

Enhanced coagulation for arsenic removal

Preliminary bench- and pilot-scale investigations showed that coagulation is a promising treatment for removing arsenic from drinking water but that further work is needed, primarily on full-scale plants.

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Arsenic is a carcinogenic metalloid that is currently regulated in drinking water by the US Environmental Protection Agency (USEPA) at the maximum contaminant level (MCL) of 0.050 mg/L. This MCL was established by the USEPA in 1977 and adopted by the state of California. How-

ever, the USEPA is planning to publish a proposed arsenic regulation in November 1995. It is anticipated that the MCL may be lowered to between 0.0005 and 0.020 mg/L, based on epidemiological studies conducted in Taiwan.¹ These studies show that the presence of arsenic will increase the risks of skin cancer

(when ingested) and of lung cancer (when inhaled). Smith² extrapolated the data from the Taiwanese study to the general US population. He concluded that the current USEPA standard of 0.050 mg/L for arsenic could increase the risk of death from lung, kidney, or bladder cancer by 13

The possible use of enhanced coagulation for arsenic removal was examined at the facilities of a California utility in 1992 and 1993. The tests were conducted at bench, pilot, and demonstration scales, with two source waters. Alum and ferric chloride, with cationic polymer, were investigated at various influent arsenic concentrations. The investigators concluded that for the source waters tested, enhanced coagulation could be effective for arsenic removal and that less ferric chloride than alum, on a weight basis, is needed to achieve the same removal.

Operational characteristics of La Verne pilot plant and demonstration plant

Parameter	Pilot Plant	Demonstration Plant
Flow	6 gpm	5.5 mgd
Velocity gradient (G)		
Rapid mix— s^{-1}	32.5	2,500
Flocculator, stage 1— s^{-1}	80	30
Flocculator, stage 2— s^{-1}	25	15
Flocculator, stage 3— s^{-1}	8	15
Flocculator, stage 4— s^{-1}		5
Detention time (basins)		
Rapid mix	1.3 min	0.84 sec
Flocculation—min	15	30
Sedimentation—min	60	99
Loading rate		
Sedimentation—gpm/sq ft		1
Filter—gpm/sq ft	6	5

per 1,000 persons, based on water ingestion of 1 L/d. The USEPA has estimated that exposure at the current MCL of 0.050 mg/L would cause an increase of 31.3 excess skin cancers per 1,000 people.³

From 1973 to 1991, the USEPA conducted bench- and pilot-scale studies to evaluate the effectiveness of various treatment processes in removing arsenic from drinking water.⁴⁻⁸ All data reported in these studies had a minimum detection limit (MDL) of 1.0–5.0 $\mu\text{g/L}$ for arsenic. The USEPA is currently assessing the practical quantitation level (PQL) for arsenic. Atomic absorption spectrometry techniques can achieve a PQL of about 4 $\mu\text{g/L}$, but preliminary indications are that a PQL as low as 2.0 $\mu\text{g/L}$ may be possible.⁹ With the potential of lowering the arsenic MCL significantly—possibly to <5.0 $\mu\text{g/L}$ —there is a renewed interest in treatment processes that can reduce arsenic below that level.

Objectives

One objective of performing tests at the bench, pilot, and demonstration scales was to determine the effectiveness of arsenic removal at each level. A second objective of this testing was to determine, if possible, what extent of treatment would be necessary to achieve the potential arsenic MCLs.

Literature review

Aqueous chemistry of arsenic. Arsenic occurs in both inorganic and organic forms in natural waters. The inorganic arsenic is a result of dissolution from the solid phase, e.g., arsenolite (As_2O_3), arsenic hydride (As_2O_5), and realgar (As_2S_2).¹⁰ Inorganic arsenic may be present in the formal oxidation states of arsenate [As(V)] and arsenite [As(III)]. The dominant arsenic species is a function of pH and redox potential. Arsenate, the thermodynamically stable form of the inorganic species in oxic waters, generally predominates

in surface waters. Arsenate exists in four forms in aqueous solutions: H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} . HAsO_4^{2-} predominates from pH 7 to 11.5, indicating that this is the form most likely to occur in surface water supplies. At pH <7, H_2AsO_4^- dominates. Arsenite is favored under reducing conditions, e.g., in anaerobic groundwater. Arsenite is present as H_3AsO_3 in aqueous solutions; this undissociated weak acid is predominant in the pH range of 2–9. Organic arsenic species occur in natural waters as a result of the use of organo-arsenical pesticides, as well as through the biomethylation mechanisms of microorganisms.^{11,12}

It is well established that the toxicity of arsenic depends on its chemical form.¹³ Arsenite, the trivalent inorganic species,

is more toxic to biological systems than arsenate, the pentavalent species. The toxicities of organo-arsenicals are lower than those of inorganic arsenic species.

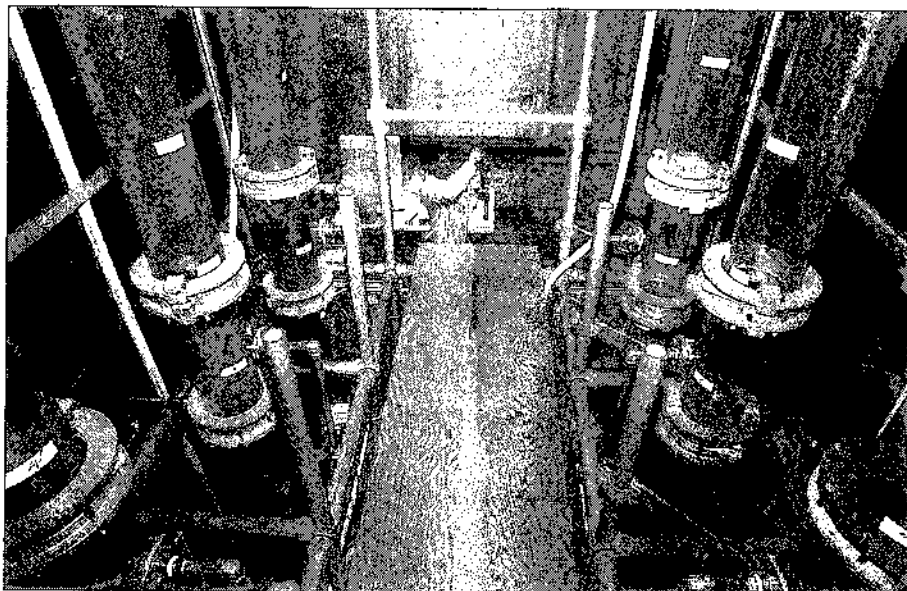
Aqueous chemistry of aluminum and iron coagulation. Amirtharajah and O'Melia¹⁴ indicated that freshly precipitated amorphous aluminum hydroxide, $\text{Al}(\text{OH})_3(\text{am})$, is formed by the addition of alum to water. According to thermodynamic data for aluminum equilibria, aluminum is least soluble around

o correlation was found between turbidity removal and arsenic removal. However, good turbidity removal is a prerequisite for good arsenic removal.

a pH of 6.2. Alum dosages of 10–30 mg/L, in the pH range of 5.0–8.0, can result in $\text{Al}(\text{OH})_3(\text{am})$ precipitate. As the alum dose is increased to nearly 30 mg/L at a final pH of 7.0–8.0, the precipitation of solid aluminum hydroxide tends to occur to a greater extent, and a sweep coagulation mechanism tends to dominate. At pH <5.0, polymeric species can predominate.

Freshly precipitated amorphous ferric hydroxide, $\text{Fe}(\text{OH})_3(\text{am})$, is formed by the addition of ferric chloride (FeCl_3) to water in the pH range of 6.0–10.0. At high pH (>10), the principal soluble species present is the monomeric anion $\text{Fe}(\text{OH})_4^-$. At low pH levels (<6), the dominant soluble species are cationic monomers such as Fe^{3+} and $\text{Fe}(\text{OH})_2^+$. Fe(III) is least soluble at a pH of about 8. Fe(III) is a stronger acid and is less soluble than aluminum.

Arsenic removal from water. A variety of treatment processes has been used for arsenic removal from water. The most commonly used technologies include coprecipitation and adsorption onto coagulated floc, lime softening, sulfide precipitation, adsorption onto activated carbon, activated alumina, ion



Pilot-scale tests were conducted to substantiate arsenic removals observed in jar tests and to collect operational data such as the effects of increased coagulant dosages on filter performance.

apparatus containing six jars, followed by sand filters.²⁰ Each jar holds approximately 2 L of water.

Both California state project water (SPW) and Colorado River water (CRW) were collected in batches and subsequently tested. Because MWDSC normally treats surface waters, and As(V) is the prevalent form of arsenic found in surface waters, all

exchange, and membrane processes such as reverse osmosis.^{4-8,15-19} One of the most common treatment processes for removing arsenic from water is conventional coagulation. Previous studies concluded that arsenate is more effectively removed than arsenite from drinking water, and oxidation of arsenite to arsenate is necessary to achieve effective arsenic removal.^{4,16} However, it must still be determined whether conventional coagulation could be applied to meet more stringent drinking water standards.

Experimental design

Bench-, pilot-, and demonstration-scale tests at various Metropolitan Water District of Southern California (MWDSC) facilities evaluated arsenic removals under varying conditions.

Bench studies. A series of jar tests was performed for arsenic removal during February and March 1993. These tests were conducted using a modified jar-test

arsenic spiking tests were performed with As(V). Although SPW and CRW contain ambient arsenic levels of approximately 3 µg/L, sufficient As(V) was spiked to raise the arsenic level to 20 µg/L in the influent. This elevated level simulates the possible degradation of MWDSC's surface waters when groundwater is introduced.

Both alum and FeCl₃ were used as coagulants in this study, and cationic polymer was used as the coagulant aid. Alum and FeCl₃ were dosed at 10, 20, and 30 mg/L. The polymer doses used in SPW were 2 mg/L for alum and 3 mg/L for FeCl₃; when CRW was used, the polymer doses were 3 mg/L for either alum or FeCl₃. These polymer dosages were determined to be optimal from the jar tests.

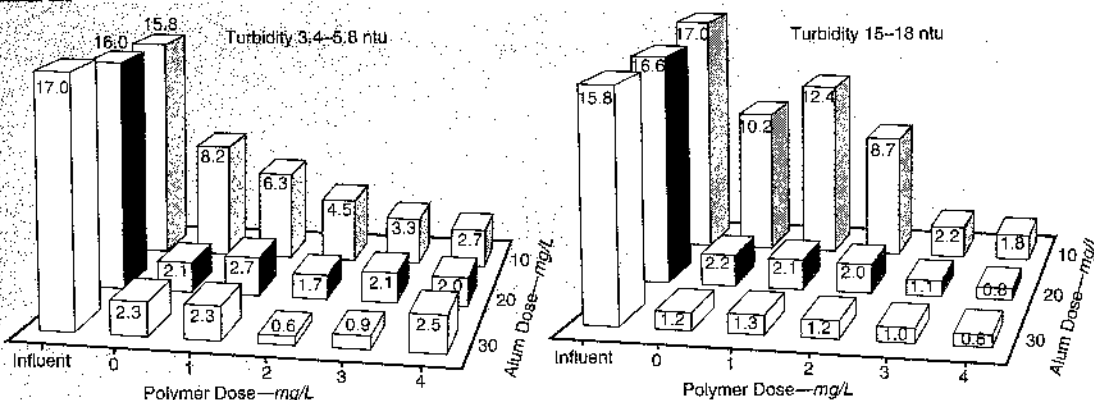
A total of four pH conditions were tested in this study: ambient (with no acid addition), 7.0, 6.3, and 5.5. All pH values mentioned hereafter refer to the pH of coagulation unless otherwise noted. Some of the

Raw water quality for SPW and CRW

Parameter	Jar Tests (2/93-3/93)			Pilot Tests (7/93-10/93)	
	SPW			SPW	CRW
	Batch 1	Batch 2	CRW		
Temperature—°C	NT*	NT	NT	24.0 ± 0.7	26.3 ± 0.5
pH	7.81 ± 0.14	7.64 ± 0.27	8.05 ± 0.28	7.89 ± 0.15	8.10 ± 0.15
Alkalinity—mg/L	68 ± 1.4	56 ± 1.4	128 ± 4.1	81.0 ± 2.0	121 ± 1.0
Turbidity—ntu	4.5 ± 1.5	16.8 ± 4.5	1.8 ± 1.2	2.0 ± 0.3	0.8 ± 0.2
Total suspended solids—mg/L	NT	NT	NT	2.33 ± 0.27	0.69 ± 0.28
Spiked arsenic—µg/L	16.9 ± 0.8	18.3 ± 1.5	19.8 ± 1.8	3.5 ± 1.0	4.4 ± 0.4
Al—µg/L	127 ± 31	496 ± 68	72 ± 30	81 ± 22	13.3 ± 2.9
Fe—µg/L	345 ± 412	NT	69 ± 12	63 ± 24	24 ± 11
TOC—mg/L	3.12 ± 0.13	3.17 ± 0.11	2.51 ± 0.17	3.59 ± 0.32	64 ± 10
UV ₂₅₄ —1/cm	0.098 ± 0.028	0.190 ± 0.020	0.051 ± 0.011	NT	2.66 ± 0.53
				NT	NT

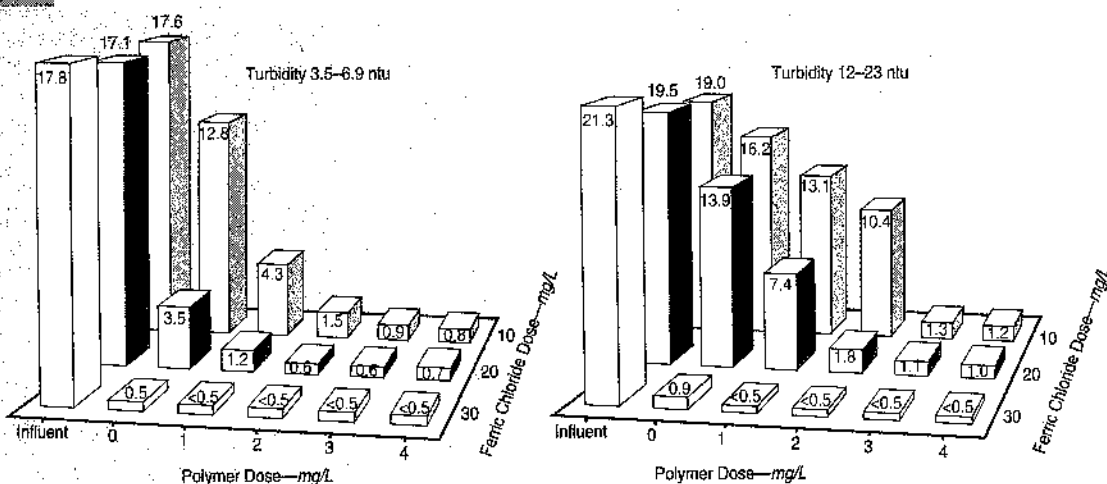
*NT—not tested

Arsenic levels using alum and cationic polymer in SPW during jar tests



Bars represent arsenic levels in micrograms per litre.

Arsenic levels using FeCl₃ and cationic polymer in SPW during jar tests



Bars represent arsenic levels in micrograms per litre.

conditions tested required pH adjustment by acid addition. Sulfuric acid (at a strength of 93 percent) was added to the influent to depress the pH. Because the added coagulants depressed the pH of the water, the desired coagulation pH was measured after the acid and the coagulants had been added. For the ambient pH tests, alum doses of 10, 20, and 30 mg/L dropped the pH of SPW and CRW to the ranges of 7.40-7.0 and 7.84-7.51, respectively. When FeCl₃ was dosed at 10, 20, and 30 mg/L, the pH of the SPW and CRW was lowered to the ranges of 7.06-6.53 and 7.55-7.03, respectively.

The coagulants were added to each jar, flash-mixed at 100 rpm (G value of 90 s⁻¹) for 1 min, and flocculated at 50 rpm for 15 min (G value of 35 s⁻¹); finally, the effluent was collected after being passed through the sand filters. The filters were backwashed with tap water and rinsed with five bed volumes of deionized (DI) water. Because the tap water contained ambient levels of arsenic (up to 3 µg/L), rinsing with

DI water was necessary to lower the background arsenic level below the <0.5-µg/L detection limit obtained during these tests.

Samples collected from each test were analyzed for pH, turbidity, ultraviolet (UV) absorbance at 254 nm (UV₂₅₄), and arsenic. Total organic carbon (TOC), alkalinity, aluminum, and iron were analyzed for selected tests to assess other operating criteria for enhanced coagulation (e.g., TOC reduction, alkalinity reduction, and aluminum and iron levels in the finished water).

Pilot-scale tests. The goals of the pilot-scale tests were (1) to substantiate the removals observed in the jar tests and (2) to collect operational data in such areas as the effects of increased coagulant dosages on filter performance (turbidity, filter run length). These tests were conducted between July and October 1993 at MWDSC's La Verne pilot plant (LVPP). The LVPP contains two trains, each capable of operating at 6 gpm, and simulates a conventional filtration

plant. Pertinent operational parameters for the LVPP are listed in Table 1.

The filters were backwashed before any runs were started. Arsenate was spiked into the plant influent in 55-gal stainless-steel containers. If pH adjustment was needed, the acid was added after this point. If pH adjustment was necessary, the coagulation pH (measured at the rapid-mix effluent) was allowed to stabilize to ± 0.1 pH units of the desired pH. Coagulants were then added to the rapid-mix tank, and the water entered the flocculation basins. The water settled in the sedimentation basins, which were equipped with tube settlers to better mimic the basins at MWDSC's full-scale plants. A nonionic polymer was then added (typically in a dose of 0.02 mg/L) to improve the filterability of the water. The filters were operated at 6 gpm/sq ft to simulate the highest rate currently allow-

able by the State of California Department of Health Services without special exemptions.

With a few exceptions, as noted later, the same coagulation conditions were tested in the bench- and pilot-scale tests. For the pilot tests, As(V) was spiked into the influent to achieve a total arsenic level of approximately 5 $\mu\text{g/L}$ in order to simulate the normal worst-case ambient arsenic levels in MWDSC's source waters. A coagulation pH of 5.5 was not tested because it was felt that MWDSC's plants could not reasonably operate at this pH on a continuous basis.

All of the sample analyses performed in the pilot-scale tests were similar to those in the bench-scale tests, with the exception of the arsenic analysis.

Demonstration-scale tests. A series of enhanced coagulation tests was performed at MWDSC's 5.5-

FIGURE 3 Arsenic levels using alum and FeCl_3 at selected pH values in SPW during jar tests¹

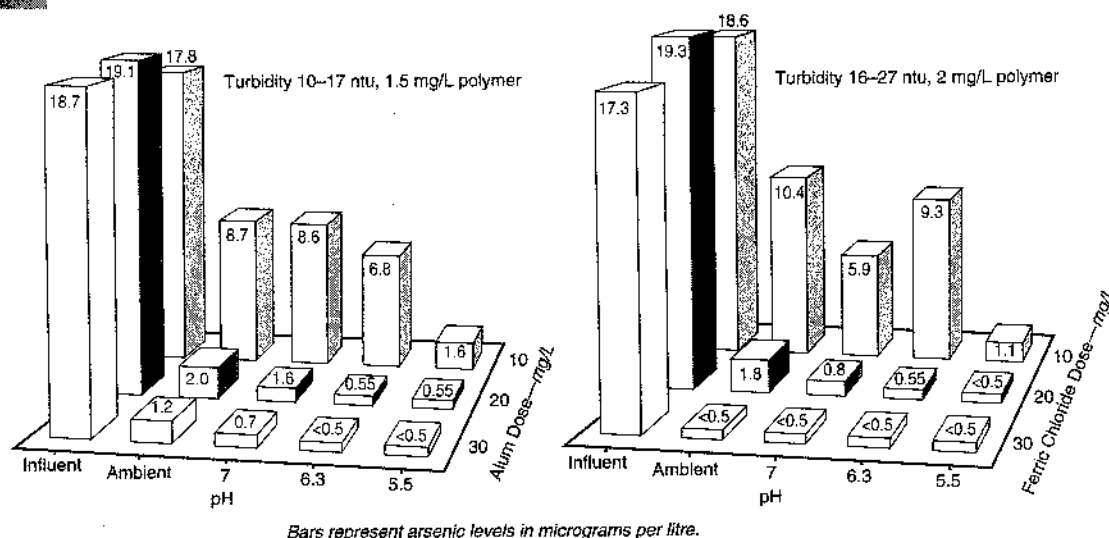
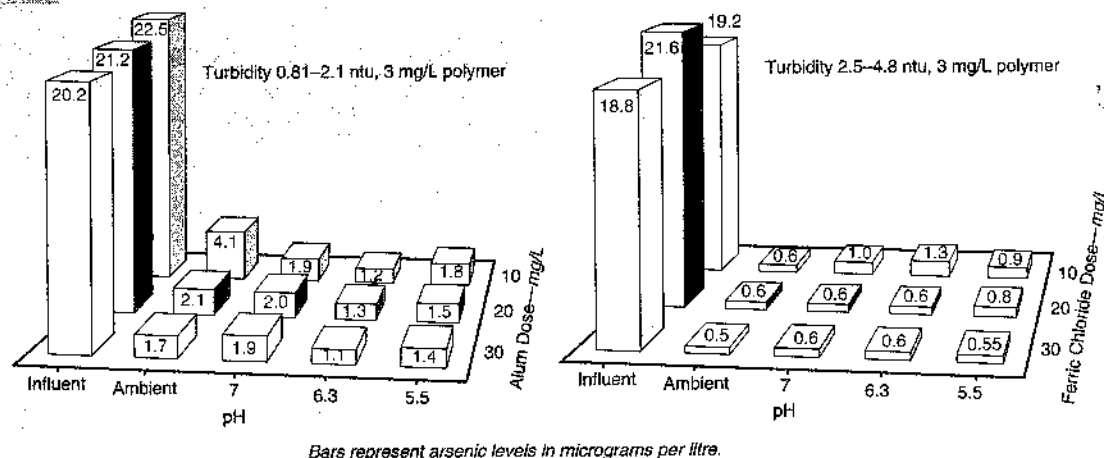


FIGURE 4 Arsenic levels using alum and FeCl_3 at selected pH values in CRW during jar tests



Operational conditions to achieve specific effluent arsenic levels during jar tests at initial arsenic concentration of 20 µg/L

Water Type	Possible MCL µg/L	Alum Dose mg/L	FeCl ₃ Dose mg/L	Minimum pH Required	
SPW	2.0-5.0	≥20	≥20	No acid added	
		10	10	5.5	
	0.5-2.0	≥20	≥20	No acid added	
CRW	2.0-5.0	20		7.0	
		10	10	5.5	
		30	10	6.3	
	0.5-2.0		20	20	5.5
			30	30	No acid added
			10	10	7.0
<0.5		>10	>10	No acid added	
		30	10	No acid added	
		10	10	7.0	
	<0.5	NP*	NP	NP	

*NP—not possible with any condition

Operational conditions to achieve specific effluent arsenic levels during pilot-plant tests

Water Type	Influent Arsenic µg/L	Possible MCL µg/L	Alum Dose mg/L	FeCl ₃ Dose mg/L	Minimum pH Required
SPW	3.5 ± 1.0	2.0-5.0	10	10	No acid added
		0.5-2.0	>10	10	No acid added
		<0.5	30	10	6.3
CRW	4.4 ± 0.4	2.0-5.0	10	10	No acid added
		0.5-2.0	10	10	No acid added
			20		7.0
	13.3 ± 2.9	<0.5	10	10	No acid added
			10	10	No acid added
			30	10	6.3
	<0.5		10	No acid added	

mgd Oxidation Demonstration Plant (ODP) from August to October 1992. Pertinent ODP operating information is shown in Table 1. These tests were performed primarily for disinfection by-product removal, and no arsenic spiking was conducted;²¹ however, limited arsenic data were collected from the tests. Only alum was used during these tests, at pH conditions of ambient (no acid addition), 7.0, 6.3, and 5.5. For the ambient tests, alum doses of 10, 20, and 30 mg/L dropped the pH of SPW to 7.8, 7.65, and 7.26, respectively, whereas 20 mg/L alum dropped the pH of CRW to 7.6. The plant was allowed to operate for 17 h before the filters were backwashed, and three detention times were allowed to elapse before the arsenic samples were collected.

Sample analyses

The turbidity and pH were measured at the jar-test influent and effluent. A turbidimeter* with an accuracy of ±2 percent was used to measure the

turbidity; it was calibrated daily, using standards of 0.80 and 6.6 ntu. A pH meter† with an accuracy of ±0.002 pH units was used; this unit was also calibrated daily, using pH 7.0 and 9.18 buffer solutions.

The UV analyses were performed with a spectrophotometer‡ set at a wavelength of 254 nm. The samples were first filtered through a prewashed 0.45-µm filter to remove turbidity, which can interfere with this measurement. The jar-test influent and effluent samples were measured for UV. The TOC analyses were performed for selected tests (with higher coagulant levels dosages); TOC was measured using a carbon analyzer.§ The aluminum and iron samples were analyzed with an atomic absorption spectrophotometer.** The detection limits for aluminum and iron were 5 and 20 µg/L, respectively. The alkalinity samples were analyzed by the procedures described in *Standard Methods*.²²

Arsenic samples were analyzed by two methods, with three detection limits. The MDL for arsenic was 1.0 µg/L during the demonstration-scale tests and was lowered to 0.5 µg/L during the

bench-scale tests. The arsenic analyses for the pilot-scale samples were performed by hydride generation, combined with inductively coupled plasma-mass spectrometry (ICP-MS), conducted by a contract laboratory†† on an ICP-MS unit‡‡ equipped with a nebulizer, water-cooled spray chamber, and electron multiplier.²³ This method has a detection limit of 0.02 µg/L.

Results and discussion

Jar tests. The SPW was collected in two separate batches, which yielded two distinct sets of raw-

*Model 2100A, Hach Co., Loveland, Colo.

†Model 920A, Orion Research, Boston, Mass.

‡Lambda 5 model, Perkin-Elmer Corp., Norwalk, Conn.

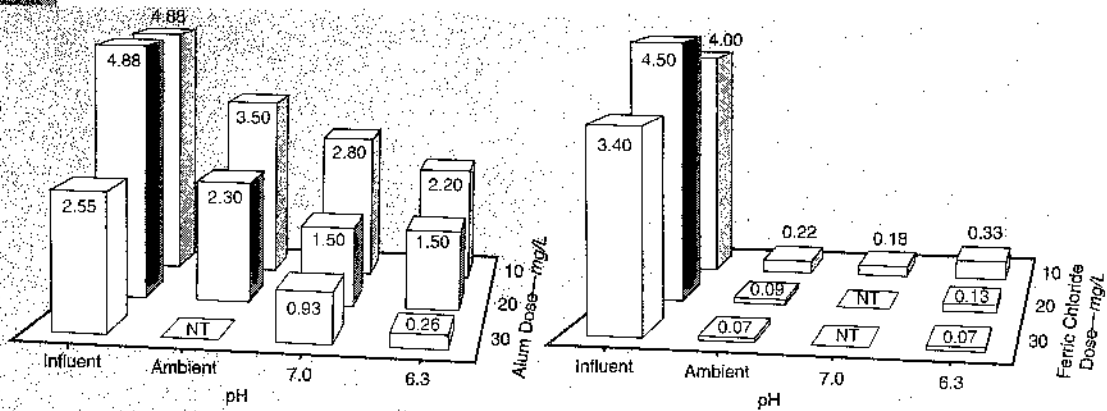
§Dohrmann model DC-180, Rosemount Analytical Corp., Santa Clara, Calif.

**SpectraAA 300/400 model, Varian Corp., Sugarland, Texas

††West Coast Analytical Services, Santa Fe Springs, Calif.

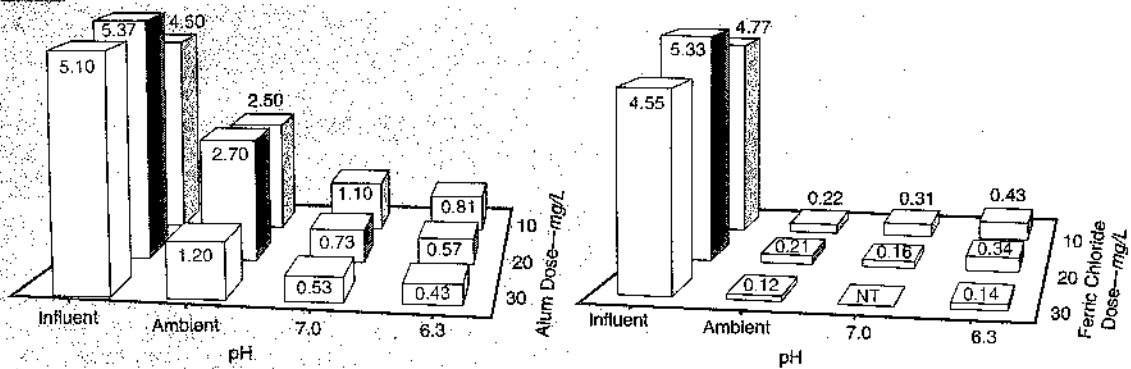
‡‡VG Plasma-Quad PQ2 Turbo Plus, Fisons Instruments, Danvers, Mass.

Comparative effluent arsenic levels using alum and FeCl₃ at selected pH values in SPW during pilot-scale tests



Bars represent arsenic levels in micrograms per litre; NT—not tested.

Comparative effluent arsenic levels using alum and FeCl₃ at selected pH values in CRW during pilot-scale tests



Bars represent arsenic levels in micrograms per litre; NT—not tested.

TABLE 2. Comparison of pilot-plant effluent turbidities at various pH and coagulant dosage conditions

Coagulant Dose mg/L	Water Type	Effluent Turbidity—ntu							
		Alum				FeCl ₃			
		Influent	No Acid Added	pH = 7.0	pH = 6.3	Influent	No Acid Added	pH = 7.0	pH = 6.3
10	SPW	1.96	0.16	0.13	0.24	2.73	0.12	0.17	0.26
	CRW	1.06	0.09	0.09	0.07	1.08	0.07	0.08	0.08
20	SPW	2.58	0.11	0.15	0.11	3.04	0.10	NT*	0.16
	CRW	1.00	0.09	0.01	0.12	1.12	0.07	0.06	0.07
30	SPW	2.65	NT	0.13	0.10	3.08	0.07	NT	0.14
	CRW	1.22	0.08	0.08	0.08	0.98	NT	0.06	0.09

*NT—not tested

water quality conditions (Table 2). Batch 1 water contained lower turbidity and higher alkalinity, whereas batch 2 water had a higher turbidity and a lower alkalinity. The difference between the water quality parameters measured for the two batches of water resulted from high-turbidity runoff water mixing with the SPW.

One purpose of the jar-test experiments was to determine the optimal dosage of polymer required for turbidity removal, using alum or FeCl₃ as the coagulant. MWDSC's effluent turbidity goal of ≤0.10 ntu was achieved by using either a low-turbidity influent or a higher dosage of coagulant. The arsenic removal was lower for waters with higher turbidity, especially

TABLE 6

Comparison of pilot-plant filter run times at various pH and coagulant dosage conditions

Coagulant Dose mg/L	Water Type	No Acid Added	Run Time—h				
			Alum		FeCl ₃		
			pH = 7.0	pH = 6.3	No Acid Added	pH = 7.0	pH = 6.3
10	SPW	22.1	22.1	9.9 (T)*	13.0	13.0	11.9 (T)
	CRW	6.3 (T)	6.6 (T)	6.7 (T)	6.9 (T)	6.7	10.7 (T)
20	SPW	10.6	13.4	9.9	9.8	NT†	9.6
	CRW	6.2 (T)	6.6 (T)	15.6 (T)	6.5 (T)	7.6	8.1 (T)
30	SPW	NT	8.3	9.6	6.2	NT	9.0
	CRW	6.2 (T)	7.61	20.6	NT	7.5	6.8 (T)

* (T) denotes filter runs ended on turbidity breakthrough (>0.25 ntu); otherwise, filter runs ended on 6 ft of head loss.
 † NT—not tested

FIGURE 7 Comparative percentages of arsenic removal at varying influent arsenic spikes using alum and FeCl₃ at selected pH values in SPW

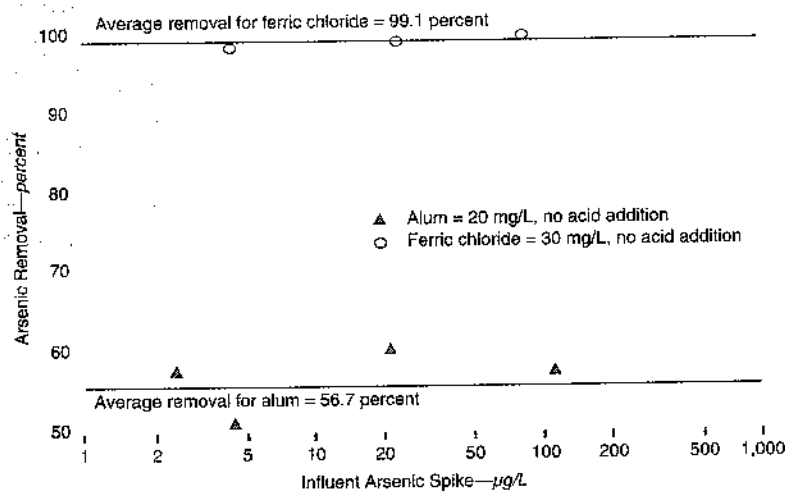
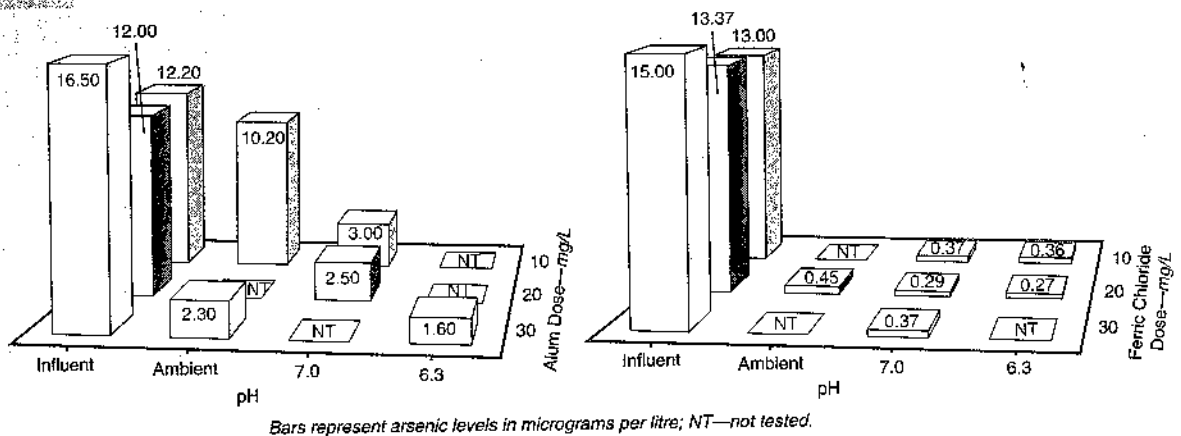


FIGURE 8 Comparative effluent arsenic levels using alum and FeCl₃ at selected pH values in CRW during high arsenic spike pilot-scale tests



at the lower coagulant dosages (Figures 1 and 2). The poor arsenic removal at the high-influent-turbidity and low-coagulant conditions appears to be linked with the poor turbidity removal observed. Because good floc formation, followed by filtration, is crucial to arsenic removal, a high-turbidity effluent indicates poor floc formation and is likely to reduce the arsenic removal attained. However, at the higher coagulant dosages, no substantial differences in arsenic removal were apparent between higher- and lower-turbidity waters. Polymer addition improved arsenic removal when a low dose of alum (<20 mg/L) or FeCl₃ (≤20 mg/L) was used under high- and low-turbidity conditions.

The influent arsenic was spiked to a level between 17.3 and 22.5 µg/L. The removals increased with increasing alum dosage and decreasing pH (Figures 3 and 4). For SPW, both alum and FeCl₃ showed similar arsenic removals (when compared on an equal-weight dosage basis), varying between 49 and >97 percent. In CRW, FeCl₃ appeared to effect better arsenic removal. It is interesting that arsenic removals with coagulant doses of >20 mg/L, at

Comparisons of bench- and pilot-scale tests for percent arsenic removal in CRW using alum

Dose mg/L	Arsenic Removal—percent								
	Bench Scale*			Pilot Scale†			Pilot Scale‡		
	No Acid Added	pH = 7.0	pH = 6.3	No Acid Added	pH = 7.0	pH = 6.3	No Acid Added	pH = 7.0	pH = 6.3
10	79	92	95	31.1	68.8	NT§	49	73.2	82
20	89	91	94	NT	79.2	NT	61.4	82.2	88.6
30	90	91	95	83.6	NT	91.6	82.9	86.1	90.4

*Average As in influent—21.3 µg/L
 †Average As in influent—13.6 µg/L
 ‡Average As in influent—4.99 µg/L
 §NT—not tested

TABLE 2 Comparisons of bench- and pilot-scale tests for percent arsenic removal in CRW using FeCl₃

Dose mg/L	Arsenic Removal—percent								
	Bench Scale*			Pilot Scale†			Pilot Scale‡		
	No Acid Added	pH = 7.0	pH = 6.3	No Acid Added	pH = 7.0	pH = 6.3	No Acid Added	pH = 7.0	pH = 6.3
10	90	95	93	NT§	97.7	96.4	94.1	93.3	92.8
20	97	97	97	97.2	98.1	97	95.6	96.6	94.8
30	97	97	97	NT	97.5	NT	97.6	NT	96.7

*Average As in influent—20 µg/L
 †Average As in influent—13.8 µg/L
 ‡Average As in influent—4.93 µg/L
 §NT—not tested

ambient pH, were almost equal to the removals achieved at lower coagulant dosages with acid addition to lower the pH.

Pilot-scale tests. The raw-water quality of both CRW and SPW remained consistent during the pilot-scale test period (Table 2). The influent arsenic was spiked to a level of 3.5 ± 1.0 µg/L in SPW and 4.4 ± 0.4 µg/L in CRW. FeCl₃ appears to result in much better arsenic removals than alum (Figures 5 and 6). An effluent arsenic concentration of <0.5 µg/L was easily met under all conditions in both waters when FeCl₃ was used. The maximum effluent arsenic level attained in SPW when FeCl₃ was used was 0.33 µg/L, and the values ranged from 0.07 to 0.33 µg/L. The maximum effluent arsenic level attained when FeCl₃ was applied to CRW was 0.31 µg/L, and the values ranged from 0.14 to 0.31 µg/L. These results also demonstrate that FeCl₃ works equally well in both SPW and CRW, achieving similar removals under the same coagulation conditions.

Achieving specific arsenic residuals. Jar tests. Three possible new MCL levels—<0.5, 0.5–<2.0, and 2.0–5.0 µg/L—were assumed, and the operational conditions required to meet each of these levels for both of MWDSC's source waters, with a 20-µg/L influent, were compared (Table 3). In all instances, except for an MCL of <0.5 µg/L in CRW, no pH adjustment was necessary. Most of the target MCLs could be met through increased coagulant addition. The lowest arsenic effluent level obtained in CRW was 0.55 µg/L with FeCl₃. For SPW, if the arsenic MCL was

set at a level of >0.5 µg/L and no pH adjustment was required, a 20-mg/L dose (or greater) of either alum or FeCl₃ could be used. For CRW, using FeCl₃ seemed to achieve better arsenic removal. If the MCL was ≥ 0.5 µg/L and CRW was the source water, no pH adjustment was needed when either 10 mg/L of FeCl₃ or 30 mg/L of alum was used.

Pilot-scale tests. A similar summary was prepared for the pilot-scale results as for the bench-scale results, with the exception that the influent arsenic concentration was different (Table 4). For CRW, both the high and normal spike conditions are listed. FeCl₃ easily met a possible MCL of 0.5 µg/L in both SPW and CRW (including the high arsenic spike scenario), requiring a dose of 10 mg/L and no pH adjustment. If alum was used as the coagulant in SPW and CRW (with a normal arsenic spike), no acid addition was necessary when the MCL remained >0.5 µg/L; an alum dose of 20 mg/L at ambient pH appeared to be sufficient. If CRW contained a high arsenic spike (>10 µg/L), no scenario examined in this study with alum was sufficient to lower the effluent arsenic level to <0.5 µg/L.

Summary. The bench- and pilot-scale data suggest that (1) FeCl₃ is more effective than alum; (2) alum is pH-dependent, and the highest As(V) removals are achieved at pH <7; and (3) FeCl₃ coagulation is not pH-dependent between 5.5 and 7.0, but increasing coagulant dosage will increase As(V) removal. Other studies also arrived at the same conclusions.^{4,5,15,16} Gullledge and O'Conner¹⁶ demonstrated that some of these observations can be

Table 5 Comparisons of effluent arsenic concentrations and percent arsenic removals at bench, pilot, and demonstration scale in SPW using alum

Dose mg/L	Effluent Arsenic Concentration (Arsenic Removal)— $\mu\text{g/L}$ (percent)							
	No Acid Added	Bench Scale*		No Acid Added	Pilot Scale†		Demonstration Scale‡	
		pH = 7.0	pH = 6.3		pH = 7.0	pH = 6.3	No Acid Added	pH = 6.3
10	8.7(49)	8.6(52)	6.8(62)	3.5(25.5)	2.8(17.6)	2.2(83.9)	NT§	<1.0(>67)
20	2.0(89)	1.6(92)	0.55(97)	2.3(51)	1.5(55.9)	1.5(41.9)	NT	<1.0(>67)
30	1.2(96)	0.7(96)	<0.5(>97)	NT	0.93(67.9)	0.26(88.2)	<1.0(>67)	<1.0(>67)

*Average As in influent—18.5 $\mu\text{g/L}$
 †Average As in influent—3.44 $\mu\text{g/L}$
 ‡Average As in influent—3.0 $\mu\text{g/L}$
 §NT—not tested

explained by less adsorption of As(V) on both $\text{Al}(\text{OH})_3(\text{am})$ and $\text{Fe}(\text{OH})_3(\text{am})$ at pH 8 than at a pH of 5–7. The pH dependence was much more pronounced for the $\text{Al}(\text{OH})_3(\text{am})$ than the $\text{Fe}(\text{OH})_3(\text{am})$. Gullidge and O'Conner¹⁶ also concluded that As(V) was removed better in the H_2AsO_4^- form than in the HAsO_4^{2-} form.

Operational considerations. Other parameters measured during the pilot-scale tests can enter into the selection of operational conditions that are optimal for removing arsenic. These factors include (but are not limited to) effluent turbidity and filter run length. Some operational data were collected by on-line instruments, including turbidimeters,* differential pressure cells for head loss measurements, and magnetic flowmeters. The data were recorded via a supervisory control and data acquisition (SCADA) system and were logged once every 4 min.

The turbidities measured on-line over a run were subsequently averaged (Table 5). Excellent turbidities were obtained under all conditions, except for a low coagulant dosage at low pH (6.3) in SPW. Generally, lower turbidities were achieved in CRW than in SPW. No significant difference in effluent turbidity can be seen between the two coagulants, and no correlation seems to exist for turbidity removal and arsenic removal.

The filter runs may be terminated under two conditions: loss of head or high turbidity. The runs are ended when either the head loss exceeds 6 ft or the turbidity reaches (and remains at) 0.25 ntu. The two waters behaved differently under the same conditions (Table 6). When alum was used, the filter runs usually terminated with head loss in SPW and with turbidity breakthrough in CRW. When FeCl_3 was used, the filter run times in SPW appeared to be shorter, whereas the filter runs in CRW appeared to remain nearly constant (between 7 and 9 h of operating time). These filter run times must be considered when the decision is made to use alum or FeCl_3 at MWDSC's treatment plants.

Arsenic removal at elevated influent concentrations. Tests were conducted on both SPW and CRW at elevated influent arsenic concentrations to determine whether the effluent arsenic concentration or the removal percentage remained constant. Two conditions in SPW, one with FeCl_3 and one with alum, were examined with varying influent spikes (2.2–128 $\mu\text{g/L}$). The removal percentage remained nearly constant over the range of influent spikes for the same test condition (Figure 7).

Higher influent arsenic spikes ($13.3 \pm 2.9 \mu\text{g/L}$) were used in CRW to determine whether arsenic removal was dependent on the influent concentration (Tables 7 and 8). Again, it appears that FeCl_3 was the better coagulant for arsenic removal (Figure 8). The removals appear to remain nearly constant between the normal ($4.4 \pm 0.4 \mu\text{g/L}$) and high arsenic spike tests for both FeCl_3 and alum.

Comparison of arsenic removals among tests. The demonstration-scale effluent data at the higher coagulant dosages compare favorably with the bench- and pilot-

Table 6 Comparisons of bench- and pilot-scale tests for percent arsenic removal in SPW using FeCl_3

Dose mg/L	Arsenic Removal—percent					
	No Acid Added	Bench Scale*		No Acid Added	Pilot Scale†	
		pH = 7.0	pH = 6.3		pH = 7.0	pH = 6.3
10	45	68	51	95.8	91	93
20	91	96	97	98.3	NT‡	96.5
30	>97	>97	>97	98.5	NT	96.8

*Average As in influent—18.4 $\mu\text{g/L}$
 †Average As in influent—3.48 $\mu\text{g/L}$
 ‡NT—not tested

*Model 1720C, Hach Co., Loveland, Colo.

Comparisons of aluminum residual in bench- and pilot-scale tests

Dose mg/L	pH	Aluminum Residual— $\mu\text{g/L}$							
		SPW				CRW			
		Bench Scale		Pilot Scale		Bench Scale		Pilot Scale	
		Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
10	No acid added	NT*	NT	NT	NT	49	23	21	178
	6.3	547	63	104.5	47	NT	NT	NT	NT
20	No acid added	137	77	64.3	93	69	50	20.5	213.5
	6.3	533	28	80	26.5	52	20	14	34
30	No acid added	NT	NT	NT	NT	74	25	21.5	110
	6.3	395	22	95	54	116	26	26.5	33.5

*NT—not tested

scale data, even with the limited data and the different influent arsenic spike levels (Table 9). The effluent levels were all $<1.0 \mu\text{g/L}$ in the three tests for coagulant dosages of $>20 \text{ mg/L}$. Only limited comparisons can be made from the percentage removal data, however, because of the relatively high detection limit of $1.0 \mu\text{g/L}$ in the demonstration-scale tests (resulting in a maximum calculated removal percentage of $>67\%$).

The bench-scale data demonstrated better arsenic removal than the pilot-scale data (Table 9). This phenomenon is consistent with the UV_{254} and TOC data collected from previous bench-, pilot-, and demon-

stration-scale tests conducted with alum.²¹ These previous results show that the UV and TOC removals were similar in pilot- and demonstration-scale tests but were consistently higher in bench-scale tests.

Conclusions

Based on this testing, the following conclusions can be drawn about the effectiveness of alum and FeCl_3 , as well as arsenic removals under various influent spikes.

- Both the bench- and pilot-test results indicate that FeCl_3 is a much more effective coagulant than alum when compared on an equal-weight dosage basis.

- The bench-scale results, based on an influent arsenic level of $20 \mu\text{g/L}$, indicate that when the FeCl_3 dosage is $\leq 10 \text{ mg/L}$, no acid addition is necessary to lower the effluent arsenic concentration to a level of $<0.5 \mu\text{g/L}$.

- Depending on the proposed arsenic MCL, pH adjustment may not be necessary. Based on the results from the pilot-scale tests, with an influent arsenic concentration of $<5 \mu\text{g/L}$, FeCl_3 lowered the arsenic level to $0.22 \mu\text{g/L}$ in both SPW and CRW with a dose of 10 mg/L and no acid addition. If alum was used, an arsenic MCL of $\leq 0.5 \mu\text{g/L}$ could not be achieved without acid addition.

- Arsenic removal percentages appear to have remained relatively constant in this study, regardless of the influent arsenic concentration (from 2.2 to $128 \mu\text{g/L}$ for SPW and from 4.4 to $13.3 \mu\text{g/L}$ for CRW).

- No correlation was found between turbidity removal and arsenic removal. However, good turbidity removal is a prerequisite for good arsenic removal.

- When alum was used, comparisons among bench-, pilot-, and demonstration-scale tests show that the bench-scale tests achieved better arsenic removal percentages. No significant differences between the bench- and pilot-scale arsenic removal data were observed with FeCl_3 , except at the low coagulant dosage in SPW.

Depending on the proposed arsenic MCL, pH adjustment may not be necessary.

stration-scale tests conducted with alum.²¹ These previous results show that the UV and TOC removals were similar in pilot- and demonstration-scale tests but were consistently higher in bench-scale tests.

Comparisons between the bench- and pilot-scale tests performed on CRW using alum show similar removals for the two sets of pilot-scale data, but the bench-scale data show higher removals (Table 7). This trend is similar to that observed when alum was used in SPW (Table 9). The removals seen in Table 8 are similar among the three sets of data and are consistent with those observed in the tests conducted with FeCl_3 and SPW (Table 10). With the exception of the lower FeCl_3 dose (10 mg/L), the removal percentages correlated well between bench- and pilot-scale tests (Table 9).

In summary, alum coagulation results in higher As(V) removals in the jar tests than in the pilot-scale tests. This difference is substantiated by the aluminum residual data (Table 11). As is the case with arsenic, aluminum is removed to a greater extent during the jar tests than during the pilot tests. The pilot-scale

• The pilot-scale results indicate that if the influent arsenic level is ≤ 5 $\mu\text{g/L}$ in both source waters, alum can reduce the effluent arsenic level to ≤ 0.5 $\mu\text{g/L}$. However, both the bench- and pilot-scale tests indicate that if the influent arsenic level is > 13 $\mu\text{g/L}$, even an alum dose of 30 mg/L and a pH of 6.3 are not sufficient to meet this effluent arsenic level.

Future work

Although these studies have generated some useful information, the tests must be regarded as a preliminary step in evaluating the feasibility of using enhanced coagulation for arsenic removal in the full-scale application. More work on full-scale facilities needs to be undertaken, particularly with alum. Testing at full-scale facilities would determine whether FeCl_3 is a better coagulant for arsenic removal. Work also needs to be done on arsenic speciation before the extent of possible arsenite removal from MWDSC's source waters can be determined.

Acknowledgment

The authors thank Dennis Hartmann, Hien Ngo, Jude Perera, Don Roth, and Leslie Ann Soo for their successful operation and maintenance of the La Verne pilot plant. The authors also acknowledge Robert Alvarez and Suzanne Teague, of MWDSC's Water Quality Laboratory, who helped in sample analyses and data review. Thanks are also extended to Peggy Kimball, who provided the review for this manuscript.

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