



## Project Summary

# Arsenic(III) and Arsenic(V) Removal from Drinking Water in San Ysidro, New Mexico

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The removal of a natural mixture of As(III) (31  $\mu\text{g/L}$ ) and As(V) (57  $\mu\text{g/L}$ ) from a groundwater high in total dissolved solids (TDS), and also containing fluoride (2.0 mg/L), was studied in San Ysidro, NM, using the University of Houston (UH)/U.S. Environmental Protection Agency (EPA) Mobile Drinking Water Treatment Research Facility. The raw water in this study was deliberately unchlorinated so as not to oxidize the As(III) present. The objective of the study was to establish a cost-effective means of removing As(III), As(V), and fluoride from this and similar waters.

Arsenic adsorption onto fine-mesh activated alumina gave better-than-expected results in view of the knowledge that As(III) is known to be poorly retained on alumina. Approximately 9000 bed volumes (BV) could be treated at pH 6 before the arsenic maximum contaminant level (MCL) (0.05 mg/L) was reached. At the natural pH of 7.2, however, only 1900 BV could be treated before exceeding the MCL. Approximately 70% of the adsorbed arsenic was recoverable by cocurrent regeneration with 6.5 BV of 4% NaOH, but after two regenerations, the column capacity was reduced to 72% of its virgin performance. Coarser, 12 x 28 mesh, alumina did not perform as well in adsorption or regeneration. The spent alumina regenerant was treated by lowering its pH to 8.5 and quantitatively coprecipitating the arsenic with the bulk Al(OH)<sub>3</sub> precipitate. The sludge produced was not hazardous as determined by the EPA's extraction procedure (EP)

toxicity test. Analyses of the spent regenerant solution showed that unavoidable oxidation of the As(III) to As(V) occurred on the alumina, which helps to explain its better-than-expected column performance.

Reverse osmosis (RO) treatment with either a cellulose triacetate (CTA) or polyamide (PA) hollow fiber membrane resulted in > 97% arsenic removal and > 94% TDS removal. Electrodialysis (ED) removed 73% of the arsenic and was able to meet the arsenic MCL on the City Water containing 89  $\mu\text{g/L}$  total arsenic; however, ED removed only 28% of the As(III) from a new well containing 100% As(III) at a level of 230  $\mu\text{g/L}$ .

Chloride-form anion exchange also performed better-than-expected but not well enough for it to be considered seriously for treatment. About 200 BV could be treated before the arsenic MCL was reached. Point-of-use (POU) RO treatment with a thin film composite (TFC) membrane was effective in removing > 91% of the arsenic and > 94% of the TDS at low (< 15%) water recovery.

Because of the small (70-dwelling) community, the difficulty of central treatment, and the poor water quality, EPA chose San Ysidro as a test community for POU RO treatment. That study (EPA/600/2-89-050) showed POU RO treatment to be a viable alternative to central treatment.

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

## Introduction

San Ysidro, NM, is a small community 45 miles northwest of Albuquerque. The current water supply, a 12-ft-deep infiltration gallery, is inadequate in quantity during the summer months and exceeds, year-round, the EPA MCL of 0.05 mg/L for arsenic. It also contains 2.0 mg/L of fluoride; at the time of this study, that also exceeded the old 1.4 mg/L MCL. Additionally, this "City Water" has high TDS (810 mg/L), hardness (282 mg/L), and alkalinity (468 mg/L). From 1975 through 1981, the mean arsenic concentration was 0.074 mg/L and fluoride ranged from 1.6 to 3.0 mg/L.

In an effort to obtain an adequate quantity of arsenic-free water, three test wells, ranging in depth from 44 to 128 ft, were drilled in 1982. Unfortunately, these new wells contained much higher levels of arsenic, fluoride, dissolved solids, iron, sulfate, chloride, and manganese than did the existing City Water from the shallow infiltration gallery.

Field research was performed in San Ysidro over a period of 9 mo using the UH/EPA Mobile Drinking Water Treatment Research Facility (Mobile Inorganics Pilot Plant). This 10-ft wide by 40-ft long trailer had been used at three previous locations to study the removals of fluoride, nitrate, and chromate from groundwater supplies. One objective of the move to San Ysidro was to attempt treatment of both the City Water and the best of the new test wells, Well No. 4, because of their differing levels of arsenic, fluoride, and iron. After having decided that the new wells were too difficult to treat, however, the basic objective of the San Ysidro arsenic removal experiments was changed to development of a simple, cost-effective way to remove the arsenic from the San Ysidro City Water and from similar waters.

## Experimental Details

Alumina adsorption, electrodialysis, reverse osmosis, and ion exchange processes were studied in San Ysidro without oxidative pretreatment of the raw water, i.e., the treatment processes were fed the natural mixture of As(III) and As(V). This was done because the next planned study in Hanford, CA, would involve oxidation of As(III) to As(V) before its removal by the same processes. The alumina adsorption and ion exchange tests were carried out in lab scale (1-in. diameter) columns rather than in the 8- or 10-in.-diameter pilot-scale columns to minimize the production of ar-

senic-contaminated sludges from alumina and ion-exchange regeneration.

## Analytical Methods

With the exception of metals analyses performed using a Perkin Elmer Model 5500 Inductively Coupled Plasma (ICP) Spectrometer at UH, and a check sample of the City Water run by an independent laboratory, all analyses were performed with mobile lab equipment. Analysis procedures from "Standard Methods for the Examination of Water and Wastewater" were used for hardness, alkalinity, silica, and sulfide. Fluoride and pH were analyzed using electrode methods from an Orion manual. All methods and instruments were standardized and calibrated daily. Generally two or more standards from different sources were used during the study.

We used a method which we had previously developed for EPA to rapidly speciate arsenic. It takes advantage of the fact that, in the pH range of 3.0 to 8.4, As(V) is ionic existing as monovalent  $\text{H}_2\text{AsO}_4^-$  or divalent  $\text{HAsO}_4^{2-}$ , whereas As(III) is uncharged arsenious acid,  $\text{H}_3\text{AsO}_3$ . When chloride-form strong-base anion resins are used for the separation, As(III) passes through the resin column unhindered whereas As(V) is completely retained by the resin. Following speciation, graphite furnace atomic absorption spectroscopy (GFAAS) is used to determine total arsenic (As(III) + As(V)) on the untreated sample and As(III) on the column effluent. Arsenic(V) is determined by difference.

## Alumina Experiments

Because the removal of natural mixtures of As(III) and As(V) by activated alumina had not been studied previously, it was the focus of this study. And, because we had experienced unforeseen oxidation of As(III) in previous lab studies, such unplanned oxidation of As(III) was also of interest in San Ysidro. The optimum pH for the adsorption of arsenic and fluoride is known to occur in the 5.5 to 6.0 range; therefore, a pH of 6.0 was fixed for most of the alumina runs. Because adsorption onto alumina is known to be a kinetically controlled process, the two common mesh sizes, 14 x 28 (1.2 x 0.6 mm) and 28 x 48 (0.6 x 0.3 mm), of Alcoa F1 alumina were compared. Finally, two concentrations of the NaOH regenerant were used to determine which was more economical in terms of the mass of arsenic removed/mass of NaOH applied.

\* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

A 100-L pilot-scale feed tank was used to adjust the pH of the incoming raw water; however, most of the tank effluent was bypassed to waste to minimize mixing, aeration, and detention time. This was done to prevent oxidation of the As(III) and to represent more closely, the actual feedwater that would exist in a full-scale treatment process. For all the alumina experiments, the feedwater pH was adjusted to 6.0 with 2%  $\text{H}_2\text{SO}_4$ . The 32-in.-deep alumina beds containing 0.4 L of media operated at a flow rate of  $80 \pm 3$  mL/min for an empty bed contact time (EBCT) of 5 minutes. Generally, the alumina runs, which lasted 20 to 25 days, were continued until the effluent MCL for arsenic (0.05 mg/L) was reached, which meant that the runs lasted far beyond fluoride exhaustion. Only total arsenic was determined on the column effluent samples, i.e., there was no speciation of As(III) or As(V).

## Desalting Tests

Arsenate, As(V), which is a large mono-, di-, or trivalent anion at pHs above 3, is known to be effectively (> 97%) rejected by RO membranes. The percent removal of arsenite, a nonionic species at neutral and acidic pH, varies widely (43% to 81%), however. Thus, it was of interest to study the removal of a mixture of As(III) and As(V) using PA, CTA, and TFC membranes. Additionally, TFC membrane performance was studied using a Culligan POU RO system. Two different RO modules were used in the study: a Dow, hollow-fiber, CTA type of membrane and a DuPont hollow-fiber, PA type. Each was operated separately as a single module at approximately 50% recovery. The Dow module was larger, producing 11,700 L/day compared with 4500 L/day for the DuPont module. Based on the recommendations from each manufacturer, the feed to the Dow unit was acidified to pH = 6.3 whereas no acid was added to the DuPont module feed. For both the Dow and DuPont systems, a deep-bed filter was used ahead of the 10- $\mu\text{m}$  cartridge filter. Also, an antiscalant, 10 mg/L sodium hexametaphosphate (SHMP), was added continuously during each run. Although no reference to arsenic rejection by ED could be found, ED was expected to effectively remove charged arsenate species but be ineffective for the removal of uncharged arsenite. There was some speculation that the potential and current generated in the ED stack might oxidize and thereby remove arsenite.

An Ionics Aquamite I ED unit with automatic current reversal to prevent fouling was used in San Ysidro. It operated with-

out pretreatment to produce 1790 L/day (475 gpd) of product water at 81% recovery utilizing internal brine recycle.

### ***Ion-Exchange Experiments***

Attempts were made to verify the expectation of very short ion-exchange runs because of (a) the presence of nonionic arsenite, (b) high TDS, and (c) high sulfate in the feedwater. Related research before this study showed As(V) is removed well by ion exchange in low sulfate/low TDS water, but the inherent danger of an elution peak of high arsenic exists if the column runs beyond breakthrough. These considerations, in addition to the interesting possibility of a sulfate/arsenate selectivity reversal due to the high TDS of the San Ysidro City Water, prompted a limited study of strong-base anion resins in the chloride form. In these experiments, the pH of the feedwater was not adjusted. The resin bed consisted of 400 mL of chloride-form, strong-base anion resin—either Ionac ASB-1, a type 1 gel resin with microporosity, or Dowex-11, an isoporous "improved porosity" type 1 resin. Following each exhaustion run, the resin was regenerated with 5 BV of 6% NaCl solution (18.3 lb/ft<sup>3</sup>), i.e., approximately 4 to 5 times the stoichiometric requirement based on total resin capacity.

### ***Arsenic Sludge Disposal Tests***

Wastewater disposal studies were performed on the spent regenerant solutions from the alumina column regenerations in an attempt to verify previous research on arsenic removal in Fallon, NV. In Fallon it was found that by simply neutralizing the alumina regenerant solution the resulting Al(OH)<sub>3</sub> precipitate would adsorb the arsenate to yield a supernatant water with less than 0.10 mg/L total arsenic. The difference between the present study and prior studies is the presence of a significant amount of As(III) which, because it is poorly adsorbed on the alumina, could cause the Al(OH)<sub>3</sub> sludge to fail the Extraction Procedure (EP) toxicity test.

In a typical Al(OH)<sub>3</sub> precipitation test, 500 mL of spent alkaline regenerant solution (pH 13) was placed into a 1-L beaker and acidified to pH 6.5 with HCl. A small amount of acid was added at 1/2- to 4-hr intervals during the next 14-hr period to maintain the pH at 6.5 to prevent redissolution of Al(OH)<sub>3</sub>. The solution was allowed to stand overnight (10 hr) before being filtered through a quantitative, paper filter. This paper filter was later dried for 12 hr at ambient temperature (22° C) and stored for future studies including the EP toxicity test. Total arsenic, As(III), and As(V) were determined on the spent regenerant

before precipitation and on the filtrate after filtration.

## **Results and Discussion**

### ***Water Quality***

Most of the values for the City Water analyses were single-point determinations, others, however, notably the As(III) and As(V) and total arsenic values, were the averages of many determinations. During the study, the mean As(III) value was 31 ± 8.6 µg/L, As(V) was 57 ± 8.2 µg/L, and the total As concentration was 88 ± 8.3 µg/L. Occasionally, oxidation of As(III) to As(V) was observed when a raw water sample was allowed to sit for several hours or more. This oxidation was not uniformly repeatable, however.

In addition to arsenic, major constituents of the City Water were TDS (810 mg/L), alkalinity (468 mg/L), hardness (282 mg/L), sodium (190 mg/L), chloride (123 mg/L), silica (60 mg/L), sulfate (37 mg/L), and fluoride (2 mg/L). Desalting with RO or ED would be required to meet the EPA secondary MCL for TDS (500 mg/L) and to lower the hardness and sodium levels. Serious precipitation and fouling problems would, however, be expected with desalting because both the City Water and Well No. 4 were found to be supersaturated with BaSO<sub>4</sub> and CaF<sub>2</sub>. Acid addition to prevent CaCO<sub>3</sub> precipitation and addition of SHMP, a precipitation inhibitor, were recommended for scale control. Furthermore the recovery would be limited to approximately 50% to prevent silica fouling.

### ***Activated Alumina Results***

#### **Typical Alumina Breakthrough Curves at pH 6.0**

Typical breakthrough curves (Figure 1) for fluoride and arsenic in the effluent from the activated alumina column showed fluoride breaking through first and reaching a maximum level of 1.4 mg/L long before arsenic reached its 0.05 mg/L MCL. If activated alumina is used in this fashion, i.e., without oxidative pretreatment, the time to reach the arsenic MCL will be typically two to three times as long as the time to reach a fluoride level of 1.4 mg/L for this particular water. This may be seen in Table 1, which contains the summary of the alumina results and a comparison of the fluoride and arsenic run lengths.

#### **Arsenic and Fluoride Breakthrough Curves**

In a related laboratory study at the UH, alumina-run simulations were made with synthetic waters similar to the San Ysidro

City Water except that the synthetic waters contained either 100% As(III) or 100% As(V). In this way, it was possible to compare the arsenic and fluoride removal performances among three runs to quantify the effect of oxidizing the San Ysidro As(III) to As(V). The run length (8760 BV) to arsenic breakthrough for the San Ysidro City Water, a mixture of As(III) and As(V), fell between that of pure As(III) (300 BV) and pure As(V) (23,400 BV). Therefore, oxidizing the San Ysidro City Water to 100% As(V) should more than double the alumina run length to about 23,000 BV at pH 6.0.

The shape of the San Ysidro arsenic breakthrough curve (Figure 1) was delayed, i.e., no leakage before 3,600 BV, and was surprisingly sharp. A much earlier As(III) breakthrough was expected based on the lab simulation data. By way of explanation, some oxidation of As(III) to As(V) occurred in the field column, as proven later by regeneration studies of eluted As(III) and As(V). Also, the trivalent arsenic concentration of the field study was only 32 µg/L, i.e., one-third the concentration in the lab study.

The fluoride capacities of the various columns were remarkably similar at 4160 to 4280 g/cm<sup>3</sup>. This occurred despite the fact that the San Ysidro water contained only 2 mg F/L whereas the laboratory waters contained 3.0 mg F/L. Finally, in these column tests, the presence of As(III) and As(V), at a level of 100 mg As(total)/L, did not seem to influence the fluoride capacity of the alumina.

#### **Effect of Mesh Size**

Figure 2, representing the arsenic breakthrough curves for Runs 1 and 2, illustrates that the mesh size of the alumina has a dramatic effect on its performance for arsenic removal. Referring again to Table 1, it can be seen that the coarse mesh grade treats 6840 BV to the arsenic MCL whereas the fine mesh can treat 8760 BV with corresponding arsenic capacities of 390 and 575 g/m<sup>3</sup>, respectively. Such large differences between coarse and fine were not noted, however, during fluoride removal.

#### **Effect of pH**

Not reducing the pH of the feedwater to the optimum range between 5 and 6 resulted in a drastic loss in both the arsenic and fluoride removal capacity of alumina. The effects of varying both arsenic concentration (from 90 to 230 µg/L) and pH (from 6.0 to 7.1) are apparent when Runs 1 and 8 using coarse alumina are compared: the high, trivalent arsenic concentration and unadjusted feedwater pH during

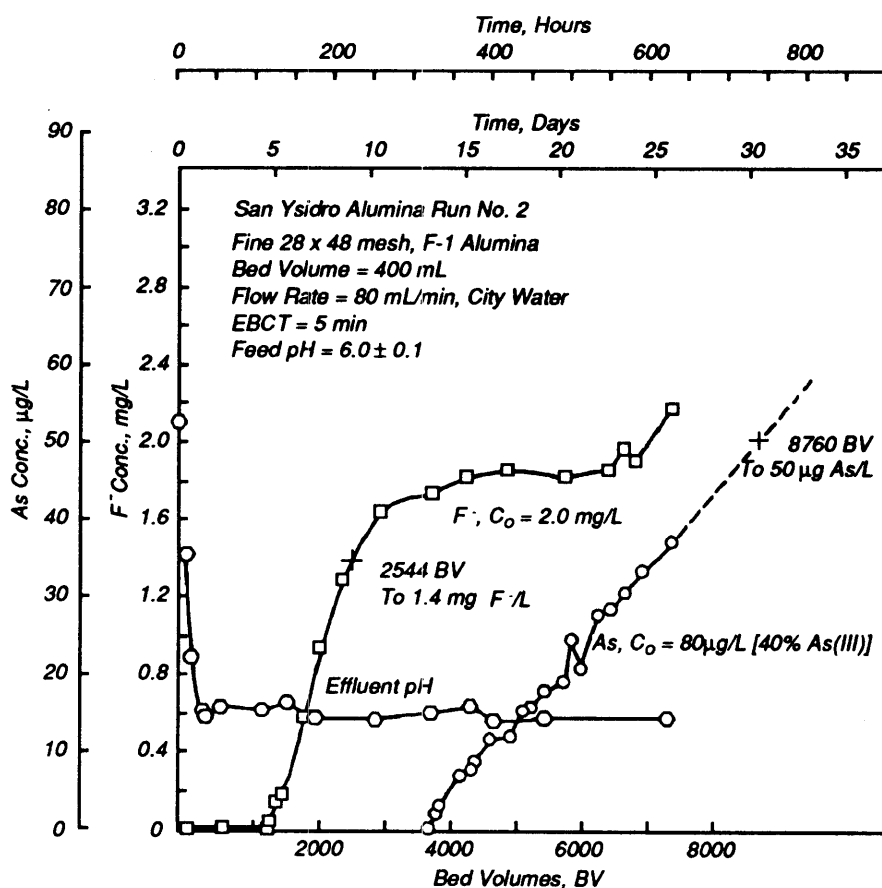


Figure 1. Breakthrough curves for fluoride and arsenic from 28 x 48 mesh activated alumina column, Run No. 2.

Table 1. Summary of Activated Alumina Results

Parameter	Run Number							
	1	2	3	4	5	6	7	8
Mesh	Coarse	Fine	Coarse	Fine	Coarse	Fine	Fine	Coarse
Mesh Size	14 x 28	28 x 48	14 x 28	28 x 48	14 x 28	28 x 48	28 x 48	14 x 28
Condition*	New	New	1 x Reg.	2 x Reg.	2 x Reg.	2 x Reg.	New	New
Feedwater†‡	CW	CW	CW	CW	CW	CW	CW	No. 4
Feed pH§	6.0	6.0	6.0	6.0	6.0	6.0	7.3	7.1
BV to 1.4 mg F-/L	3080	2540	2380	2380	1740	2040	547	—
Days to 1.4 mg F-/L	10.8	9.0	8.1	8.1	6.0	7.1	1.9	—
g F-/m <sup>3</sup> Adsorbed to 1.4 mg F-/L	3870	4160	3063	3870	2260	3130	925	—
BV to 50 mg As/L	6840	8760	5880	8040	4500	6300	1944	252
Days to 50 µg As/L	23.8	30.4	20.4	27.9	15.6	21.9	6.8	0.9
g As/m <sup>3</sup> Adsorbed to 50 µg/L As	390	575	380	575	305	493	175	53

\* 1 x Reg. = once regenerated; 2 x Reg. = twice regenerated.

† For runs 1 through 7, San Ysidro City Water (CW) with 92 ± 10 µg As/L was pH adjusted to 6.0 before using.

‡ For Run 8, Well No. 4 water with 230 µg As/L was fed.

§ No pH adjustment was made for runs 7 and 8.

Run 8 resulted in a run length (252 BV) which was only 4% of that using City Water at pH 6.0 (8760 BV). These unadjusted-pH runs were made to illustrate the short run lengths that would occur in the simplest POU treatment systems compared with a pH-optimized system. Allowing the natural pH (7.3) feedwater to contact fine alumina produced a similar reduction in both arsenic and fluoride removal capacity. For example, at the optimum pH of 6.0, the arsenic and fluoride run lengths were 8760 and 2540 BV, respectively; whereas at pH 7.3, the run lengths were reduced to only 22% of the optimum values.

### Regeneration of Alumina

Fluoride is more easily and completely eluted from the exhausted alumina during NaOH regeneration than is arsenic. This is evident in Figure 3 containing typical regeneration elution curves. The fluoride elution curve always begins slightly ahead of the arsenic curve, and the arsenic curve has a much longer tail. Only 60% to 70% of the arsenic was recovered from fine- or coarse-mesh alumina even when using excessive (10 - 17 lb NaOH/ft<sup>3</sup> alumina) regenerations. For both fluoride and arsenic removal, 3.0 gram-equivalents of the dilute (1%) NaOH/L alumina (7.5 lb NaOH/ft<sup>3</sup>) eluted more arsenic than did the concentrated (4%) NaOH, and the fine-mesh alumina permitted slightly higher arsenic recoveries with both the 1% and 4% NaOH solutions.

Neutralization of the NaOH-laden column with a relatively concentrated 2% H<sub>2</sub>SO<sub>4</sub> (0.4 N) solution applied at the same flow rate (3.9 BV/hr) as the regenerant

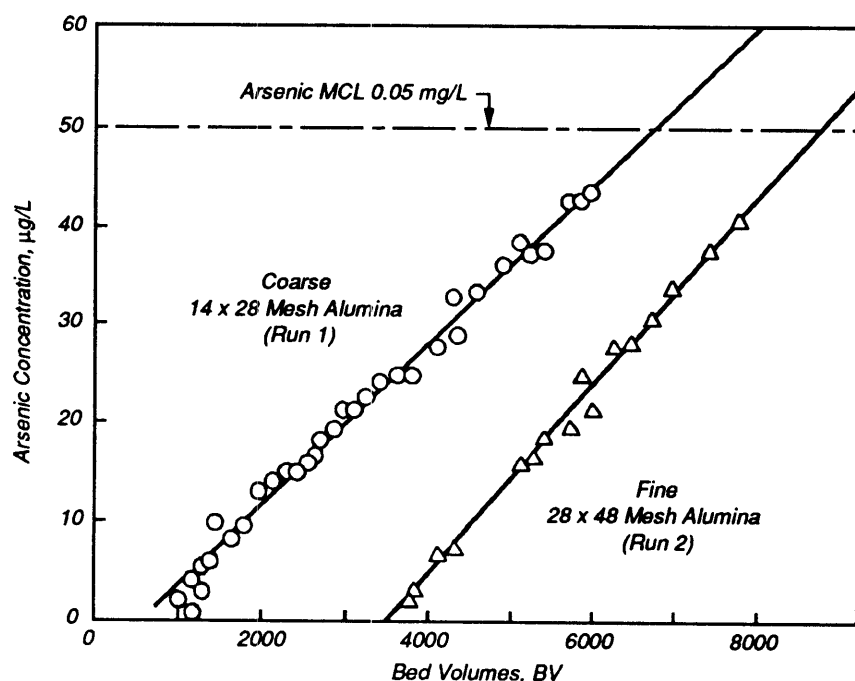


Figure 2. Comparison of arsenic breakthrough curves for coarse (14 x 28) and fine (28 x 48) mesh aluminas.

immediately following regeneration works well. This procedure is simpler than gradually decreasing the concentration of acid following NaOH regeneration, a procedure used in other fluoride removal applications.

The breakthrough curves for fluoride adsorption on fine alumina are only slightly affected by one or two regenerations. Regenerations had a clearly negative effect, however, on the run length to arsenic breakthrough. After two regenerations, the BV to 50 µg As/L for the coarse-mesh alumina dropped to 4500 from 6840, i.e., a 34% reduction. The reduction in arsenic capacity was smaller (28%) for the fine- as compared with the coarse-mesh alumina.

#### Treatment of Spent Regenerant

The spent-regenerant solution was acidified to pH 6.5 with HCl, settled for 24 hr, and filtered before being analyzed for arsenic. The coprecipitation/filtration procedure removed essentially all of the As(V) but only 36% of the As(III), and 97% of the arsenic remaining after precipitation was As(III). Therefore, if this procedure is to be used in a full-scale application, any As(III) in the regenerant should be oxidized to As(V). Based on results of our earlier As(III)

oxidation studies, chlorine should be added after the pH has been reduced to 6.5 to take advantage of the much faster As(III) oxidation in the 6 to 10 pH range.

The settled, arsenic-contaminated alum sludge produced in this manner amounted to approximately 12% of the total initial solution volume. Other investigators, using a similar precipitation procedure on a 4% NaOH spent regenerant (more concentrated), found the settled sludge to be 25% and the filtered sludge solids to be less than 1% of the original wastewater volume. Following the 24-hr extraction procedure, the arsenic (total) concentration in the EP test filtrate was 0.6 mg/L, i.e., far below the 5.0 mg/L limit for classification as a hazardous waste.

#### Arsenic Coprecipitation from Raw Water

Iron hydroxide floc and hydrous iron oxide solids can be used to remove arsenic from water by a mechanism of coprecipitation or adsorption. Moreover, As(V) is much more effectively removed by ferric hydroxide than is As(III). Based on this knowledge, an attempt was made to remove at least part of the arsenic from

San Ysidro City Water and Well No. 4 water by oxidation and precipitation of the natural-iron present. The City Water (containing 0.06 mg/L Fe(II)) did not contain enough iron to give a visible precipitate, and no arsenic was removed by chlorination and filtration at either pH. Well No. 4 water containing 2.0 mg/L Fe(II) is partially treatable by this arsenic removal method. At pH 7.1, 60% of the arsenic was removed; at pH 8.5, somewhat less, 52%, was removed.

#### Desalting Results

Based on percent removal of contaminants, the polyamide RO membrane clearly gave the best TDS removals (97%) and arsenic removals greater than 99% at 50% recovery with a single pass. As predicted, ED gave the poorest removal of arsenic—presumably because molecular As(III) could not be transported out of the feedwater using electrical current. ED cannot be recommended if As(III) removal is a major criterion. For example, with Well No. 4 water containing 188 mg As(III)/L, only 28% of the arsenic was removed. This conclusion contrasts with those made when ED was used to remove fluoride, nitrate, or chromate; in previous studies, ED performed as well as or better than RO for contaminant rejection. If ED is to be used for As(III) removal, preoxidation with chlorine, for example, is required to convert molecular As(III) to ionic As(V).

#### Ion-Exchange Results

Although immediate breakthrough of essentially all the As(III) was expected, it did not occur. Significant, immediate arsenic leakage was apparent, but it did not reach the 25 to 36 mg As(III)/L present in the feedwater. Rather, about 200 BV was treated before a level of 30 µg/L total arsenic was reached in the column effluent. The 93 µg/L total arsenic level in the feed was not reached in the effluent until 570 BV was treated. Most importantly, the arsenic concentration in the effluent never exceeded that of the influent. Thus, chromatographic peaking did not occur because of sulfate driving arsenic off the column as has been regularly observed in our prior laboratory studies. (An arsenic peak, however, cannot be ruled out later in the run.) In spite of the better-than-expected performance of these resins, they did not perform well enough to be considered seriously as a viable treatment alternative (at least 400 BV).

Fluoride was not removed to any significant extent by the chloride-form anion resins. During treatment by Dowex-11 or ASB-1 resins, fluoride reached 1.4 mg/L at approximately 4 and 18 BV, respectively.

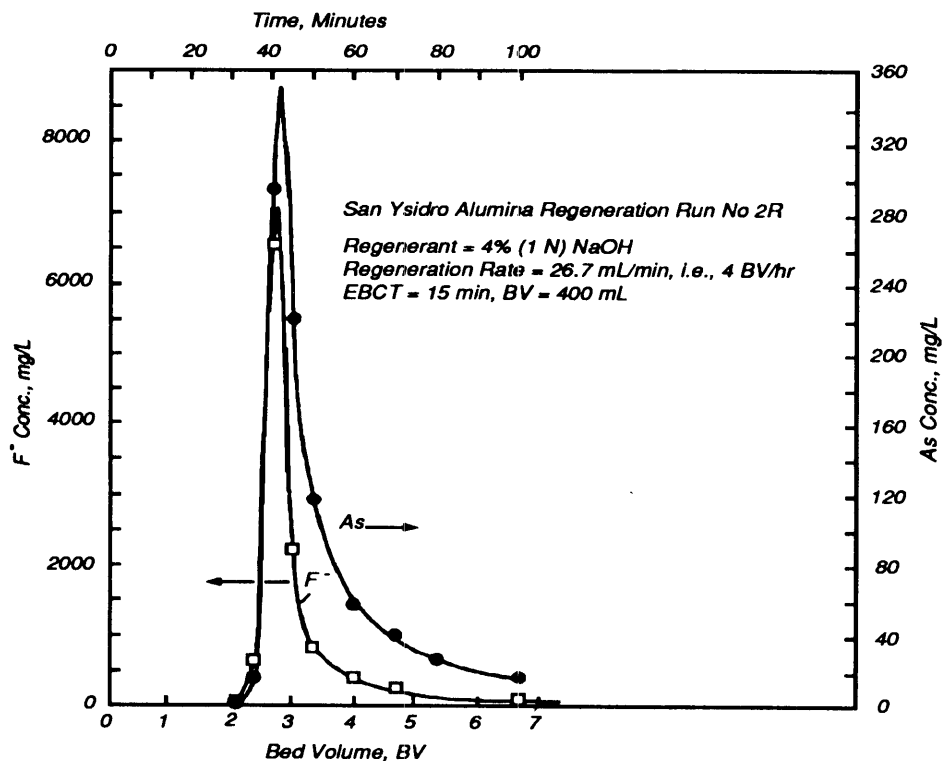


Figure 3. Arsenic and fluoride elution during a regeneration of fine-mesh alumina using 4% NaOH. Run 2R—regeneration following exhaustion Run No. 2.

Such early breakthroughs resulted from the very low affinity of fluoride for these typical strong-base anion resins which clearly cannot be recommended for fluoride removal.

The exhausted ion exchange columns were completely and easily regenerated with the use of approximately 3 BV of 1.0 N (6%) NaCl (11 lb NaCl/ft<sup>3</sup>) in a cocurrent (downflow) mode. The adsorbed arsenic (presumably As(V)) was easily eluted from the exhausted resin.

The ease with which anion exchange columns were regenerated in this study and the fact that arsenic did not peak after breakthrough suggested that ion exchange should be further studied. These and previous results with strong-base anion exchange resins indicate a real potential for chloride-form anion exchange for As(V) removal. For example, our previous experience suggests that approximately 400 to 500 BV should be attainable before the arsenic MCL is reached if the As(III) is oxidized to As(V) prior to ion exchange.

### Point-of-Use (POU) Treatment

Six months after the San Ysidro project began, the test results suggested no easy solution to the combined arsenic/fluoride contamination problem. Even if the water was chlorinated to produce As(V), which would yield alumina runs exceeding 20,000 BV, the fluoride present would force the alumina runs to end at 2,000 BV so as not to exceed 1.4 mg/L.

The complexity of the alumina adsorption/regeneration cycle for a small community, the anticipated short alumina runs due to fluoride, the ineffectiveness of ion exchange, and the anticipated sludge disposal problem led to the consideration of POU treatment employing RO. The Culligan H-82 POU RO system that was tested had a nominal capacity of 8 gal/day product water. The system comprised a 10- $\mu$ m cartridge filter; a granular activated carbon (GAC) filter; a TFC RO membrane; a second, smaller GAC filter; and, finally, a pressurized storage tank. (Other manufacturers supply similar equipment.)

A salient feature of POU-RO units is their low percent water recovery—typically 10% to 15%. This is both an advantage and a disadvantage. With such low recovery, there is no significant concentration of the brine; therefore, membrane scaling and fouling problems are minimal compared with central treatment utilizing the typical 70% to 80% recovery. The disadvantage is that only 10% to 15% of the feedwater is recovered for drinking.

The initial results of the POU-RO pilot test indicated 8  $\mu$ g/L arsenic in the product water when the feed water contained 90  $\mu$ g/L. Subsequent arsenic analyses on the product water from this unit yielded undetectable arsenic levels, i.e., < 2  $\mu$ g/L.

### Conclusions

The existing San Ysidro City Water that contains 810 mg/L TDS, 282 mg/L CaCO<sub>3</sub> hardness, and 190 mg/L sodium and is contaminated with 57  $\mu$ g As(V)/L, 31  $\mu$ g As(III)/L, and 2.0 mg F/L can employ activated alumina adsorption, RO, or possibly ED to remove arsenic. The first two treatment methods can be applied either in central treatment or at POU. Preoxidation using chlorine to convert As(III) to As(V) will definitely aid in removing arsenic but is not essential. Significant oxidation of As(III) to As(V) appears to have occurred in all the processes tested and consequently better-than-expected removal of arsenic occurred in all cases.

About 8800 bed volumes of unchlorinated San Ysidro City Water adjusted to pH 6 could be continuously passed through a virgin, fine mesh (28 x 48) activated alumina column before the arsenic MCL was reached. Under similar conditions, a run length of 6800 BV was obtained for the coarse (14 x 28) mesh alumina.

Feedwater pH was the most significant variable in activated alumina treatment for arsenic removal. At the natural pH of 7.3, only 1900 BV could be treated before the arsenic MCL was reached; this compares to 8800 BV at pH 6.

In all the activated alumina tests, fluoride broke through long before arsenic. For example, using the fine-mesh alumina at pH 6, fluoride reached 1.4 mg/L at 2500 BV whereas arsenic did not reach its 0.05 mg/L MCL until 8800 BV.

Even with excessive cocurrent regenerations employing 1% or 4% NaOH, a maximum of 70% of the adsorbed arsenic was recovered, and subsequent runs to arsenic breakthrough were shorter than with virgin alumina. During the third exhaustion cycle, the run lengths were reduced to 72% and 66% of the virgin capacity for the fine- and coarse-mesh

aluminas, respectively. Countercurrent upflow regenerations were not attempted in San Ysidro but would probably have been more effective assuming that channeling was avoided and adequate flow distribution was achieved.

In the spent NaOH regenerant solution, 99.8% of the As(V) and 36% of the As(III) were removed by coprecipitation with the Al(OH)<sub>3</sub>, which was produced when the spent regenerant solution was acidified to pH 6.5 using HCl. The total arsenic remaining in solution after precipitation was 0.92 mg/L, of which 97% was As(III). The arsenic-contaminated Al(OH)<sub>3</sub> sludge resulting from the pH 6.5 precipitation procedure on the dilute (1% NaOH) regenerant was 12% of the solution volume after 24-hr settling. The dried sludge (7.8 g/L of spent regenerant) was subjected to the EPA EP toxicity test and easily passed.

ED with no pretreatment except cartridge filtration reduced the City Water arsenic by 73%, from 85 down to 23 µg/L, while reducing the TDS by 72%. ED was not effective, however, in removing As(III) from the anaerobic Well No. 4 water. There arsenic was only reduced by 28%, from 188 µg/L down to 136 µg/L.

Both the CTA and the PA hollow fiber RO membranes did an excellent job (> 97% and > 99% removal, respectively) in removing arsenic from the City Water without prechlorination to convert As(III) to As(V). Greater than 94% removals for both TDS and fluoride were also obtained. For all contaminants, the PA membrane performance was superior. Thus, RO with pretreatment consisting of SHMP addition, cartridge filtration, and possible pH adjustment to 6.0 is a technically effective, but costly, means of treating waters like San Ysidro City Water.

Even though the City Water contained 40% As(III) which is nonionic at the natural pH of 7.2, ion-exchange with chloride-form strong-base resins worked reasonably well in reducing the total arsenic concentration. Before the arsenic MCL was reached, 160 to 220 BV could be treated. Arsenic leakage, primarily As(III), was substantial, however, and the runs were too short to seriously consider ion exchange as a treatment method. (Chlorine oxidation of the As(III) would probably increase the run lengths to 500 BV.)

A POU RO system containing a TFC membrane achieved 95% overall reduction in TDS and a 91% removal of arsenic, which appeared to improve with time. POU RO treatment is attractive for this application because of the small size of the community, the multiple contaminants in the

water, and the fact that no pretreatment of the raw water would be necessary.

## Recommendations

A POU RO treatment system study was recommended in San Ysidro as a result of the findings of this research. Such a study was undertaken in San Ysidro with the result that POU RO treatment was found to be an "effective, economical, reliable and viable alternative to central treatment" for removing arsenic and other contaminants (K. R. Rogers, EPA/600/2-89-050, March 1990).

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*The complete report, entitled "Arsenic(III) and Arsenic(V) Removal from Drinking Water in San Ysidro, New Mexico," (Order No. PB91-181925/AS Cost: \$23.00, subject to change) will be available only from:*

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