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ARSENIC(III) AND ARSENIC(V) REMOVAL FROM DRINKING WATER IN SAN YSIDRO, NEW MEXICO

by

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for the planning, implementing, and managing of research, development, and implementation programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

Toxic arsenic in the forms of arsenite and arsenate is occasionally found in groundwater used for drinking water supply. This report describes research on the methods of removing arsenic from a community water supply to protect the public health. Successful central treatment processes for combined arsenite and arsenate removal include adsorption onto activated alumina, and reverse osmosis hyperfiltration. In-home treatment devices utilizing reverse osmosis hyperfiltration were also tested and found to be effective.

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ABSTRACT

The removal of a natural mixture of As(III) (25-39 μg/L) and As(V) (49-65 μg/L) from groundwater high in total dissolved solids (TDS), and also containing fluoride (2.0 mg/L) was studied in San Ysidro, New Mexico using the University of Houston/U.S. 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 mean concentration of total arsenic in the San Ysidro water during this study was 89 μg/L.

This is a companion study to two other EPA-funded arsenic removal pilot studies--Fallon, Nevada and Hanford, California where As(V) removal was studied following chlorination of the raw water. The original objectives of this study were to establish cost-effective means of removing As(III), As(V) and fluoride from this and similar waters. When Maximum contaminant level (MCL) for fluoride was set at 4.0 mg/L, the fluoride-removal objective was dropped.

Arsenic adsorption onto fine-mesh (28 x 48) 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 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 of 0.05 mg/L. 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 $Al(OH)_3$ precipitate. The sludge produced was not hazardous as determined by the 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 or polyamide 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 μg/L total arsenic but only removed 28% of the As(III) from a new well containing 100% As(III) at a level of 230 mg/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 RO treatment with a thin film composite membrane was effective in removing >91% of the arsenic and >94% of the TDS at low (3-12%) water recovery.

Due to the small size (70 dwellings) of the community, the difficulty of central treatment, and the poor water quality, San Ysidro was chosen by EPA as a test community for point-of-use RO treatment. That study showed point-of-use RO treatment to be a viable alternative to central treatment.

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ABBREVIATIONS AND SYMBOLS

AAl	--	activated alumina, Alcoa F-1 in this study
As	--	arsenic, also referred to as As(Tot), i.e., total arsenic including As(III) and As(V)
As(III)	--	trivalent arsenic, i.e., arsenite ($H_2AsO_3^-$) or arsenious acid (H_3AsO_3) with $pK_a = 9.2$
As(V)	--	pentavalent arsenic, i.e., arsenate ($H_2AsO_3^-$, $HAsO_4^{2-}$ or AsO_4^{3-}) or arsenic acid with pKa values of 2.2, 7.1 and 11.5
BV	--	bed volume, i.e., the volume including voids occupied by an adsorbent in a column, or an equal volume of solution passed through the column
C	--	concentration, mg/L, meq/L or µg/L
C_o	--	initial concentration or conc. at process inlet
C-1	--	column No. 1
CTA	--	cellulose triacetate
d	--	days
EBCT	--	empty bed contact time, min.
ED	--	electrodialysis, the general process description
EDR	--	electrodialysis with current reversal, all ED in this study was EDR
EDTA	--	ethylenediaminetetraacetate, a chelating agent
eff	--	effluent
EP	--	Extraction Procedure, the standard EPA test procedure to establish to toxicity of a sludge
EPA	--	U.S. Environmental Protection Agency
F^-	--	fluoride ion
F-1	--	the grade or designation of the Alcoa activated alumina used in these tests
g	--	grams
GAC	--	granular activated carbon
GFAAS	--	graphite furnace atomic absorption spectroscopy
HF	--	hollow fiber, in reference to an RO membrane
HPIC	--	high pressure ion chromatography
hr	--	hours
IC	--	ion chromatography
ICP AES	--	inductively coupled plasma atomic emission spectroscopy
IX	--	ion exchange
kPa	--	kilopascals
kg	--	kilogram
L	--	liters

m	-- molar, one gram mol/L
m^3	-- cubic meters
MCL	-- maximum contaminant level
mg	-- milligrams
meq	-- milliequivalents
mL	-- milliliters
min	-- minutes
mol	-- mole, one gram molecular weight
N	-- normal, one gram equiv/L
P	-- pressure, psig or kPa
PA	-- polyamide, in reference to an RO membrane
P-E	-- Perkin Elmer
mg/L	-- parts per million or mg/kg, a concentration unit equivalent to mg/L when the solution density is 1.00
µg/L	-- parts per billion or µg/kg, a concentration unit equivalent to µg/L when the solution density is 1.00
ppt	-- precipitation or precipitate
P-1	-- pump No. 1
Q_i	-- volumetric flow of i-th stream, L/min
R	-- suffix designating a regeneration, Run No. 1R
regen	-- regeneration or regenerated
RO	-- reverse osmosis
RO-1	-- RO module No. 1, DuPont HF PA
RO-2	-- RO module No. 2, Dow HF CTA
SDI	-- silt density index
T-Alk	-- total alkalinity, mg/L as $CaCO_3$
TDS	-- total dissolved solids, mg/L
T-Hard	-- total hardness, mg/L as $CaCO_3$
T-1	-- tank No. 1
V-1	-- valve No. 1
V	-- volume, m^3 or L
µ	-- micro
µg	-- micrograms
µS	-- microSiemens, conductivity unit equivalent to µmho/cm
µmho	-- micromho, 10^{-6} reciprocal ohms

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INTRODUCTION

THE SAN YSIDRO ARSENIC PROBLEM

San Ysidro, NM is a small community of 67 dwellings located 50 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 around, the U.S. EPA maximum contaminant level (MCL) of 0.05 mg/L for arsenic. It also contains 2.0 mg/L of fluoride which at the time of this study also exceeded the old 1.4 mg/L MCL. Additionally, this "City Water" has high levels of total dissolved solids (TDS = 810 mg/L), hardness (282 mg/L) and alkalinity (468 mg/L). Historical arsenic and fluoride data from the State of New Mexico files are presented in Table 1 along with values for the inorganic contaminants which do not exceed their MCL's. During the six-year period summarized, the mean arsenic concentration was 0.074 mg/L while fluoride ranged from 1.56 to 3.04 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 the existing City Water from the shallow infiltration gallery. The State of New Mexico analyses for these test wells are summarized in Table 2. As can be seen in the table, the water quality deteriorated with depth. Therefore, what little research we did on these wells was done on the shallowest (44 ft) one.

Not only do the new wells contain two to four times the arsenic levels found in the City Water, but also our subsequent arsenic speciation tests revealed that they contain 100% trivalent arsenic while the City Water is more aerobic in nature and contains only 40% trivalent arsenic. The significance of the speciation is that trivalent arsenic, i.e., arsenite or As(III), is considered to be as much as 60 times as toxic as pentavalent arsenic, i.e., arsenate or As(V) [1].

TABLE 1. HISTORICAL ARSENIC AND FLUORIDE DATA FOR SAN YSIDRO CITY WATER

Collection Date	Arsenic mg/L	Fluoride mg/L	Others mg/L
9-08-75	0.084	1.56	
4-08-76	0.10		Boron 1.36
8-05-76	0.06		Boron 0.44
2-07-77	0.025		Se 0.006
3-21-77	0.02		
8-05-77	0.06		
2-28-78	0.08	1.55	Ba 0.28, Cd <0.001, Pb <0.005, Hg 0.002, Cr <0.005, Ag <0.001, and Se <0.001
5-16-78	0.082		
5-26-78	0.092		

(continued)

TABLE 1. (continued)

Collection Date	Arsenic mg/L	Fluoride	Others mg/L
5-31-78	0.083		
6-27-78	0.041		
11-14-78	0.101		Pb 0.039
1-29-79	0.054		
6-21-79	0.095		
8-02-79	0.067		
1-03-80	0.081		
1-08-80	0.087		
1-29-80	0.088		
12-11-80	0.069		(repeat analysis with identical results)
12-11-80	0.017		(repeat analysis with identical results)
12-21-80	0.092		
2-03-81	0.078		
2-03-81	0.103		
6-29-81	0.075	3.04	NO_3-N 0.25, Ba <0.10, Cd <0.001, Cr <0.005, Pb <0.005, Hg <0.0005, Se <0.005, and Ag <0.001
8-10-81		3.14	(no arsenic analysis)
10-07-81		2.59	(no arsenic analysis)
11-11-81		2.35	(no arsenic analysis)

* All analyses by State of New Mexico EIA Laboratory.

† For arsenic: mean = 0.074 mg/L, std dev = 0.023 mg/L.

§ Samples are from various locations in the distribution system.

‡ The City Water source is a 12-ft deep infiltration gallery.

TABLE 2. CHEMICAL ANALYSES OF TEST WELLS IN SAN YSIDRO, NEW MEXICO

Contaminant	Well No. 4 44 ft	Well No. 2 100 ft	Well No. 1 128 ft
Arsenic	0.163	0.235	0.235
Fluoride	5.22	6.60	5.18
Iron	2.50	7.2	8.9
Sulfate	120.0	367.0	371.0
Chloride	289.0	864.0	1257.0
Manganese		0.32	0.68

* All values in mg/L

† All analyses by State of New Mexico EIA Laboratory

§ All three wells were drilled within a 5 foot radius, and are located behind the San Ysidro City Hall.

LIME SOFTENING TESTS ON WELL NO. 4

Neptune Microfloc Corp. of Corvallis, Oregon performed a pilot study of arsenic and fluoride removal from Well No. 4 water in San Ysidro in July, 1983. In the study they used a combined lime-softening, crossflow filtration device called a HYDROPERM unit. The theory behind the operation of the unit is that: (a) lime ($(CaOH)_2$) is added to precipitate $CaCO_3$, thereby reducing hardness and alkalinity; (b) lime and magnesium sulfate are added to precipitate both magnesium hydroxide ($Mg(OH)_2$) and $CaCO_3$; and (c) the gelatinous $Mg(OH)_2$ floc adsorbs both fluoride and arsenate. Thus, if the arsenite is first oxidized to arsenate using chlorine, the HYDROPERM process should theoretically reduce the TDS, hardness, alkalinity, arsenic, fluoride, iron, and manganese levels.

Their tests indicated that reductions in all these contaminants did indeed occur. However, to reduce the arsenic from 0.22 mg/L to 0.03 mg/L required enormous chemical dosages: 900 mg/L $MgSO_4 \cdot H_2O$, 750 mg/L $Ca(OH)_2$ and 3 mg/L Cl_2. Fluoride was still relatively high at 2.8 mg/L, and the TDS reduction was only slight. Even without reducing the product water pH down from 10.4, the capital plus operating costs were estimated at $1.74/1000 gallons. These costs were for a 100 gpm unit operated 8 hours/day, and arsenic sludge disposal costs were not included. Clearly the HYDROPERM was not a feasible treatment alternative. In this range of treatment costs, reverse osmosis (RO) and (ED) electrodialysis would be economically competitive and yield a much superior product water.

MOBILE INORGANICS PILOT PLANT

Part of our original plan in moving the UH/EPA Mobile Drinking Water Treatment Research Facility 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. This unit, also called the Mobile Inorganics Removal Pilot Plant, is shown in Figures 1 and 2. After much consideration, however, a decision was made to work almost exclusively with the existing City Water supply. Any feasible treatment scheme for Well No. 4 would have been too complicated and too expensive to be operated successfully in such a small community where money and skilled labor are in short supply.

HAZARDOUS WASTE DISPOSAL CONSIDERATIONS

The 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(IV). We chose to perform the alumina adsorption and ion exchange tests in lab scale (1-inch diameter) columns rather than in the 8- or 10-inch diameter pilot-scale columns. Use of these smaller columns, several of which could be run simultaneously, was begun in Scottsdale, Arizona where an ion-exchange run could last as long as 120 days. Therefore, running one large column at a time, which is all the pilot-scale design allows, would have taken several years to complete all the required tests. The high quality of the Scottsdale 1-inch column data in terms of its contaminant leakage and breakthrough curves compared to the 10-inch diameter columns prompted their use in San Ysidro but for different reasons. Here the small columns were required so as to minimize the production of arsenic-contaminated sludges from alumina and ion-exchange regeneration. This was done to avoid having to stockpile 55-gallon drums of spent regenerant solutions for later treatment to precipitate the arsenic with $Al(OH)_3(s)$ followed by filtration and subsequent disposal of filtrate and sludge.

The ion-exchange regeneration in San Ysidro yielded spent regenerant salt solutions containing less than 2.0 mg/L arsenic and therefore were also considered non-hazardous wastes since they were below 5.0 mg/L arsenic.

Prior to the determination that we would not be producing hazardous wastes in San Ysidro, we corresponded with State of New Mexico officials who in turn made inquiries of Federal officials regarding our need to obtain hazardous waste permits to operate in San Ysidro. In the final analysis no permits or discharge plans were required because we did not create significant quantities of arsenic-contaminated sludges. One hundred and seventy grams of arsenic-containing $Al(OH)_3$ sludges were eventually filtered, dried and stored for future study in the pilot plant. Also, because the desalting processes simply separate groundwater into product and brine streams which were recombined for surface discharge into a nearby arroyo, no discharge permits were required. Sanitary wastes from the living trailer were disposed of in the septic-tank, tile-field system.

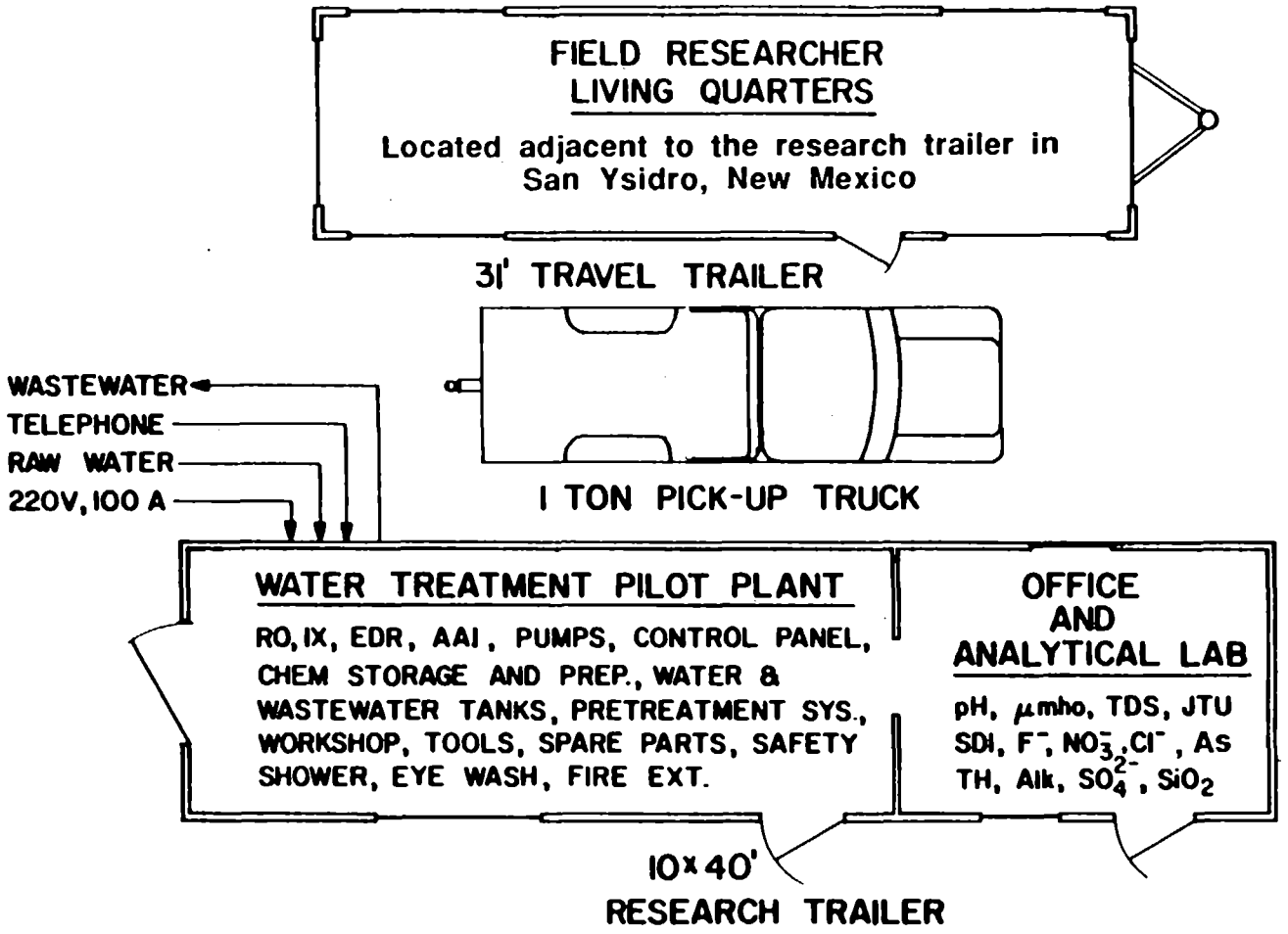


Figure 1. . Mobile research concept including transportable pilot plant/ laboratory, travel trailer, and pickup truck.

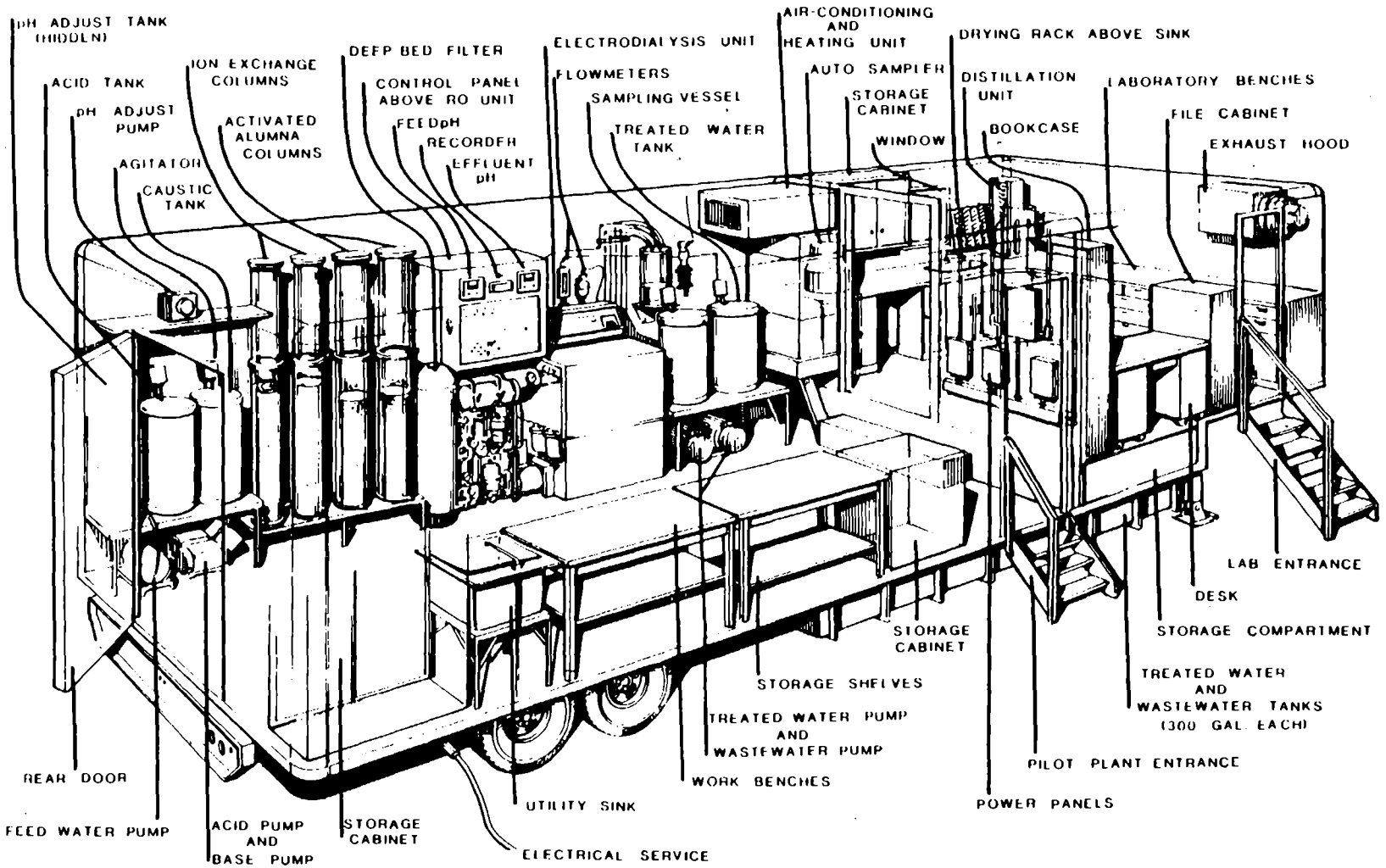


Figure 2. Interior layout of the UH/EPA Drinking Water Treatment Research Facility. While in San Ysidro, NM and Hanford, CA, the graphite furnace atomic absorption spectrophotomerer (GFAA) was located under the exhaust hood.

CONCLUSIONS

The existing San Ysidro city water containing 810 mg/L TDS, 282 mg/L $CaCO_3$ hardness, 190 mg/L sodium and contaminated with 57 µg/L As(V), 31 µg/L As(III) and 2.0 mg/L fluoride can be successfully treated for arsenic removal by means of activated alumina adsorption, reverse osmosis and possibly electrodialysis. The first two treatment methods can be applied either in central treatment or at the point of use. Pre-oxidation using chlorine to convert As(III) to As(V) will definitely aid in the removal of arsenic but is not essential. Since the MCL for fluoride has been set at 4.0 mg/L, fluoride removal is no longer a problem.

The best new San Ysidro well (No. 4) has water of such poor quality that its treatment should not be considered. Its major troublesome contaminants are 1400 mg/L TDS, 230 µg/L As(III), 6.6 mg/L F^- and 2.0 mg/L Fe. Desalting using ED or RO preceded by extensive pretreatment would be technically feasible but too costly.

Although one objective of the San Ysidro experiments was to avoid raw water oxidation and study the removal of both As(III) and As(V), significant oxidation appears to have occurred in all the processes tested and consequently beter-than-expected removal of arsenic occurred in all cases.

Electrodialysis 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%. Electrodialysis 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. Any installation of ED for arsenic removal should include chlorine (or equivalent) oxidation of As(III) to As(V). Calcium carbonate scaling of the reversible ED membranes did occur but was easily removed by acid cleaning.

Both the cellulose triacetate (CTA) and the polyamide (PA) hollow fiber RO membranes did an excellent job, 99% and >99% removal, respectively, in removing arsenic from the city water without prechlorination to convert As(III) to As(V). Greater than 94% TDS and fluoride removal were also obtained. For all contaminants, the PA membrane performance was superior. Thus, RO with pretreatment consisting of sodium hexamethaphosphate addition, cartridge filtration and possible pH adjustment to 6.0 is a technically effective, but costly, means of treating the San Ysidro city water. About 25% of the raw water could be bypassed and then blended with the RO product water to provide a stable water for distribution thereby reducing the treatment costs.

About 8800 bed volumes of pH 6, unchlorinated San Ysidro city water could be continuously passed through a virgin fine mesh (28 x 48) activated alumina column before the arsenic MCL was reached. This is intermediate between the short run of 300 BV obtained from laboratory studies on a simulated water containing 100 µg/L As(III) and the long (23,400 BV) run for a simulated water containing 100 µg/L As(V). Coarse (14 x 28) mesh alumina did not perform as well on the San Ysidro water. Under similar conditions a run length of 6800 BV was obtained for the coarse alumina.

In all the activated alumina tests, fluoride broke through long before arsenic. For example, using the fine-mesh alumina at pH 6, fluoride reached the interim MCL of 1.4 mg/L at 2500 BV while arsenic did not reach its 0.05 mg/L MCL until 8800 BV. Even though fluoride was driven off the alumina by the more-preferred arsenic, the fluoride elution peak was not large. The highest fluoride concentration observed in the alumina column effluent was

2.4 mg/L while the feed was 1.9 mg/L. Therefore, the revised fluoride MCL of 4.0 mg/L would not be exceeded during an alumina run to the arsenic MCL.

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 prior to the arsenic MCL compared to 8800 BV at pH 6.

Partial regeneration of the arsenic spent alumina is possible. When using a considerable excess, 6.7 BV of 4% (1.0 N) NaOH, 63% of the adsorbed arsenic was eluted during a cocurrent (downflow) regeneration of spent, fine-mesh alumina. A larger volume of more dilute NaOH was also effective in partially regenerating the alumina. Cocurrent regeneration with 15-19 BV of 1% (0.25 N) NaOH recovered 67-70% of the adsorbed arsenic. 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. Also, in practice, lesser volumes of regenerant could be used followed by a displacement rinse with raw water to conserve regenerant.

Even with these excessive regenerations, 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 respectively for the fine- and coarse-mesh aluminas.

A material balance on the arsenic adsorbed and eluted from the alumina indicated that 34% of the As(III) fed to the column was adsorbed, and 65% of the As(III) adsorbed was eventually oxidized to As(V) on the alumina. Only a small percentage (8.6%) of the arsenic in the spent regenerant solution was As(III).

99.8% of the As(V) and 36% of the As(III) in the spent NaOH regenerant solution were removed by coprecipitation with the $Al(OH)_3$ 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 consisting of 97% As(III).

The arsenic-contaminated $Al(OH)_3$ 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 U.S. EPA extraction procedure (EP) toxicity test and easily passed. Even though the sludge contained As(III), the final leachate arsenic concentration was 0.6 mg/L, i.e., far below the 5.0 mg/L limit for classification as a toxic waste.

Attempts were made to coprecipitate the arsenic from the city water with the $Fe(OH)_3(s)$ resulting from chlorine oxidation of the Fe(II) originally present. This failed because of the low (0.06 mg/L) iron content of the city water. The arsenic content (200 µg/L) of the Well No. 4, containing 2.0 mg/L Fe(II), was, however, reduced 69% by this procedure.

Even though the city water contained 40% As(III) which is non-ionic at the natural pH of 7.2, ion-exchange with chloride-form strong-base resins worked reasonably well in reducing the total arsenic concentration. 160-220 BV could be treated before the arsenic MCL was reached. 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.) Fortunately, due to the high TDS of the raw water, the effluent arsenic concentration did not exceed the influent concentration when it broke through. Finally, fluoride broke through almost immediately (4-18 BV) but was also subject to significant peaking.

A point-of-use (POU) reverse osmosis (RO) system containing a thin-film-composite (TFC) membrane achieved 91% removal of arsenic and 95% reduction in TDS. The arsenic removal appeared to increase with time.

Although coarse-mesh alumina is nearly as good as the fine-mesh variety for fluoride removal, it is particularly important to use a fine-mesh (28 x 48) activated alumina for arsenic removal. The coarse-mesh alumina was exhausted much sooner and was much more difficult to regenerate.

RECOMMENDATIONS

Although these results for activated alumina indicate a beter-than-expected removal of a natural mixture of As(III) and As(V), future pilot studies and central municipal arsenic removal installation should always include chlorine or alternative means of oxidation of As(III) to As(V).

San Ysidro, a small, remote community of 67 families should be considered as a test site for evaluation of point-of-use (POU) treatment using reverse osmosis and possibly activated alumina adsorption. In this case no cental pretreatment needs to be provided and the water need not be chlorinated to oxidize As(III). The objectives of the POU RO study would be to determine the actual operating costs and evaluate the long term (e.g., 2 years) effectiveness of treatment by monitoring all the units installed for TDS (conductivity), arsenic, product water flow rate, and membrane life. Occasional samples are also recommended for bacterial monitoring, and all system maintenance requirements should be carefully recorded.

Point-of-use testing of activated alumina at San Ysidro or a similar community with a natural mixture of As(III)/As(V) and moderate, i.e., <4 mg/L fluoride contamination is recommended now that the fluoride MCL has been set at 4.0 mg/L. Even without chlorination of the feedwater, POU devices should operate much longer than was observed in these studies, before the arsenic MCL is reached. This is because of the intermittent nature of operation of POU systems. The "off" (no flow) periods will provide time for oxidation of As(III) and relaxation of the solid-phase concentration gradient which will result in improved adsorption during the "on" periods.

Countercurrent (upflow) regeneration of arsenic-spent alumina should be studied on a pilot or full-scale using a relatively concentrated (e.g., 4%) NaOH solution. The objective of such a study would be to determine if countercurrent regeneration alone (i.e., not countercurrent followed by cocurrent) can eliminate or reduce the earlier leakage which was observed following cocurrent regeneration.

EXPERIMENTAL DETAILS

OVERVIEW OF THE SAN YSIDRO ARSENIC REMOVAL EXPERIMENTS

The basic objective of the San Ysidro arsenic removal experiments was to develop a simple cost-effective way to remove the arsenic from the city water, after having decided that the new wells were too difficult to treat. A few experiments were, however, performed using Well No. 4 for comparison. Because an extensive study of Arsenic(III) oxidation was planned in Hanford, CA, oxidative pretreatment using chlorine was not studied in San Ysidro. A chronological list of the San Ysidro experiments is presented in Table 3.

Arsenic(V) is easily removed from water even in the presence of high TDS and strongly competitive ions like fluoride [Singh and Clifford, 1981; Rosenblum and Clifford, 1984]. It was of particular interest to study the removal of natural mixtures of As(III) and As(V) by activated alumina since this had not been studied previously. Also of interest was any unplanned oxidation of arsenic(III) which might occur in the adsorption columns. 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 and 28 x 48) of Alcoa F1 alumina were used for comparison. Finally, two concentrations of the NaOH regenerant were used to determine which was most economical in terms of the mass of arsenic removed/mass of NaOH applied.

Fox [1979] and Sorg [1981] have shown that arsenic is well removed by RO membranes, but the percent removals of arsenite, a non-ionic species at neutral and acidic pH, varied widely (43-81%). Arsenate, on the other hand, typically showed greater that 97% rejection. This is not unexpected since arsenate exists predominantly as a large anion at pH's above about 3.0. Thus, it was of interest to study the removal of a mixture of As(III) and As(V) using polyamide (PA), cellulose triacetate (CTA) and thin-film composite (TFC) membranes. TFC membrane performance was studied using a Culligan Point of Use RO system. Reverse osmosis was of particular interest because of the high TDS of the water and the presence of multiple contaminants.

TABLE 3. CHRONOLOGICAL LIST OF SAN YSIDRO EXPERIMENTS

Run/(Date) (1984)	Description
EDR Run (Preliminary) (March, 1984)	Well No. 4 feed, no chemical pretreatment, feed pH 7.1, product flow 1450 L/day, 80% recovery. Preliminary run to determine As(III) passage (it passes--90%).
EDR Run 1 (March 12-17)	City water, no chemical pretreatment, feed pH 7.1, product flow 1450 L/day, 81% recovery. Objectives: to determine % rejections and fouling.
RO Run 1 (April 1-9)	DOW HF CTA, pH 6.3, 10 mg/L SHMP, product flow 11700 L/day, 50% recovery. Objectives: to determine % rejections and fouling.

(continued)

TABLE 3. (continued)

Run /(Date) (1984)	Description
AAl Run 1 (4/12 - 5/3)	12 x 28 mesh, pH 6.0, EBCT 5 min. Objectives: to determine F^- and As breakthroughs.
AAl Run 2 (4/12 - 5/8)	28 x 48 mesh, pH 6.0, EBCT 5 min. Objectives: to compare breakthroughs for fine and coarse mesh alumina.
AAl Run 1R (May 14)	6 BV 1.0 N (4.0 %)NaOH, EBCT 15.4 min. Objective: to determine F^- and As recoveries and regeneration efficiency.
AAl Run 2R (May 14)	6 BV 1.0 N (4.0 %)NaOH, EBCT 15.4 min. Objective: to determine F^- and As recoveries and regeneration efficiency.
AAl Run 3 (5/16 - 6/3)	12 x 28 mesh, used, pH 6.0, EBCT 5 min. Objective: to determine F^- and As capacities compared to Run 1.
AAl Run 4 (5/16 - 6/11)	28 x 48 mesh, used, pH 6.0, EBCT 5 min. Objective: to compare F^- and As capacity to Run 2.
AAl Run 3R (June 15)	16 BV 0.25 N (1.0 %) NaOH, EBCT 15.4 min. Objective: to compare 1.0 N to 0.25 N regenerants on coarse mesh.
AAl Run 4R (June 18)	16 BV 0.25 N (1.0 %) NaOH, EBCT 15.4 min. Objective: to compare 1.0 N to 0.25 N regenerants on fine mesh.
AAl Run 5 (6/19 - 7/7)	12 x 28 mesh, used, pH 6.0, EBCT 5 min. Objective: to compare F^- and As capacities to Run 3.
AAl Run 6 (6/19 - 7/12)	28 x 48 mesh, used, pH 6.0, EBCT 5 min. Objective: to compare F^- and As capacities to Run 4.
AAl Run 5R (July 23)	15 BV 0.25 N (1.0 %) NaOH, EBCT 12 min. Objective: to compare F^- and As recoveries to regeneration 3R.
AAl Run 6R (July 23)	14 BV 0.25 N (1.0 %) NaOH, EBCT 12.4 min. Objective: to compare F^- and As recoveries to regeneration 4R.
AAl Run 7 (7/16 - 7/23)	28 x 48 mesh, new, pH 7.3 (no adjustment), EBCT 5 min. Objective: to determine F^- and As run lengths at natural pH.
AAl Run 1 (4/12 - 5/3)	12 x 28 mesh, pH 6.0, EBCT 5 min. Objective: to determine F^- and As breakthroughs.

(continued)

TABLE 3. (continued)

Run/(Date) (1984)	Description
RO Run 2 (8/2 - 8/7)	DuPont HF PA, pH 7.6 (natural), 10 mg/L SHMP, product flow 4500 L/day, 50% recovery. Objective: to determine % rejections and fouling.
IX Run 1 (8/14 - 8/15)	Dowex 11, used, pH 7.2. Objective: to determine if As(III) breaks through immediately as expected.
IX Run 2 (8/23 - 8/25)	Dowex 11, new, pH 7.3. Objective: to verify unusual results of IX Run 1 using fresh resin.
IX Run 1R (Sept. 4)	5 BV 1.0 N (6 %) NaCl, 4.5 BV/hr. Objective: to establish amount of NaCl required and F^- and As recoveries.
IX Run 2R (Sept. 4)	4 BV 1.0 N (6 %) NaCl, 4.7 BV/hr. Objective: to compare to regeneration Run 1R.
AAI Run 8 (9/20 - 9/21)	Well No. 4, 12 x 28 mesh, new, pH 7.1 (no adjustment), EBCT 5 min. Objective: to determine As run length at natural pH on high As(III) source water.
$Al(OH)_3$ precipitation	Reduce pH of spent regenerant solution to 6.5 to precipitate $Al(OH)_3$ and coprecipitate As. Objective: to determine if As can be removed from regenerant solution.
EP Toxicity	Leach $Al(OH)_3$ sludge at pH 5. Objective: to determine if As leaches from sludge to yield a hazardous waste.
$Fe(OH)_3$ precipitation	Increase pH of raw water to 8.5 after oxidizing As(III) and Fe(II) with Cl_2. Objective: to determine if As can be removed from city water and Well No. 4 by coprecipitation with $Fe(OH)_3$.

The electrodialysis (ED) desalting process is usually considered as direct competition to RO for brackish water treatment. Removal of individual nonionic contaminants by ED, however, may not be competitive. Such is the case with the nonionic arsenite which is not expected to be removed by ED because it does not transport a charge across the membrane. Arsenate anions such as $H_2AsO_4^-$ or $HAsO_4^{2-}$ transport one or two changes depending on pH. In this regard, it was of interest to study the ED process on both the mixed As(III)/As(V) city water and the pure As(III) Well No. 4 water. The published ED literature contains no data on arsenic rejection and there was some speculation that the potential and current generated in the ED stack might oxidize and thereby remove arsenite.

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. Previous studies by Horng [1983] showed arsenic(V) to be well removed by ion exchange, but 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, prompted a study of strong-base anion resins in the chloride form for the treatment of the San Ysidro city water.

Although precipitation processes are not included in the pilot scale equipment, bench scale tests were performed because arsenate has been found to be removed from water by coprecipitation with $Fe(OH)_3$ [Buswell, 1943; Rosehart and Lee, 1972; Gullege and O'Connor, 1973]. The removal of arsenic from Well No. 4 water containing 2.0 mg/L of iron, and city water containing 0.06 mg/L of iron by the precipitation of the naturally occurring iron was tried after oxidizing the arsenite to arsenate using chlorine.

Finally, wastewater disposal studies were performed on the spent regenerant solutions from the alumina column regenerations. It was of particular interest in these experiments to determine if the results of Rubel and Hathaway [1985] from their Fallon, Nevada arsenic removal studies could be duplicated. They found that, by simply neutralizing the alumina regenerant solution, the resulting aluminum hydroxide precipitate would adsorb the arsenate yielding a supernatant water with less than 0.10 mg/L total arsenic. Their filtered, $Al(OH)_3(s)$ sludge passed the EPA Extraction Procedure (EP) test as a non-hazardous waste. (The difference between our study and Rubel's was the presence of a significant amount of arsenic(III) which might have been poorly adsorbed on the alumina, thus causing the $Al(OH)_3(s)$ sludge to fail the EP toxicity test. Fortunately, most of the As(III) retained by the alumina was unintentionally oxidized to As(V), and our sludges also passed the EP test.)

ANALYTICAL METHODS

Summary of Methods

With the exceptions of metals analyses done using a Perkin Elmer Model 5500 Inductively Coupled Plasma (ICP) Spectrometer at the University of Houston, and a check sample of the city water run by Water Test Corporation of New London, NH, all analyses were done with equipment in the Mobile research facility. The methods used are summarized in Table 4 with their respective references.

Arsenic Determinations

The method used for arsenic speciation was developed by Clifford, Chow and Ceber [1983] especially for use in field situations. The method makes use of the fact that in the pH range of 3.0 to 8.4, As(V) exists as monovalent $H_2AsO_4^-$ or divalent $HAsO_4^{2-}$ whereas As(III) exists as the uncharged arsenous acid, H_3AsO_3. When chloride-form strong-base anion resins are used for the separation, As(III) passes through the column unhindered while As(V) is completely retained by the resin. In the simplest determination, 100 mL of sample are passed at 10 mL/min through a small column containing 5 mL of resin beads with a depth of 10 cm.

GFAAS is used to determine total arsenic (As(III) + As(V)) on the untreated sample and As(III) on the column filtrate. Arsenic(V) is determined by difference, and it can be

TABLE 4. LIST OF ANALYTICAL METHODS USED IN THE SAN YSIDRO ARSENIC STUDY

Test	Method	Reference
Total Arsenic	GFAAS, P-E 372 with HGA-2200	Appendix A
Arsenic(III)	IX separation then GFAAS	Appendix A
Arsenic(IV)	IX separation then GFAAS	Appendix A
pH	Orion 231 Digital pH meter with combination glass electrode and ATC	Orion Research Manual
TSS	Glass Fiber Filtration Reeve Angel-934 AH, 4.25 cm	
TDS	Evaporation at 105° C	
Conductivity	Hach Conductivity Meter-16300	Hach Manual
SDI	Filtration with Millipore-HA, 0.45 µm	DuPont RO Manual
Turbidity	Hach Turbidimeter-2100A	Hach Manual
Silica	Molybdosilicate	Standard Method 14th Ed., p 487, 1975
Total Hardness, TH	EDTA Titration	Standard Method 14th Ed., p 487, 1975
Total Alkalinity, T. alk	Hach Digital Titrator-AL-DT	Hach Manual
Sulfide	Methylene Blue	Standard Method 14th Ed., p 503, 1975
Bicarbonate	Hach Digital Titrator-AL-DT	Hach Manual
Fluoride	Electrode, Orion-96-09-00	Orion Research Manual
Chloride, Bromide, Sulfate, Nitrate	Dionex HPIC-2010i	Dionex Manual
Na, Ba, K, Mn, Fe, Ca, Sr	ICP AES at UH	P-E Manual
Magnesium	Difference of TH and Ca	

checked by elution of the column with 50 mL of 0.5 N HCl followed by GFAAS analysis of the As(V) in the eluate.

Ferric iron interferes by adsorbing As(III) if the pH is above 3.1. Fortunately, the interference due to the presence of up to 1.0 mg/L Fe^{3+} may be completely eliminated by adjusting the sample pH into the 2.8 to 3.1 range. Distilled water could not be used for reagent preparation, rinsing and dilution because it contained traces of chlorine carryover from the tap water from which it was distilled. These traces of Cl_2 completely oxidized any As(III) present. Deionized water, i.e., water from a standard mixed bed demineralizer preceded by an activated carbon adsorber, was found to be satisfactory, however, for reagent preparation and dilution.

Complete details of the As(III)/As(V) ion-exchange separation method can be found in "Arsenic(III)/Arsenic(V) Separation by Chloride-Form Ion-Exchange Resins" (Clifford et. al., 1983). Although it is not a "standard method", it has been used successfully over a period of three years on hundreds of As(III)/As(V) samples in the University of Houston Laboratories and in San Ysidro. Furthermore, the method has been validated by an independent testing laboratory in Fresno, California--Twining Laboratories. In evaluating the method for determination of the arsenic speciation of Hanford, CA groundwaters, they found the procedure to be "very good" as evidenced by the average recovery of As(III) of 99±1%, and As(V) of 100±2%. Their 4-page evaluation report including analysis of Hanford's Well No. 31 is included in Appendix A.

QUALITY ASSURANCE

The basic quality assurance procedure used was participation in the EPA's Quality Assurance Surveys. Regarding arsenic, fluoride and nitrate analyses, the field researcher has achieved acceptable results for these parameters while using the analytical equipment in the UH/EPA trailer during three years of research prior to the San Ysidro study. This indicates that our standards and analytical procedures are of acceptable accuracy.

While in San Ysidro, the field researcher determined arsenic, fluoride and nitrate with the results in Table 5. All UH analysis values were within the acceptable range as determined by the EPA Quality Assurance Officer. Appropriate blanks and standards were run at least once each day when the analytical tests were performed.

TABLE 5. QUALITY ASSURANCE RESULTS

Survey No. (Date)	Analysis	Sample #1 UH	Sample #1 True Value	Sample #2 UH	Sample #2 True Value
WS 014 (5/18/84)	Arsenic, µg/L	22.0		73.0	
	Fluoride, mg/L	1.0		0.41	
	Nitrate, mg/L	9.87		0.66	
	Chromium, µg/L	37.0		67.0	
WS 013 (11/18/843	Arsenic, µg/L	12.5		104.0	
	Fluoride, mg/L	2.17		0.223	
	Nitrate, mg/L	6.05		0.404	
WS 012 (5/23/83)	Arsenic, µg/L	19.0	18.0	51.0	48.1
	Fluoride, µmg/L	1.51	1.50	0.89	0.86
	Nitrate, mg/L	2.12	2.1	1.13	1.13
	Chromium, µg/L	13.8	14.3	81.7	78.6

ELECTRODIALYSIS APPARATUS AND PROCEDURES

The pilot-scale electrodialysis (ED) unit used in San Ysidro is an Ionics Inc. Aquamite I unit with automatic current reversal (EDR) to prevent fouling. It was operated to produce 1790 L/day (475 gpd) of product water at 81% recovery utilizing internal brine recycle. The flow

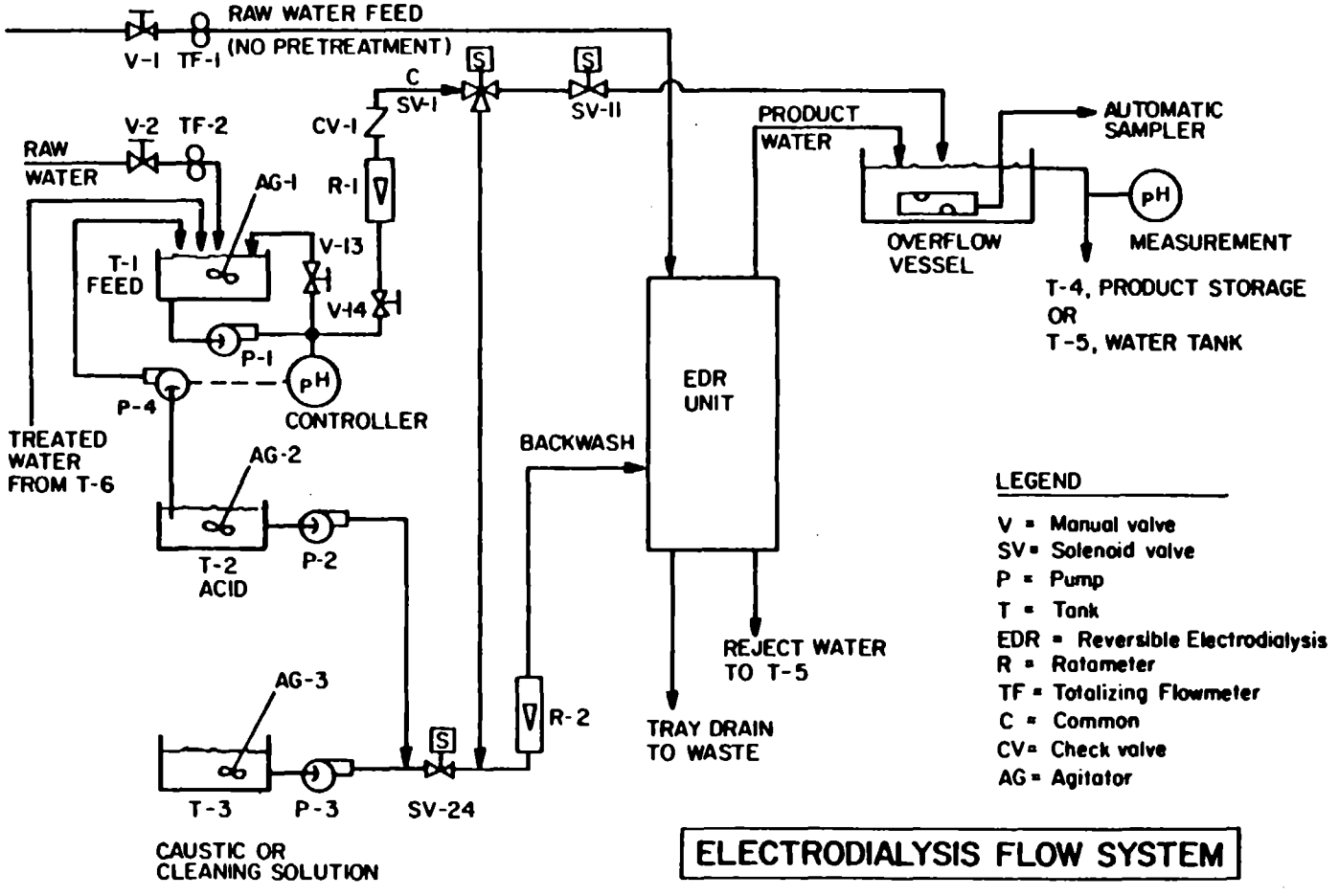


Figure 3. Process and instrumentation flow diagram for the reversible electrodialysis system. An internal flow schematic can be found in Appendix B--Figure B1.

scheme is shown in Figure 3. Further details, including an internal flow schematic for the unit and a list of specifications, are presented in Appendix B as Figure B1 and Table B1, respectively.

Raw water without pH adjustment or antiscalant addition was fed directly through valve V-1 to the unit. This lack of pretreatment was done at the manufacturer's suggestion and to verify their claim that pretreatment is not required. Actually, since the internal flow schematic (Figure B1) contains a 10-micion cartridge filter and a granular activated carbon column (for dechlorination), some pretreatment does occur.

Prior to the tests in San Ysidro, the ED unit had been operated intermittently for four years in three previous locations. However, the membrane stack had to be replaced approximately six months prior to its use in San Ysidro because it was improperly stored and allowed to dry out. Thus, it was effectively a relatively new unit.

The ED unit was severely challenged in San Ysidro by operating it without pretreatment on both the city water and Well No. 4. The result was that membranes did scale up and needed to be acid cleaned prior to use in Hanford, California, the subsequent field location. The cleaning procedure is outlined in Appendix B following the EDR specifications.

REVERSE OSMOSIS APPARATUS AND PROCEDURES

The RO system flow schematic is given in Figure 4 and the list of specifications are presented in Appendix B, Table B2. Two different modules were used in the study--a Dow, hollow-fiber, cellulose triacetate-membrane type and a DuPont hollow-fiber, polyamide-membrane type. Each was operated separately as single module at approximately 50% recovery. The Dow module (RO-1) was larger, producing 11,700 L/day compared to 4500 L/day of product for the DuPont module (RO-2). Based on the recommendations from each manufacturer, the feed to the Dow unit was acidified to pH = 6.3 while no acid was added to the DuPont module feed. Their respective computer projections and pretreatment requirements are reproduced in Appendix Tables B3 through B6 following the RO system details.

For both the Dow and Dupont systems, the deep-bed AG-media filter was used ahead of the 10-μm cartridge filter. Also, an antiscalant, 10 mg/L sodium hexametaphosphate (SHMP), was added continuously during each run by pumping from tank T-3 into the recirculating feed tank T-1.

During the EDR and RO runs, product water samples were taken automatically from the overflow vessel by the ISCO automatic sampler at predetermined volumes and time intervals. Feed and brine samples were taken manually at least once per day. No preservatives were used in the sample bottles.

ALUMINA APPARATUS AND PROCEDURES

As previously discussed, 1-inch diameter columns rather than the 8- or 10-inch diameter pilot columns were used for all the alumina and ion exchange runs to minimize the production of arsenic wastes in San Ysidro. The flow schematic for the alumina system is given in Figure 5. The 100-L pilot-scale feed tank T-1 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 in T-1. This was done to prevent oxidation of the As(III), and to represent more closely, the actual feedwater which would exist in a full-scale treatment process.

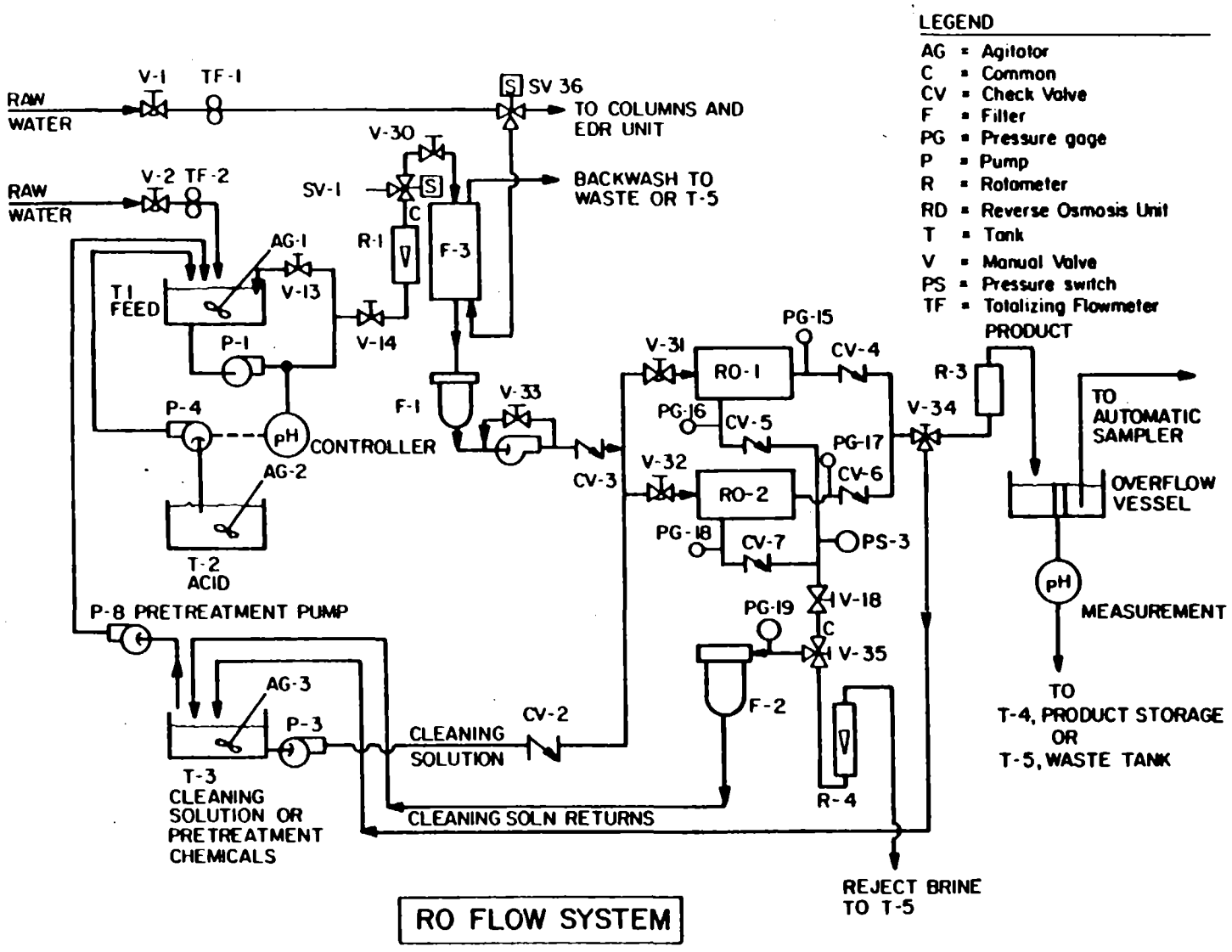


Figure 4. Process and instrumentation flow diagram for the reverse osmosis (RO) system.

For all the alumina experiments, the feedwater pH was adjusted to 6.0 with 2% H_2SO_4 added from T-2 using an Ecodyne model 2500C metering pump, P-3. The feedwater metering pumps, P-C1 and P-C2, which fed the alumina columns, operated at a flow rate of 80±3 mL/min for an EBCT of 5 minutes--typical of full-scale operations. Two different mesh sizes of alumina were used, but the bed volumes were always 400 mL resulting in a bed depth of 81.5 cm (32 in).

Generally, the alumina runs were continued until the MCL for arsenic (0.05 mg/L) was achieved in the effluent. This meant that the runs were continued far beyond fluoride exhaustion. This was not considered a serious violation of the fluoride MCL (1.4 mg/L in 1984) because the feed fluoride level was only 2.0 mg/L. Now that the MCL for fluoride is 4.0 mg/L, potential fluoride violations are not a problem with the San Ysidro city water. In these experiments, the alumina runs lasted from 20-25 days. Only total arsenic was determined on the column effluents, i.e., there was no speciation of As(III) or As(V).

ION EXCHANGE APPARATUS AND PROCEDURES

The ion exchange runs were done to verify that immediate arsenic(III) breakthrough would result because of the molecular (nonionic) nature of arsenious acid. To insure that oxidation would not occur, the holding time in the feedwater tank T-1 was reduced to 6 seconds by replacing T-1 (100 L) with a 2-L beaker to receive the raw feed. This is shown in Figure 6--the ion exchange system schematic. 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. Two different resins were used: Ionac ASB-1, a type 1 gel resin with microporosity, and Dowex-11, an isoporous "improved porosity" type 1 resin.

Following each exhaustion run, the resin was regenerated with 5 BV of 1.0 N (6 %) NaCl solution, i.e., approximately 4-5 times the stoichiometric requirement based on total resin capacity. During each regeneration the elution curves for fluoride and arsenic were monitored. Arsenic was speciated occasionally during the exhaustions and regenerations.

FERRIC IRON PRECIPITATION TESTS

Batch oxidation/precipitation tests were run on 500-mL samples of city water and Well No. 4 water. These consisted of adding an excess of chlorine (bleach) to the raw water, adjusting the pH of one half of the chlorinated water to 8.5 and filtering the samples prior to the determination of arsenic in the filtrate. This was done to determine the amount of arsenic which was adsorbed onto any precipitate that was formed at the adjusted pH of 8.5 and the unadjusted precipitation pH of approximately 7.2 for both the city water and Well No. 4. Diluted Purex® bleach was used for the oxidation, and a fine, quantitative-analysis filter paper was used for the filtration step.

ARSENIC SLUDGE DISPOSAL TESTS

In a typical $Al(OH)_3$ precipitation test, 500 mL of spent alkaline regenerant solution (pH 13) was placed into a 1-L beaker and acidified to pH 6.5 using about 7 mL of concentrated reagent-grade HCl. In order to maintain the pH ≤ 6.5 and to prevent redissolution of $Al(OH)_3$, a small amount of acid was added at 1/2 to 4 hour intervals during the next 14-hour period. The solution was allowed to stand overnight (10 hours) prior to filtration. The precipitate with its absorbed arsenic was then filtered through a quantitative, paper filter which was later dried

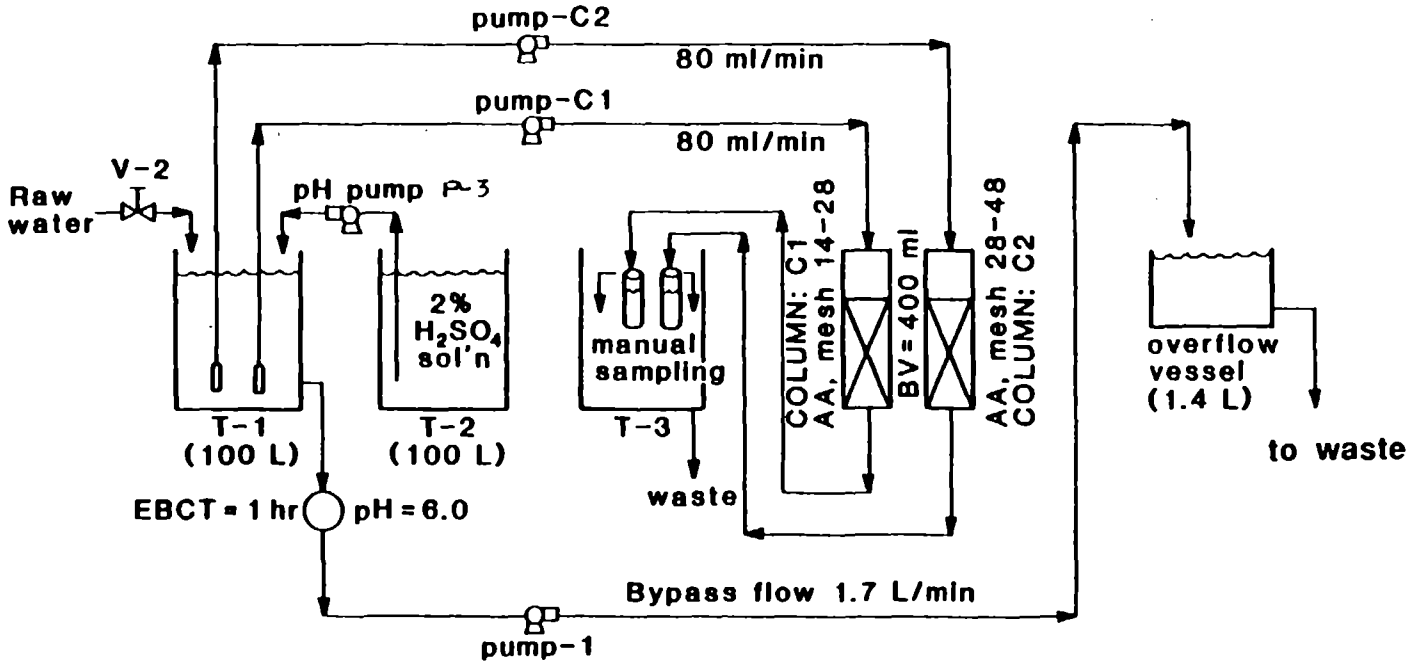


Figure 5. Flow schematic for the activated alumina system.

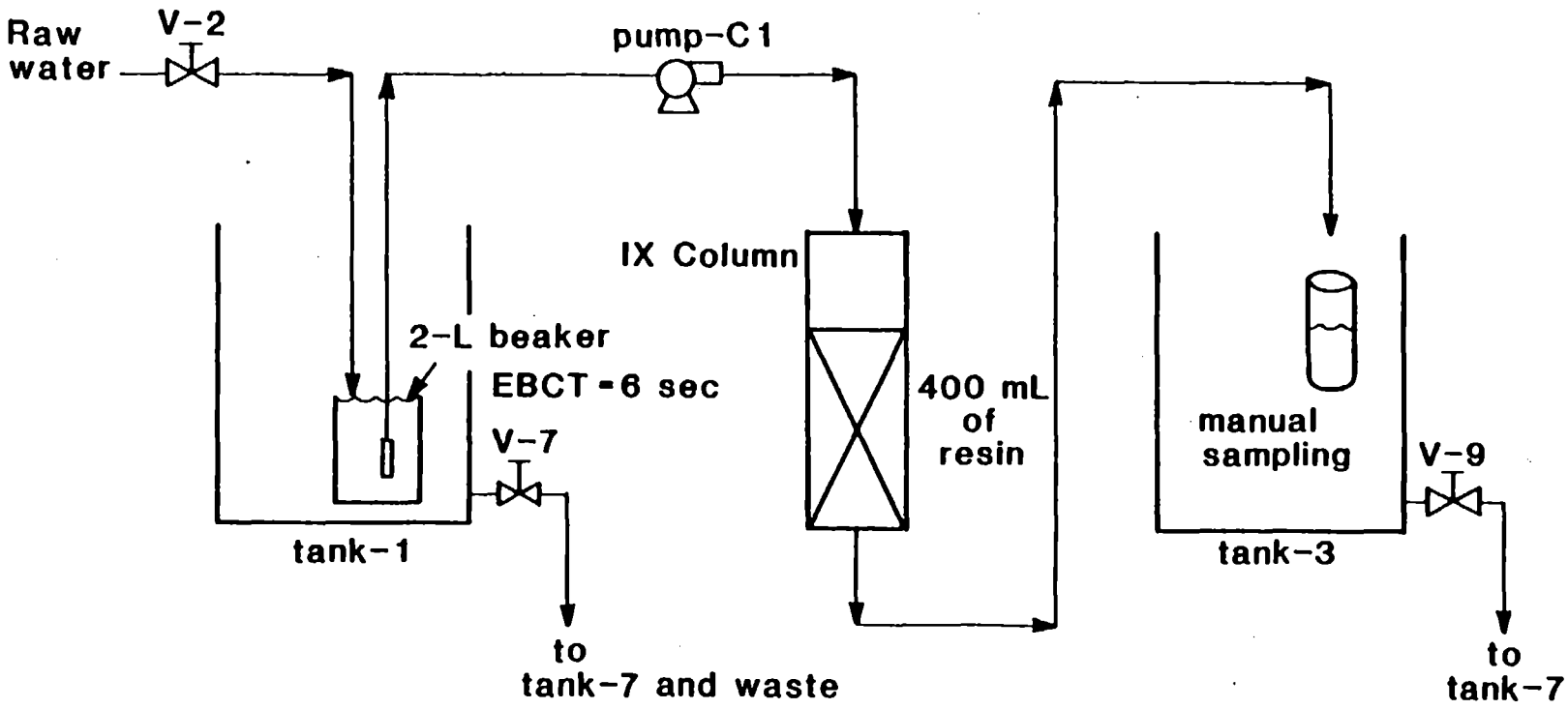


Figure 6. Flow schematic for the ion-exchange (IX) system.

for 12 hours at ambient temperature (22° C) and stored for the future studies including the Extraction Procedure (EP Toxicity) Test (U.S. EPA 1980). Total arsenic, As(III) and Arsenic(V) were determined on the spent regenerant prior to precipitation and on the filtrate after filtration. This procedure was used as a screening test only, i.e., to quantify the amount of As(III) and As(V) coprecipitated with the $Al(OH)_3$ near its pH of minimum solubility, i.e., 6.5.

EP TOXICITY TEST PROCEDURE FOR $Al(OH)_3$ SLUDGE

The $Al(OH)_3$ sludge dried for 12 hours at ambient temperature was subjected to the Extraction Procedure (EP Toxicity) test (Appendix A). Briefly, the procedure consists of extracting the sludge with 16 times its weight of distilled water after adjusting the pH to 5 using acetic acid. If, at the end of the first 24-hour extraction period, the pH is greater than 5.2, more acid is added and the extraction is continued. Subsequent to the extraction step, the sludge is filtered and the arsenic measured in the filtrate. If the total arsenic concentration exceeds 5.0 mg/L, the sludge is considered a hazardous waste and must be disposed of in a hazardous waste landfill. Although the sludge passed the EP test, there were no such landfills in the State of New Mexico. So, the results of the test had important disposal-cost implications.

RESULTS AND DISCUSSION

SAN YSIDRO WATER QUALITY

The compositions of the city water and Well No. 4 are shown in Table 6. Most values are single-point determinations while others, notably the As(III) and As(V) and total arsenic values are the averages of several determinations. Table 7 lists the separate As(III) and As(V) values for the city water which were used to compute the averages. The mean As(III) value was 31±8.6 µg/L while As(V) was 57±8.2 µg/L, and the total As concentration was 89±8.3 µg/L. The total arsenic value, 89 µg/L, was slightly higher than the sum of As(III) + As(V) (31 + 57 = 88) because more samples were included in the As(total) average. Finally, the data indicate that the total arsenic concentration appeared to be increasing during the course of the study.

Other particularly troublesome constituents of the city water are TDS (810 mg/L), hardness (282 mg/L), total alkalinity (468 mg/L) and sodium (190 mg/L). To achieve the U.S. EPA secondary MCL's would require desalting, e.g., with EDR or RO. With desalting, however, problems also exist, depending on the concentration factor encountered in the reject brine and the amount of precipitation inhibitor, SHMP, used for scale control. Both the Dow and DuPont RO computer projections indicate that the City Water is supersaturated with respect to $BaSO_4$ and CaF_2. For Well No. 4 water, these same two compounds were computed to be at supersaturation. Further elaboration of the scaling problem can be found in the discussion of EDR and RO performance.

TABLE 6. RAW WATER ANALYSES IN SAN YSIDRO, NM

Contaminant	City Water * † §	Well No. 4
Arsenic(III), µg/L	31	230
Arsenic(V), µg/L	57	0
Arsenic Total, µg/L	88	230
pH	7	7.2
Dissolved solids, TDS	810	1393
Suspended solids, TSS	0.05	0.05
Conductivity, µS	1530	2860
Silt Density Index, SDI	1.13	0.7
Turbidity, NTU	0.11	4.4
Silica, SiO_2	60	66
T. Hardness as $CaCO_3$	282	126
T. Alkalinity as $CaCO_3$	468	642
Sulfide	0	0.032

(continued)

TABLE 6. (continued)

Contaminant	City Water	Well No. 4
Bicarbonate	571	783
Fluoride	2.0	6.6
Chloride	123	300
Nitrate as N	0.22	0
Sulfate	37	101
Bromide	0.35	0.83
Strontium	0.85	0.56
Calcium	85	38
Magnesium	17	7.5
Iron	0.06	2
Manganese	0.02	0.16
Potassium	12	15
Barium	0.2	0.06
Sodium	190	510

* All concentration are mg/L unless otherwise specified.

† See Table 5 for analytical methods used.

§ Values shown are averages of several samples taken during the course of the study, 1/84 through 9/84.

ARSENIC(III) OXIDATION

As Table 7 indicates, the As(III) concentration was quite variable (22-44 µg/L) during the course of the study. If the raw water sample was allowed to sit for several hours or more, prior to speciation, some or all of the As(III) was occasionally found to oxidize to As(V). Consequently, concern existed that the water in the raw water recirculation tank, T-1, with a typical retention time of one hour, would be subject to air oxidation of As(III). There was, however, no clear indication that oxidation took place in this tank. Comparing the As(III) values of samples taken directly from the tap (24, 24, 34 and 28 µg/L) to the samples from T-1 shows the tap samples on the average to be lower in As(III) than those from T-1. This is probably due to the fact that the tap samples were all taken in the earlier part of the study when both the As(III) and As(V) values were somewhat lower than they were near the end of the study.

The variability of As(III) oxidation presents a problem with treatment to remove total arsenic. As previously discussed, As(III) is known to be poorly removed by alumina, chloride-form ion-exchange, and ED -- especially ED. Nevertheless, to assess the direct applicability of these processes, they were all tried in San Ysidro without chlorine pretreatment, i.e., on the natural water as it came from the ground. It was suspected early in the study that point-of-use (POU) treatment using RO might be the only feasible alternative in the small

community of San Ysidro. This is because POU RO devices are operated at such low water recovery (10-20%) that membrane scaling and fouling are minimal compared to central RO treatment with 50-80% recovery. The reduced scaling at lower water recovery is, of course, due to the reduced brine concentration factor.

TABLE 7. ARSENIC(III) AND ARSENIC(V) CONCENTRATIONS IN THE SAN YSIDRO CITY WATER

No.	Date (1984)	As(III) µg/L	As(IV) µg/L	Total As µg/L	% As(III)
1 *	3-12	24	59	83	29
2 *	3-13	24	59	83	29
3 *	3-15	34	51	85	40
4	4-4	44	47	91	48
5	4-5	38			
6	4-6	44	47	91	48
7 *	4-19	28	46	74	38
8	4-20			75	
9	4-22	36	50	86	42
10	5-8			85	
11	5-22	22	62	84	26
12	5-28	26	60	86	30
13	6-2	28	63	91	31
14	6-4	26	74	90	18
15	6-5	40	56	96	42
16	6-7			98	
17	6-27	28	62	90	31
18	7-20			107	
19	7-23			101	
	$\overline{X}$, mean	31	57	89	35
	n, samples	14	13	18	
	s, std dev.	8.58	8.16	8.33	

* Samples 1, 2, 3 and 7 were taken directly from the tap; all others were from tank T- 1 where feedwater was exposed to air.

DESALTING PROCESS RESULTS

Electrodialysis Process Performance on Well No. 4

Immediately after the research trailer moved into San Ysidro and before the speciation tests, Well No. 4 water was treated using EDR to produce drinking water for Lin's family. EDR was used because it required no pretreatment and could simply be "turned on" to produce potable water. The product water was low in TDS and tasted good. Use of this water for drinking was stopped immediately, however, when arsenic analysis revealed 136 µg/L As(total) in the EDR product from a 188 µg/L As(total) feedwater. The supposition is that, although not yet speciated, the feed contained primarily molecular As(III) which was not removed by electrodialysis. Later, it was determined that the arsenic in Well No. 4 was 100% As(III). Thus, in retrospect, only 28% of the As(III) was removed by the EDR unit possibly by means of oxidation or adsorption/precipitation onto the membranes.

Electrodialysis Process Performance on City Water

The Ionics EDR unit was run for five days on city water with the results shown in Figure 7. The only pretreatment was the standard 10-micron cartridge filter and the granular activated carbon (GAC) filter for dechlorination (which was unnecessary since there was no Cl_2 in the feed). Averaging the effluent concentration histories in Figure 7, the EDR performance data in Table 8 were generated.

The overall removal of arsenic was 73%, which was higher than expected. No As(III) was found in the ED product water; when speciated, it was 100% As(V) even when analyzed within 30 minutes after sampling. The arsenic in the product water was probably As(III) that remained in the ED feedwater as it became product water during its passage through the membrane stack. The mechanism by which this As(III) was oxidized to As(V) in the product water was not determined in this study. Assuming 90% rejection of As(V), the calculated rejection of As(III) was 60% whereas we expected only 30% As(III) rejection based on the performance of ED on Well No. 4.

TABLE 8. ELECTRODIALYSIS PERFORMANCE DATA ON CITY WATER*

Constituent	Feed	Brine	Product	% Removal
pH	7.1	--	6.8	--
TDS, mg/L	810	--	227	72
As(total), µg/L	85	200	23	73
Fluoride, mg/L	2.4	8.0	0.43	82
Sulfate, mg/L	36	125	3.6	90
Bicarbonate, mg/L	552	1300	99	82
Chloride, mg/L	142	475	17	88

* Water recovery was 81%; run length was 5 days, and feed temperature was 12° C. Feedwater As(III) concentration was 34 µg/L.

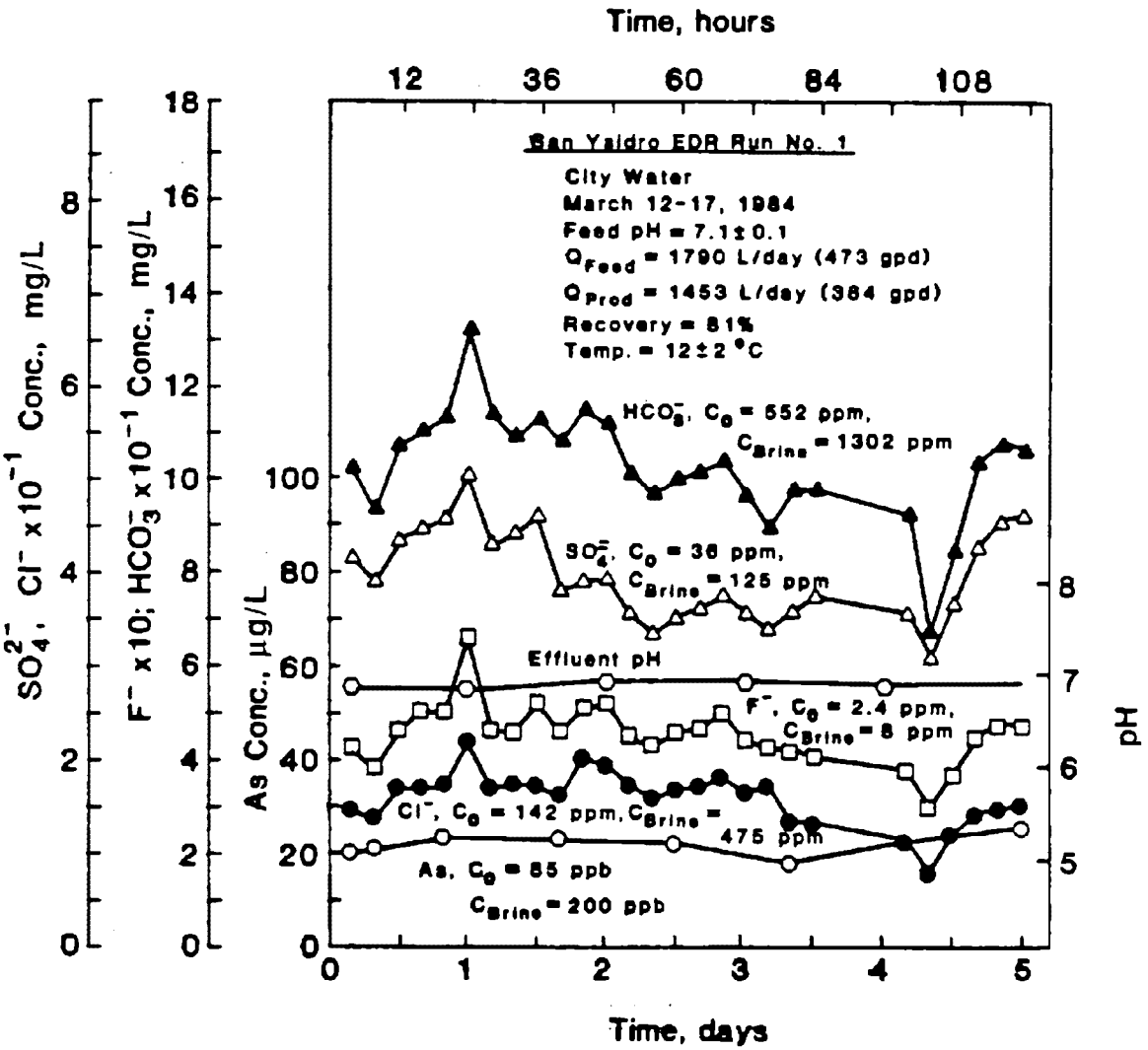


Figure 7. Results of EDR run no. 1, effluent concentration histories for anions during the EDR run with City Water feed and 81% recovery.

Close examination of the effluent concentration histories in Figure 7 reveals that the data during hours 86 through 96 were not plotted. During this time the stack becomes fouled due to membrane scaling by calcium carbonate, and the scale was removed using 10% HCl recycled through the unit. This acid cleaning procedure successfully regenerated the unit.

CELLULOSE TRIACETATE MEMBRANE RO RESULTS

Effluent concentration history data from an 8-day run of the Dow hollow fiber, cellulose triacetate (CTA) membrane module are plotted in Figure 8. The average performance of the system during the last 5 days of the run after the unit stabilized are shown in Table 9.

Although 20-50% As(III) passage was expected with the CTA membrane, it averaged less than 5%. In fact, nearly half the product water samples tested exhibited total arsenic values below the detection limit. During the last 5 days of the run, arsenic never exceed 4 µg/L. Because this Dow module had been used in four previous desalting studies, some residue or scale may have developed on the membrane and aided in the arsenic removal. However, based on the generally good overall performance of the Dow module (and the DuPont RO module) this excellent arsenic removal performance is expected from typical commercial installation of these units.

TABLE 9. DOW HF CTA RO PERFORMANCE DATA

Constituent	Feed	Brine	Product	% Removal
pH	6.3	--	5.0	--
TDS, mg/L	922	1785	57.0	94
As(total), µg/L	91	168	1.0	99
Fluoride, mg/L	2.4	4.8	0.15	94
Sulfate, mg/L	286	543	6.5	98
Bicarbonate, mg/L	256	487	18.0	93
Chloride, mg/L	138	267	9.0	93

* Sulfuric acid was added for pH adjustment, water recovery was 50% and feed temperature was 12°C. Feedwater As(III) was 42 µg/L.

POLYAMIDE MEMBRANE RO RESULTS

The performance of the DuPont hollow fiber polyamide (PA) RO module is shown in Figure 9 and summarized in Table 10. The DuPont polyamide membrane clearly performed better than the other desalting processes for all contaminants, especially arsenic which was undetectable in the product water. Again, this essentially complete removal of arsenic, including As(III), was not expected. The high arsenic rejection agreed with the results obtained with the Dow module and the Culligan point-of-use RO system. The better performance of the PA membrane compared to CTA may have been due to the higher pH of the feedwater for PA (pH = 7.6) compared to CTA (pH = 6.3).

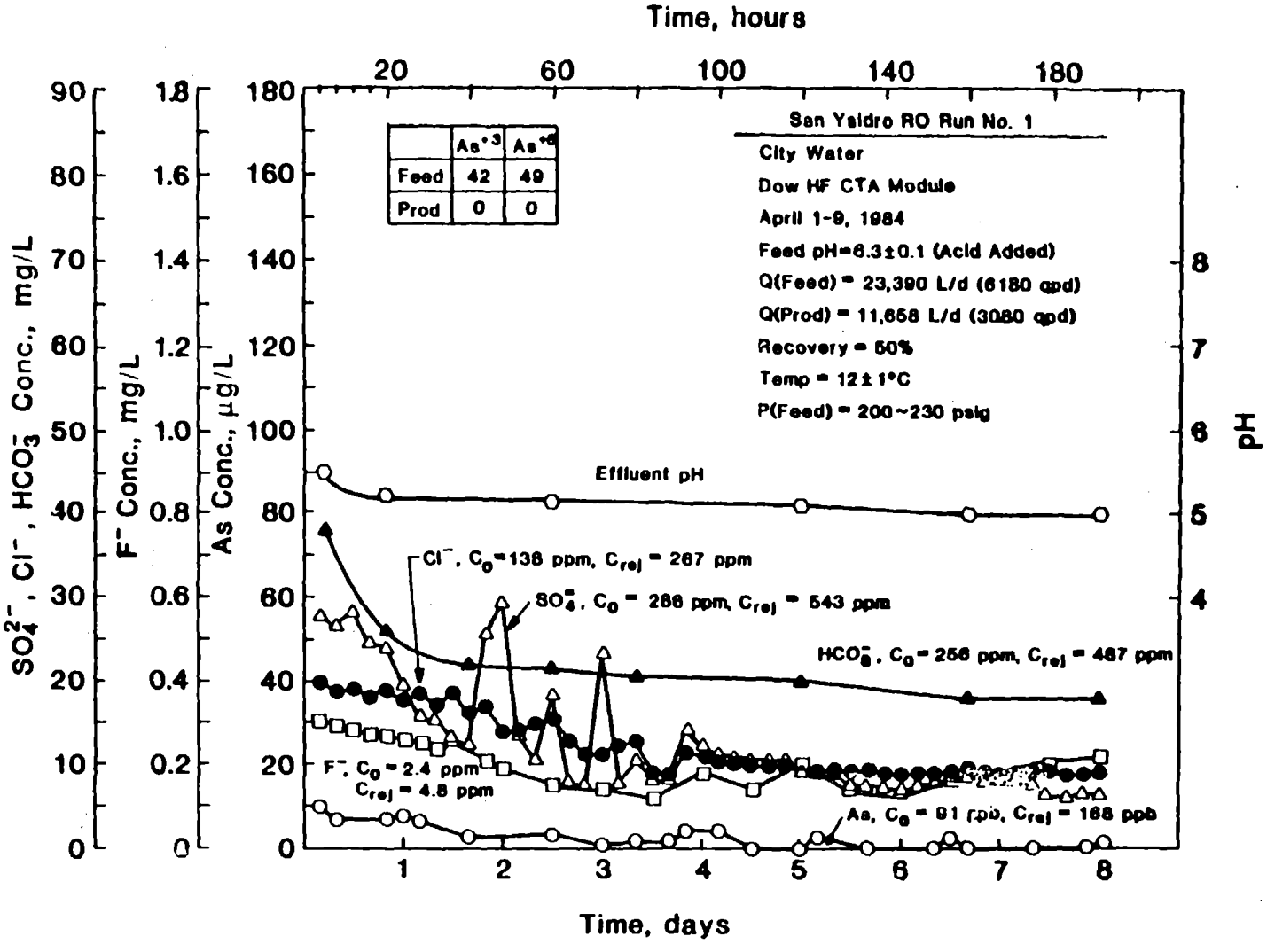


Figure 8. Results of DOW RO Run, effluent, concentration histories for the DOW HF CTA RO system operated at 50% recovery on San Ysidro City Water.

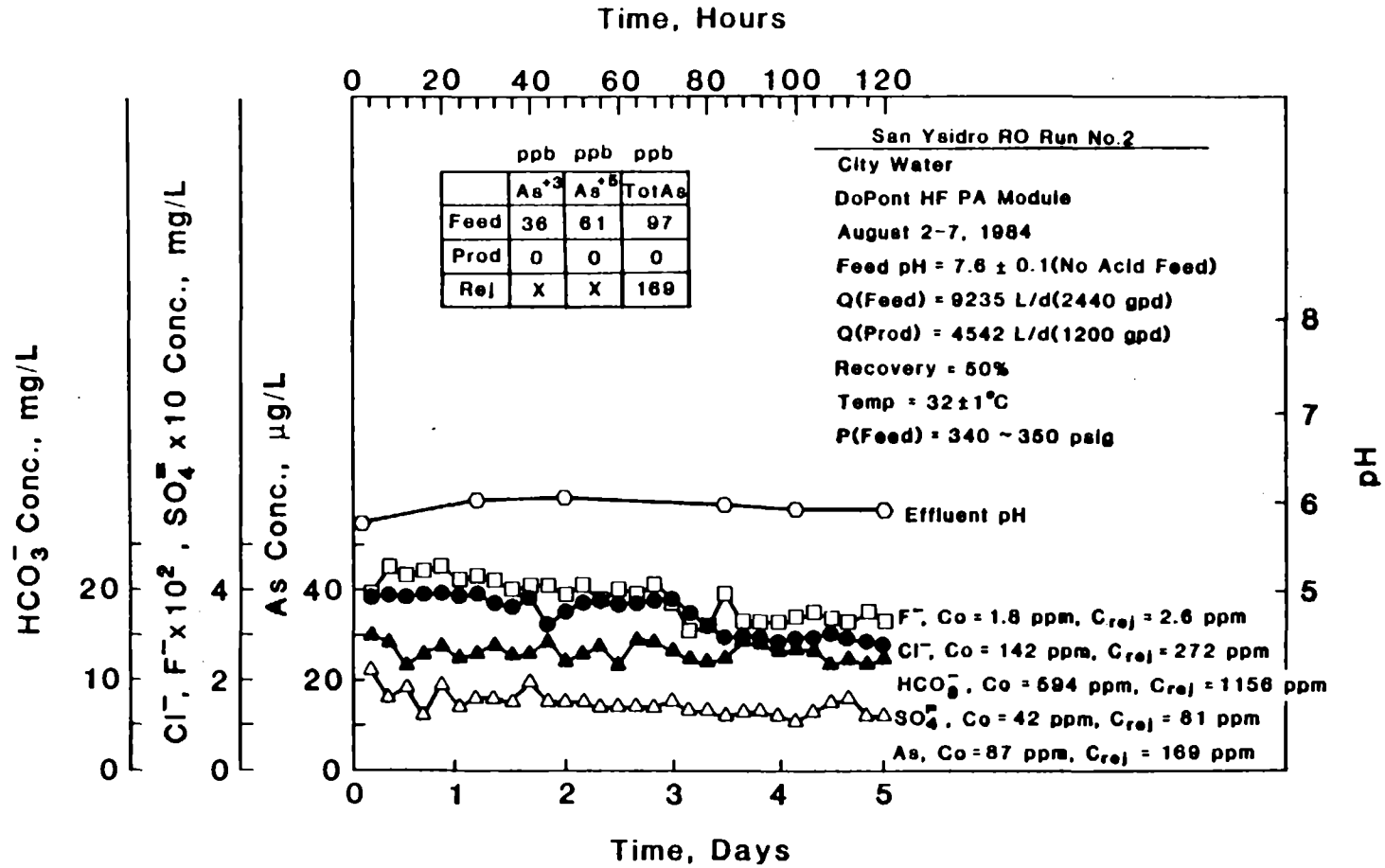


Figure 9. Results of DuPont RO run no. 2, effluent concentration histories for the DuPont HF PA RO system operated at 50% recovery on San Ysidro City Water.

TABLE 10. DUPONT HF PA RO PERFORMANCE DATA

Constituent	Feed	Brine	Product	% Removal
pH	7.6	--	6.0	--
TDS, mg/L	924	1841	27.0	97
As(total), µg/L	87	169	nd	> 99
Fluoride, mg/L	1.8	2.6	0.04	98
Sulfate, mg/L	42	81	0.15	> 99
Bicarbonate, mg/L	594	1156	12.0	98
Chloride, mg/L	142	272	3.5	98

* nd = not detected. Run length was 5 days. No acid was added, feed temperature was 23ºC, and feedwater As(III) was 36 µg/L.

A Comparison of the Desalting Processes

Table 11 summarizes and compares the performance of the EDR and RO units. Based on percent removal of contaminants, the polyamide membrane was clearly the best giving 97% TDS removal and greater than 99% arsenic removal at 50% recovery with a single pass. As predicted, electrodialysis gave the poorest removal of arsenic--presumably because molecular As(III) could not be transported out of the feedwater using electrical current. The lower TDS removal by the ED process is in part attributed to the higher (80%) water recovery compared to the RO unit (50%). Electrodialysis cannot be recommended if As(III) removal is a major criterion. This conclusion is in contrast to those made using ED for fluoride, nitrate or chromate removal in previous studies where ED performed equal to 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).

TABLE 11. SUMMARY OF EDR AND RO RESULTS ON SAN YSIDRO CITY WATER

Parameter	ED §	Dow RO HF ‡ Cellulose Triacetate	Dow RO HF Polyamide
Run Length, days	5	8	5
Pretreatment *	Filt	pH, SHMP, Filt.	SHMP, Filt.
Water Recovery, %	81	50	50
TDS Removal, % †	72	94	97
Arsenic Removal, %	73	> 97	> 99

(continued)

TABLE 11. (continued)

Parameter	ED §	Dow RO HF ‡ Cellulose Triacetate	Dow RO HF Polyamide
Fluoride Removal, %	82	94	98
Sulfate Removal, %	90	98	> 99
Bicarbonate Removal, %	82	93	98
Chloride Removal, %	88	93	98
Conductivity Reduction, %	80	94	97
Feed pH	7.2	6.3	7.6
Product pH	6.8	5.0	5.9
Temperature, °C	12.0	12.0	23.0

* For pretreatment, pH means pH reduction using sulfuric acid; SHMP means addition of 10 mg/L sodium hexametaphosphate; Filt is 10 micron cartridge filtration.

† removal shown are based on average product concentration after the run stabilized.

§ ED is electrodialysis with intermittent current reversal.

‡ HF is Hollow Fiber.

ACTIVATED ALUMINA RESULTS

Typical Alumina Breakthrough Curves at pH 6.0

Figure 10 presents the typical breakthrough curves for fluoride and arsenic in the effluent from the activated alumina column during Run No. 2, one of eight alumina runs made. Fluoride broke through first and reached 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 12 -- the summary of the alumina results, and in Table 13 -- a comparison of the fluoride and arsenic run lengths.

Complete effluent concentration histories (breakthrough curves) of all the alumina runs are presented in chronological order in Appendix C, where exhaustion runs are the even-numbered figures and regenerations are the odd-numbered figures in the C1-C15 series.

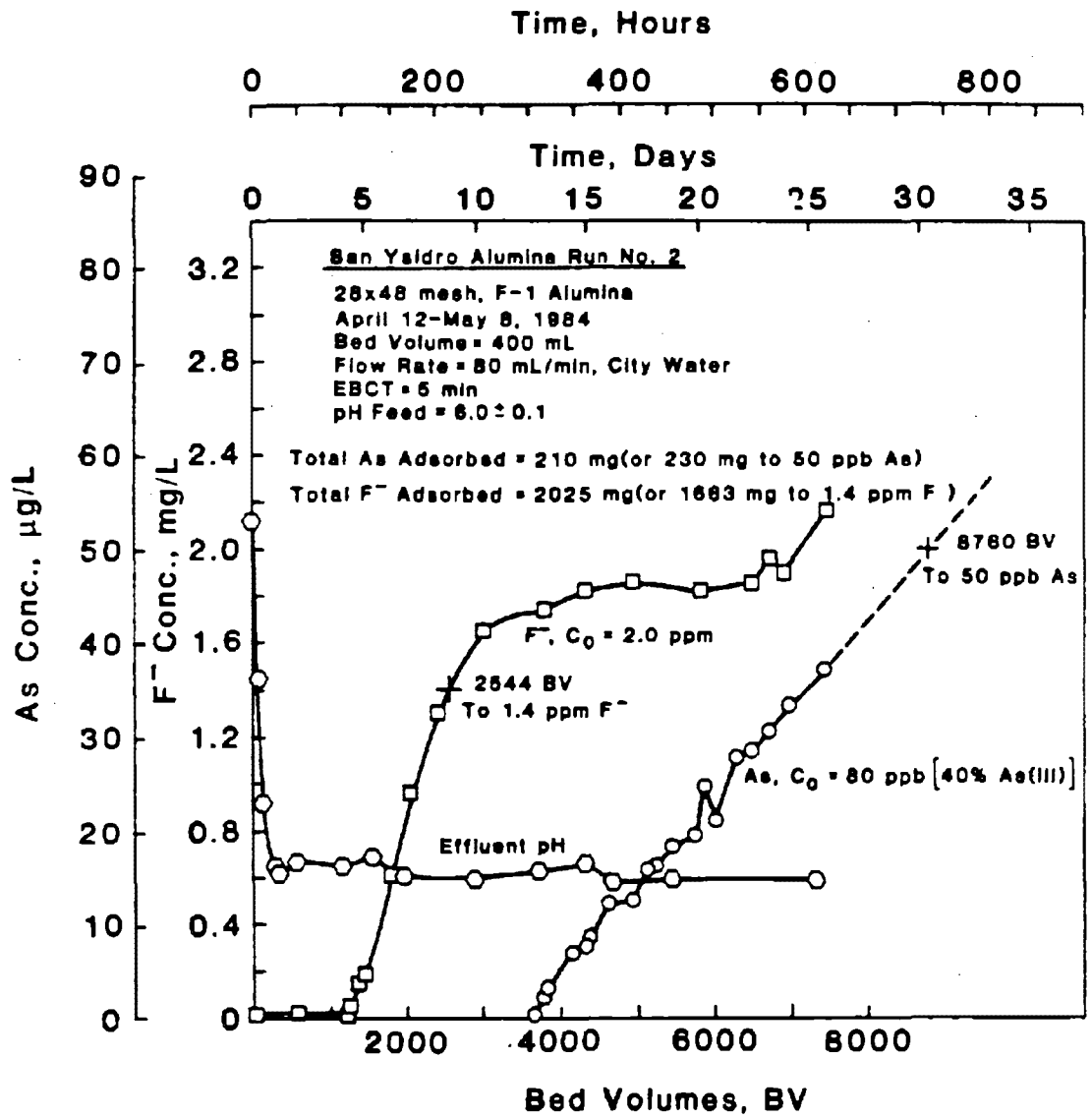


Figure 10. Breakthrough curves for fluoride and arsenic from 28 x 48 mesh activated alumina columns, Run No. 2.

TABLE 12. SUMMARY OF ACTIVATED ALUMINA RESULTS

Run No.	1	2	3	4	5	6	7	8
Mesh Size	1428 Coarse	28-48 Fine	14-28 Coarse	28-48 Fine	14-28 Coarse	28-48 Fine	28-48 Fine	14-28 Coarse
Condition §	new	new	1xReg.	2xReg.	2xReg.	2xReg.	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/L F^-	3084	2544	2376	2376	1740	2040	547	–
g/m^3 F^- Adsorbed to 1.4 mg/L F^-	3870	4160	3063	3870	2260	3130	925	–
BV to 50 µg/L As	6840	8760	5880	8040	4500	6300	1944	252
g/m^3 As Adsorbed to 50 µg/L As	390	575	380	575	305	493	175	53

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

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

§ 1 x Reg. = once regenerated; 2 x Reg. = twice regenerated.

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

TABLE 13. COMPARISON OF FLUORIDE AND ARSENIC RUN LENGTHS USING ACTIVATED ALUMINA

Run	Mesh	Condition	Days to 1.4 mg/L F^-	Days to 50 µg/L As
1	Coarse	New	10.8	23.8
3	Coarse	1 x Regenerated	8.1	20.4
5	Coarse	2 x Regenerated	6.0	15.6
2	Fine	New	9.0	30.4
4	Fine	1 x Regenerated	8.1	27.9
6	Fine	2 x Regenerated	7.1	21.9

Expected Breakthrough Curves for As(III) and As(V)

In a related study [Frank and Clifford, 1986] laboratory alumina-run simulations were made using 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). This comparison is presented in Figure 11, and a list of the potentially competing anions in the various feedwaters is given in Table 14. Finally, the bed volumes (BV) to fluoride and arsenic breakthrough for the As(III) and As(V) laboratory waters and the San Ysidro City Water are summarized in Table 15.

TABLE 14. BACKGROUND WATER ANALYSES FOR FIGURES 11 AND 12

Constituent	Simulated Groundwaters As(III)	Simulated Groundwaters As(V)	San Ysidro City Water
As(III), µg/L	100	0	32
As(V), µg/L	0	100	57
As(total), µg/L	100	100	89
Fluoride, mg/L	3.0	3.0	2.0
Sulfate, mg/L	384	384	365
Chloride, mg/L	71	71	123
pH	6	6	6

* Sulfate was measured after pH adjustment to 6.0 using sulfuric acid.

TABLE 15. COMPARISON OF LABORATORY AND FIELD DATA FOR FLUORIDE AND ARSENIC REMOVAL

	UH Laboratory Tests Simulated Groundwaters As(III)	UH Laboratory Tests Simulated Groundwaters As(V)	Field Test San Ysidro City Water
BV to 0.05 mg/L As	300	23,400	8,760
Arsenic capacity, g/m^3	18	1,610	575
BV to 1.4 mg/L F^-	1,600	1,550	2,520
Fluoride capacity, g/m^3	4,190	4,280	4,160

* The anionic composition of the waters is given in Table 14.

From the above comparison, the arsenic breakthrough curve for a mixture of As(III) and As(V) falls between that of pure As(III) and pure As(V). Furthermore, oxidizing the San

Ysidro city water to 100% As(V) will approximately triple the alumina run length to about 24,000 BV at pH 6.0.

The shape of the San Ysidro arsenic breakthrough curve (Figure 10) was delayed and surprisingly sharp. A much earlier As(III) breakthrough was expected based on the lab simulation data--Figure 11, As(III), Run No. 1. 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. Furthermore, in the lab study the pentavalent arsenic breakthrough curve (Figure 11, As(V), Run No. 2) showed early leakage of As(V). This was probably due to the lab column's shorter EBCT (3 min compared to 5 min in the field), its shallow bed depth (15.8 cm) and the fact that its adsorption zone was a large fraction of the bed depth.

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

Effect of Mesh Size on Arsenic and Fluoride Removal

Figure 12, representing the arsenic breakthrough curves for San Ysidro Runs 1 and 2 illustrates that the mesh size of the alumina has a dramatic effect on its performance for arsenic removal. The summary data are listed in Table 12 where it can be seen that the coarse mesh grade treats 6840 BV to the arsenic MCL while the fine mesh can treat 8760 BV with resulting arsenic capacities of 390 g/m^3 for the coarse and 575 g/m^3 for the fine-mesh adsorbent. Such large differences between coarse and fine were not noted during fluoride removal, however.

Figure 13 compares the fluoride breakthrough curves for coarse- and fine-mesh aluminas. Considering the entire run, i.e., up to about 6000 BV, the coarse and fine-mesh aluminas adsorbed almost exactly the same amount of fluoride--4830 g/m^3 and 5060 g/m^3 respectively. The adsorption kinetics of the fine mesh alumina are better, of course, so less fluoride leakage resulted during the first 2000 BV compared to the coarse variety. This improved fluoride removal by the fine-mesh alumina early in the run is, however, compensated for by a slightly superior performance of the coarse alumina during the later portion of the run. Similar behavior might have been observed for arsenic had we run the columns far beyond the MCL of 0.05 mg/L. In theory, the mesh size of the alumina should not significantly affect the equilibrium adsorption capacity.

Effect of pH on Alumina's Adsorption Capacity

Not reducing the pH of the feedwater to the optimum range of 5-6 results in a drastic loss in both the arsenic and fluoride removal capacity of alumina. This loss is evident in Table 16 and in the arsenic breakthrough curves for City Water (Figure C11) and Well No. 4 water (Figure C13) at their natural pH's of 7.3 and 7.1, respectively.

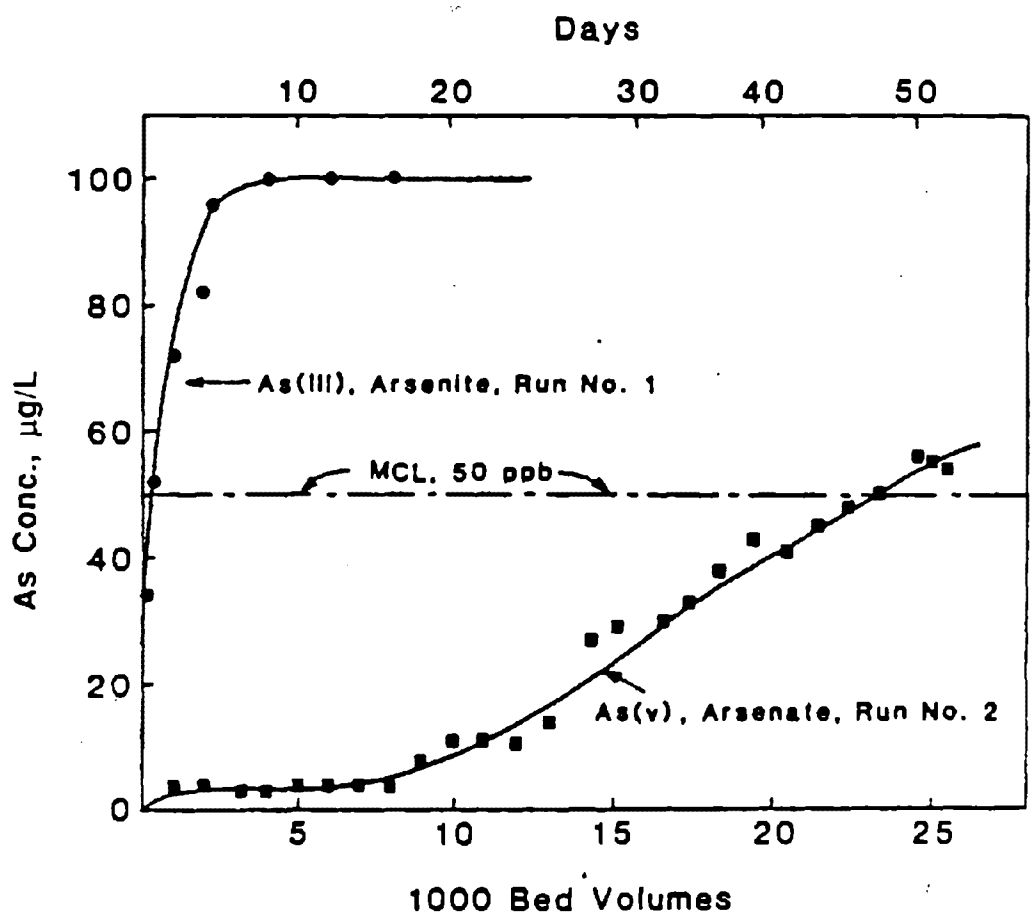


Figure 11. Comparison of pure As(III) or pure As(V) breakthrough curves from minicolumns of activated alumina being fed synthetic waters containing 100 µg/L arsenic and 3 mg/L fluoride.

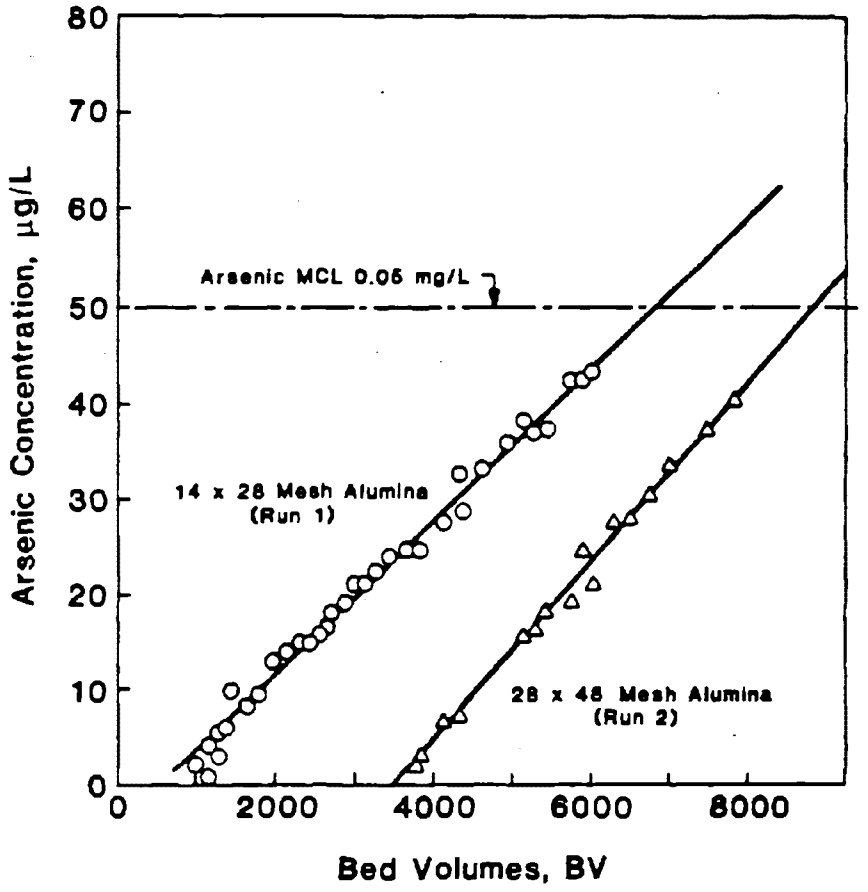


Figure 12. Comparison of arsenic breakthrough curves for coarse (14 x 28) and fine (28 x 48) mesh aluminas.

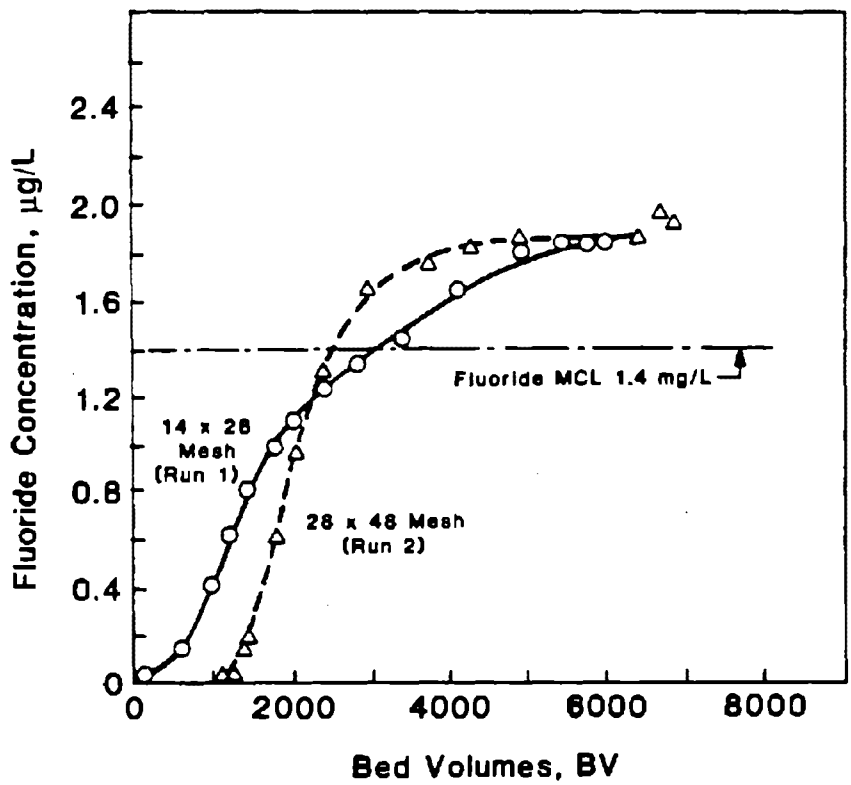


Figure 13. Comparison of fluoride breakthrough curves for coarse (14 x 28) and fine (28 x 48) mesh aluminas.

TABLE 16. CHANGES IN ADSORPTION CAPACITY AS A FUNCTION OF pH AND ARSENIC CONCENTRATION

Run No.	Mesh	Feed Condition µg/L As	pH	BV to 50 µg/L As	BV to 1.4 mg/L F^-
2	Fine	90	6.0	8760	2544
7	Fine	90	7.3	1944 (22%)	547 (22%)
1	Coarse	90	6.0	6840	
8*	Coarse	250	7.1	252 (4%)	

* Run No. 8 was made with Well No. 4 water (100% As(III); Runs 2, 7 and 1 were with City Water (40% As(III)).
(%) Values in parentheses are % of optimum BV at pH 6.0.

The effect of varying both arsenic concentration (from 90 to 250 µg/L) and pH (from 6.0 to 7.1) are seen by comparing Runs 1 and 8 in Table 16. The high, trivalent arsenic concentration and unadjusted feedwater pH during Run 8 resulted in a run length (252 BV) which was only 4% of that using city water at pH 6.0. These unadjusted-pH runs were made to illustrate the short run lengths which would occur in the simplest point-of-use treatment systems compared to a pH-optimized system.

The Regeneration of Spent Alumina

Fluoride is more easily and completely eluted from the exhausted alumina during NaOH regeneration than is arsenic. This is evident in Figure 14 containing typical regeneration elution curves and in the series of exhaustion-followed-by-regeneration figures in Appendix C. The fluoride elution curve always begins slightly ahead of the arsenic curve and the arsenic elution curve has a much longer tail. The alumina regeneration conditions are summarized in Table 17 where the percent arsenic recoveries are also summarized.

TABLE 17. ACTIVATED ALUMINA REGENERATION SUMMARY § # @

Run	NaOH Conc. N	BV NaOH	Equiv.NaOH / L Alumina	Arsenic Adsorbed mg	Arsenic Recovered mg	Arsenic Recovered %
1* ‡	1.0	6.5	6.5	146	85	58
3*	0.25	18.0	4.5	142	92	65
5*	0.25	16.0	4.0	136	91	67
2† ‡	1.0	6.7	6.7	210	132	63
4†	0.25	19.0	4.8	212	148	70
6†	0.25	15.3	3.8	198	133	67

* Coarse activated alumina (14 x 28 mesh) was used for the sequence of runs 1, 3 and 5.

† Fine activated alumina (28 x 48 mesh) was used for the sequence of runs 2, 4 and 6.

§ All regenerations were cocurrent (downflow) at a rate of 0.5 gal/minft^3(EBCT=15.4min).

‡ The regeneration times were 100 minutes for runs 1 and 2 and 240 minutes for the others.

@ All regenerations were excessive in order to remove as much arsenic as possible and to provide the data to establish Figures 15a-d and 16a-b.

All regenerations were followed by neutralization with 2% H_2SO_4 (0.41 N) until effluent pH was 5.0 or less.

To convert equiv. NaOH/L alumina to lbs NaOH/ft^3 alumina, multiply by 2.50.

The higher efficiency of fluoride compared to arsenic recovery is more clearly illustrated in Figures 15a-d. Where, at any give dose of NaOH (on the x-axis) a higher percentage of fluoride is eluted compared to arsenic. In these figures, fluoride or arsenic recovered is plotted as a function of the equivalents of NaOH added per liter of spent alumina. Figures 15a and 15b are for 4% (1.0 N) NaOH regenerant while Figures 15c and 15d are for 1% (0.25 N) NaOH. The weaker regenerant (1% NaOH) is usually recommended for fluoride removal [Rubel, 1984] because higher concentrations are considered wasteful and unnecessariily corrosive. The higher (4% NaOH) concentration was used because, although more corrosive to the alumina, it had been found to be more effective than 1% NaOH for arsenic(V) recovery from alumina [Clifford and Chou, 1987].

In all the Figures (15a-d), the percent recovery is based on what was eluted during the entire regeneration not on what was adsorbed during the exhaustion. This approach is not unreasonable because, as can be seen in the Appendix C regeneration curves (even-numbered figures in the C1-C15 series), the amounts of regenerant used were always in excess of that which was considered necessary. Thus, we expect that nearly all the fluoride or arsenic "reasonably" recoverable was, in fact, recovered during these excess regenerations. Fluoride was always more efficiently eluted than arsenic, i.e., less NaOH was invariably required to elute fluoride compared to arsenic. With the coarse alumina, for example, it can be seen in Figure 15a that 3 BV of 4% NaOH elute 94% of the recoverable fluoride but only 77% of the arsenic. Note that in Figures 15a-d the BV of regenerant is measured from the time of first appearance of fluoride or arsenic.

A comparison of the fluoride and arsenic recovery efficiencies is presented in Table 18. For both fluoride and arsenic removal, 3.0 equiv. of the dilute (1%) NaOH/L alumina eluted more arsenic than the concentrated (4%) NaOH. The fine-mesh alumina permitted higher arsenic recoveries with both the 1% and 4% NaOH solutions.

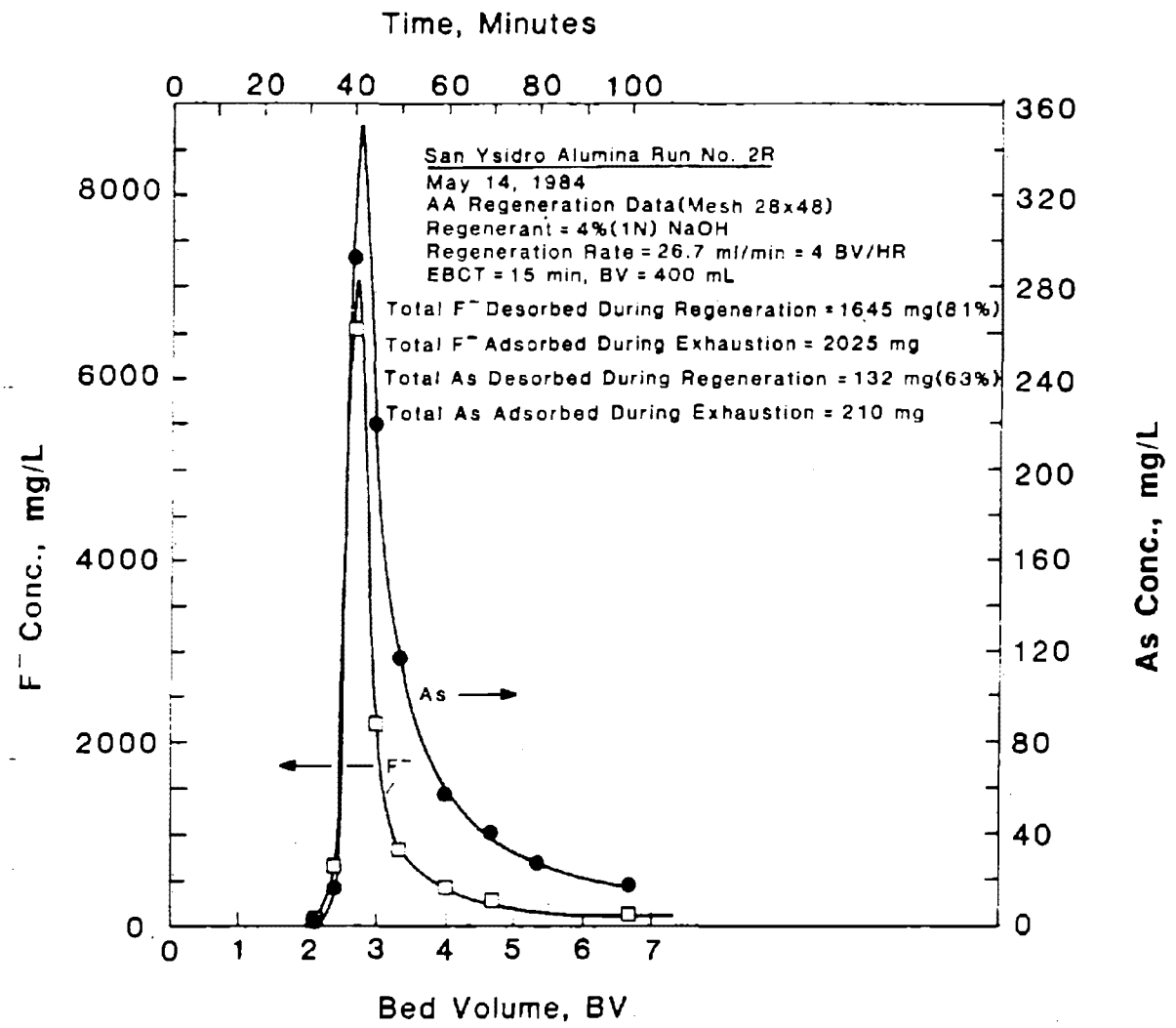


Figure 14. Arsenic and fluoride elution during a regeneration of fine-mesh alumina using 4% NaOH. Run 1R--regeneration following exhaustion Run No. 2.

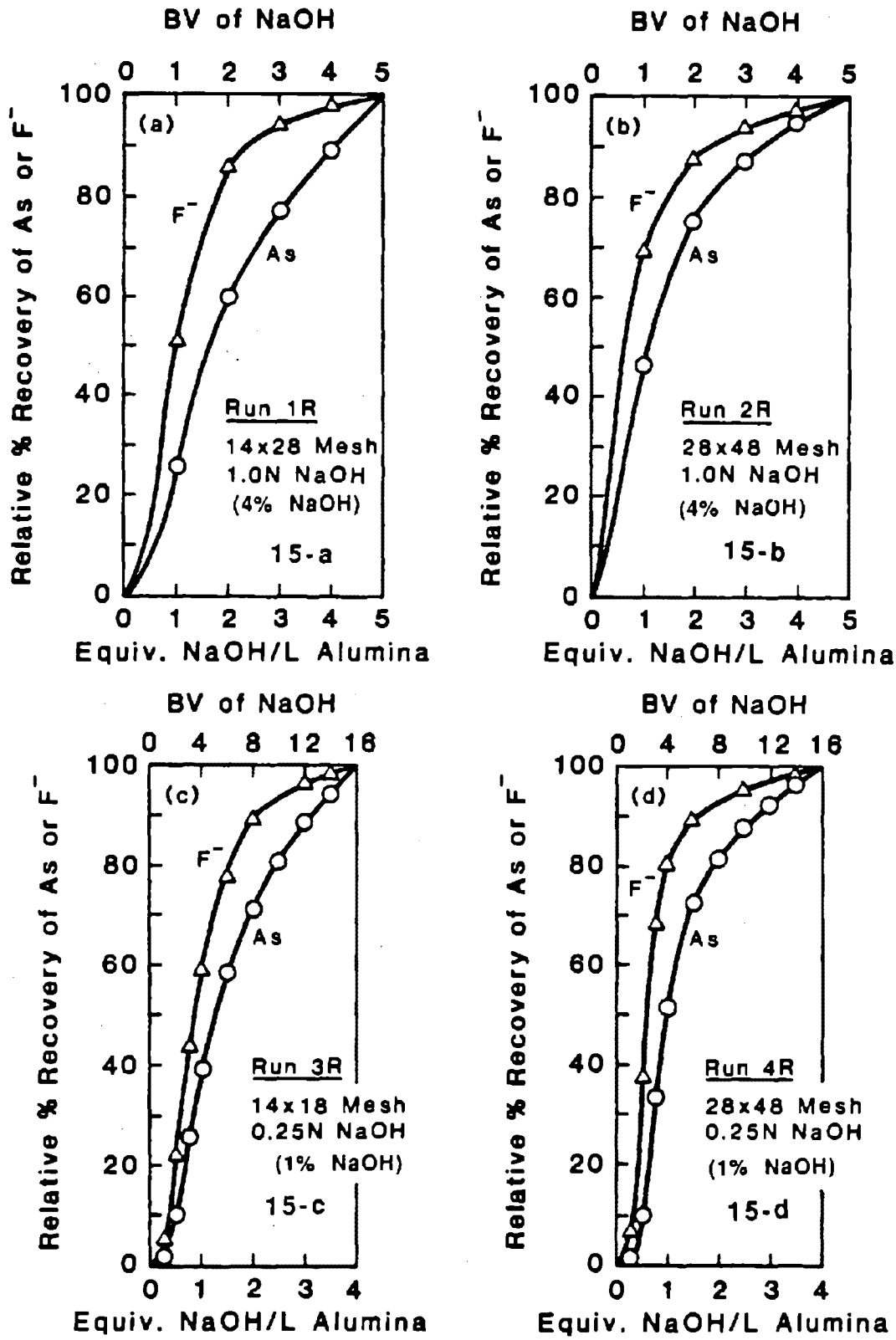


Figure 15. Relative % arsenic or fluoride recovery as a function of quantity of NaOH regenerant.

TABLE 18. RELATIVE PERCENT RECOVERIES OF FLUORIDE AND ARSENIC USING 3.0 EQUIV. NaOH/L ALUMINA

Species Eluted	Relative % Recoveries for fine alumina		Relative % Recoveries for coarse alumina	
	1% NaOH	4% NaOH	1% NaOH	4% NaOH
Fluoride	97	93	96	94
Arsenic	93	87	89	77

* 3.0 equiv. NaOH/L media represents 3 BV of 4% (1.0 N) NaOH and 12 BV of 1% (0.25 N) NaOH. % recoveries are relative to the recovery of As or F^- at a maximum regeneration level of 5 equiv. NaOH/L alumina.

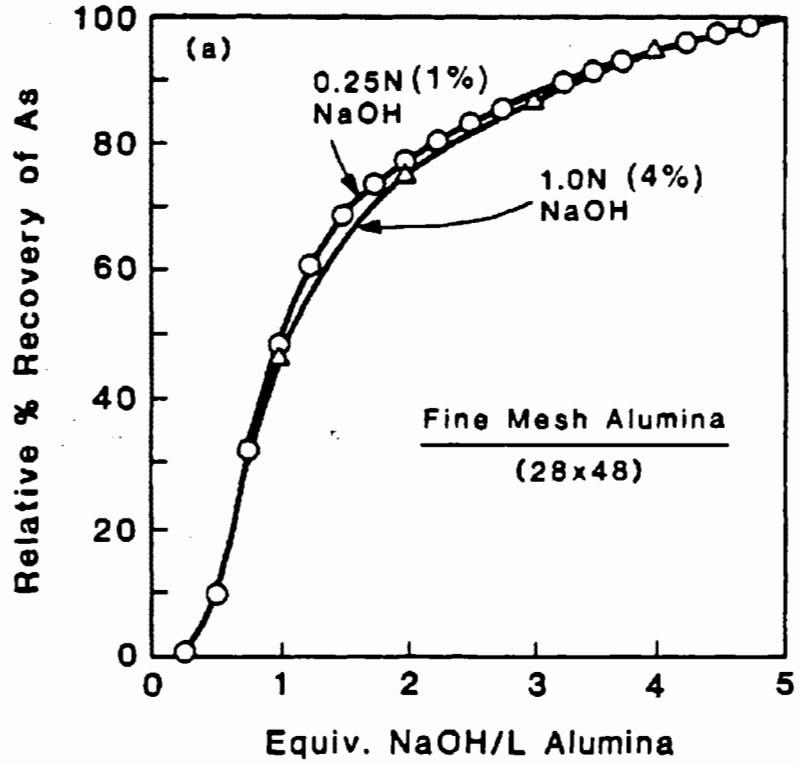
It is useful to compare the slopes of the fluoride and arsenic recovery curves at 100% relative recovery in Figures 15a-d. In all cases, the fluoride slope is flatter than that for arsenic, indicating a small percent increase in fluoride recovery with the last increment of regenerant applies. The percent increase in arsenic recovery, on the other hand, is quite large for the last increment of regenerant added especially with the coarse alumina (Figure 15a).

An interpretation of the data in Figure 15d, fine-mesh alumina regenerated with 1% NaOH, lends support to the regeneration recommendations of Rubel [1984] in his fluoride removal design manual. Rubel recommends 4 BV of 1% NaOH (i.e., 1.0 equiv. NaOH/L alumina) for fluoride elution in a procedure consisting of:

2 BV	1% NaOH, upflow
4 BV	water slow rinse, upflow
2 BV	1% NaOH, downflow
24 BV	pH 2.5 H_2SO_4, neutralization downflow

Assuming that the NaOH is still effectively regenerating the alumina during the slow rinses as suggested by Clifford and Chou [1987], about 8 BV of "effective regenerant" are being applied during Rubel's procedure. In Figure 15d it may be seen that 8 BV of 1% NaOH elutes a respectable 93% of the recoverable fluoride in agreement with his recommendation. We do not believe, however, that upflow regeneration is necessary for fluoride removal systems. This complicated procedure is generally used only to eliminate contaminant leakage during the subsequent exhaustion run--an unnecessary consideration in fluoride removal where fluoride leakage is tolerable due to the high MCL, and is unavoidable due to alumina's poor adsorption kinetics. Upflow regeneration may, however, be of some use in arsenic removal applications but that is yet to be proven, and it is doubtful that the upflow-then-downflow sequence is necessary even for arsenic removal.

The debate as to whether 1% or 4% NaOH is preferred for regeneration of arsenic-spent alumina is at least partially resolved by examining Figures 16a and 16b. For the fine mesh alumina (Figure 16a), the percent recoveries of arsenic for 1% and 4% NaOH were the same as a function of the equivalents of NaOH added per liter of alumina. However, for the coarse alumina (Figure 16b) the dilute NaOH was a slightly more efficient regenerant.



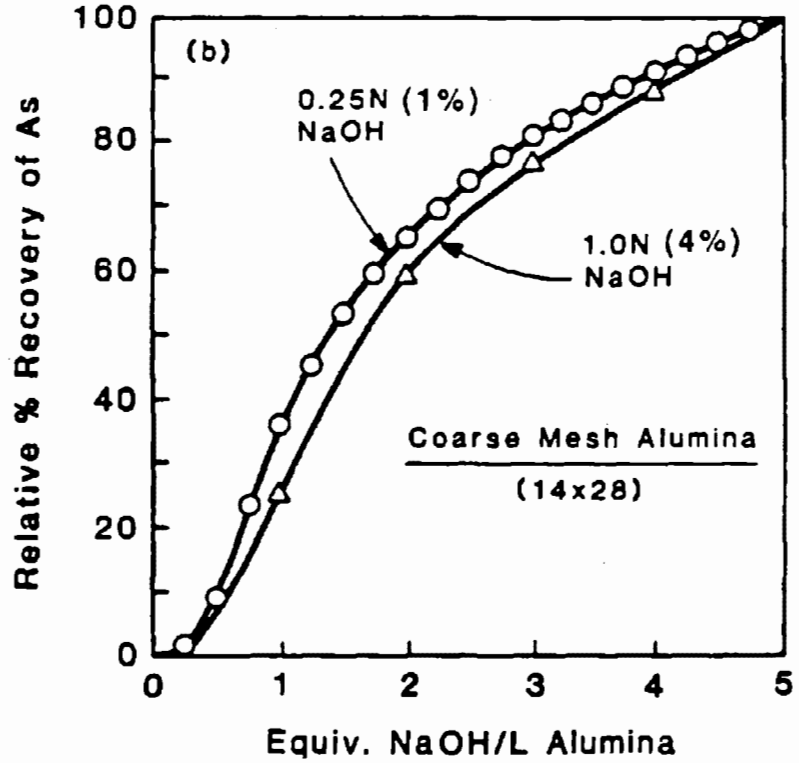


Figure 16. Comparison of arsenic recovery efficiencies of 1% and 4% NaOH for regeneration of fine- (16-a) and coarse-mesh (16-b) aluminas.

Dilute 1% NaOH (0.25 N) is less hazardous and less corrosive to the alumina; these are further reasons to prefer it to the 4% (1.0 N) NaOH for regeneration. It was, however, found in a previous laboratory study of alumina regeneration [Clifford and Chou, 1987] that the dissolution of alumina by NaOH (and H_2SO_4) is a function of exposure time and concentration. Thus, dilute regenerants can be just as corrosive as concentrated ones at correspondingly longer regeneration times. For example, using equal regenerant flow rates and equivalents of NaOH/L alumina, the 1% solution would take four times longer to apply than a 4% solution, and nearly the same degredation (dissolution) of the media would result. Furthermore, a dilute regenerant yields a proportionately larger volume of spent regenerant, and this can be a critical, negative factor in application where spent regenerants are difficult to dispose of.

In summary, both 1% and 4% regenerants are feasible for regeneration. The 1% solution is probably somewhat less corrosive and hazardous, although one has to deal with it, 100% NaOH (flakes or pellets) or concentrated (40-50%) NaOH liquid when preparing either solution. The advantage of 4% NaOH is that regeneration time and spent regenerant volume are reduced. Rubel and Hathaway [1985] used 4% NaOH to successfully regenerate As(V) spent alumina in their Fallon, Nevada pilot study. Of course, regenerant concentrations are not limited to 1% and 4% NaOH.

The comments regarding the strength of NaOH also apply to the H_2SO_4 used for neutralization following regeneration. Neutralization of the NaOH-laden column with a relatively concentrated 2% H_2SO_4 (0.4 N) solution applied at the same flow rate (3.9 BV/hr) as the regenerant immediately following regeneration is preferred. This procedure is believed to be simpler than the procedure recommended above by Rubel [1984] for fluoride removal applications.

Effect of Regeneration on Adsorption Capacity

The breakthrough curves for fluoride adsorption on fine alumina are only slightly affected by one or two regenerations as shown in Figure 17. A single curve has been drawn through the fluoride effluent data points for fresh, once- and twice-regenerated alumina. It appears that very little change in fluoride capacity has occurred due to the regeneration procedure. However, a slight but clear tendency exists toward earlier fluoride breakthrough with subsequent regenerations.

Regenerations have a clearly negative effect, however, on the arsenic breakthrough curves as shown in Figures 18 and 19. After two regenerations, the BV to 50 μg/L As for the coarse-mesh alumina (Figure 18) dropped to 4500 from 6840, i.e., a 34% reduction. A summary of the reduction in arsenic capacity is presented in Table 19 where the reduction in arsenic capacity was smaller for the fine- as compared to the coarse-mesh alumina. The data in Table 19 shows the reduction due to the first regeneration (7 BV of 4% NaOH) were smaller than those for the second regeneration (18 BV of 1% NaOH) for both the coarse and fine aluminas. This observation suggests that a shorter regeneration (100 minutes) with stronger caustic (4%) is preferred to the longer regeneration (240 minutes) with dilute (1%) caustic. However, this suggestion is based on using little data. Furthermore, the decay of arsenic capacity upon regeneration may simply be nonlinear. More work on this area was done during the arsenic removal study in Hanford, California [Clifford and Lin, 1987].

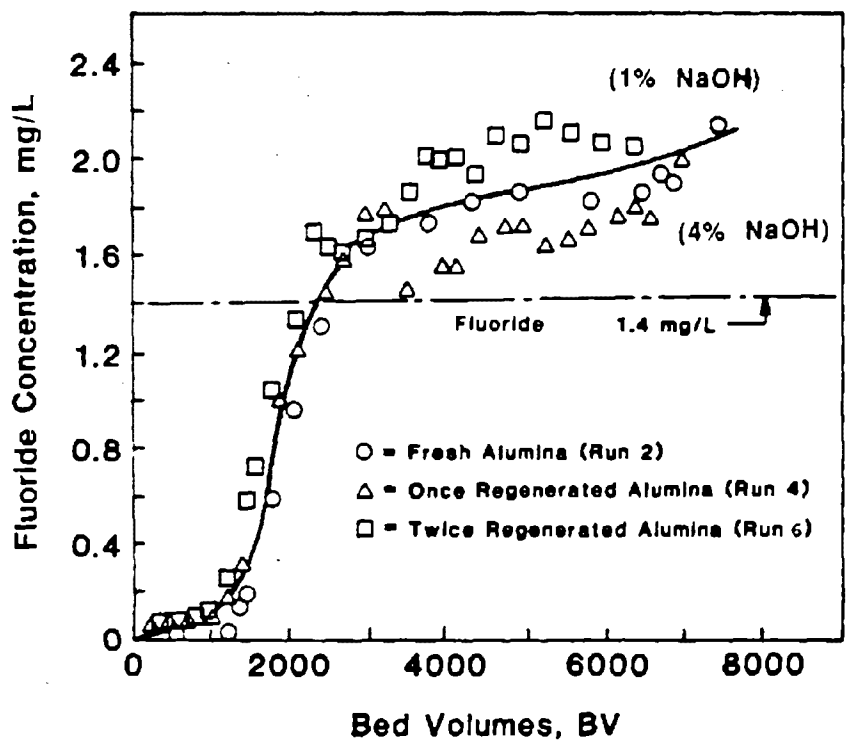


Figure 17. Effect of cocurrent regenerations on the fluoride breakthrough curves for fine-mesh (14 x 28) aluminas. First regeneration was made with 4% while the second was made with 1% NaOH.

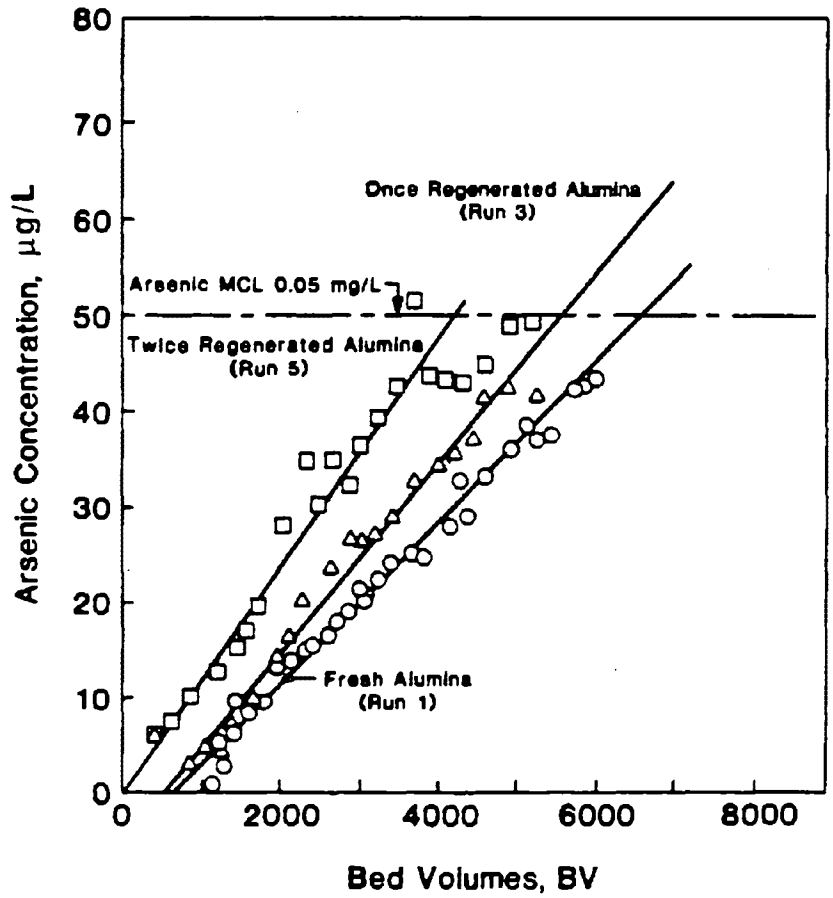


Figure 18. Effect of cocurrent regenerations on the arsenic breakthrough curves for coarse-mesh (14 x 28) alumina. First regeneration was made with 4% while the second was made with 1% NaOH.

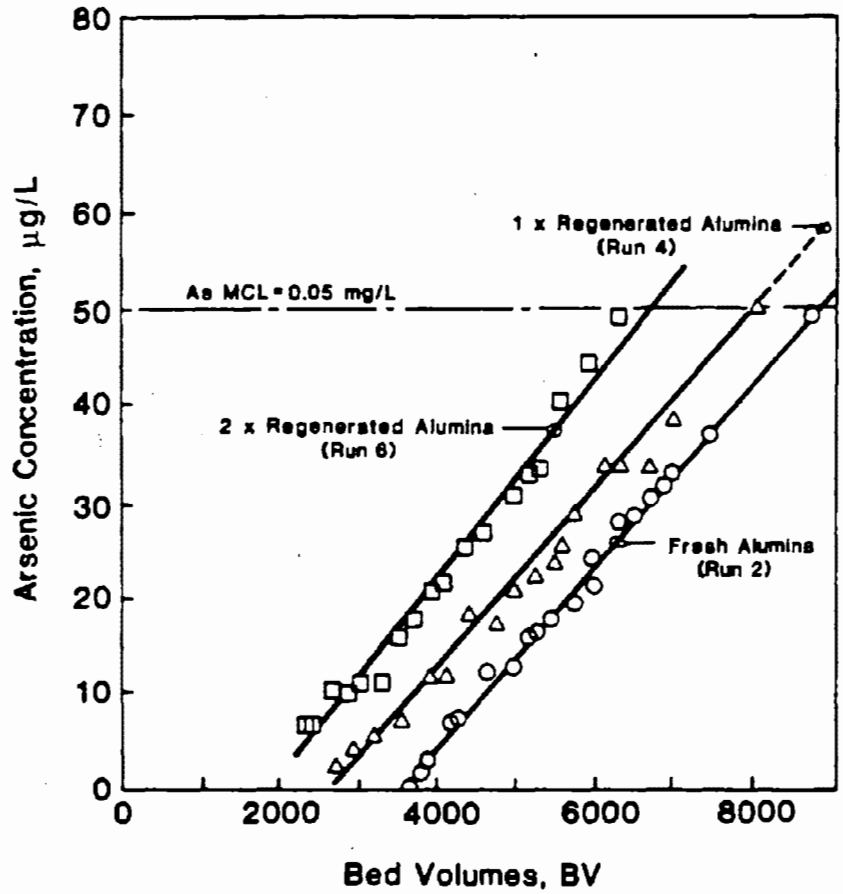


Figure 19. Effect of cocurrent regenerations on the arsenic breakthrough curves for fine-mesh (14 x 28) alumina. First regeneration was made with 4% while the second was made with 1% NaOH.

TABLE 19. REDUCTION IN ALUMINA'S ARSENIC REMOVAL CAPACITY WITH REGENERATION

Run No.	Mesh	Condition	BV to 50 µg/L As *	Percent of Original BV
1	Coarse †	Fresh	6840	100
3	Coarse	After first (4%) regen.	5880	86
5	Coarse	After second (1%) regen.	4500	66
2	Fine †	Fresh	8760	100
4	Fine	After first (4%) regen.	8040	92
6	Fine	After second (1%) regen.	6300	72

* BV to 50 µg/L As are based on the data in Table 12.

† For each series, i.e., coarse or fine alumina, the first regeneration was made with 4% while the second was made with 1% NaOH.

Rubel and Hathaway [1985], in their recently completed As(V) removal study in Fallon, Nevada, used 4-5% NaOH upflow followed by downflow for regeneration of arsenic-spent alumina. Although the regeneration time and amount of regenerant were undisclosed, they reported 80% recovery of arsenic (all As(V)) and no significant loss of arsenic removal capacity upon two subsequent arsenic removal runs at pH 5.5. Their reported better performance with regenerated alumina may have been due to one of several differences: (a) the initial upflow step in the regeneration sequence, (b) the absence of As(III) from the feedwater, (c) the amount of regenerant used or, (d) the exhaustion pH--5.5 compared to our value of 6.0. In any case, their results suggest that an As(V)-spent alumina column can be restored to essentially its virgin capacity for As(V) even though only 80% of the As(V) is recovered during a presumably intense regeneration with 4-5% NaOH.

Results of $Al(OH)_3$ Precipitation from Spent Regenerant

The spent-regenerant solutions from regeneration runs 5R and 6R (Figures C8 and C10) were combined, acidified to pH 6.5 with HCl, settled for 24 hours and filtered prior to analysis of the arsenic remaining. The results are presented in Table 20.

The coprecipitation/filtration procedure removes essentially all of the As(V) but only 36% of the As(III), and 97% of the arsenic remaining after precipitation is 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). Using the results of Frank and Clifford [1986], 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 6-10 pH range.

TABLE 20. ARSENIC COPRECIPITATION WITH $AL(OH)_3$

Sample	Total As mg/L	As(V) mg/L	As(III) mg/L	As(III) Percent
Combined Regenerants from Runs 5R and 6R	16.2	14.8	1.4	8.6
Filtrate after $Al(OH)_3$ Precipitation	0.92	0.03	0.89	97.0
Arsenic Removal (%)	94.0	99.8	36.0	

The arsenic-contaminated alum sludge produced in this manner amounted to approximately 12% of the total initial solution volume. Rubel [1982], 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.

Results of Extraction Procedure (EP) Toxicity Test

The details of the $Al(OH)_3$ precipitation of arsenic and a summary of the EPA Extraction Procedure Toxicity test are given in Appendix A. After drying at room temperature, the $Al(OH)_3$ sludge solids amounted to 7.8 g/L of regenerant solution (which was originally 1% NaOH). Following the 24-hour extraction procedure, the arsenic (total) concentration in the filtrate was 0.6 mg/L, i.e., far below the 5.0 mg/L limit for classification as a toxic waste. Rubel and Hathaway [1985] found even less arsenic (0.036 mg/L) in their EP toxicity test filtrate from an As(V)-contaminated $Al(OH)_3$ sludge which they derived by adjusting the pH (to 6.5) of a spent alumina regenerant solution (originally 4% NaOH). The higher, but nevertheless acceptable, total arsenic concentration was presumably due to the presence of As(III), in the original regenerant solution and in the $Al(OH)_3$ sludge. Furthermore, both studies resulted in a low-volume non-toxic arsenic sludge from the regenerant wastewater.

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 [Buswell, 1943]. Moreover, As(V) is much more effectively removed by ferric hydroxide than is As(III) [Pierce and Moore, 1982]. 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 results of these tests are summarized in Table 21. A relatively high dosage, 10 mg/L, of free chlorine from household bleach (5.25% NaOCl, equivalent to 50,000 mg/L Cl_2) was used to assure oxidation of all chlorine demanding substances present, viz., ferrous iron, sulfides and arsenite. The unadjusted pH following chlorination was 7.1. In one test the pH was adjusted to 8.5 corresponding to the minimum solubility of $Fe(OH)_3(s)$.

TABLE 21. ARSENIC COPRECIPITATION WITH $Fe(OH)_3$ FROM NATURAL Fe PRESENT

Sample	Raw Water Fe(II) mg/L	Percent Arsenic Removal pH 7.1	pH 8.5
City Water *	0.06	0	0
City Water + Cl_2	0.06	0	0
Well No. 4 †	2.0	0	0
Well No. 4 + Cl_2	2.0	60	52

* City water samples contained 86 µg/L As(total).
† Well No. 4 water samples contained 200 µg/L As(total).

The City Water 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. Sixty percent arsenic removal was achieved at pH 7.1 while somewhat less, 52%, removal was observed at pH 8.5. The lower removal at the higher pH, 8.5, is in accord with the observations of Pierce and Moore [1982] who suggest that the optimal pH for As(V) removal by ferric hydroxide is 4.0, and that As(V) is removed by specific adsorption rather than electrostatic attraction. No further tests were done at lower pH's, however, because the Well No. 4 water was of such poor quality.

ION EXCHANGE RESULTS

Performance of the Anion Exchange Columns

Chloride-form strong-base anion exchange tests were conducted to a limited extent (3 experimental runs) to verify the prediction that anion exchange is not effective for the removal of nonionic As(III) in the raw water. Based on prior laboratory studies, immediate breakthrough of essentially all the As(III) was expected, but did not occur. The typical breakthrough curves for arsenic, fluoride, bicarbonate and pH from a 76-cm (30-in) deep bed of Dowex-11 resin are presented in Figure 20. The performance of all three runs is summarized in Table 22 and the breakthrough curves for the remaining runs are presented in Appendix D--Figures D1 (Run 1), D2 (Run 2, expanded), D4 (Run 3), and D5 (Run 3, expanded).

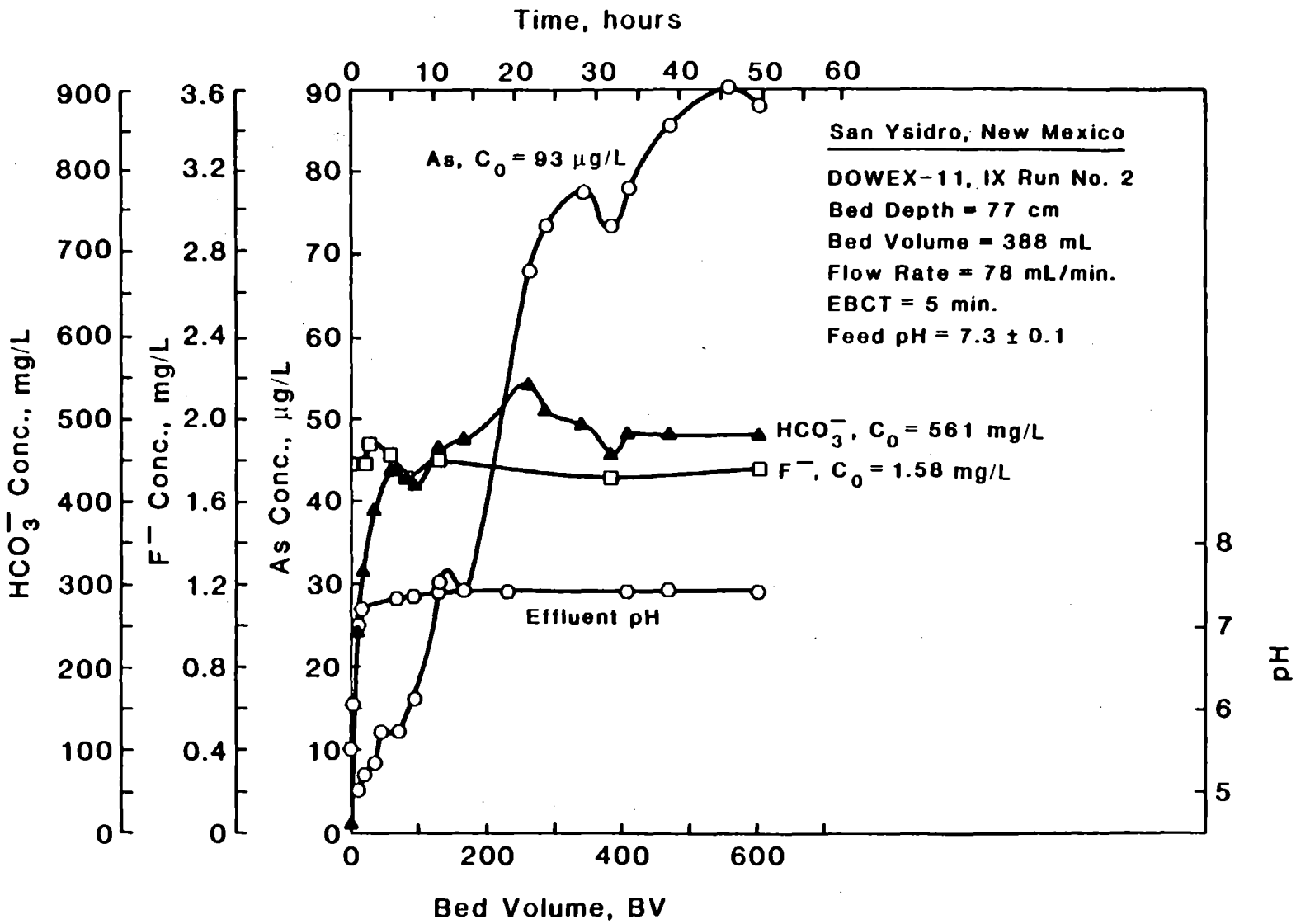


Figure 20. Results of IX Run No. 2, effluent concentration histories for arsenic, fluoride, bicarbonate and pH from a chloride-form strong-base anion resin, Dowex-11.

TABLE 22. SUMMARY OF CHLORIDE-FORM ANION EXCHANGE RESULTS IN SAN YSIDRO, NEW MEXICO * †

IX Run No.	Resin Type	Condition	BV to 1.4 mg/L F-	BV to 50 µg/L As
1	Dowex-11 §	New	--	223
2	Dowex-11 §	Regenerated	3.6	223
3	ASB-1 ‡	New	18.0	156

* No pH adjustment was made for the IX runs.

† San Ysidro City Water with 92 µg/L As was fed (33% As(III), 67% As(V)) in all runs.

§ Dowex-11 is an improved porosity strong-base, Type-1 resin with an exchange capacity of 1.3 meq/mL.

‡ Ionac ASB-1 is a gel, strong-base, Type-1 resin with an exchange capacity of 1.1 meq/mL.

Referring to Figure 20 it is clear that immediate breakthrough of the 25-36 µg/L As(III) present in the feedwater did not occur. Rather, about 200 BV was passed 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 passed through the bed. Most importantly, the arsenic concentration in the effluent never exceeded that of the influent. Thus, chromatographic peaking did not occur due to sulfate driving arsenic off the column as has been regularly observed in laboratory studies [Horng, 1983]. We are not, however, completely ruling out the possibility of an arsenic peak much later in the run.

Neither the sulfate nor the chloride breakthrough curves are shown in the figures because their effluent concentrations as analyzed by ion chromatography did not make sense. Sulfate appeared to be breaking through before chloride (the presaturant), and the sulfate that apparently eluted during the first 200 BV was nearly five times the sulfate fed to the column during that period. No reason existed to believe that there was sulfate on the column due to regeneration because reagent grade NaCl was used to put the resin in the chloride form. The analytical problem was never resolved, but it seems safe to assume that sulfate eluted from the column prior to arsenic elution. The early sulfate elution was undoubtedly due to a selectivity reversal of the usual preference for sulfate over chloride. This reversal is expected for such a high TDS (810 mg/L) high ionic-strength (I = 0.017 M) water.

For both the Dowex-11 runs, the 50 µg/L arsenic MCL was not reached until 220 BV. For Run 3, Ionac ASB-1 the run was shorter, 156 BV, before the MCL was reached. 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 (400 BV+). Also, in spite of the fact that arsenic did not peak, its breakthrough was not sharp; an ever increasing level of arsenic leaked from the column right from the start of the run.

As(III) Leakage During Ion Exchange

Table 23 summarizes the As(III) and As(total) in the feedwater and the column effluent during Run 2 (Figure 20). The early leakage was nearly all (93%) As(III), and later dropped to a value (26%) near that of the feed (33%). Oxidation of As(III) to As(V) within the bed

appears to have occurred because there was 31 μg/L As(III) in the feed and only 8-20 μg/L As(III) in the effluent during the first 400 BV.

TABLE 23. ARSENIC COMPOSITION OF EFFLUENT AND FEED FOR ION EXCHANGE RUN NO.2

Run Time Hours	BV	Effluent As(III) μg/L	Effluent As(total) μg/L	Effluent As(III) Percent
3.0	36	7.8	8.4	93
6.0	72	9.6	12.3	78
33.5	402	18.9	72.0	26
Feedwater		31.0 (As(III))	93.0 (As(total))	33 %(As(III))

pH Reduction in Ion Exchange Effluent

At the beginning of all the ion exchange runs, the effluent pH was quite acidic-pH 5.5 for Runs 1 and 2, and pH 4.3 for Run 3. After about 20 BV, however, the pH rose to near its influent value of 7.2. It is believed that this low initial pH is a verification of the previously observed [Horng, 1983] conversion of bicarbonate to carbonate within the resin according to the following reaction:

$$2\,RCl + HCO_3^- = R_2CO_3 + 2\,Cl^- + H^+ \qquad (1)$$

where RCl is resin in the chloride form, and R_2CO_3 is resin in the carbonate form.
A strong acid, HCl, is produced which both lowers the pH and reacts with any bicarbonate remaining in the aqueous phase according to reaction (2):

$$HCl + HCO_3^- = H_2CO_3 + Cl^- \qquad (2)$$

The aqueous CO_2, i.e., carbonic acid (H_2CO_3) generated passes unhindered through the remainder of the bed. To the extent that reactions (1) and (2) proceed, and HCO_3^- is exchanged for chloride, the alkalinity of the column effluent is reduced. Initially the effluent alkalinity is zero, but eventually it rises to the influent value when the column is completely exhausted.

This rise in effluent alkalinity to the influent value, indicating equilibrium between the feedwater and the resin, did not occur in any of the runs, i.e., the columns were not completely exhausted even at 600 BV throughput. The implication of this observation is that, at complete exhaustion when the carbonate wave reaches the end of the bed, an arsenic peak might occur as carbonate displaces arsenic. This is, however, merely a possibility to be considered in the event ion exchange is used to treat the San Ysidro water.

Fluoride Removal by Ion Exchange

In all the ion-exchange runs (Figures 20, D1, D2 and D3) fluoride was not removed to any significant extent by the chloride-form anion resins. In Figure D2, an expanded plot of the first 80 BV of Run 2, fluoride is seen to reach 1.4 mg/L (the old MCL) at approximately 4 BV. Such an early breakthrough is expected due to the very low affinity of fluoride for the usual strong-base anion resins. Further data on fluoride removal are presented in Table 22 where one can observe that, although the performance of ASB-1 was poor for arsenic removal, it performed better than Dowex-11 for fluoride removal. Neither resin could be used for municipal defluoridation, however. Their fluoride capacities are simply too low.

Ion-Exchange Regeneration Results

The exhausted ion exchange columns were completely and easily regenerated using approximately 3 BV of 1.0 N (6%) NaCl in a cocurrent (downflow) mode. Figure 21 presents the arsenic and fluoride elution curves during regeneration Run 1R following the first exhaustion of Dowex-11 resin during Run No. 1. The arsenic elution curve is particularly sharp and denotes the ease with which the adsorbed arsenic is 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 suggests that ion exchange should be further studied. These and previous results with strong-base anion exchange resins [Horng, 1983] indicate a real potential for chloride-form anion exchange for As(V) removal. Results from this study suggest that approximately 400-500 BV could be attained prior to the arsenic MCL if the As(III) had been oxidized to As(V) prior to anion exchange.

POINT-OF-USE TREATMENT

In August 1984, 6 months after the San Ysidro project started, 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 in excess of 20,000 BV, the fluoride present would force termination of the alumina runs at 2,000 BV so as not to exceed the existing MCL of 1.4 mg/L. (Now the MCL is 4.0 mg/L [U.S. EPA, 1986] and fluoride is no longer a problem in San Ysidro.)

The anticipated short alumina runs due to fluoride, the complexity of the alumina adsorption/regeneration cycle for a small community and the anticipated sludge disposal problem led to the consideration of point-of-use treatment using reverse osmosis. A Culligan Model No. H-82 was installed and tested in San Ysidro. The system used had a nominal capacity of 8 gal/day product water and contained a thin-film-composite RO membrane. The entire H-82 system comprises a 10 μm 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, and no endorsement is implied.

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

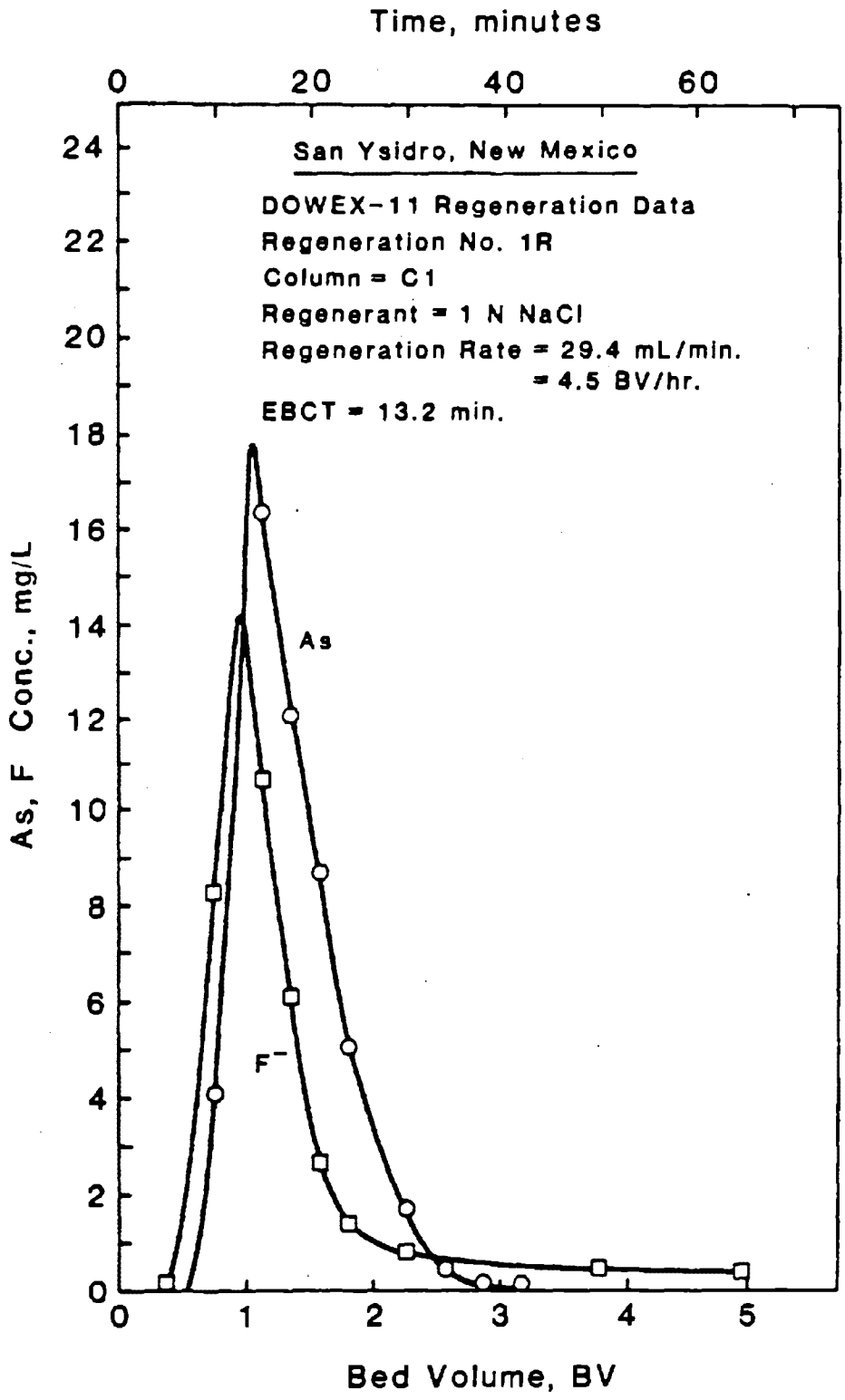


Figure 21. Arsenic and fluoride elution during a typical ion exchange regeneration with 6% (1.0 N) NaCl.

The initial results of the POU-RO pilot test are presented in Table 24. Subsequent arsenic analyses on the product water from this unit yielded undetectable arsenic levels, i.e., <0.2 µg/L.

TABLE 24. RESULTS OF POINT-OF-USE REVERSE OSMOSIS PILOT TEST

Parameter	Feed	Product	Percent Removal
pH	7.2	5.5	
Water flow, gal/day	50	6	
Conductivity, µS	1430	120	92
TDS, mg/L	750	35	95
Arsenic, µg/L	90	8	91

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Appendix A

Analytical Procedures

Sample: Water, Well 31, 2-17-84

Purpose: The valence of arsenic in water is determined with separation by chloride form ion-exchange resin [1]. It is important to distinguish the inorganic valence state of arsenic (As) because As(III) is considered to be much more toxic than As(V) [2].

Procedure: The pH of the water is immediately adjusted to 3.0 and passed through an ion-exchange column that will elute the molecular As(III) into a collection flask and retain the ionized As(V) on the resin. The As(V) is eluted later from the column with 0.5N HCl into another collection flask. The arsenic is determined on each fraction using atomic absorption spectrophotometry with hydride generation following EPA guidelines. [3]

The precision and accuracy of the procedure was performed using laboratory prepared reagents [As_2O_3 for As(III) and NaH_2AsO_4 for As(V)]. A series of seven columns were prepared as follows: 1.) deionized water; 2.) 0.05 mg As(III)/l solution (twice); 3.) 0.05 mg As(V)/l solution (twice) and; 4.) 0.05 mg As(III) + 0.05 mg As(V)/l solution (twice). See Table 1.

A series of seven columns were prepared to speciate the arsenic in well 31 as follows: 1.) deionized water; 2.) well 31 (twice); 3.) 0.05 mg As(III)/l solution; 4.) 0.05 mg As(V)/l; 5.) well 31 + As(III) spike (0.05 mg/l); and 6.) well 31 + As(V) spike (0.05 mg/l). See Table 2.

The total arsenic concentration was also performed on the water from well 31.

Results: The precision and accuracy of the procedure for arsenic speciation is very good as evidenced by the % recovery from Table 1. The average As(III) recovery is 99 ± 1%. The average As(V) recovery is 100 ± 2%.

From Table 2, the average % As(III) in well 31 is 98 ± 2 and the average % As(V) is 1 ± 2. The arsenic in well 31 is predominately trivalent arsenic [As(III)].

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2c: Herewith

Table A-1. Laboratory Experimental Analysis

Sample	mgAs(111)/l found	%As(111) recovered	mgAs(V)/l found	%As(V) recovered
1. Deionized Water	None		None	
2. 0.05mgAs(111)/l	0.050	100	None	---
3. 0.05mgAs(111)/l	0.049	98	None	---
4. 0.05mgAs(V)/l	None	---	0.051	102
5. 0.05mgAs(V)/l	None	---	0.049	98
6. 0.05mgAs(111) & 0.05mgAs(V)/l	0.050	100	0.049	98
7. 0.05mgAs(111) & 0.05mgAs(V)/l	0.049	98	0.051	102

Table A-2. On Site Analysis

Sample	mgAs(III)/l found	%As(III) IN Well 31	mgAs(V)/l found	%As(V) IN Well 31
1. Deionized Water	None		None	
2. Well 31	0.036	100	None	0
3. Well 31	0.035	97	0.001	3
4. 0.05mgAs(III)/l	0.050	---	None	---
5. 0.05mgAs(V)/l	None	---	0.050	---
6. Well 31 + 0.05 mgAs(III)/l	0.085	97	None	None
7. Well 31 + 0.05 mgAs(V)/l	0.036	100	0.050	None

NOTE: Total arsenic concentration for well 31: 0.036 mg/l

The Twining Laboratories, Inc.

Fresno Modesto Stockton Visalia

EP Toxicity Test Procedure (U.S. EPA, 1980)

A 100-g sample (wet weight) of centrifuged or filtered sludge was placed in a 4-liter Ehrlenmeyer flask with 16 times its weight of denionized water. The sludge + water mixture was stirred on a magnetic stirrer with sufficient mixing to keep the sludge particulates in solution. The initial pH of the mixture was measured, and if it was greater than 5.0 + 0.2, 0.5 N acetic acid was added to lower the pH to 5. The pH of the solution was checked at intervals of 0.25, 0.5, 1, 2, 3, 4, 5 and 6 hours after the start of the test. If necessary, 0.5 N acetic acid was added to lower the pH to 5; however, the maximum limit for total acid addition was 4 mL per gram of solids. The sludge-water mixture was stirred for 24 hours at 25°C. At the end of 24 hours, the solution pH was checked, and if the pH was not below 5.2 and the maximum amount of acid had not been added, the solution pH was again adjusted into the range of 5.0-5.2 and the extraction was continued for 4 more hours with pH adjustment every hour.

At the end of the 24-hour (or 28-hour) extraction period, deionized water was added to the extractor in an amount determined by:

$$V = 20W - 16W - A$$

where: V = ml deionized water to be added.

W = weight in grams of the solid being extracted.

A = ml of 0.5 N acetic acid added during the extraction.

The supernatant was then filtered through a 0.45 μm membrane filter, acidified to a pH < 2 with 1:1 HNO_3, and stored in a plastic bottle at 4°C for later GFAAS analysis of total arsenic.

Appendix B

Equipment Specifications

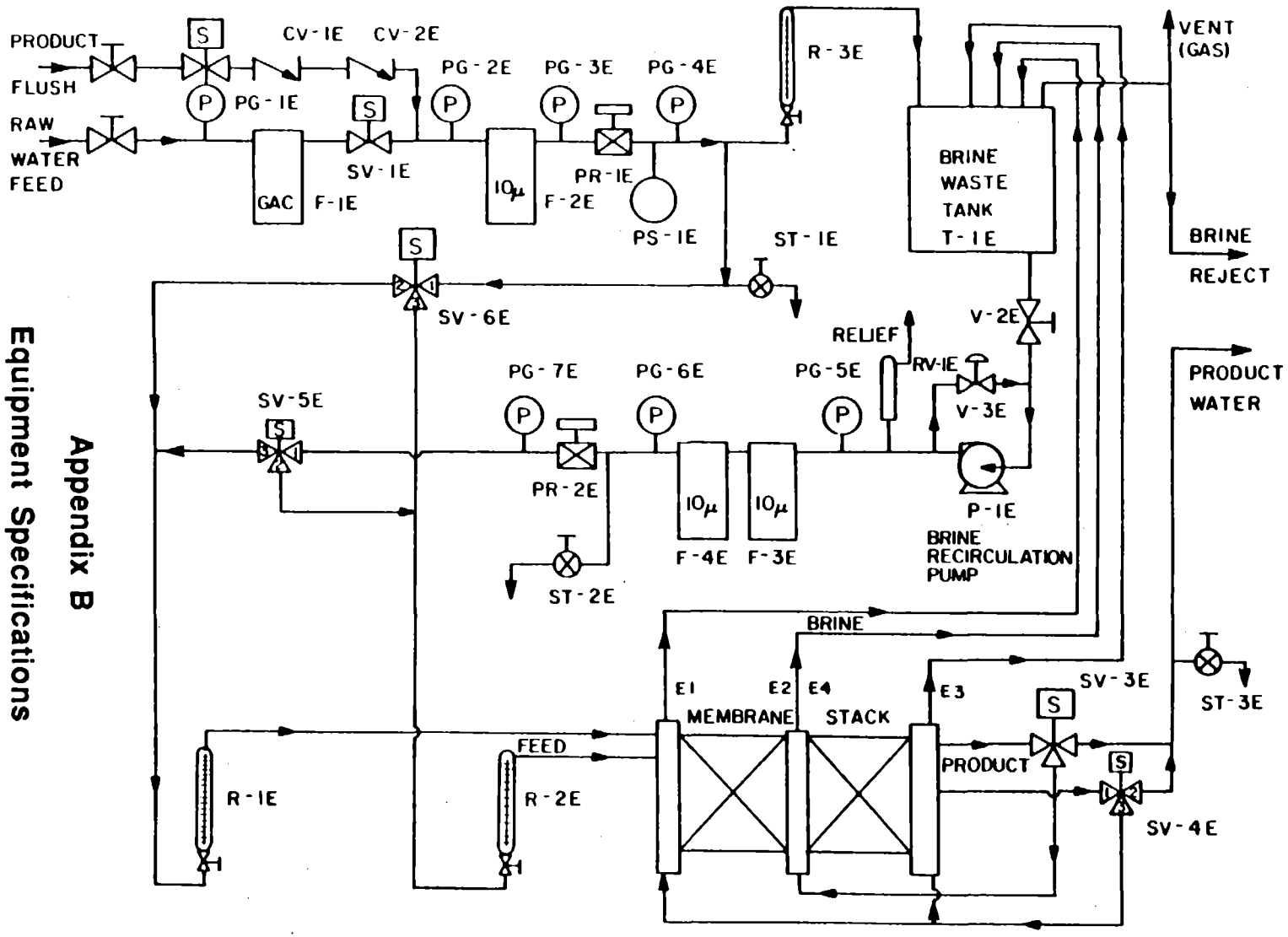

Figure B1. Internal flow schematic for the Ionics Aquamite I EDR unit--electrodialysis with current reversal.

TABLE B1. REVERSIBLE ELECTRODIALYSIS SYSTEM SPECIFICATIONS

Manufacturer: Ionics, Inc., Aquamite I

Pairs of Membranes: 200

Number of Hydraulic Stages: 6 in series

Stack Dimensions: 40.6 cm long x 24.1 cm wide x 30.5 cm high (16 in long x 9.5 in wide x 12 in high)

Product Flow: 1.9 m^3/day (500 gal/day at 2500 mg/L TDS feed)

Typical Product TDS: 100 mg/L at 50% recovery, 2500 mg/L TDS feed

% Recovery: 50 percent without brine recycle
80 percent with brine recycle

Polarity Reversal: Once each 15 minutes

Power Characteristics: 120V, Single Phase

Power Consumption: 8 kWhr/1000 gal

Temperaure Range: 0-45°C (32-110°F)

Operating Pressure: 311 kPa (45 psig)

Stack Pressure Drop: 173 kPa (25 psig)

pH Range: 1 - 13

Chlorine Tolerance: Cl_2 must be removed

Filter: One 10 cartridge type

TABLE B2. REVERSE OSMOSIS SYSTEM SPECIFICATIONS

Number of Modules: Two in parallel
Mode of Operation: Module 1 or Module 2

Module 1: duPont Model No. 0420-21
- Membrane Type: B-9 Aramid
- Membrane Configuration: Hollow Fiber
- Shell Dimensions: 13.3 cm OD x 63.5 cm long (5.25 in OD x 25 in long)
- Product Water Capacity: 7.95 m^3/day (2,100 gpd at 1500 ppm TDS)
- Operating Pressure: 0-2760 kPa (0-400 psig)
- Operating Temperature: 0-35°C (32-95°F)
- pH Range, Continuous: 4-11
- Minimum Brine Rate: 4.2 L/min (1.11 gpm)
- Chlorine Tolerance: Cl_2 must be removed
- Silt Density Index, SDI: ≤ 3.0

Module 2: Dow Model Dowex 4K
- Membrane Type: Cellulose Triacetate
- Memrane Configuration: Hollow Fiber
- Shell Dimensions: 15.88 cm OD x 122 cm long (6.25 in OD x 48 in long)
- Product Water Capacity: 15.14 m^3/day (4,000 gpd at 1500 ppm TDS)
- Operating Pressure: 0-2760 kPa (0-400 psig)
- Operating Temperature: 0-30°C (32-86°F)
- pH Range, Continuous: 4.0 - 7.5
- Minimum Brine Rate: 1.9 L/min (0.5 gpm)
- Chlorine Tolerance: ≤ 1.0 mg/L
- Silt Density Index, SDI: ≤ 4.0

RO Pump: Moyno 9P3, 316 ss Rotor
- Maximum Pump Pressure; 5520 kPa (800 psig)
- Pump Operaing Pressure; 2760 kPa (400 psig)
- Pump Motor: 3 hp, 220 v, Single Phase
- High Pressure Cutoff: 3105 kPa (450 psig)
- High Pressure Relief: 3105 kPa (450 psig)
- Low Pressure Cutoff: 2070 kPa (300 psig)

RO Pretreatment Filters: Two Provided--One Deep Bed, One 10 Cartridge
- Deep Bed Filter: 35.6 cm OD x 165 cm height (14 in OD x 65 in height)
- Filter Media: 76.2 cm AG over 10 cm flint gravel (30 in AG over 4 in flint gravel)
- Filtration Rate: 117-293 m/day (2 - 5 gal/min ft^2)

TABLE B3. Du Pont RO Projections for City Water

Du Pont Co. PERMASEP Projection GLA
SAN YSIDRO NM - City Water
APRIL 2, 1984

Design Temp = 59.0 F (15.0 C)
Feed Pressure = 400.0 psig
Overall Conversion = 45.0%
Plant Capacity = not specified
Permeator Model = 0420-021

Max Temp = 59.0 F (15.0 C)
Product Pressure = 10.0 psig
Term = 10,000 hrs.
Bal. Tube = 20 psig
Salt Passage = 10.0%

LSI = .78 pH ; A.FD. = 7.20
H_2SO_4 Added (AS 100%) = 0.0
Ionic Strength Acid Feed = .0177

pH Brine = 7.44 ; pH sat.= 6.67
PPM = 0.0 lbs/kgals. Product
Brine = .0321

Max. Allow. Conv.:	Without NaHMP	With NaHMP
$CaSO_4$	95.5%	96.9%
$BaSO_4$	-88.7%	87.1%
$SrSO_4$	97.8%	99.4%
CaF_2	-2.3%	77.9%

Max. Allow. Conv.:	Lit. Data	Oper. Data
SiO_2	0%	52.4%

Staging Ratio: 2.0

Stage No.	Permeators Per Stage	Percent Conversion	Perm Press Drop (psi)	---Flow/Perm (gpm)--- Feed	Brine	Product
1	2.0	45.0	3.4	2.2	1.2	1.0

Stage No.	MFRC	---Feed--- psig	kgpd	---Brine--- psig	kgpd	---Product--- psig	kgpd
1	.868	400.0	6.4	396.6	3.5	10.0	2.9
TOTAL							2.9

TABLE B3. (Continued)

	Raw Feed as ppm	Acid Feed As ppm		Brine as ppm		Product as ppm	
Cations	Ions	Ions	$CaCO_3$	Ions	$CaCO_3$	Ions	$CaCO_3$
Ca	85.00	85.00	212.10	153.10	381.90	1.80	4.50
Mg	17.00	17.00	69.90	80.60	125.90	.40	1.50
Na	190.00	190.00	413.30	330.90	719.70	17.80	38.70
K	11.70	11.70	15.00	20.80	26.60	.60	.80
Sr	.90	.90	1.03	1.62	1.85	.02	.02
Ba	.18	.18	.13	.32	.24	.00	.00
Fe	.02	.02	.04	.04	.06	.00	.00
TOTAL	304.80	304.80	711.40	537.30	1256.20	20.60	45.50
Anions							
HCO_3	571.00	571.00	467.60	1003.70	822.00	42.20	34.50
SO_4	60.50	60.50	63.00	109.00	113.50	1.30	1.30
CL	123.00	123.00	173.40	218.80	307.80	6.50	9.20
F	2.70	2.70	7.10	4.80	12.60	.20	.40
NO_3	.20	.20	.20	.40	.30	.00	.00
TOTAL	757.50	757.50	711.40	1336.20	1256.20	50.20	45.50

TDS ION	1122.30	1122.30	1978.70	75.60
SiO_2 ppm	60.00	60.00	105.20	4.80
CO_2 ppm	58.90	58.90	58.90	58.90
pH	7.20	7.20	7.44	6.07
Osmotic Pressure, PSI		8.60	14.90	.60
Equiv. NaCl, PPM		771.00	1341.00	57.00

TABLE B4. Du Pont RO Projections for Well No. 4 Water

Du Pont Co. PERMASEP Projection GLA
SAN YSIDRO NM - WELL #4
APRIL 2, 1984

Design Temp = 59.0 F (15.0 C)
Feed Pressure = 400.0 psig
Overall Conversion = 45.0%
Plant Capacity not specified
Permeator Model = 0420-021

Max Temp = 59.0 F (15.0 C)
Product Pressure = 10.0 psig
Term = 10,000 hrs.
Bal. Tube = 20 psig
Salt Passage = 10.0%

LSI = .36 pH; A.FD. = 7.02
H2SO4 added (As 100%) = 0.0
Ionic Strength Acid Feed = .0283

pH Brine = 7.26 ; pH Sat. = 6.90
PPM = 0.0 lbs/kgals Product
Brine = .0512

Max. Allow. Conv.:	Without NaHMP	With NaHMP
$CaSO_4$	96.1%	97.2%
$BaSO_4$	-60.5%	91.8%
$SrSO_4$	97.3%	99.2%
CaF_2	-41.8%	69.4%

Max. Allow. Conv.:	Lit. Data	Oper. Data
SiO_2	-10.0%	47.6%

Staging Ratio: 2.0

Stage No.	Permeators Per Stage	Percent Conversion	Perm Press Drop (psi)	--- Flow/Perm (gpm) --- Feed	Brine	Product
1	2.0	45.0	3.3	2.2	1.2	1.0

Stage No.	MFRC	----Feed---- psig	kgpd	----Brine---- psig	kgpd	----Product---- psig	kgpd
1	.868	400.0	6.2	396.7	3.4	10.0	2.8
TOTAL							2.8

TABLE B4. (Continued)

	Raw Feed as ppm	Acid Feed As ppm		Brine as ppm		Product as ppm	
Cations	Ions	Ions	$CaCO_3$	Ions	$CaCO_3$	Ions	$CaCO_3$
Ca	38.00	38.00	94.80	68.40	170.70	.80	2.10
Mg	7.50	7.50	30.80	13.50	55.50	.20	.70
Na	510.00	510.00	1109.30	895.30	1947.40	39.00	84.90
K	15.00	15.00	19.20	26.60	34.00	.30	1.00
Sr	.56	.56	.64	1.01	1.15	.01	.01
Ba	.06	.06	.04	.11	.08	.00	.00
Fe	2.00	2.00	3.58	3.60	6.45	.04	.08
TOTAL	573.10	573.10	1258.30	1008.60	2215.30	40.90	88.80
Anions							
HCO_3	783.00	783.00	641.30	1363.10	1116.40	74.00	60.60
SO_4	169.80	169.80	176.70	305.60	318.20	3.70	3.90
CL	300.00	300.00	423.00	532.10	750.20	16.40	23.10
F	6.60	6.60	17.30	11.60	30.50	.50	1.30
TOTAL	1259.40	1259.40	1258.30	2212.40	2215.30	94.50	88.80

TDS ION	1898.50	1898.50	3336.60	140.80
SiO_2 ppm	66.00	66.00	115.60	5.40
CO_2 ppm	122.20	122.20	122.20	122.20
pH	7.02	7.02	7.26	6.00
Osmotic Pressure, psi		15.90	27.70	1.20
Equiv. NaCl, ppm		1434.00	2493.00	110.00

TABLE B5. Dow RO Projections for City Water

Dowe X* R.O. Permeator System Design

Project: City Water Analysis
Date: Mar 23, 1984 9:50:10

This is the design of a 1 stage reverse osmosis system with 1 permeator type SP9605 (initial standard test performance of 5000. GPD, 96.0% salt rejection.) The system is operating at a recovery of 54.%, feed pressure of 400. psi and interstage pressure drops of:

Stage 1 - 2 = 50. psi
The feed water temperature range is 15.0 C to 15.0 C.
Acidification ion for carbonate scale ctrl: 1.96 lbs H_2SO_4 (100 pct)/kgal feed.
The design results below reflect system performance after 3.0 years.

WATER ANALYSIS

ION	PPM ION IN RAW FEED	PPM ION IN TREATED FEED	PPM $CaCO_3$ IN TREATED FEED	PPM ION IN PERMEATE	PPM ION IN CONCEN-TRATE
Ca^{++}	85.00	85.00	212.24	2.44	179.99
Na^{+}	190.00	190.00	413.63	7.13	400.40
Mg^{++}	17.00	17.00	69.99	0.40	36.10
Fe^{++}	0.02	0.02	0.04	0.00	0.04
Mn^{++}	0.02	0.02	0.04	0.00	0.04
K^{+}	11.70	11.70	14.98	0.58	24.50
Ba^{++}	0.18	0.18	0.13	0.00	0.38
Sr^{++}	0.85	0.85	0.97	0.02	1.81
Total +	304.77	304.77	712.07	10.56	643.27
Cl^{-}	140.24	140.24	198.02	4.10	296.88
F^{-}	2.67	2.67	7.03	0.09	5.64
SO_4^{--}	37.00	271.52	282.92	5.78	577.25
NO_3^{-}	0.22	0.22	0.18	0.03	0.44
SiO_2	60.00	60.00	99.96	4.29	124.10
PO_4^{---}	0.00	0.00	0.00	0.00	0.00
HCO_3^{-}	570.60	279.02	228.80	14.53	583.33
CO_3^{--}	0.19	0.01	0.02	0.00	0.02
Total -	810.93	693.68	716.97	24.53	1463.56
TOTAL	1115.70	1058.45	814.48	39.38	2230.93
pH	7.17	6.22		5.41	6.49
CO_2		273.14	310.60	204.85	351.70
Langelier Index					-0.20

OPTIMIZED DESIGN CONFIGURATION AND RATINGS

STAGE NO	MODULES PER STAGE	FEED PRESSURE PSI	MODULE DELTA P PSI	PIGTAIL DELTA P PSI	INTER-STAGE DELTA P PSI	TOTAL PRODUCT FLOW GPD	TOTAL BRINE FLOW GPD
1	1	400.	2.	48.	50.	3443.	2992.

STAGE	AVG PROD FLOW (GPD)	AVG BRINE FLOW (GPM)	PRODUCT QUAL (PPM)	EXIT BRINE CONC (PPM)	PERCENT RECOVERY	PERCENT NaCL
1	3443.	3.27	39.	2231.	53.50	96.28

Maximum recovery to avoid saturation with:

Gypsum	93.3%
Anhydrite	96.5%
$BaSO_4$	0.0%
$SrSO_4$	95.5%
SiO_2	53.9%
CaF_2	0.0%

These maximum recoveries assume the addition of a scale inhibitor.

** A pigtail is an artificial pressure drop consisting of nylon or stainless steel tubing which allows all permeators in a given stage to operate at approximately the same recovery.

Notes:

A. The Dowex* RO System should be operated in such a manner as to prevent the precipitation of any salts within the permeator.
Specifically we recommend:
1) Acid addition for carbonate scale control
2) Scale inhibitor addition for sulfate scale control
3) An automatic flush of the permeators at low pressure (50-100 psi) with permeate water on system shut down for silica and other scales.

B. Iron should be maintained at less than 0.1 ppm at all times, including start up and shut down.

C. Barium and strontium should be analyzed at the 0.01 and 0.1 ppm level of detection respectively. If an accurate analysis was not available at the time of this design, please note that it may be neccesary to lower the overall system recovery to prevent barium and strontium sulfate scale formation.

D. The maximum level of free chlorine which can be tolerated in the RO feedwater varies with temperature as follows: 1 ppm at 4-25 degrees C, 0.5 ppm at 26-30 degrees C, 0 ppm at 31-35 degrees C.

E. The feedwater should be sterile.

F. The feedwater should be pretreated to a silt density index < 4.

This estimate of an appropriate design configuration and expected performance of Dowex* RO permeators is based upon the particular feedwater analysis submitted to the Dow Chemical Co. The design and expected performance are presented in good faith, but no warranty is expressed or implied. Although these criteria should assure proper performance of the Dowex* RO permeators, the ultimate success of any RO facility depends upon an adequately engineered system that is properly operated and maintained.

* Trademark of the Dow Chemical Company

TABLE B6. Dow RO Projections for Well No. 4 Water

Dowe X* R.O. Permeator System Design
Project: Well #4 Analysis
Date: Mar 23, 1984 9:41:08

This is the design of a 1 stage reverse osmosis system with 1 permeator, type SP9605 (initial standard test performance of 5000. gpd, 96.0% salt rejection.) The system is operating at a recovery of 48.%, feed pressure of 400. psi and interstage pressue drops of:

Stage 1-2 = 50. psi
The feedwater temperature range is 15.0 C to 15.0 C.
Acidification for carbonate scale ctrl: 1.76 lbs H_2SO_4 (100 pct) /Kgal feed the design results below reflect system performance after 3.0 years.

WATER ANALYSIS

ION	PPM ION IN RAW FEED	PPM ION IN TREATED FEED	PPM $CaCO_3$ IN TREATED FEED	PPM ION IN PERMEATE	PPM ION IN CONCEN-TRATE
Ca^{++}	38.00	38.00	94.89	1.12	72.04
Na^{+}	510.00	510.00	1110.27	19.14	963.10
Mg^{++}	7.50	7.50	30.88	0.17	14.27
Fe^{++}	0.10	0.10	0.18	0.00	0.19
Mn^{++}	0.16	0.16	0.29	0.01	0.30
K^{+}	15.00	15.00	19.20	0.72	28.19
Ba^{++}	0.06	0.06	0.04	0.00	0.11
Sr^{++}	0.56	0.56	0.64	0.01	1.07
Total +	571.38	571.38	1256.42	21.17	1079.27
Cl^{-}	348.25	348.25	491.73	13.62	657.14
F^{-}	6.59	6.59	17.36	0.21	12.48
SO_4^{--}	101.00	311.48	324.57	5.67	593.77
NO_3^{-}	0.00	0.00	0.00	0.00	0.00
SiO_2	66.00	66.00	109.96	4.58	122.70
PO_4^{---}	0.00	0.00	0.00	0.00	0.00
HCO_3^{-}	782.62	520.90	427.14	24.88	978.76
CO_3^{--}	0.19	0.03	0.05	0.00	0.06
Total -	1304.64	1187.25	1260.84	44.39	2242.20
TOTAL	1876.02	1824.63	1368.59	70.14	3444.16
pH	7.02	6.44		5.60	6.68
CO_2		310.23	352.77	232.67	381.82
Langelier Index					-0.20

OPTIMIZED DESIGN CONFIGURATION AND RATINGS

STAGE NO	MODULES PER STAGE	FEED PRESSURE PSI	MODULE DELTA P PSI	PIGTAIL DELTA P PSI	INTER-STAGE DELTA P PSI	TOTAL PRODUCT FLOW GPD	TOTAL BRINE FLOW GPD
1	1	400.	3.	47.	50.	3334.	3612.

STAGE	AVG PROD FLOW (GPD)	AVG BRINE FLOW (GPM)	PRODUCT QUAL (PPM)	EXIT BRINE CONC (PPM)	PERCENT RECOVERY	PERCENT NaCL
1	3334.	3.67	70.	3444.	48.00	96.16

Maximum recovery to avoid saturation with:

Gypsum	97.1%
Anhydrite	98.3%
$BaSO_4$	22.6%
$SrSO_4$	97.4%
SiO_2	48.4%
CaF_2	0.0%

These maximum recoveries assume the addition of a scale inhibitor.

** A pigtail is an artificial pressure drop consisting of nylon or stainless steel tubing which allows all permeators in a given stage to operate at approximately the same recovery.

Notes:

A. The Dowex* RO System should be operated in such a manner as to prevent the precipitation of any salts within the permeator.
Specifically we recommend:
   1) Acid addition for carbonate scale control
   2) Scale inhibitor addition for sulfate scale control
   3) An automatic flush of the permeators at low pressure (50-100 psi) with permeate water on system shut down for silica and other scales.

B. Iron should be maintained at less than 0.1 ppm at all times, including start up and shut down.

C. Barium and strontium should be analyzed at the 0.01 and 0.1 ppm level of detection respectively. If an accurate analysis was not available at the time of this design, please note that it may be neccesary to lower the overall system recovery to prevent barium and strontium sulfate scale formation.

D. The maximum level of free chlorine which can be tolerated in the RO feedwater varies with temperature as follows: 1 ppm at 4-25 degrees C, 0.5 ppm at 26-30 degrees C, 0 ppm at 31-35 degrees C.

E. The feedwater should be sterile.

F. The feedwater should be pretreated to a silt density index < 4.

This estimate of an appropriate design configuration and expected performance of Dowex* RO permeators is based upon the particular feedwater analysis submitted to the Dow Chemical Co. The design and expected performance are presented in good faith, but no warranty is expressed or implied. Although these criteria should assure proper performance of the Dowex* RO permeators, the ultimate success of any RO facility depends upon an adequately engineered system that is properly operated and maintained.

* Trademark of the Dow Chemical Company

San Ysidro Arsenic Removal Report

Appendix C

Activated Alumina Runs

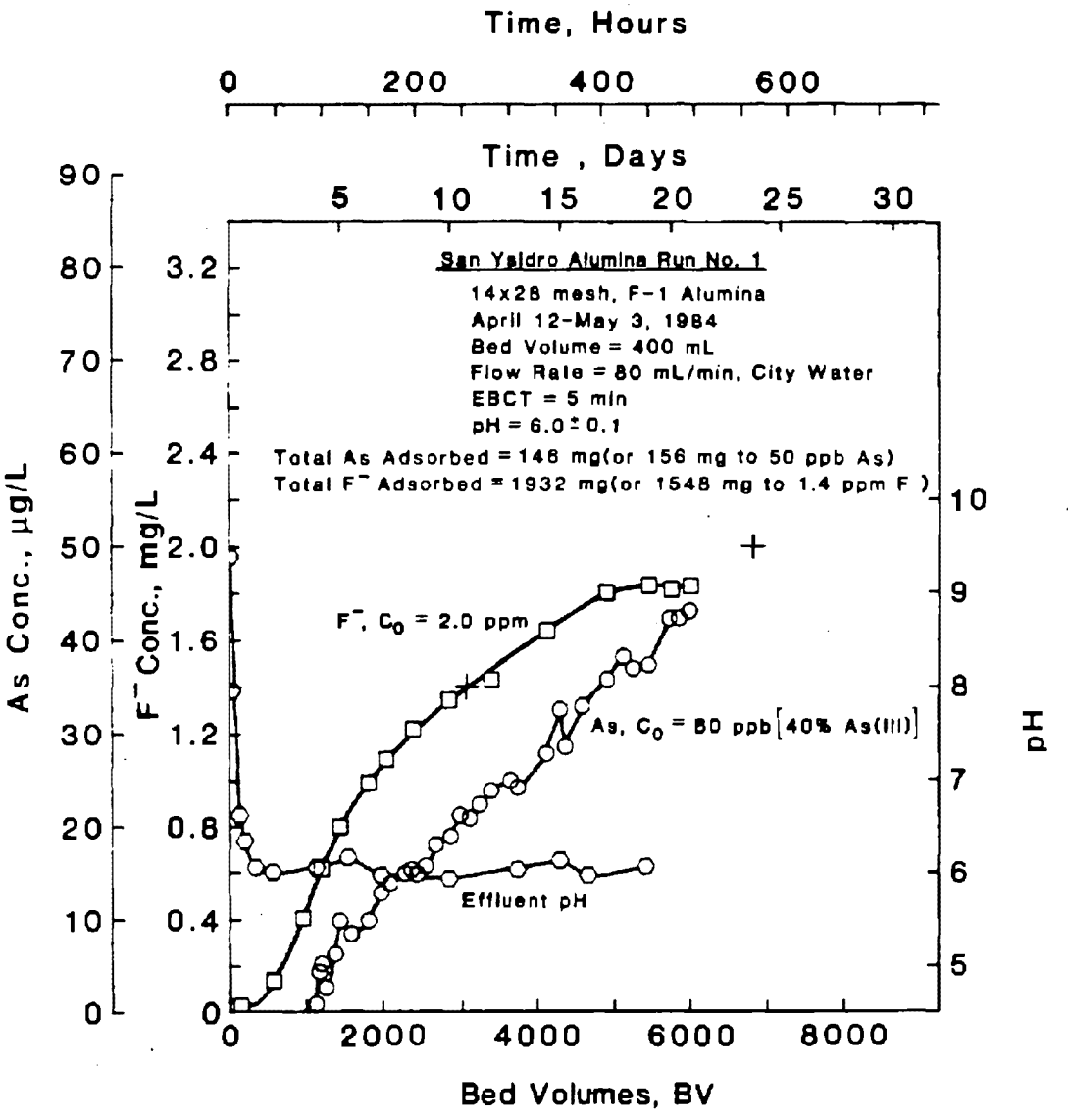

Figure C1. Breakthrough curves for fluoride and arsenic during Run No. 1--new, coarse-mesh alumina.

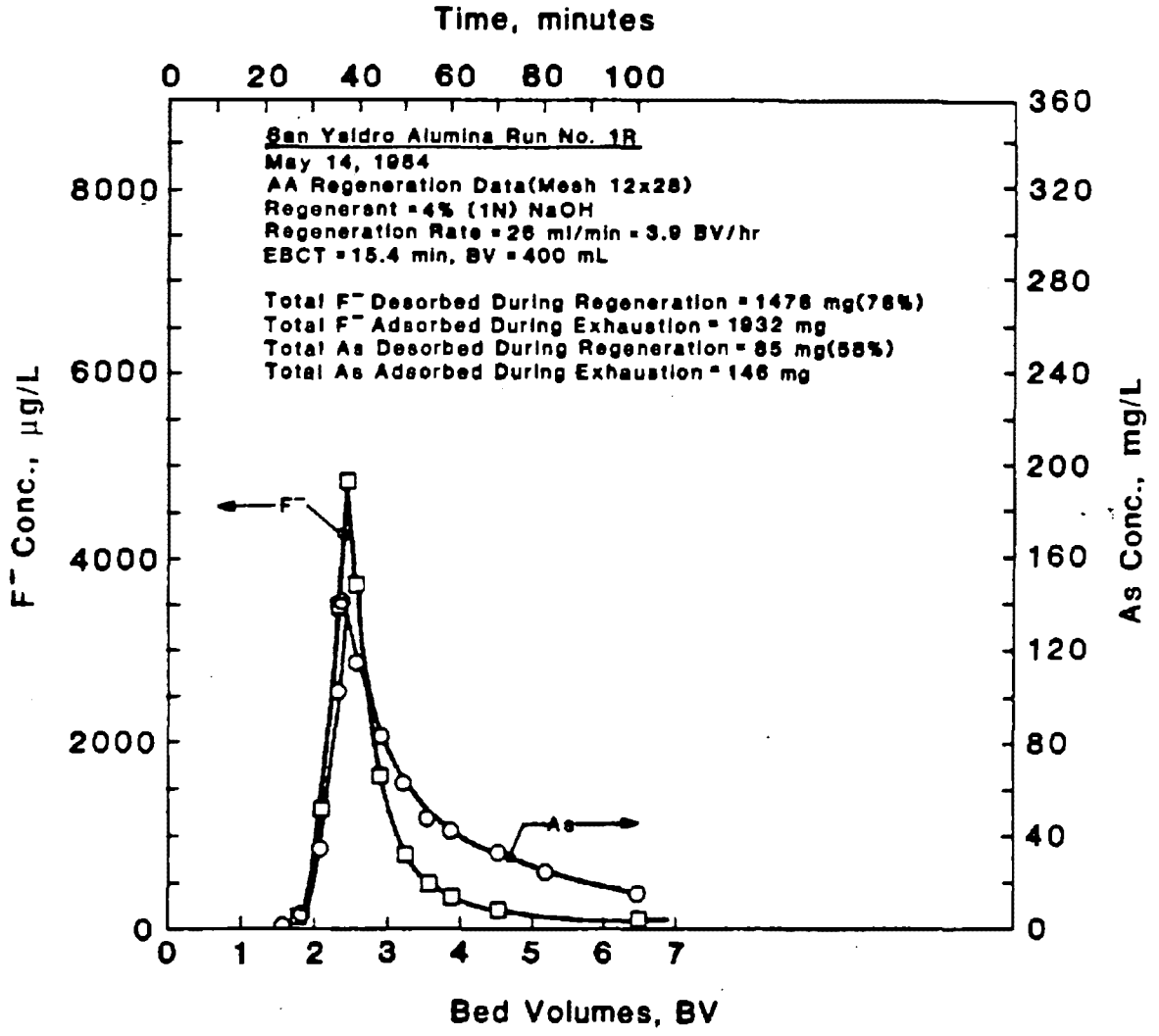

Figure C2. Arsenic and fluoride elution during a regeneration of fine mesh alumina using 4% NaOH. Run 1R--regeneration following exhaustion run No. 1.

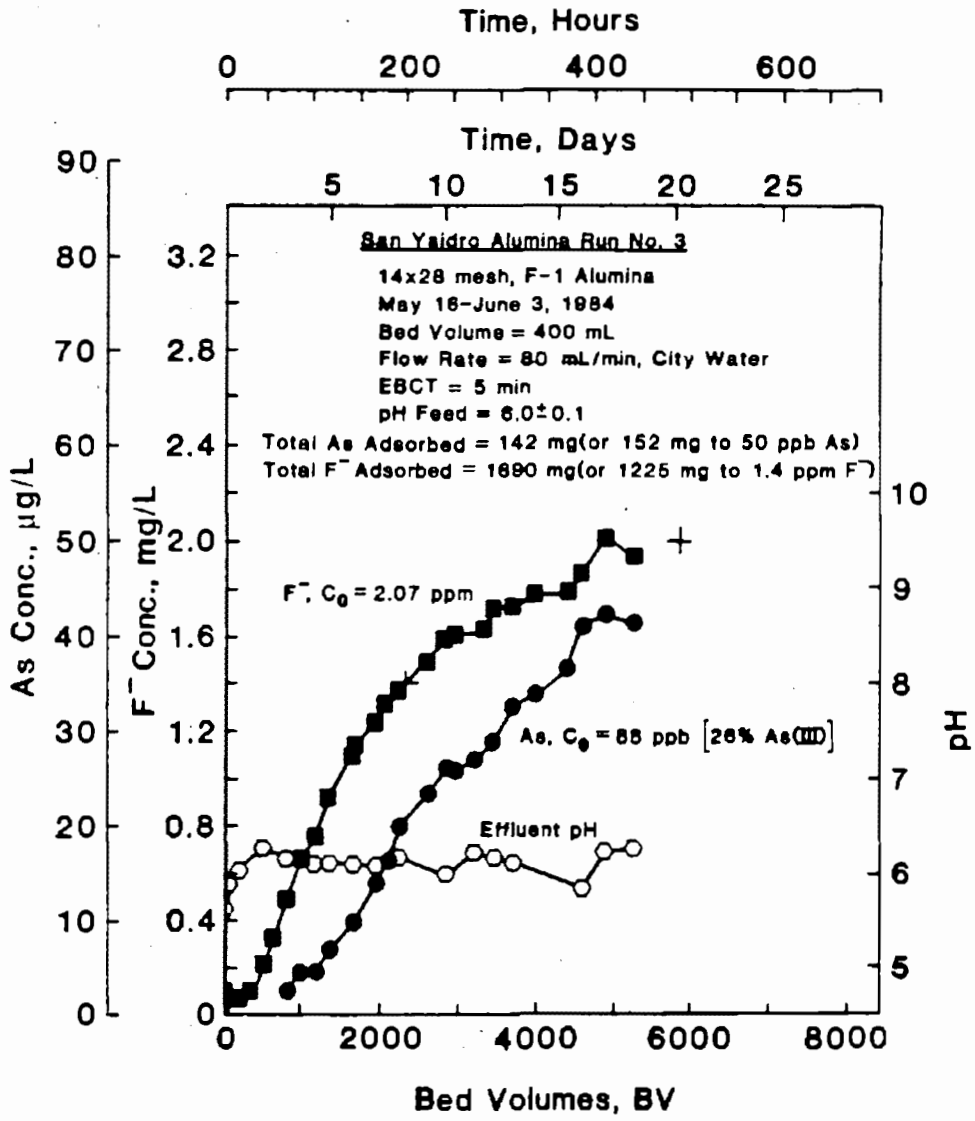

Figure C3. Fluoride and arsenic breakthrough curves for Run No. 3--once-regenerated, coarse-mesh alumina.

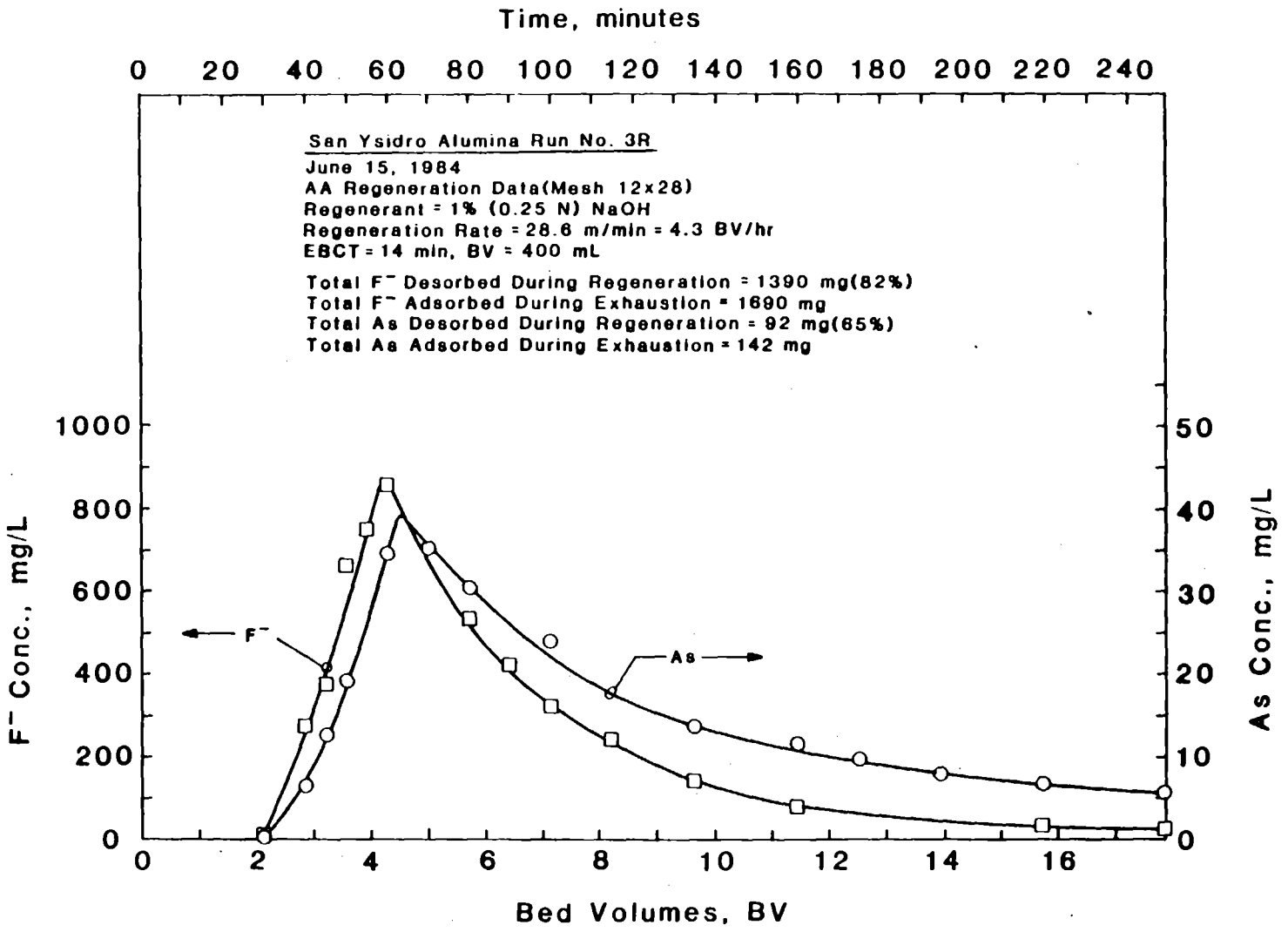

Figure C4. Fluoride and arsenic elution during 1% NaOH regeneration of coarse-mesh alumina following exhaustion Run No. 3.

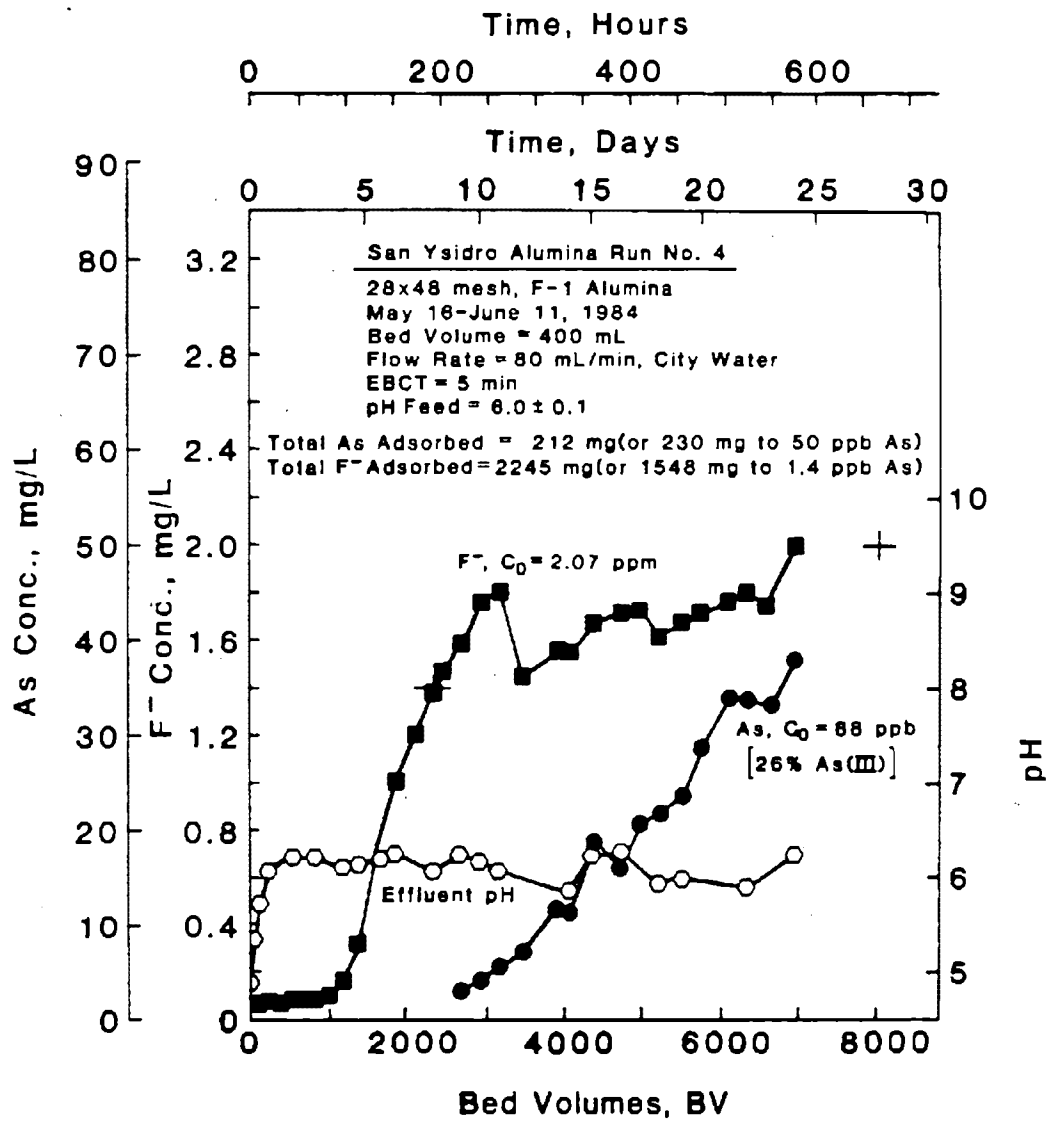

Figure C5. Breakthrough of fluoride and arsenic during Run No. 4--once-regenerated fine-mesh alumina

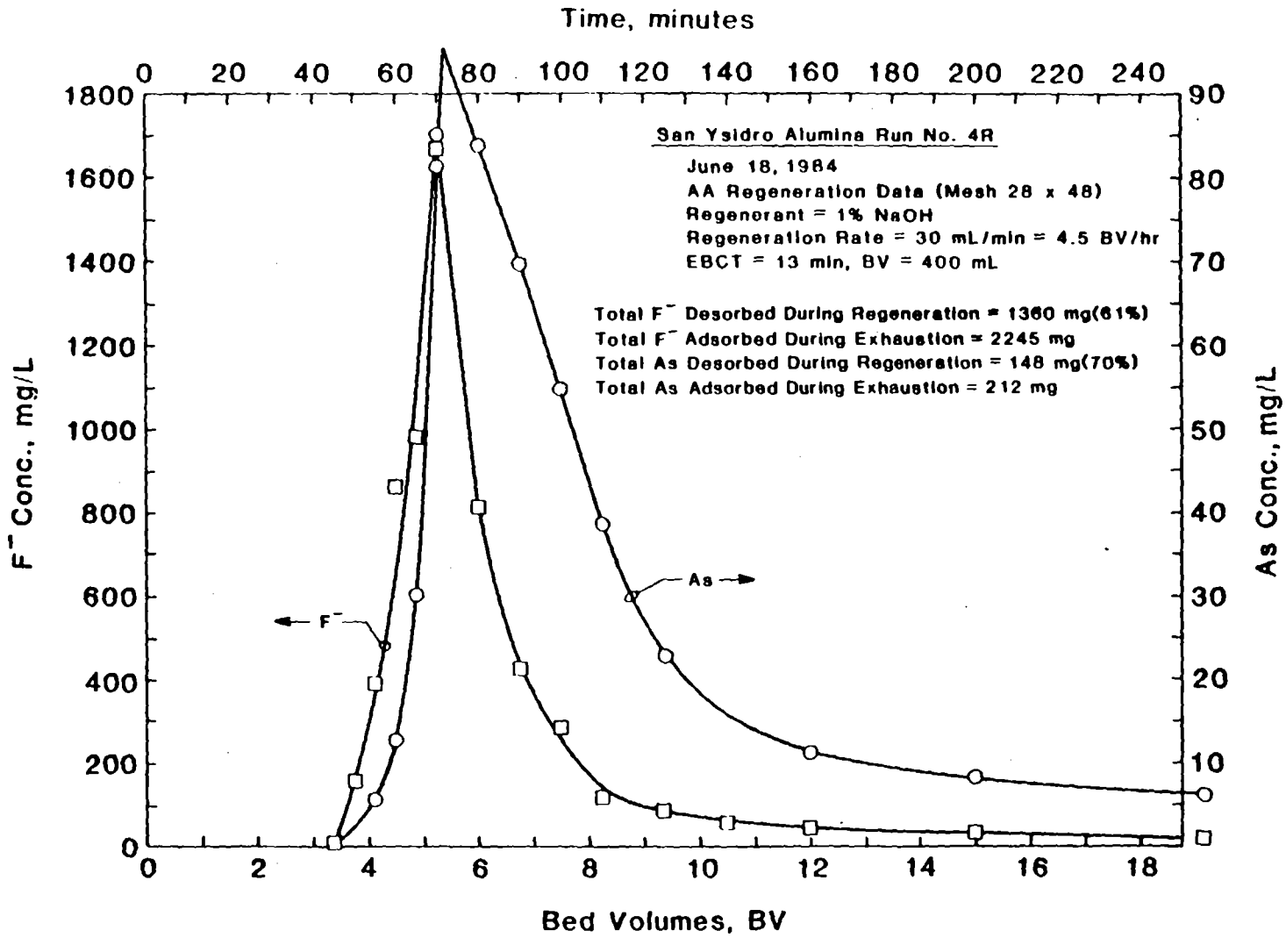

Figure C6. Fluoride and arsenic elution curves during regeneration of spent, fine-mesh alumina following exhaustion Run No. 4.

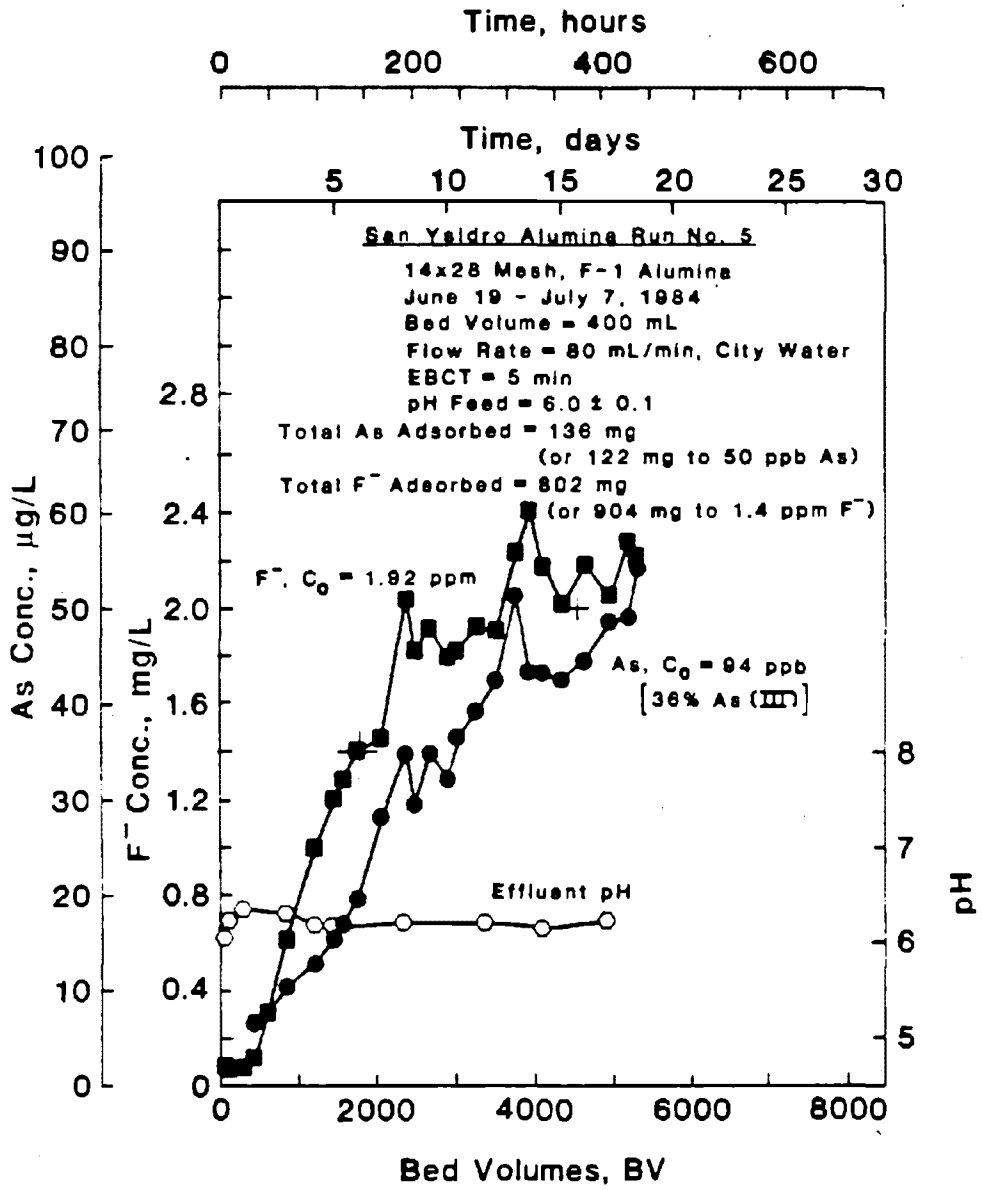

Figure C7. Breakthrough curves for fluoride and arsenic during Run 5--twice-regenerated coarse-mesh alumina.

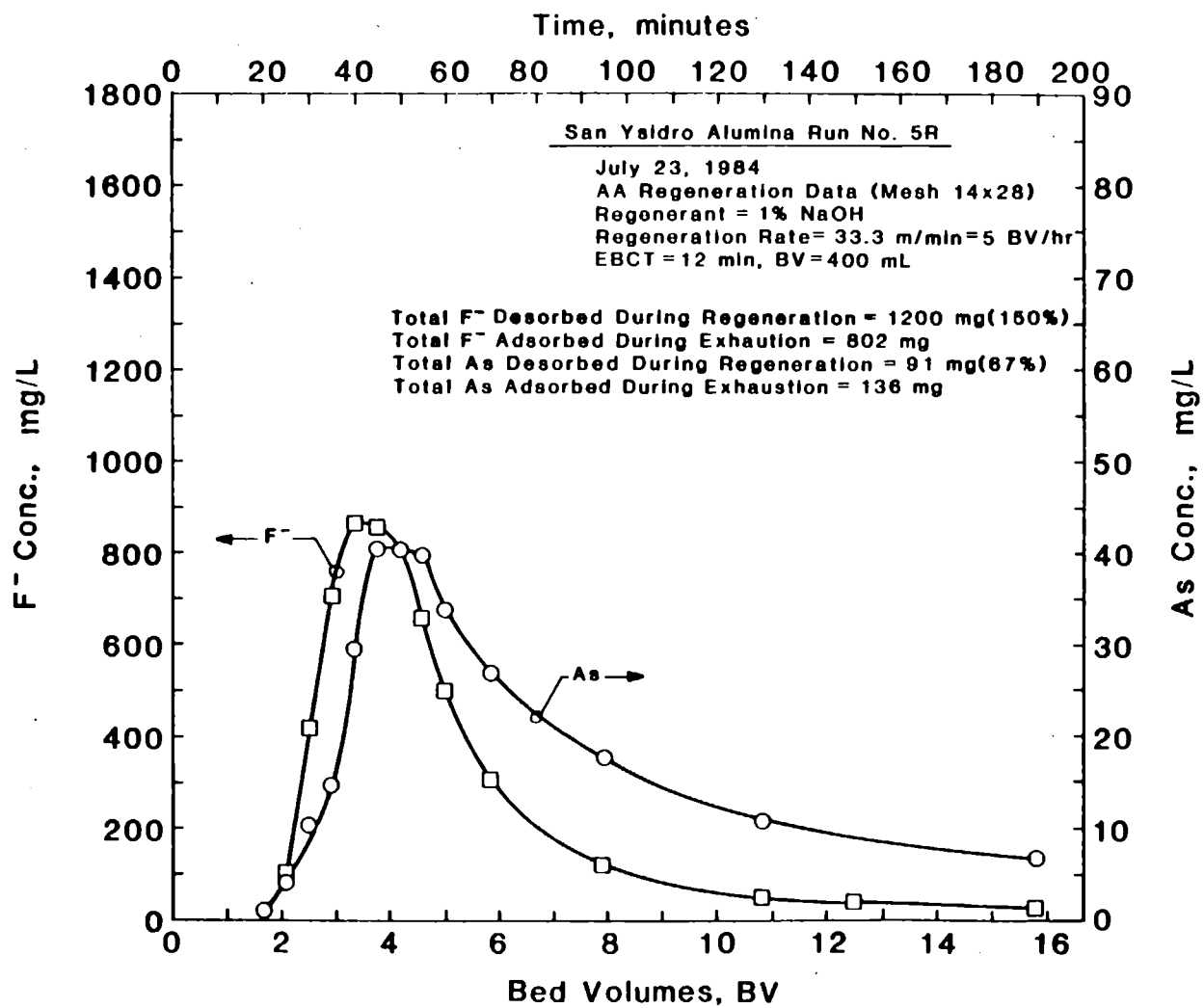

Figure C8. Fluoride and arsenic elution during 1% NaOH regeneration of coarse-mesh alumina following exhaustion Run No. 5.

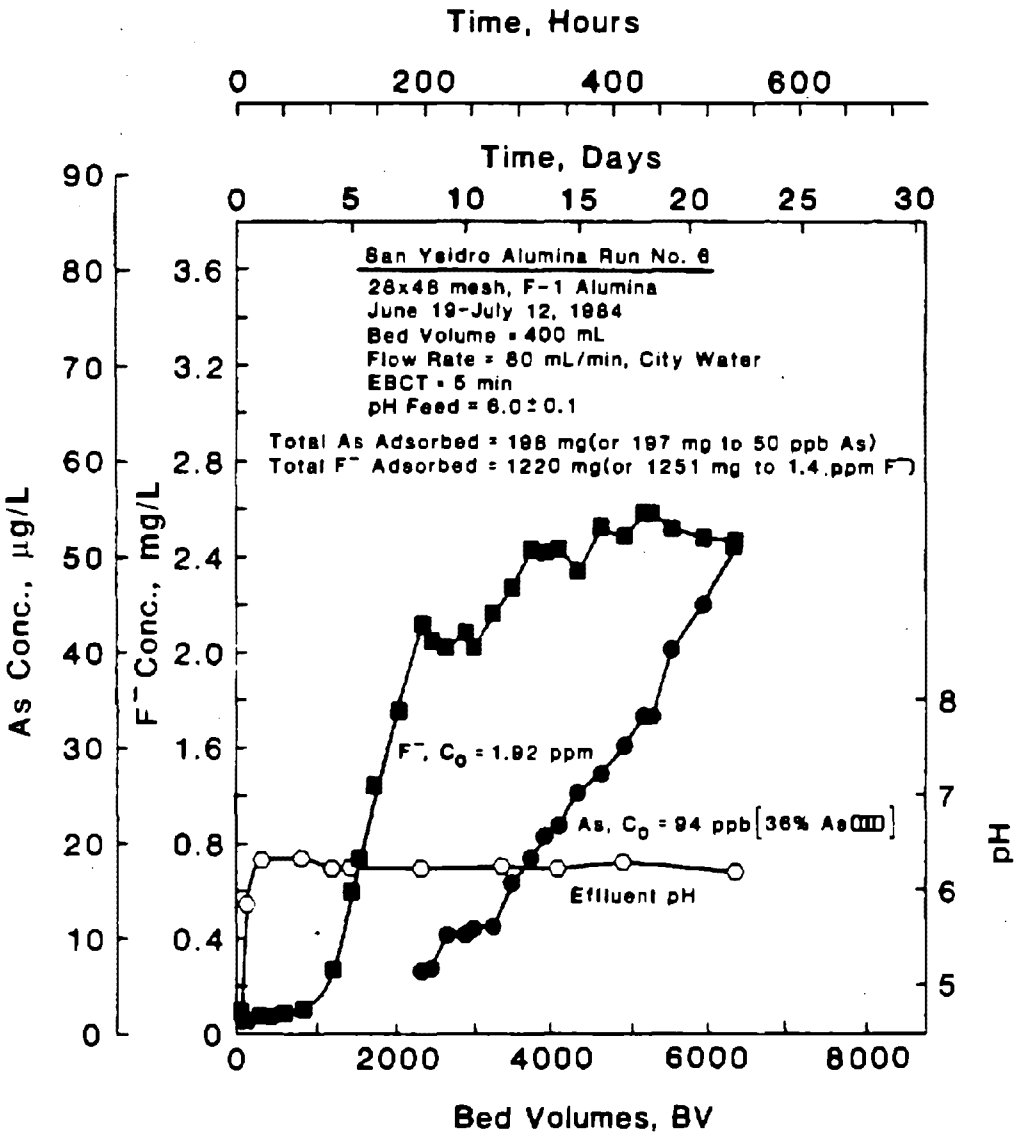

Figure C9. Breakthrough curves for fluoride and arsenic during exhaustion Run No. 6--twice-regenerated fine-mesh alumina.

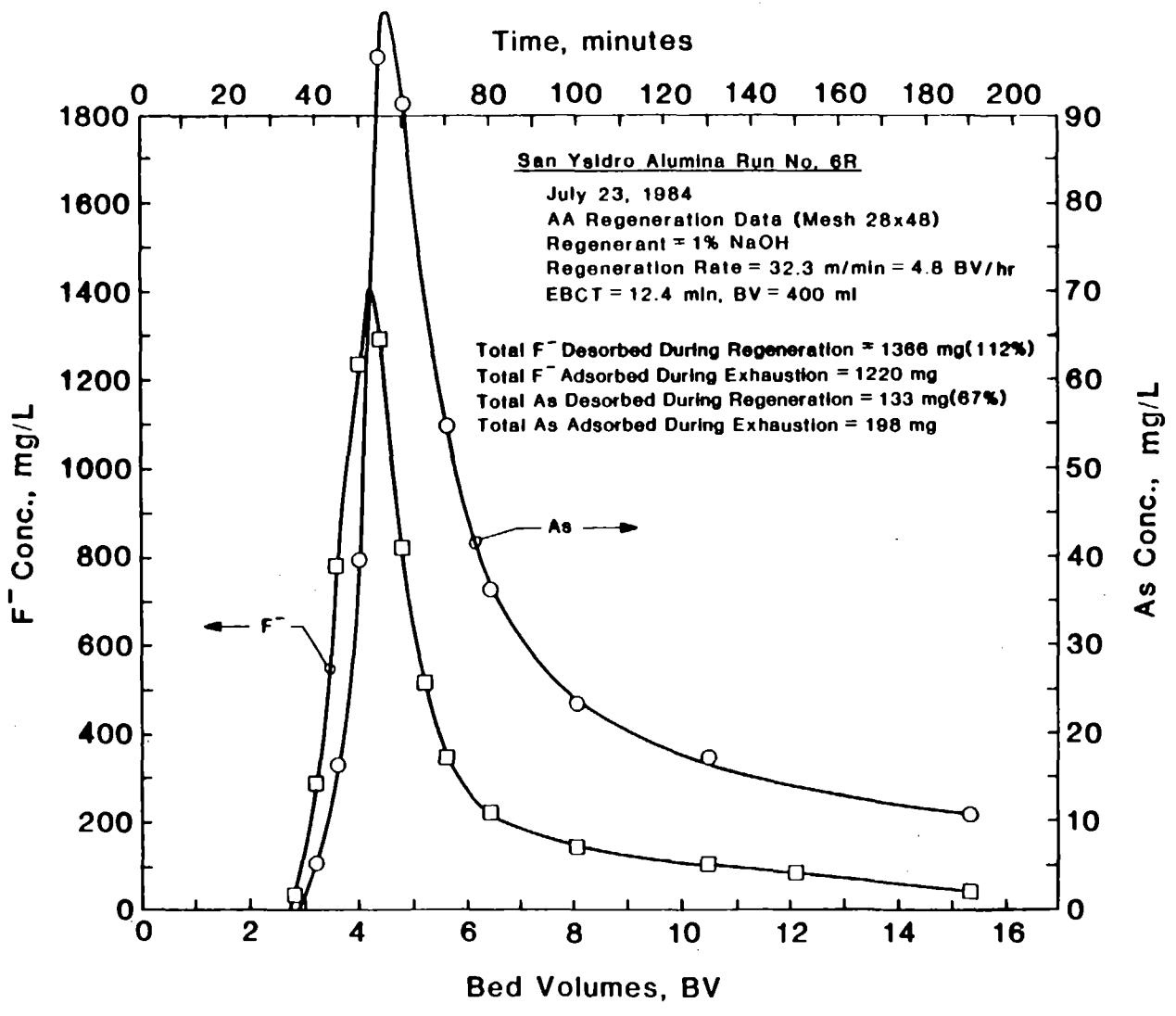

Figure C10. Fluoride and arsenic elution during 1% NaOH regeneration of fine-mesh alumina following exhaustion Run No. 6.

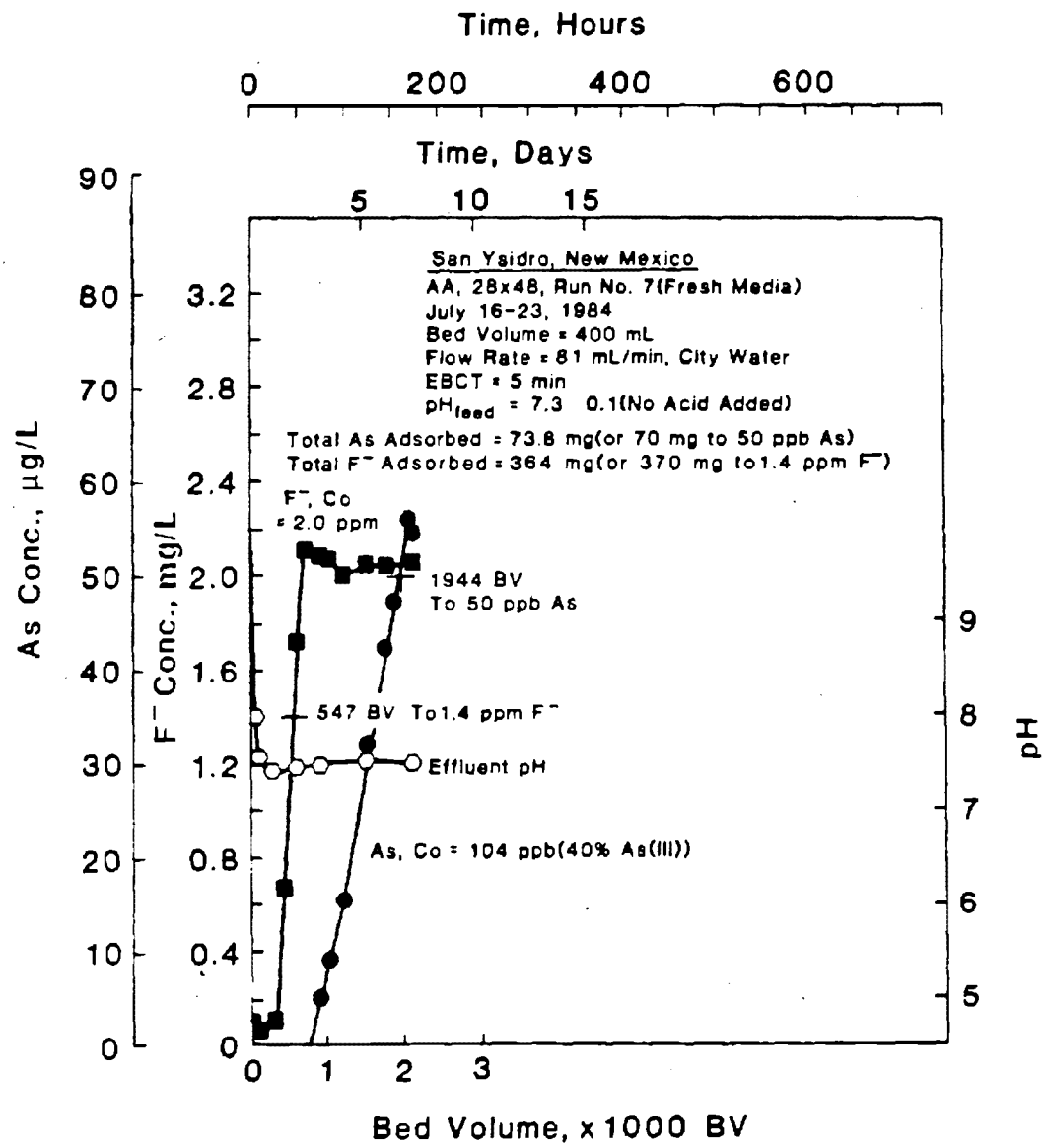

Figure C11. Breakthrough curves for fluoride and arsenic during exhaustion Run No. 7--fine-mesh alumina and unadjusted feed pH.

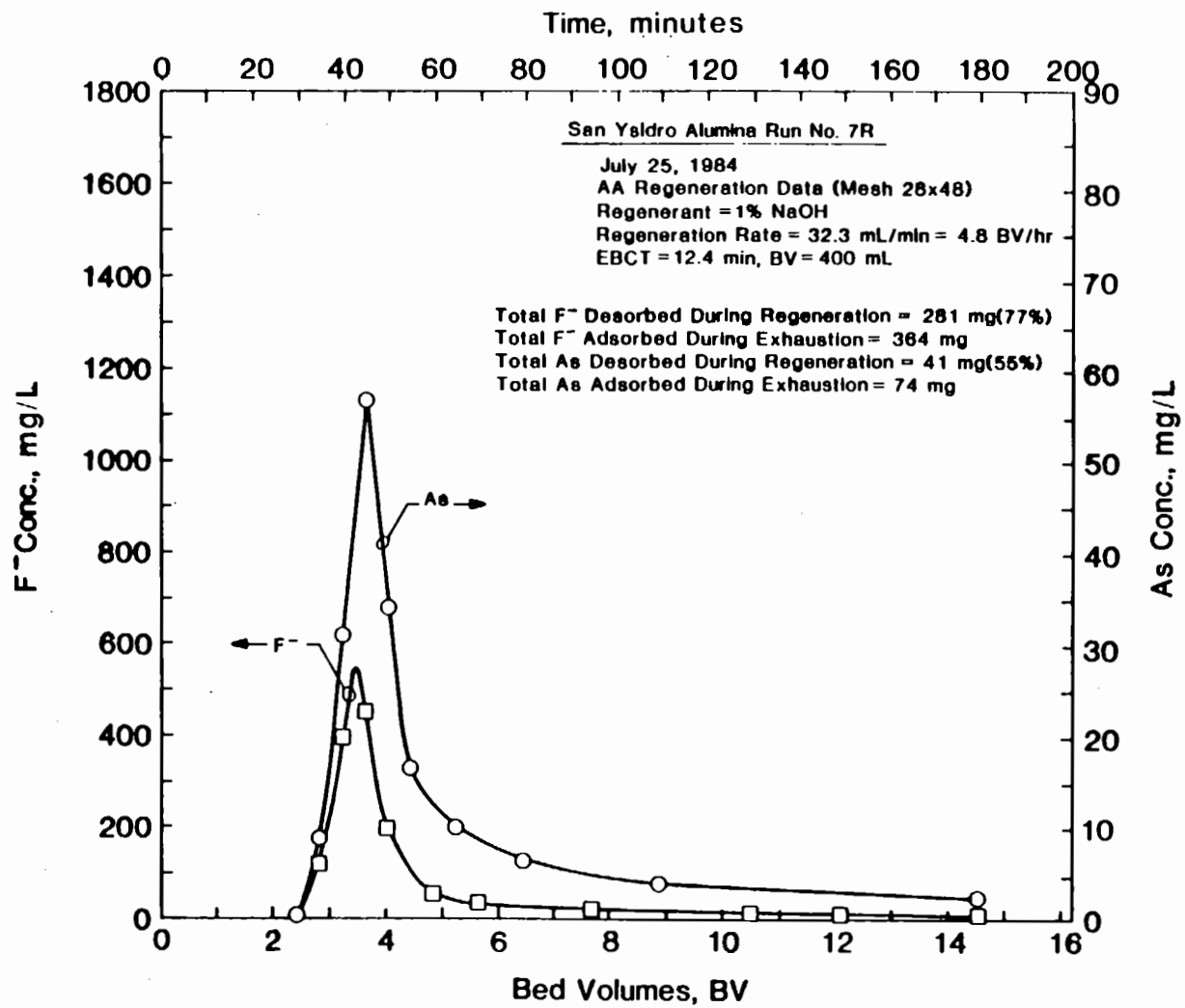

Figure C12. Fluoride and arsenic elution during 1% NaOH regeneration of fine-mesh alumina following exhaustion Run No. 7.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before complete)

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15. SUPPLEMENTARY NOTES

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16. ABSTRACT

The removal of a natural mixture of As(III) (31 ug/L) and As(V) (57 ug/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 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 into fine-mesh activated alumina gave better-than-expected results. 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.

Reverse Osmosis (RO) treatment 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 ug/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 ug/L.

Chloride-form anion exchange also performed better-than-expected (200 BV) but not well enough for it to be considered seriously for treatment. Point-of-use (POU) RO treatment was effected in removing >91% of the arsenic and >94% of the TDS at low (<15%) water recovery.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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