate is a surfactant that might interfere with the adsorptive filtration process by interacting either with the metals or the surface of the media. The presence of 0,15, or 30 mg/L of this surfactant had no noticeable effect on metal sorption.

An attempt was made to investigate the behavior of media on which biogrowth had occurred. To induce the biogrowth, a column was operated for 25 days with a feed containing 50mg/L acetate and 20 mg/L yeast extract. At the end of this period, substantial biogrowth was visible above and within the media. The column was then backwashed to remove the easily dislodged particles, potentially leaving behind a biofilm attached to the media. The biofilm apparently reduced the capacity of media for the metals by about 50%. It is expected that this interference could be partially reversed by exposing the column to a high pH solution, which would probably solubilize a substantial amount of the biofilm. In any case, the interference is relatively small considering that the biofilm

was grown under very favorable conditions.

One test was conducted in which the media were exposed to motor oil, to simulate a situation where, by accident, a large amount of some oily substance entered an adsorptive filtration column. Normally, such substances would be removed upstream of the column. To investigate a worst-case scenario, a damp sample of the coated sand was exposed to a 10% by volume mixture of SAE 30 motor oil in water and was then packed into a column. Oil remained attached to the media, and air bubbles were trapped in the column. When the influent was applied, severe channeling was observed, and breakthrough occurred almost immediately. The coated sand was then removed from the column and cleaned by rinsing it twice in isopropanol. The cleaned sand was returned to the column, and the standard ammonia-complexed influent was applied. The media performed reasonably well, but a little more than half of the sorption capacity was lost. It is not known whether this loss was due to residual oil on the media, which might be removed by more strenuous cleaning efforts, or whether it reflects a permanent loss of capacity.
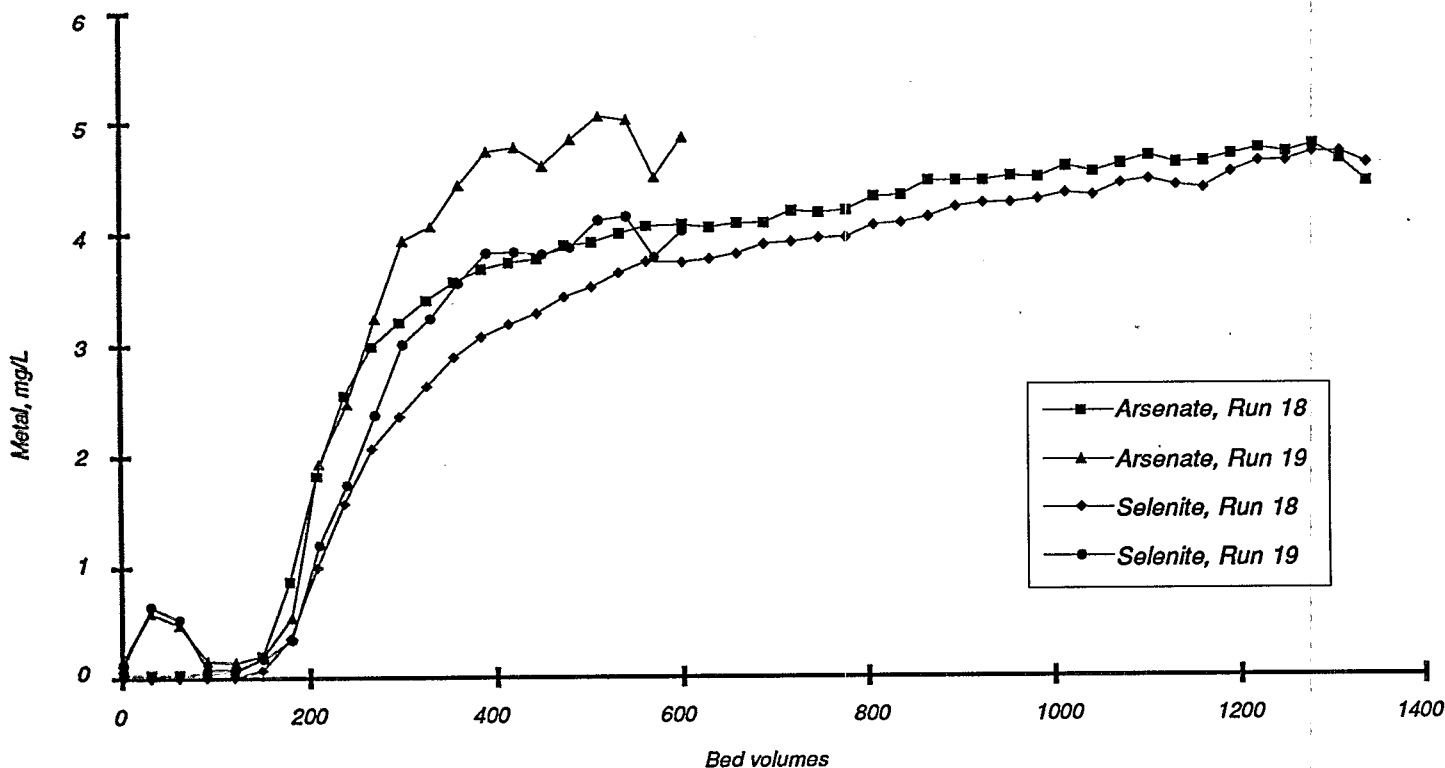
Figure 5. Breakthrough curve for arsenate and selenite in Runs 18 and 19. EBDT = 2 min, pH = 3.5.

Adsorbent Longevity

During the course of these runs, the media were backwashed over 20 times and regenerated about 10 times over a period of a few months, with no apparent deterioration in performance. Although this result is fairly qualitative, it is possible that, over the course of several months of testing, any significant changes in column behavior resulting from repeated regeneration would have been observed.

Treatment of A Real Superfund Solution

Once reasonable operating parameters for the technology were established, a real waste from a Superfund site was collected and treated. The untreated water at this site contains tens of mg/L of ferrous iron in addition to a few mg/L Zn and less than 1 mg/L of several other metals. It is treated at the site by conventional precipitation/ coagulation at pH around 8.0, and, since the ferrous iron is oxidized and precipitated in the process, the metals are exposed to a large amount of iron oxide in the process. As a result, a significant fraction of the metals that can adsorb onto iron oxide do so in the treatment process.
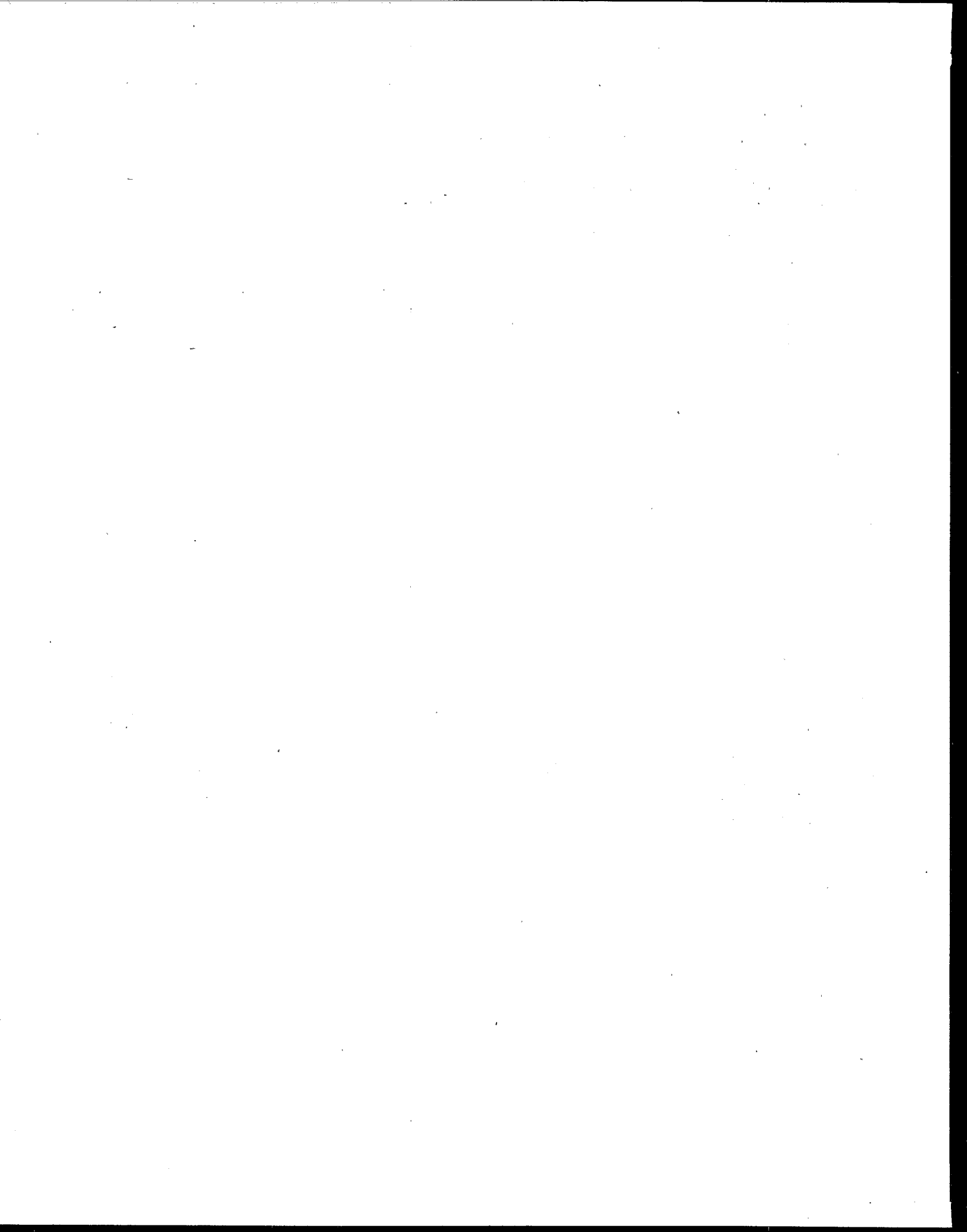
We chose to treat the effluent from the precipitation/coagulation process being used on site. The water was treated, as received, at pH near 8.0, which is well below the pH that would have been optimal for metal removal. This test gives an indication of the additional metal removal that can be obtained by using adsorptive filtration as a polishing step after a conventional treatment process.

Zn was the only metal present in significant quantities. The total and soluble Zn concentrations in the samples collected were in the ranges 0.6 to 4.0 and 0.3 to 0.6 mg/L, respectively. The corresponding Zn concentrations in the effluent were around 0.2 and <0.1 mg/L, respectively (Figure 6). Thus, even though the test might have been run under nonoptimal pH conditions and exposure to relatively high concentrations of iron oxide solids for adsorptive filtration, the process removed Zn to concentrations considerably lower than those achieved by known conventional processing.

Conclusions

Simultaneous sorption and filtration of Cu, Cd, and Pb are feasible with the use of iron-oxide-coated sand under reasonable engineering conditions. Total and soluble effluent concentrations of less than 100 µg/L, and sometimes considerably less, are achievable. The media can be backwashed to recover most of the particulate metals and be regenerated by exposure to an acid solution to recover the remaining particulates and most of the adsorbed metals. The regenerant solution typically contains metal concentrations a few hundred times as concentrated as the influent. In tests with 5 mg/L of each of three metals in the influent, filtration limited process performance more than sorption did. It should be recognized that this outcome is not generalizable: the limiting factor in any application depends on the specific operating conditions and chemical composition of the influent solution. Modifications to the influent, such as adjusting solution pH or adding a polymeric filter aid, and modifications to the operation, such as adjusting the hydraulic loading rate, would certainly affect the relative importance of headloss and effluent concentration limits. There was no indication that such factors could prevent adsorptive filtration from serving as a viable treatment technology.

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