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Capsule Report

Aqueous Mercury Treatment

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Capsule Report:

Aqueous Mercury Treatment

National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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Chapter 1
Executive Summary

1 .1 Purpose

This report describes established technologies and identifies evolving methods for treating aqueous mercury. The information provided encompasses full-, pilot- and bench-scale treatment results as presented in the technical literature. The report describes alternative technologies in terms of (1) governing physical and chemical principles (e.g., solubility, oxidation-reduction potential, volatility), (2) key treatment parameters (e.g., speciation, pH, precipitating agent type and dosage, or adsorbent type and dosage), (3) pretreatment requirements, treatment performance, advantages and disadvantages, design considerations, and economics when available. This information can be useful for evaluating mercury treatment alternatives for industrial wastewater, groundwater, and soil washing extract.

This document assumes that the reader is already well versed with the technologies described and is using this report to better understand each technology's applicability for aqueous mercury removal. Thus, the report does not provide basic descriptions of each technology; such information can be found elsewhere in the literature. In addition, the report does not present recommended values for the common design parameters of technologies. Values for such parameters as (1) contact time, (2) volumetric loading rates, (3) dosages, (4) reaction times, (5) breakthrough times, and (6) mixing requirements can be determined by conducting treatability studies using the wastewater to be treated.

1.2 Summary

A broad spectrum of mercury treatment technologies has been described in the technical literature, ranging from established full-scale applications to innovative approaches investigated to date only at bench or pilotscale. The literature, however, provides only limited information on actual full-scale treatment technology performance and almost no full-scale economic data or information on mercury recovery.

Well-established and widely reported full-scale technologies are precipitation, coagulation/co-precipitation, and activated carbon adsorption. Representative data from aqueous mercury treatment operations using these methods are provided in this report.

Another technology is ion exchange treatment, which has historically been limited to the use of anion resins to process industrial wastewater that contains inorganic mercury in the complex mercuric chloride form. Chapter 8 provides a case study illustrating the use of an ion exchange system for mercury removal.

Other, less-established methods for treating aqueous mercury that are discussed in this report include chemical reduction, membrane separation, and emerging technologies involving macrocycles adsorption, biological treatment, and membrane extraction.

Each of the mercury treatment technologies described in this report achieves different effluent mercury concentrations. The effectiveness of treatment provided by each type of technology depends on the chemical nature and initial concentration of mercury as well as the presence of other constituents in the wastewater that may interfere with the process. As indicated by example data provided, co-precipitation and ion exchange achieve the lowest effluent mercury concentrations for many waste streams, ranging from 0.5 to 5.0 μg/L. Membrane technology typically achieves 80 to 90 percent rejection of mercury. Other factors, however, such as residuals management and costs, weigh heavily in selecting the appropriate treatment approach.

Chapter 2
Precipitation Treatment Process

This chapter presents information on precipitation and coagulation/co-precipitation technologies, which are among the most well-established approaches for removing mercury from wastewater. The information provided includes example data from aqueous mercury treatment operations using these methods.

2.1 Sulfide Precipitation

One of the more commonly reported precipitation methods for removal of inorganic mercury from wastewater is sulfide precipitation. In this process, sulfide (e.g., as sodium sulfide or another sulfide salt) is added to the wastestream to convert the soluble mercury to the relatively insoluble mercury sulfide form:

$$Hg^{2+} + S^{2-} \rightleftharpoons HgS_{(s)} \qquad [2\text{-}1]$$

As with other precipitation treatment, the process is usually combined with pH adjustment and flocculation, followed by solids separation (e.g., gravity settling, filtration). A typical process flow diagram for sulfide precipitation is shown in Figure 2-l. The sulfide precipitant is added to the wastewater in a stirred reaction vessel, where the soluble mercury is precipitated as mercury sulfide. The precipitated solids can then be removed by gravity settling in a clarifier as shown in Figure 2-1. Flocculation, with or without a chemical coagulant or settling aid, can be used to enhance the removal of precipitated solids.

Table 2-l presents example sulfide treatment results. For initial mercury levels in excess of 10 mg/L, sulfide precipitation can achieve 99.9+% removal. Even with polishing treatment such as filtration the minimum effluent mercury achievable appears to be approximately 10 to 100 μg/L. The most effective precipitation, with regard to minimizing sulfide dosage, is reported to occur in the near-neutral pH range. Precipitation efficiency declines significantly at pH above 9 (Patterson, 1985). Sulfide precipitation appears to be the common practice for mercury control in many chlor-alkali plants. removal efficiencies of 95 to 99.9 percent are reported for well designed and managed

Figure 2-1 Sulfide precipitation.

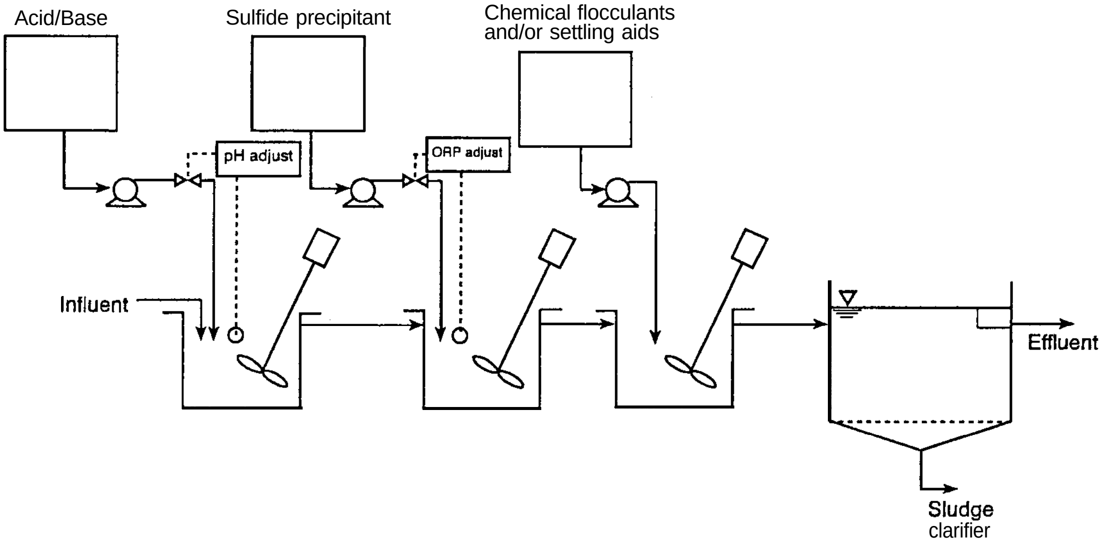


Table 2-1. Sulfide Precipitation Treatment for Mercury (After Patterson, 1985)

	Mercury Concentration (µg/L)				
Treatment Chemical	Initial	Final	Percent Mercury Removal	Treatment pH	Additional Treatment
Sodium sulfide	NA	<3	NA	NA	Vacuum filter
	300-6,000	IO-125	58-99.8	NA	Pressure filter
	1,000-50,000	10	99999.9	NA	Flocculation + activated carbon
Sodium hydrosulfide	131,50	20	>99.9	3.0	"Filter"
Magnesium sulfide	5,000-10,000	1 O-50	99-99.9	10-11	None
"Sulfide" salt	300-6,000	10-125 (50 avg)	58-99.8	5.1-8.2	Filtration
	NA	100-300	NA	NA	None
	NA	100	NA	NA	None
	NA	1 O-20	NA	NA	Activated carbon

NA = Not available.

treatment Mercury systems (Perry, 1974; U.S. EPA, 1974). A mercury effluent level of about 65 μg/L has been reported for sodium sulfide treatment of wastewaters from the chlor-alkali industry; influent mercury concentration was not reported (U.S. EPA, 1974). Costs of using the sulfide process for the treatment of chlor-alkali wastewater were reported to be $0.79/1,000 gal (1987 basis), exclusive of sludge management. Capital cost (adjusted to 1995 basis) for a chlor-alkali plant utilizing sodium sulfide addition plus diatomaceous earth filtration for a 100-gpm flow was $2,767.47 /1 ,000 gpd capacity (Perry, 1974). One consequence of the application of sulfide precipitation technology is stockpiles of mercury-laden process sludges, which must be either disposed of in an environmentally acceptable manner or processed for mercury recovery. Thus, the sludge management approach chosen is a key factor in evaluating the sulfide process for treating such wastewater.

In addition to its inability to reduce mercury below 10 to 100 μg/L, other drawbacks of this method include: (1) the formation of soluble mercury sulfide species at excess dosage of sulfide, due to the common ion effect, (2) the difficulty of real-time monitoring of reactor sulfide levels, (3) the generation of toxic residual sulfide in the treated effluent (a potential problem), (4) the difficulty of clarification and sludge processing, and (5) the need to dispose of sulfide sludges. Investigators have reported that mercury can resolubilize from sulfide sludges under conditions that can exist in landfills (Hansen and Stevens, 1992). This could in mercury contamination of leachate and potential result ground-water pollution.

2.2 Coagulation/co-precipitation

Information is available in the literature on the removal of both inorganic and organic mercury by coagulation/co-precipitation for a variety of mercury-containing wastewaters (Patterson, 1985). Coagulants employed include aluminum sulfate (alum), iron salts, and lime. For alum and iron, the dominant mercury removal mechanism is most likely by adsorptive co-precipitation (Patterson et al., 1992). Here, one ion is adsorbed into another bulk solid, formed, for example, by addition of alum and precipitation of aluminum hydroxide or by addition of an iron (ferrous or ferric) salt and precipitation of iron hydroxide. The adsorption process is isothermal, and treatment performance can be enhanced by optimal bulk solids formation and by pH manipulation to optimize bulk solid surface change and soluble mercury speciation.

In studies on the treatment of inorganic mercury dosed to domestic sewage, both iron and alum co-precipitation, followed by filtration, reduced initial mercury levels of 50 to 60 μg/L by 94% to 98%. Lime coagulation treatment, applied at a higher mercury level of 500 μg/L, achieved 70 percent removal upon filtration (Patterson, 1985). Treatment data for coagulation/co-precipitation are summarized in Table 2-2. Effluent levels of mercury achieved by alum treatment range from 1.5 to 102 μg/L, with a typical 5 to 10 μg/L value, and by iron treatment from 0.5 to 12.8 μg/L.

Table 2-2. Coagulation/co-precipitation Treatment Results for Mercury (After Patterson, 1985)

		Mercury, µg/L				
Coagulant Salt	Coagulant Dosage **(mg/L)**	Initial	Final	Percent **Mer**cut-y **Re**moval	Treatment **pH**	Additional Treatment
Alum	1,000	11,300	102	99	3	Filtration
	100	90	11	88	NA	—
	100	NA”	10	NA	NA	—
	21-24	5.9-8.0	5.3-7.4	1 o-34	6.7-7.2	Filtration
	NA	50	26.5	47	7.0	Filtration
	220	60	3.6	94	6.4	Filtration
	20-30	3-8	1.5-6.4	50-81	NA	—
	20-30	3-16”	2.3-21.3	**<23**	NA	—
Iron	34-72	4.0-5.0	2.5	38-50	6.9-7.4	Filtration
	NA	50	3.5	93	8.0	Filtration
	40	50	1.0	98	6.2	Filtration
	20-30	1-17	0.5-6.8	50-97	NA	—
	20-30	2-17’	1.2-12.8	40-93	NA	—
Lime	415	500	150	70	11.5	Filtration
	NA	0.66	co.2	**>69**	8.3	—

“Organic mercury.
NA = Not available.
- = None

Chapter 3
Adsorption Processes

Adsorption processes have the potential to achieve high efficiencies of mercury removal and/or low effluent mercury levels. The predominant adsorption process utilizes activated carbon, but the use of other adsorbents also are reported in the literature. These include processed vegetable or mineral materials such as bicarbonate-treated peanut hull carbon (BPHC), modified *Hardwickia binata* bark (MHBB), coal fly ash, and the Forager sponge (Namasivayam and Periasamy, 1993; Sen and De, 1987; Deshkar et al., 1990; U.S. EPA, 1994b). Metal hydroxides are also used as adsorbents. When metal hydroxides are employed for adsorptive treatment,, the process is commonly termed coagulation or co-precipitation. (This process is discussed in Chapter 2.) An inherent advantage of adsorptive treatment, particularly when the adsorbent displays isothermal or quasi -isothermal behavior, is that increased treatment efficiency results from incremental adsorbent dosage. Isothermal behavior is observed when, for a fixed initial pollutant concentration, decreasing residual soluble concentrations are observed as the dosage of adsorbing treatment material is added. Unless adsorbent recovery is feasible, these incremental dosages also result in production of increased wastewater treatment residuals, requiring ultimate disposal. Variables other than adsorbent type and'dosage can also affect adsorption efficiency. Common variables include wastewater pH and pollutant speciation.

4.1 Activated Carbon Adsorption

Granular activated carbon (GAC) is the most commonly used adsorbent system for treating industrial waste (U.S. DOE, 1994). This process is used in a variety of configurations, as demonstrated in Figures 3-1 and 3-2. GAC systems may be either pressure or gravity type. They may

Figure 3-1. Types of GAC column design (Calgon Carbon Corp.)

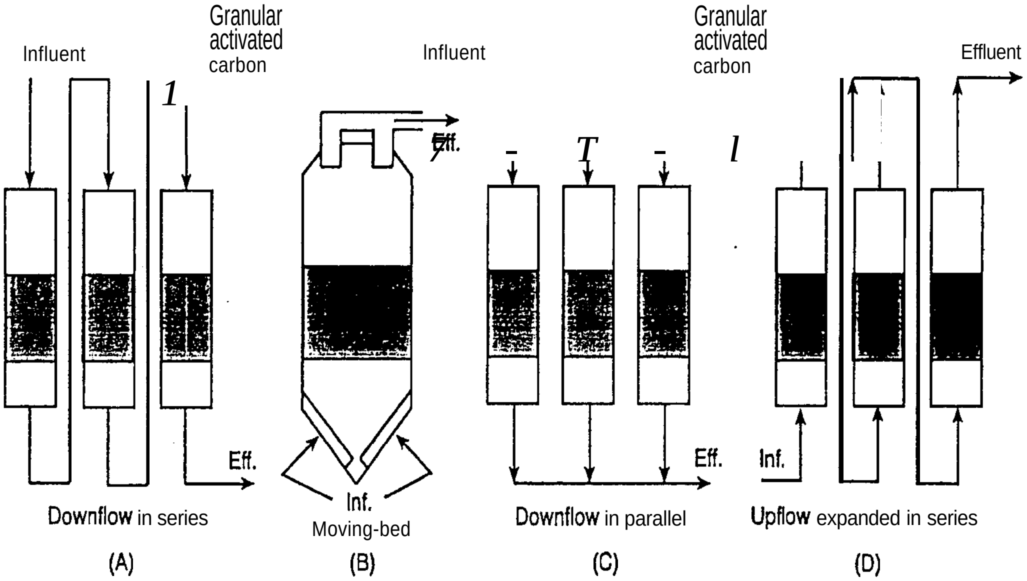
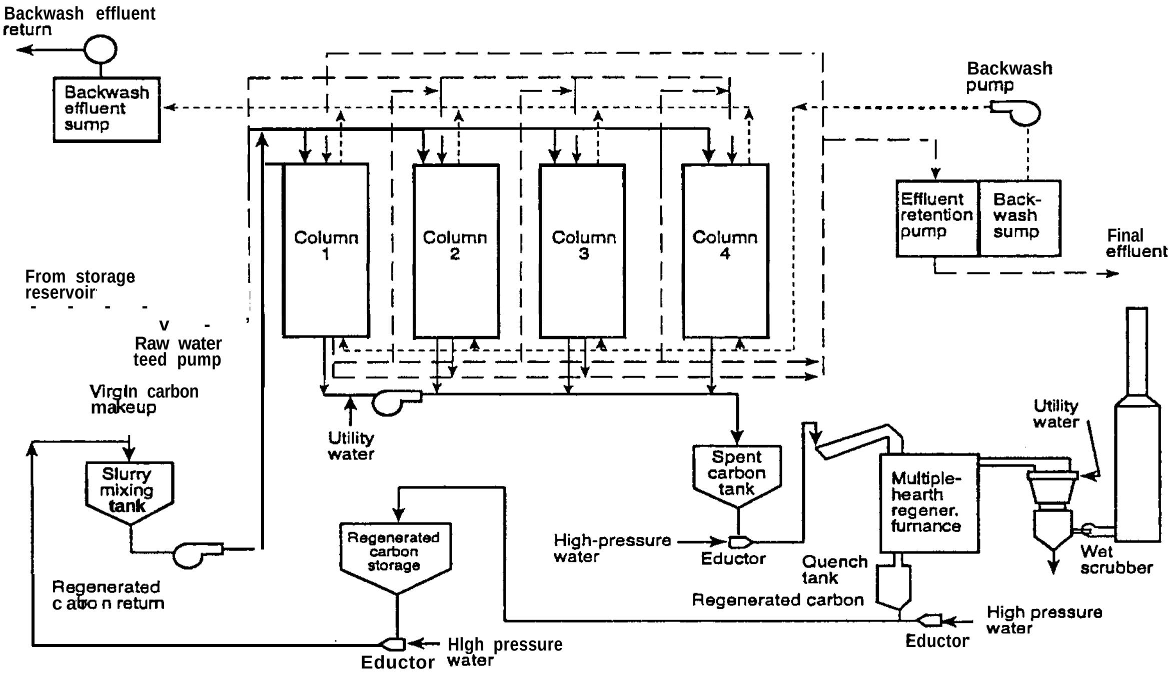


Figure 3-2. GAC process flowsheet (after Eckenfelder, 1989)



be upflow counter-current type with packed or expanded carbon beds, or upflow or downflow fixed-bed units with multiple columns in series (Figure 3-l). Contaminated water is passed through the columns until the key contaminant is detected at a predetermined level in the effluent. When multiple columns are placed in series, the first column can be loaded to a greater capacity, while residual levels of the contaminant are removed in the downstream columns. When a column has been loaded to its design capacity, it may be regenerated or the spent carbon can be replaced while another column is brought online. An alternative method of carbon treatment involves use of powdered activated carbon (PAC). The PAC is typically added as a slurry into a contact reactor, and the PAC solids subsequently are removed in a solids separation stage. The PAC is normally not regenerated for' reuse due to unfavorable economics including poor recovery of the PAC.

Table 3-1 summarizes example activated carbon mercury treatment data. The removal of mercury from potable water using PAC was studied by Thiem and colleagues (1976). Treating a spiked water solution containing 10 μg/L total mercury, they achieved approximately 80% removal at a pH of 7 and a PAC dosage of 100 mg/L. The study also demonstrated that the addition of mercury chelating agents, such as ethylene diamine triacetic acid (EDTA) or tannic acid, prior to contact with the PAC increased mercury removal efficiency. Concentrations as low as 0.02 mg/L EDTA and 1 mg/L tannic acid increased mercury removal efficiencies by 10% to 20% . The mercury removal efficiencies by concentrations of 50 to 200 mg/L also increased mercury removal efficiencies by 10% to 20% over those obtained by PAC alone.

The removal of mercury (II) from synthetic wastes by 11 different brands of commercial activated carbon was studied by Huang and Blankenship (1984). Among the 11 different types of activated carbon, Nuchar SA and Nuchar SN exhibited a high percent (>99.9) mercury (II) removal over a wide pH range (2.5 to 11). The other activated carbons studied displayed maximum total mercury (II) removal at pH 4 to 5, and the percent mercury (II) removal dropped markedly at pH values greater than and less than 4 to 5.

Pretreatment or modification of activated carbon with carbon disulfide solution before use, has been shown to enhance mercury removal. Humenick and co-investigators (1974) utilized an activated carbon that was presoaked in carbon disulfide and then dried and used as PAC. The pretreated activated carbon removed mercury from an initial concentration of 10 mg/L down to 0.2 μg/L, versus the 4 mg/L effluent value obtained with the untreated carbon. The enhanced mercury removal was attributed to chemisorption reactions. Sulfur atoms have a high affinity for mercury, as evidenced by the Ksp of HgS (see Table 2-2). The mercury removal mechanism proposed by Humenick and colleagues (1974) involves transport and diffusion to the carbon disulfide sites and subsequent formation of a chemical bond between a carbon disulfide molecule and the mercury ion.

Table 3-l. Activated carbon mercury treatment results

Activated Carbon Type	Mercury Concentration ($\mu g/L$)		Percent Removal	Additional Treatment	Other Conditions	Reference
	initial	Final				
PAC	10,000	4,000	60	None	SW, BS	Humenick et al., 1974
PAC	10,000	0.2	>99.9	5 μm filtration, PAC presoaked in CS_2 and dried	SW, BS	Humenick et al., 1974
PAC	2,000	NA	-100	Centrifugation or 0.45 μm filtration	SW, BS	Huang and Blankenship, 1984
PAC	10	NA	-80	0.45 μm filtration	SW, BS	Thiem et al., 1976
PAC	1.0	0.5	50	Settling	PW, BS	Guarino et al., 1988
GAC	O-100	<1.0	>41	None	SF, FS	E.C. Jordan Co., 1989
GAC	1.7 1.5	0.9 0.8	47 47	Filtration	PW, BS	Guarino et al., 1988

PAC = Powdered activated carbon.
GAC = Granular activated carbon.
BS = Bench scale.
SW = Synthetic wastewater.
PW = Petrochemical wastewater.
SF = Superfund wastewater.
FS = Full scale.
NA = Not available.

A study was conducted by Guarino and co-investigators (1988) to establish the feasibility of using activated carbon as an advanced treatment method for petrochemical wastewater. This study investigated petrochemical wastewater at bench scale, utilizing GAC and PAC. Low initial mercury levels of 1.5 and 1.7 $\mu g/L$ were reduced to 0.8 and 0.9 $\mu g/L$, respectively, using GAC, while an initial mercury concentration of 1 .O $\mu g/L$ was reduced to 0.5 $\mu g/L$ using PAC. The performance data reported in the literature suggests that activated carbon treatment can achieve a residual mercury level of 0.5 to 20 $\mu g/L$, dependent in part on the initial wastewater mercury level (Patterson et al.).

Gates and colleagues (1995) conducted laboratory work to investigate the feasibility of using inexpensive sulfur-impregnated activated carbon beads, known as Mersorb, for mercury removal from aqueous waste. These studies were conducted to evaluate the treatability of mercury-containing aqueous and solid mixed wastes stored at DOE sites, such as the Oak Ridge Y-12 site. The from aqueous solutions to below 0.2 mg/L. Mersorb worked under acidic conditions (pH of 2), but its capacity at low pH was reduced by 50% compared with neutral conditions. Mersorb beads reportedly had favorable process economics compared with ion exchange.

3.2 Xanthate Treatment

An alternative adsorption material to activated carbon is starch xanthate, yielding mercury-starch xanthate. One modification is termed the Metals Extraction by Xanthate Insolubilization and Chemical Oxidation (MEXICO) process, also termed the Advanced MEXICO Precipitation Process (Macchi et al., 1985; Tiravanti et al., 1987). Most published data on this process appears to be from bench- and pilot-scale studies. No published information was available on full-scale application.

Example data for starch xanthate treatment are presented in Table 3-2. Campanella and colleagues (1986) were able to reduce the mercury concentration in a synthetic wastewater at bench scale from 10 to 23 $\mu g/L$

Table 3-2. Starch Xanthate Treatment for Mercury

Mercury Concentration (mg/L)					
Initial	Final	Treatment pH	Additional Treatment	Other Conditions	Reference
10	0.023	1	Sedimentation	SW, BS	Campanella et al., 1986
100	0.001	5	0.45 μm filtration	SW, BS	Tiravanti et al., 1987
9.5	0.01-0.1	5	Sedimentation	cw, PS	Tiravanti et al., 1987
9.5	0.005-0.02	5	Sedimentation plus 0.45 μm filtration	cw, PS	Tiravanti et al., 1987
6.3	-0.2	11	10 μm filtration	cw, BS	Macchi et al., 1985
6.3	0.01	11	Sodium hypochlorite addition	CW, BS	Macchi et al., 1985
6.3	0.001	NA	Activated carbon	CW, BS	Macchi et al., 1985

SW = Synthetic wastewater.
BS = Bench scale.
cw = Chlor-alkali wastewater.
PS = Pilot scale.

following sedimentation. Tiravanti and co-investigators (1987) were able to reduce mercury at bench scale from 100 to 1 μg/L following 0.45 μm filtration. These researchers also conducted pilot-scale (15 m^3/d) experiments on chlor-alkali wastewater and were able to reduce the mercury concentration from 9.5 mg/L to a range of 10 to 100 μg/L following sedimentation, and to a range of 5 to 20 μg/L following sedimentation and 0.45 μm laboratory filtration (to estimate residual soluble mercury). Macchi and colleagues (1985) conducted bench-scale experiments on chlor-alkali wastewater and were able to reduce the mercury concentration from 6.3 to 200 μg/L following 10 μm filtration, to 10 μg/L following sodium hypochlorite addition, and to 1 μg/L following activated carbon treatment. The process appears able to achieve an effluent mercury level of 5 to 20 μg/L.

Macchi and colleagues (1985) also reported that mercury can be recovered from the mercury-xanthate sludges by treating the precipitate with 5 M hydrochloric acid and sodium hypochlorite. The cost of sodium hypochlorite is relatively insignificant for the chlor-alkali industry, and the redissolved mercury reportedly could be recycled to the head of the chlor-alkali plant.

3.3 Other Adsorption Processes

Various other adsorbent alternatives to activated carbon have been reported to perform in comparable fashion for mercury treatment. These adsorbents include BPHC, MHBB, coal fly ash, and the Forager sponge. Each of these adsorbents is described in the following sections.

Table 4-3 presents mercury adsorption Freundlich parameter values for these adsorbents, except the Forager sponge. The Freundlich adsorption equation is:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C_e \qquad [3\text{-}1]$$

Where:

x = the amount of solute (mercury) adsorbed
m = the amount of adsorbent required to adsorb x
k and $\frac{1}{n}$ = empirical constants (Freundlich parameters)
C_e = equilibrium concentration (mercury) The Freundlich parameters k and $\frac{1}{n}$ are equal to the intercept and slope of the line obtained by plotting $\log \frac{x}{m}$ vs. log C,.

Table 3-3. Freundlich Isotherm Parameters for Mercury Adsorption

Adsorbent	k	$\frac{1}{n}$	Reference
GAC	4.68	3.16	.Namasivayam and Periasamy, 1993
BPHC	42.17	3.50	Namasivayam and Periasamy, 1993
Coal fly ash (pH 2.2)	1.014	0.053	Sen and De, 1987
Coal fly ash (pH 3.1)	1.094	0.333	Sen and De, 1987
Coal fly ash (pH 4.2)	1.230	0.361	Sen and De, 1987
MHBB	1.07	0.324	Deshkar et al., 1990

GAC = Granular activated carbon.
BPHC = Bicarbonate-treated peanut hull carbon.
MHBB = Modified *Hardwickia binata* bark.

The value of k is roughly an indicator of sorption capacity, and $\frac{1}{n}$ is an indicator of sorption intensity.

3.3.1 BPHC Adsorption

From bench-scale study, using a stock mercury solution feed of 10 to 20 mg/L, Namasivayam and Periasamy (1993) reported BPHC to be seven times more effective than GAC for mercury (II) removal. This result was attributed to the higher porosity plus moderate ion exchange capacity of BPHC as compared to GAC. The Freundlich parameters shown in Table 3-3 quantify the sorption capabilities of BPHC. The desorption capabilities of BPHC also were reported to be promising. Percent recoveries of mercury from BPHC and GAC using 0.6 M HCI were 47% and 13%, respectively, and 87% and 24%, respectively, using 1.0% KI (potassium iodide). No full-scale data were available on this material.

3.3.2 MHBB Adsorption

A modified *Hardwickia Binata* bark was studied at bench-scale for its adsorption of mercury (II) from water (Deshkar et al., 1990). Although the media was shown to be effective in removing mercury (II) from water, it is not as effective as GAC, as indicated by the Freundlich parameters listed in Table 3-3. No information was reported on the desorptive properties of the *Hardwickia binafa* bark.

3.3.3 Coal Fly Ash Adsorption

Coal fly ash, an industrial waste solid, was shown to adsorb mercury (II) (Sen and De, 1987). Coal fly ash did not perform as well as GAC, however, as shown by the Freundlich parameters listed in Table 3-3. Maximum mercury adsorption by coal fly ash was observed in the pH range 3.5 to 4.5 (Sen and De, 1987).

3.3.4 Forager Sponge Adsorption

The Forager sponge is an open-celled cellulose sponge with an amine-containing polymer that reportedly has a selective affinity for aqueous heavy metals in both cationic and anionic states. The polymer is reported to form complexes with ions of transition-group heavy metals, providing ligand sites that surround the metal and form a coordination complex. The polymers order of affinity for metals is reportedly influenced by solution parameters such as pH, temperature, and total ionic content. Mercury is one of the metals that is claimed to be removed by the sponge. In general, the following affinity sequence for representative ions is expected (U.S. EPA, 1994b):

$Cd^{2+}>Cu^{2+}>Fe^{3+}>Au^{3+}>Mn^{2+}>Zn^{2+}>Ni^{2+}>Co^{2+}>Pb^{2+}>Au(CN)_2^{-}$
$^{6}>SeO_4^{2-}>AsO_4^{3-}>Hg^{2+}>CrO_4^{2-}>Ag^{+}>Al^{3+}>Ca^{2+}>Mg^{2+}$

The sponge can be used in columns, fishnet-type enclosures, or rotating drums. When used in a column, flow rates of 3 bed volumes per minute are reported to be obtained at hydrostatic pressure only 2 feet above the bed and without additional pressurization. Therefore, sponge-packed columns are claimed to be suitable for unattended field use.

Adsorbed ions can be eluted from the sponge using techniques typically employed to regenerate ion exchange resins and activated carbons. Following elution, the sponge can be reused in the next adsorption cycle. The number of useful cycles is reported to depend on the nature of the adsorbed ions and the elution technique used. Alternatively, the metal-saturated sponge could be incinerated. Metals volatilization would be of concern. The sponge may be dried and reduced in volume to facilitate disposal (U.S. EPA, 1994b).

Chapter 4
Ion Exchange Treatment

Resins containing the iminodiacetic acid group will exchange for cationic mercury selectively over calcium and magnesium, but copper and cobalt are also readily exchanged. Mercury in the form of anionic complexes, such as $HgCl_3^-$, can be treated by anion exchange resins. The thiol resin, Duolite GT-73, is reported to be selective for mercury in any of its three oxidation states (Ritter and Bibler, 1992).

Ion exchange processes are typically operated as packed columns. Usually four operations are carried out in a complete ion exchange cycle: service,. backwash, regeneration, and rinse. In the service step, the ion exchange resin in the packed column is contacted with the water containing the mercury to be removed. After a target concentration of mercury in the column effluent is reached, the resin is said to be spent. A backwash step is then initiated to expand the bed and to remove fines that may be clogging the packed bed. The spent resin is then regenerated by exposing it to a concentrated solution of the original exchange ion, so that a reverse exchange process occurs. The rinse step removes excess regeneration solution before the column is brought back online for the next service cycle.

Reported advantages and disadvantages of ion exchange include (Clifford et al., 1986):

Advantages

- Operates on demand
- Is relatively insensitive to variability
- Can achieve essentially a zero level of effluent contaminant
- Is available in a large variety of specific resins
- Can normally achieve beneficial selectivity reversal upon regeneration

Disadvantages

- Has potential for chromatographic effluent peaking
- Results in spent regenerant brine that must be disposed of
- Can yield variable effluent quality
- Cannot typically be used for waters with a high total dissolved solids content

Ion exchange technology for mercury removal has historically been limited to the use of anion resins to treat industrial wastewater that contains inorganic mercury in the complex mercuric chloride form. For the process to be effective, the chloride content of the wastewater must be high, such as that generated by a chlor-alkali plant. This will yield negatively charged mercury chloride complexes. If the chloride content of the wastewater is low, either chlorine or chloride salt could be added to improve removal process efficiency (Sorg, 1979).

Cation exchange of mercury may be effective if the anion content of the wastewater is low (Sorg, 1979). Certain cation exchange resins (Amberlite IR-120 and Dowex-50W-X8) are reported to be effective for ion exchange treatment of mercury present in industrial wastewater (Patterson, 1985). Also, Duolite GT-73, a cationic resin, contains the thiol (-SH) group and reacts with ionic mercury. The thiol functional group has a high selectivity for mercury as well as a strong tendency to bind certain other metal ions such as copper, silver, cadmium, and lead.

A chelate resin is an insoluble polymer to which is attached a complexing group or groups. This, in turn, can bond metal cations within the structure so as to form a ring (or chelate) into which the metal is incorporated. The reaction involves both ion-exchange and chemical reactions. Table 4-1 lists some chelate resins that are reported to have a high selectivity for mercury; the table includes the order of selectivity.

Example ion exchange treatment data for drinking water are presented in Table 4-2. Mercury removal from ground water was studied in point-of-entry treatment (POET) systems installed on private water supply wells (Sites and Obeholtzer, 1992). Table 4-2 indicates that Ionac SR-4, Purolite S-920, AFP-329, and ASB-2 were able to remove mercury from the relatively low initial ground-water concentrations to below 1 μg/L, following prefiltration.

A full-scale ion exchange process at a defense processes facility has consistently removed mercury via ion exchange from 0.2 to 70 mg/L down to levels of 1 to 5 μg/L, following 0.2 μm prefiltration (Ritter and Bibler, 1992). This system utilizes a macroporous, weakly acidic, polystyrene/divinylbenzene cation resin, with thiol (SH) functional groups. High levels of mercury in a synthetic wastewater

Table 4-l. Summary of mercury-selective chelate resins (After Calmon, 1981)

Resin	Order of Selectivity
Duolite ES-466	$Hg^{2+}>Cu^{2+}>Fe^{2+}>Ni^{2+}>Pb^{2+}>Mn^{2+}>Ca^{2+}>Mg^{2+}>Na^{+}$
Dowex A-l	$Cu^{2+}>Hg^{2+}>Ni^{2+}>Pb^{2+}>Zn^{2+}>Co^{2+}>Cd^{2+}>Fe^{2+}>Mn^{2+}>Ca^{2+}>Na^{+}$
Nisso Alm-525	$Hg^{2+}>Cd^{2+}>Zn^{2+}>Pb^{2+}>Cu^{2+}>Ag^{+}>Cr^{3+}>Ni^{2+}$
Diaion CR-l 0	$Hg^{2+}>Cu^{2+}>Pb^{2+}>Ni^{2+}>Cd^{2+}>Zn^{2+}>Co^{2+}>Mn^{2+}>Ca^{2+}>Mg^{2+}>Ba^{2+}>Sr^{2+}>>>Na^{+}$
Amberlite IRC-718	$Hg^{2+}>Cu^{2+}>Pb^{2+}>Ni^{2+}>Zn^{2+}>Cd^{2+}>Co^{2+}>Fe^{2+}>Mn^{2+}>Ca^{2+}$
Unicellex UR-10	$Hg^{2+}>Cu^{2+}>Fe^{3+}>A1^{3+}>Fe^{2+}>Ni^{2+}>Pb^{2+}>Cr^{3+}>Zn^{2+}>Cd^{2+}>Ag^{2+}>Mn^{2+}>Ca^{2+}>Mg^{2+}>>>Na^{2+}$
Sirorez-Cu	pH>5, Cu^{2+}; pH>0, Hg^{2+}
Sumichelate Q-l 0	$HgCl_2>AuCl^-_4>Ag^+>Cr_2O_7^{2-}$

Table 4-2. ion Exchange treatment for mercury in drinking water

		Mercury **Concentration** (μg/L)				
ion Ex-change Resin	**Resin Type**	**Initial**	**Final**	**Additional Treatment**	**Other Conditions**	**Reference**
Ionac SR-4	Weak acid chelating resin	14.88”	0.43”	Prefiltration	GW, FS[b]	**Sites and Oveholtzer, 1992**
Purolite s-920	Hg-specific chelating resin	10.67”	0.34”	Prefiltration	GW, FS[b]	Sites **and** Obeholtzer, 1992
AFP-329	Weak base anion resin	12.21”	0.44[a]	Prefiltration	GW, FS[b]	Sites and Oveholtzer, 1992
ASB-2	Strong base anion resin	14.31”	0.70”	Prefiltration	GW, FS[b]	Sites and Oveholtzer, 1992
Duolite GT-73	Weak acid cation thiol	200-70,000	1-5	0.2 μm pretilter	DFW, FS	Ritter and Bibler, 1992
Amberlite IRC 718	Iminodiacetic acid resin	11,800	15-35	None	SW, BS	Becker and Eldrich, 1993
IRC 718 and GT 73	(See above)	14,000	15-l ,200	GT 73 used as polishing	SMW, BS	Becker and Eldrich, 1993

‘Average value
[b] 3 to 4 gpm

GW = Ground water.
FS = Full scale.
DFW = Defense facility wastewater.
SW = Synthetic wastewater.
BS = Bench scale.
SMW = Smelter wastewater.

were removed to levels as low as 15 μg/L after 77 bed volumes of usage, and 35μg/L after 157 bed volumes of usage (Becker and Eldrich, 1993). This system utilized Amberlite IRC 718 in bench-scale testing. In further bench-scale testing, smelter wastewater containing 14.0 mg/L of mercury at a flow rate of 6.7 mL/min was treated with IRC 718 followed by a polishing ion exchange column containing GT 73. This system removed mercury to concentrations of 15 to 46 μg/L after 289 bed volumes, and 1,200 μg/L after 325 bed volumes. This study further showed that at pH 1.5, the iminodiacetic acid resin (IRC 718) was highly selective for mercury (II) over zinc, lead, and cadmium, and that mercury recovery from wastewater on such a resin is feasible provided strongly complexing anions such as chloride are absent. Regeneration with 3 M NaCl or other complexant for mercury at near neutral pH yields a solution for which mercury can reportedly be recovered via reduction to an insoluble and commercially valuable form (Becker and Eldrich, 1993).

Chapter 5
Other Processes

In addition to precipitation, adsorption, and ion exchange treatment technologies, the following processes are also reported to be applicable to remove mercury from wastewater: (1) chemical reduction, (2) membrane separation, and (3) various emerging technologies.

5.1 Chemical Reduction

The standard electrode potential of metals determines their placement in the electromotive series, which is a series of elements in descending order of their standard potential. Ionic mercury can be displaced from solution via reduction by another metal higher in the electromotive series, and then separated by filtration or other solids separation technique. Reducing agents include aluminum, zinc, iron, hydrazine, stannous chloride, and sodium borohydride. Example data on these reductants are presented in Table 5-1.

Although the literature includes much discussion of reduction processes, only limited actual treatment data are presented. The main advantage claimed for reduction is that mercury can be recovered in the metallic state (Patterson, 1985). The data in Table 5-1, however, indicate that most reduction processes cannot effectively achieve mercury levels below 100 μg/L, and their use would likely require second-stage polishing.

Experiments were conducted by Gould and colleagues (1984) at bench scale on Chemical Oxygen Demand (COD) test wastewater using iron wire (nominal diameter 0.229 mm). Due to the high initial mercury levels (735 to 2,030 mg/L), high recovery efficiencies were observed (96% to 99%); however, high residual mercury levels were also observed (22 to 33 mg/L). Experiments were conducted by Grau and Bisang (1995) on synthetic wastewater with iron felt formed by compressing iron wool. As for other studies, a high removal efficiency resulted at the high initial mercury concentration, leaving 68 to 91 μg/L residual mercury.

As noted in Chapter 4, ‘mercury removal from ground water was studied in POET systems that were installed on private water supply wells (Sites and Oberholtzer, 1992). Table 5-l shows that a bimetallic oxidation/ reduction compound, KDF, which consists of a finely ground alloy of 55% copper and 45% zinc, was able to remove low levels of mercury down to a range of 0.4 to 1.08 μg/L, following prefiltration. This process may be applicable only for exceptionally clean solutions, however.

5.2 Membrane Separation

Several membrane processes have been applied for water and wastewater mercury treatment. These include ultrafiltration, charged filtration, crossflow microfiltration, magnetic filtration, and reverse osmosis. Example treatment data for these processes are shown in Table 5-2.

Ultrafiltration systems are pressure-driven membrane operations that use porous membranes for the removal of dissolved and colloidal material (Metcalf and Eddy, 1991). These systems differ from reverse osmosis systems by the relative driving pressures, usually under 150 psi (1034 kN/m^2). Ultrafiltration is normally used to remove colloidal material and large molecules with molecular weights in excess of 5,000. Recent studies indicate that effluent from ultrafiltration using spiral wound elements is suitable as a feed source for reverse osmosis (Metcalf and Eddy, 1991).

Chelation in combination with ultrafiltration is a process that has been described for the removal of heavy metals, including mercury (Kosarek, 1981). This concept is based on reacting ligands with cationic metallic constituents to form a metal-containing complex (chelate), and then removing these metal-containing complexes by ultrafiltration (Kosarek, 1981). The opposite charges of the ionized ligand and metal attract each other to form a stable chelate complex. The properties that facilitate ultrafiltration membrane rejection of the metal-containing complex (including mercury complexes) are thought to be (1) the increased size of the metal chelate complexes, (2) alteration in the ionic shape of the metal, (3) modified solubility, and (4) reversal of charge from cationic metal to a functionally anionic or electroneutral chelate species (Kosarek, 1981).

Charged membrane ultrafiltration incorporates a noncellulosic, high flux membrane that is negatively charged as a result of dissociated subgroups within the membrane structure. A beneficial aspect of the charged ultrafiltration membrane is that the negative polarization minimizes membrane fouling (Kosarek, 1981). Bhattacharyya and colleagues (1979) conducted bench-scale investigations to determine the feasibility of the simultaneous separation of various heavy metals from scrubber blowdown wastewater generated in the primary copper industry. They studied the application of low pressure ultrafiltration with commercially available, negatively charged noncellulostic membranes. Typical mercury values

Table 5-1. Performance of Reduction Processes for Mercury Treatment.

	Mercury (μg/L)			
Reductant	Initial	Final	Treatment pH	Reference
Zinc	5,000-10,000	5-10	NA	Patterson, 1985
	1,800	140	11.5	Patterson, 1985
	12,500	830	10.0	Patterson, 1985
	12,500	750	6.0	Patterson, 1985
	12,500	470	2.5	Patterson, 1985
	NA	600	NA	Patterson, 1985
Iron	734,000-2,030,000	22,000-33,000	NA	Gould et al., 1984
Iron felt	100,000	68-91	NA	Grau and Bisang, 1995
KDF’	6.17-12.11	0.4-l .08	NA	Sites and Oberholtzer, 1992
Stannous chloride	2,800	500	NA	Patterson, 1985
Sodium borohydride	10,000	220	NA	Patterson, 1985
	4,000	420	NA	Patterson, 1985
	26,000	820	NA	Patterson, 1985
	4,700	200	NA	Patterson, 1985
	NA	<10	NA	Patterson, 1985

‘Bimetallic copper-zinc oxidation/reduction compound.
NA = Not available.

in the scrubber blowdown were found to be 1.5 to 2.0 mg/L. Mercury removals for a full-scale system were calculated by computer simulation based on laboratory-scale data and were reported to be 91% to 93% (AP = 5.6 x 10^5 N/m*, channel velocity, U = 250 cm/s, and pH = 4.5). For a 3.6 x 10^5 kg/d (400 ton /day) copper production plant, the net operating costs for a closed-loop scrubber blowdown water recycle system was estimated to be $2,508 /day or $0.0070/kg Cu production (1995 basis updated assuming cost components follow change in skilled labor cost index).

The crossflow microfiltration system is based on the concept of using a dynamic membrane to form a filtration medium. This process, whose patented form is called Exxflow, is a solid-liquid separation process in which the feed suspension sweeps across the face of a filter membrane while pressure differences cause the liquid phase to pass through the membrane, leaving the solids to be flushed away in the residual flow. By this means, the solids are concentrated up in the suspension flow, which is commonly recycled to the feed end. This contrasts with “barrier” filtration systems in which the solids build up on the filtering surface, gradually restricting the flow through the filter (Squires, 1992). A schematic of the microfiltration process is shown in Figure 5-l.

Mercury removal via crossflow microfiltration was reported for a full-scale plant designed to process 200 m^3 /day of mixed plating wastewater (Broom et al., 1994). A process schematic of the plant is shown in Figure 5-2. The filtrate from the rotary vacuum filter was combined with the supernatant from a preclarification stage and stored in a 80 m^3 balance tank, where the pH was adjusted to 11 to 12, primarily to precipitate cadmium. Sodium hydrogen sulfide (NaHS) was also added to precipitate any soluble metals remaining. This conditioned filtrate was then pumped to the crossflow microfiltration unit, where it was recycled at an average pressure of 150 kPa. The reject flow was effectively a concentrate produced by the passage of clean permeate through the filter. With mercury feed concentrations to the microfiltration plant of 1.27, 0.967, 0.15, and 2.28 mg/L, permeate concentrations of 0.015, 0.015, 0.088, and 0.03 mg/L were achieved, respectively. This represents a removal efficiency of about 95 %. Removal may have been enhanced by mercury co-precipitation in the balance tank.

Table 5-2. Performance of Membrane Processes for Mercury Treatment.

Membrane Process	Mercury (µg/L) Initial	Mercury (µg/L) Final	Percent Removal	Comments	Reference
Reverse osmosis	5,000	880[a]	82.4	BS, SW	Sorg, 1979
	9,000	1,503[a]	83.3	BS, SW	
	8	1.5[a]-1.7[a]	79-81	PS	
Charged ultrafiltration	1,500-2,000	NA	91-93	CS	Bhattacharyya et al., 1978
Crossflow microfiltration	1,270	15	99.8[a]	FS, PW	Broom et al., 1994
	967	15	98.5[a]	FS, PW	
	150	88	41.3[a]	FS, PW	
	2,280	30	98.7[a]	FS, PW	
Magnetic filtration	15,000	3-117	99.2-99.9	BS, GSW	Terashima et al., 1986

[a] Calculated from removal efficiency data (% removal = $\frac{\text{(Initial - Final)}}{\text{Initial}}$ x 100%

BS = Bench scale.
SW = Spiked wastewater (secondary effluent).
PS = Pilot scale.
CS = Computer simulation.
FS = Full scale.
PW = Plating wastewater.
GSW = Gas scrubber wastewater from solid waste incineration plant.
NA = Not available.

Magnetic filtration of soluble species such as ionic metal is accomplished by forming a magnetic precipitate through coagulation and magnetic seed addition, and then passing the wastewater through a filter made with ferromagnetic wires, which represent a magnetic field. The magnetic precipitate can be rapidly and efficiently removed by magnetic filtration, even if the precipitate is quite fine (Terashima et al., 1986). This occurs because of the strong magnetic forces that act on the magnetic particles as they move through the magnetic field. The magnetic particles are captured on the filter matrix by the magnetic force, which overcomes other competing forces of gravitation, hydrodynamics, and inertia (Terashima et al., 1986). Terashima and colleagues (1986) report mercury removals in a bench-scale magnetic filtration unit fed gas scrubbing wastewater from a municipal solid waste incineration plant. For an influent mercury concentration of 15.0 mg/L, effluent mercury concentrations of 0.003 to 0.117 mg/L were achieved.

Reverse osmosis (RO) is a physical separation technique whereby an applied pressure in excess of the inherent solution osmotic pressure forces water to permeate a semipermeable membrane, which rejects the bulk of the dissolved and suspended constituents. The pressures applied to the membrane in RO processes range from 200 to 800 psi (Kosarek, 1981). The operation of an RO membrane system is significantly affected by fouling, scaling, pH-temperature-pressure-related hydrolysis, and chemical or biochemical deterioration of the membranes. The RO process has very strict feed water requirements, particularly related to the concentration of suspended solids and materials (e.g., oil or grease), which will foul the membrane surface (Kosarek, 1981).

A literature review by Sorg (1979) described several laboratory and pilot-plant RO studies for the removal of metals from water or wastewater, but only one study provided data on the removal of mercury. Investigators ran a series of RO pilot-plant tests to evaluate the technique for the removal of heavy metals, pesticides, and other toxic chemicals from secondary waste water effluent. The results of one-day batch tests with spiked concentrations of 5 and 9 mg/L of inorganic mercury showed removals of 82.4% and 83.3%, respectively.

Sorg (1979) also reported that EPA's Drinking Water Research Division (DWRD) conducted two one-day tests for inorganic mercury (influent at 0.008 mg/L) removal from Glendale, Ohio, well water, with two small-scale RO systems. The first system used a spiral-wound (SW) membrane and the second a hollow fiber (HF) membrane. The SW system had a raw water flow of 2.2 Lpm and operated at 1,400 to 1,600 kPa (200 to 230 psi) and 7% to 9% recovery. The HF system had a higher raw water flow

Figure 5-1. Principles of the Crossflow Microfilter (Broom, et al, 1994).

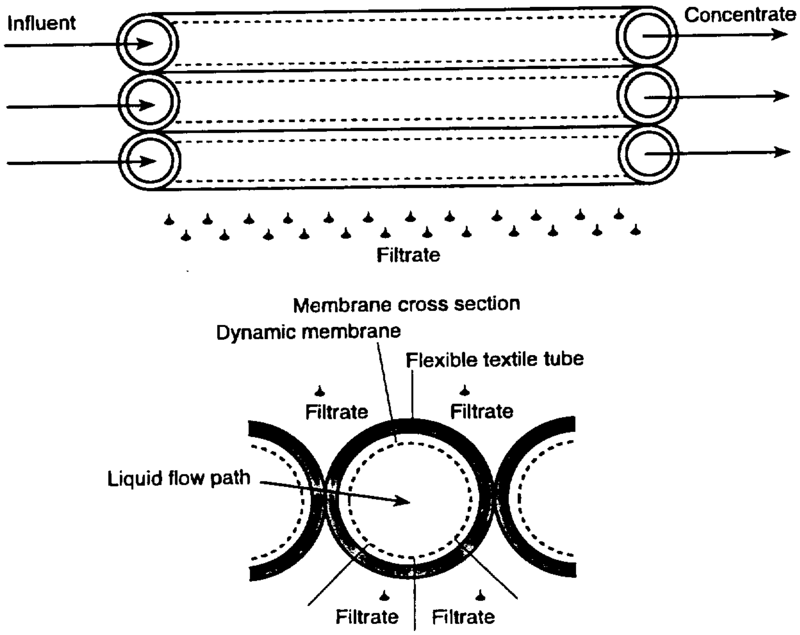
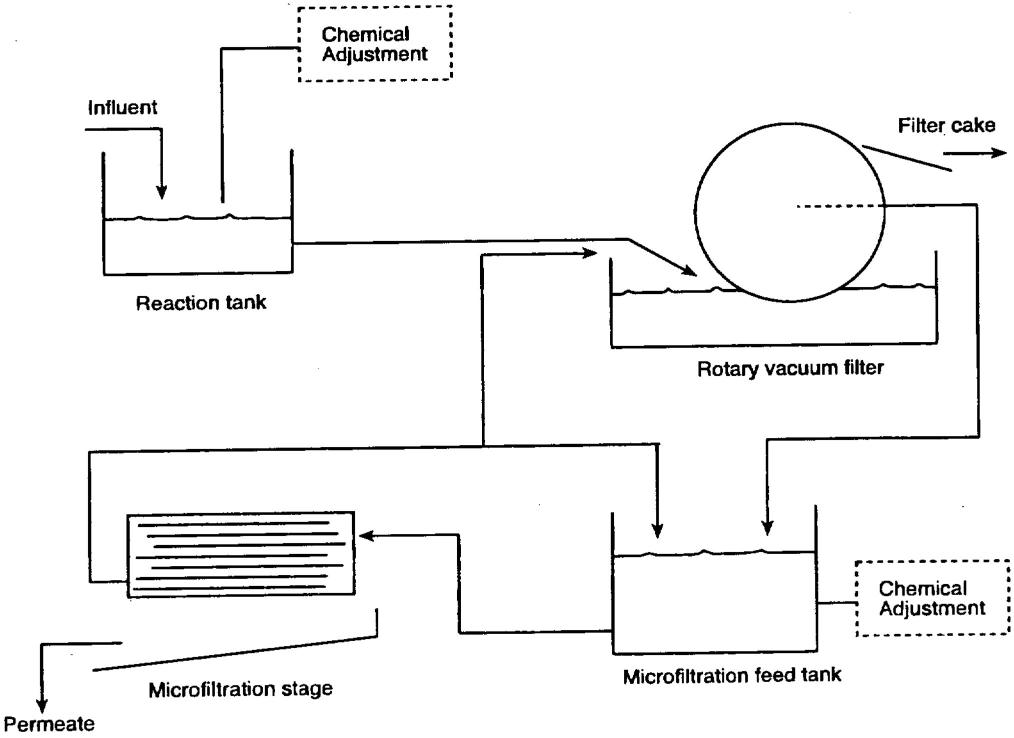


Figure 5-2. Filtrate Polishing using Micro filtration.



of 5 L/min and operated at 1,200-1,400 kPa (170 to 200 psi) and 40% to 50% recovery. The test results showed 25% mercury removal with the SW system and 79% to 81% with the HF system.

The results for these two limited scope studies are not as high as the 95% to 98% rejected range for organic mercury that Sorg (1979) reports as equipment manufacturer estimates. Sorg also states, however, that full-scale RO systems operated at high pressure and recovery should achieve greater removals than pilot-scale units performing under less than optimum conditions. A summary of membrane process performances by Kosarek (1981) cites mercury removals of 95% to 97% by RO. Based on these mercury treatment results, a broader range of 80% to 99% membrane rejection is indicated.

5.3 Emerging Technologies

Various other mercury treatment processes are cited in the technical literature; however, actual mercury treatment data are extremely limited. These processes include solvent extraction with high molecular weight amines, the use of silicon alloys for reduction of elemental mercury, and adsorption onto ground rubber and wool (Patterson, 1985). Other processes include the use of bound macrocycles (Izatt et al., 1991), biological detoxification (Hansen and Stevens, 1992), and microemulsion liquid membrane extraction (Larson and Wiencek, 1994). Selected processes are briefly reviewed below.

5.3.1 Macrocycles Adsorption

The use of aza macrocycles bonded to silica gel columns to selectively remove heavy metals from contaminated waters was reported (Izatt et al., 1991). Bench-scale tests using synthetic wastewater removed mercury from 4 μg/L to less than 1 μg/L.

5.3.2 Biological Treatment Systems

Biological treatment systems using mercury-resistant bacteria in a completely mixed, aerobic treatment process was studied by Hansen and Stevens (1992). Methods for recovering mercury from the vapor phase of the bioreactor are discussed by Hansen and Choudhury (1990). In bench-scale studies, three influent mercury concentrations (nominal levels of 2, 20, and 40 mg/L), three mean cell residence times (12, 20, and 28 hours), and three temperatures (15, 22.5, and 30°C) were employed in a 2^3 factorial design at a nominal influent COD of 2,500 mg/L (Hansen and Stevens, 1992). Effluent mercury concentrations ranged form 0.010 to 18.6 mg/L, with mercury removal efficiencies ranging form 6.8% to 99.5%.

Genetically engineered plants have been used in laboratory studies to reduce mercury concentrations in soil. Certain soil bacteria are known to reduce highly toxic action of a mercuric ion reductase called MerA. Researchers modified the bacterial MerA gene and inserted it into *Arabidopsis thaliana* plants. The results showed that the genetically engineered plants not only absorbed and concentrated Hg^{2+} ions from soil, but also reduced them to less toxic elemental mercury (Anonymous, 1996).

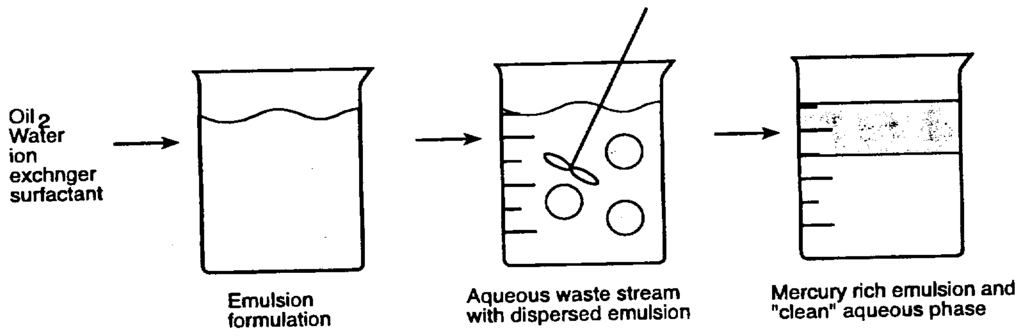
5.3.3 Membrane Extraction

Microemulsion liquid membrane extraction of mercury is an example of a liquid-liquid extraction technique. Schematic representations of mercury extraction using an emulsion liquid membrane are shown in Figures 5-3 and 5-4. A microemulsion forms spontaneously when oleic acid tetradecane, DNP-8 surfactant, and 6N sulfuric acid are mixed. The microemulsion is then dispersed in the aqueous stream containing mercury. After extraction, the emulsion and aqueous phase are separated. The microemulsion is then demulsified to recover the internal aqueous phase, which is concentrated in mercury. During the extraction process, mercury ion reacts with the oleic acid at the surface of the emulsion droplet. The mercury/oleic acid complex diffuses to the interior of the emulsion until it encounters an internal droplet containing sulfuric acid. A hydrogen ion is exchanged for the mercury ion on the oleic acid molecule, which is then free to diffuse back to the surface of the emulsion and extract another mercury ion (Larson and Wiencek, 1994). As a result, mercury can be pumped against its concentration gradient, with countertransport of hydrogen ions.

To demonstrate the efficiency of a microemulsion liquid membrane compared to conventional solvent extraction, Larson and Wiencek (1994) formulated a microemulsion with 0.32 molar (M) oleic acid intetradecane, 10 weight % DNP-8, and 6 normal (N) sulfuric acid. At equilibrium, a clear microemulsion phase and excess aqueous phase could be observed. The aqueous content of the microemulsion phase was 11 weight %. The organic phase of the control experiment consisted of 0.32 M oleic acid. There was no internal phase. Extraction of the feed phase with this formulation reduced the mercury content to 8.2 mg/L from 460 mg/L. After extraction with microemulsion liquid membrane, however, the feed phase was reduced to 0.25 mg/L. A second-stage extraction may be required to reduce mercury levels to a required limit via the microemulsion liquid membrane process.

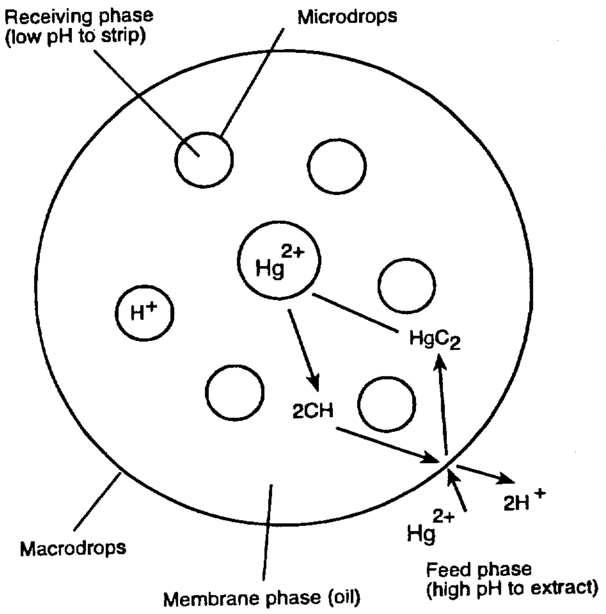
The demulsification and recovery of mercury via electrostatic coalescence and butanol addition were evaluated by Larson and colleagues (1994). They concluded that electrical demulsification with heat was not effective for microemulsions due to the small size of the internal phase droplets in microemulsions. They further reported that

Figure 5-3. Shematic representation of mercury extraction with an emulsion liquid membrane.



microemulsions can be demulsified using butanol as an an additive. The demulsification kinetics were found to be proportional to the butanol concentration and the temperature, and inversely proportional to the surfactant concentration.

Figure 5-4. Schematic representation of mercury ion extraction with an emulsion liquid membrane.



Chapter 6
Comparison of Treatment Processes

The preceding chapters describe a variety of mercury treatment technologies. The most widely recognized full-scale technologies are precipitation, coagulation/co-precipitation, and activated carbon adsorption. Other processes include starch xanthate adsorption, ion exchange, reduction, and membrane separation. Relatively limited full-scale performance data are available for these technologies and only general comparisons are possible. This chapter presents brief comparisons of treatment technologies based on (1) treatment effectiveness, (2) residuals management, and (3) economics. An example of a cost comparison from the literature is provided.

6.1 Treatment Effectiveness

Each of the mercury treatment technologies described in the preceding chapters achieves different effluent mercury levels. The effectiveness of treatment provided by each type of technology depends on the chemical nature and initial concentration of mercury as well as the presence of other constituents in the wastewater that may interfere with the process. Table 6-1 summarizes achievable effluent mercury concentrations. Co-precipitation and ion exchange achieve the lowest effluent mercury concentrations, ranging from 0.5 to 5.0 μg/L. Membrane technology typically achieves 80% to 90% rejection of mercury.

Table 6-1. Summary of Achievable Effluent Mercury Concentrations

Treatment Process	Achievable Concentration (μg/L)
Sulfide precipitation (+ filtration)	10-100
Co-precipitation	0.5-5.0
Activated carbon	0.5-20
Starch xanthate	5-20
Ion exchange	0.5-5.0
Reduction	10->100
Membrane separation	[a]

[a] Membrane technology typically achieves 80 to 90 percent rejection, which is a measure of salt rejected into the brine.

6.2 Residuals Management

Each mercury treatment technology yields a waste residual requiring further management.

Types of waste residuals include:

- Sludge produced by chemical precipitation and co-precipitation reactions.
- Spent carbon from activated carbon adsorbers.
- Concentrated ion exchange regenerant solutions.
- Concentrated brine solutions generated from membrane separation processes.

This section discusses potential options for mercury recovery from these residuals.

6.2.1 Mercury Sludges

The amount of metal sludge produced from a precipitation or co-precipitation process is typically estimated by performing treatability studies. The amount of sludge produced, the mass of mercury within the sludge, and the physical handling characteristics must be examined for each treatability method to effectively evaluate sludge management options. Mercury sludges associated with precipitation or co-precipitation are typically landfilled, although thermal processing to volatilize mercury for recovery would appear to be an option. The MEXICO process generates voluminous sludge, but mercury recovery from the sludge for reuse has been proposed (Macchi et al., 1985).

6.2.2 Spent Activated Carbon

Activated carbon columns may be regenerated either chemically or thermally, but options to concurrently recover mercury are not addressed in the literature. PAC is not normally regenerated for reuse due to unfavorable economics. GAC regenerated chemically would yield a mercury-rich regenerant solution. If regenerated thermally, a mercury-enriched vapor phase would result.

6.2.3 Concentrated Brine Solutions

Ion exchange and membrane processes both yield concentrated residual mercury solutions requiring further management. These solutions are typically high in total dissolved solids. Reduction or thermal processing for mercury recovery may be applicable to these brines.

6.3 Economics

As for the performance-related aspects of mercury control technologies, relative economics are not well defined. As an example, a cost comparison of the xanthate treatment process in comparison with the sulfide precipitation process is presented below.

A technical-economic evaluation of the xanthate treatment process in comparison with sulfide precipitation processes was conducted by Tiravanti, et. al. (1987) for the treatment of chlor-alkali wastewater. Investigators assumed a continuous treatment of 50 m^3/d of wastewater containing mercury at 3.0 mg/L, according to the flow diagram depicted in Figure 6-1. An investment capital cost of $280,000 (1987 basis) was assumed for all plants. Cost data derived for the treatment processes are presented in Table 6-2. The results indicate that total annual costs, assuming the same disposal route for the residual sludge, are comparable. The amount of sludge generated via xanthate treatment, however, may be greater than by sulfide treatment and this could affect sludge disposal costs. It should also be taken into account that the sludge produced by the xanthate process can reportedly be treated for mercury recovery and reuse.

Figure 6-1. *Flow chart of unit operations utilized for technical-economical analysis (Travanti, et. Al. 1987).*

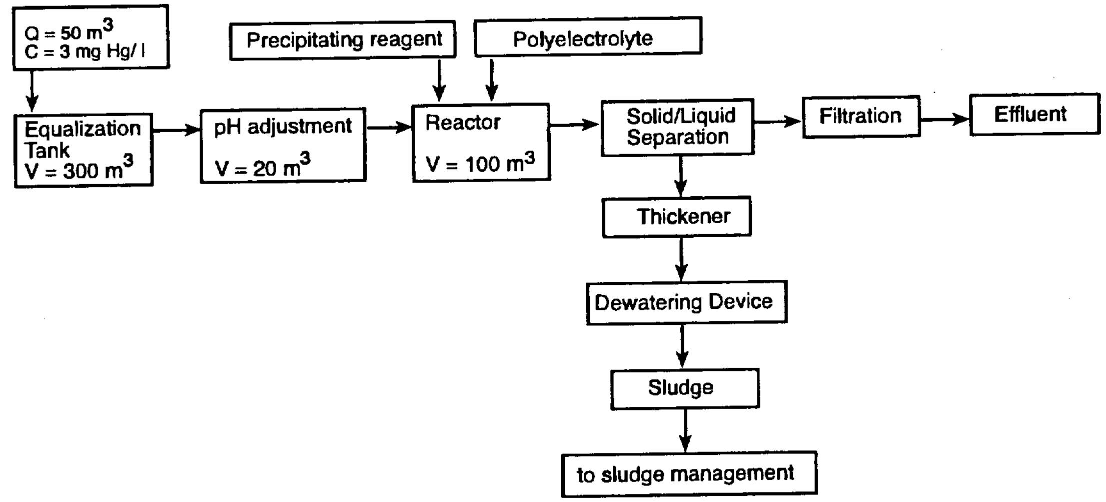


Table 6-2. Operating Costs (U.S. $/year, 1987) of Processes for Mercury Removal from Chlor-alkali Wastewaters (after Tiravanti et al., 1987).

Cost Item	Mexico	Sodium Sulfide
Chemicals		
Precipitating reagent	$ 7,267	$ 466
Polyelectrolyte	10,200	2,067
Ferric sulfate	—	733
Sludge Treatment		
Lime	267	1,134
Ferric chloride	333	1,667
Transportation[a]	933	4,600
Sludge disposalb[b]	5,533	27,400
Maintenance[c]	8,400	8,400
Manpower[d]	20,000	20,000
Electric energy[e]	24,533	24,533
Total	$77,466	$91,000

[a] Average distance = 30 km; unit cost = 16.7 ¢/kg.
[b] Including inertization and disposal of sludge unit cost = 10 ¢/kg.
[c] 3 percent of the total investment costs.
[d] Plant is operated by the chloride production team; manpower has been increased by one operator.
[e] Average power consumption = 0.6 KWh/m^3; unit cost = 9.33 ¢/kWh.

Chapter 7
Case Study

7.1 Ion Exchange Removal of Mercury from Wastewater at DOE's Savannah River Site Effluent Treatment Facility

DOE's Savannah River Site (SRS) is a facility that produces nuclear materials for national defense. The SRS houses two separation areas where uranium and plutonium are separated from fission products. Mercury is used at SRS as a catalyst in the dissolution of fuel elements composed of uranium-aluminum alloys. As a result, mercury is present in varying concentrations in some SRS wastestreams. Mercury is but one of several constituents being addressed in a system involving various treatment processes. Mercury is primarily removed by a cation exchange treatment system.

Depending on the stream, mercury may be present in solution as Hg°, Hg^{2+}. The site's Effluent Treatment Facility (ETF) is designed to treat several dilute wastestreams associated with the nuclear materials operation. The ETF uses cation exchange resins to selectively remove mercury in each oxidation state. Hg^{2+} and Hg_2^{2+} are removed by typical ion exchange mechanisms. Hg° is believed to be removed either by oxidation via dissolved oxygen and subsequent ion exchange, or by van der Waals attraction between Hg° and the matrix of the resin.

The discussion in this section focuses on (1) the ETF, (2) ETF feed streams, (3) ETF discharge limits, and (4) the role of ion exchange at the ETF. Actual ETF treatment data are not presented in this report because they were unavailable; however, the effluent limitations on which the ETF system was designed are described.

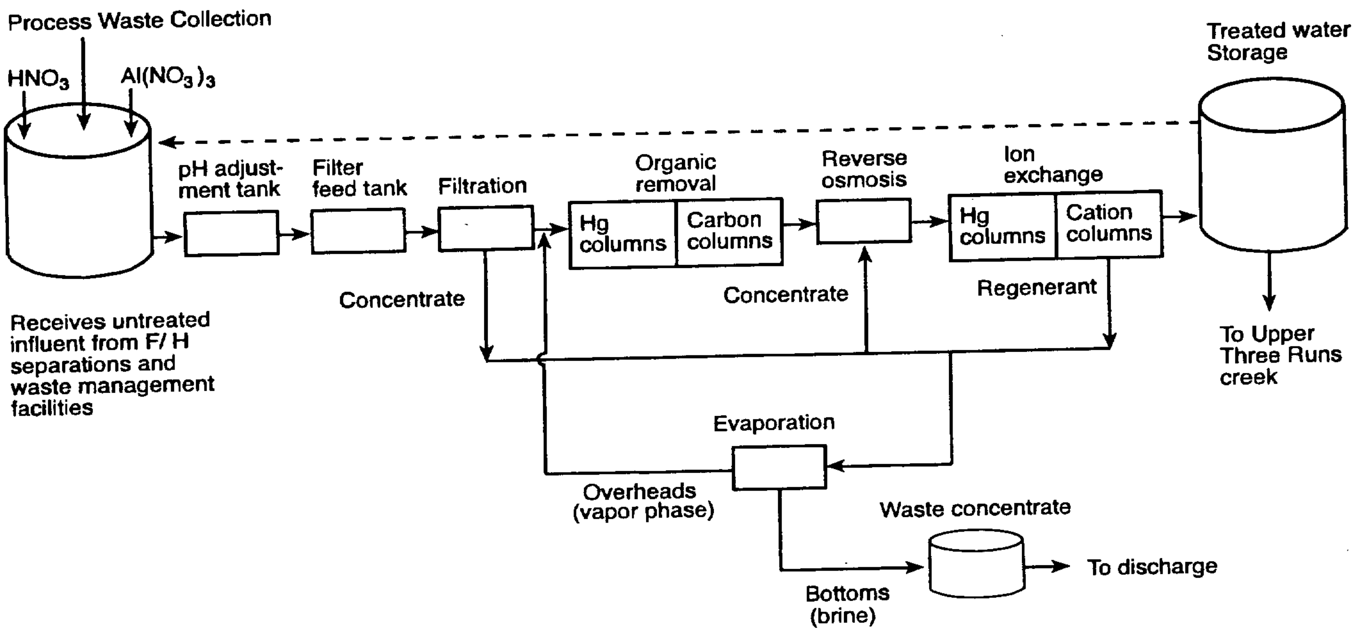
7.1.1 The ETF

Treatment at the ETF involves a four-stage process of filtration, organics removal, RO, and ion exchange. A process flow diagram for the ETF is shown in Figure 8-1. Process influent feed is collected in two 450,000-gal feed tanks, which normally operate at 40% to 50% capacity. No agitation is provided in the tanks. Mixing is accomplished by recirculation, using a sump pump. The pH of the influent wastewater typically ranges from 2.5 to 5.0; however, pH values in the range of 1.5 to 13 are observed. Nitric acid is added to the wastewater in the feed tank to reduce the pH to the range of 2.0 to 2.5. Aluminum nitrate [$Al(NO_3)_3$] (available on site) is added in liquid form to yield a final concentration of Al^{3+} of 35 mg/L. $Al(NO_3)_3$ is added as a coagulant and, reportedly, to reduce biofouling in the treatment system.

The wastewater is pumped from the feed tank into two pH-adjustment tanks that operate in series. The volume of the first tank is 1,500 gallons and the volume of the second tank is 2,500 gallons. The pH is adjusted to 3.5 in the first tank and to 7.5 in the second tank to precipitate ions present in the feed, such as Al^{3+} and Fe^{3+}. These metal precipitates are removed by the filtration system, which is located upstream of the organic removal, RO, and ion exchange systems. Some mercury removal may occur at this point via co-precipitation. The wastewater flows from the second pH-adjustment tank into a 2,500-gal filtration feed tank that operates 50% full. The wastewater is then pumped from the feed tank to the filtration system, which includes α-alumina membrane filters operating in the crossflow mode. The filtration system operates at a wastewater flux ranging from 200 to 500 gpd/ft^2. A feed pump provides the required filtration pressure. The pressure differential is approximately 30 to 40 psi. The filtration system includes three treatment trains, each with three stages in series. Each stage has four parallel modules. Each module has two bundles of 10 filters. The filtration system has recirculation on each stage and blowdown on the third stage. During each filtration run, the filter is backpulsed for about 30 seconds every 10 minutes. As headloss increases and flux decays, the filtration system is taken offline to be cleaned. The filtration tubes are cleaned first by oxalic acid and then by caustic and household bleach before they are put back online. In the past, irreversible biofouling of the tubes was observed and the tubes were replaced after being online for 3 years.

The concentrate (brine) exiting the filtration system goes into the filter concentration tank and then to the evaporator feed tank. The filtrate flows out of the filtration system radially to the organic removal feed tank, which also receives overheads from the evaporator. The organic removal system was not originally included in the ETF. RO was the main component of the process, intended to remove cesium. It was subsequently determined, however, that the waste water contained organics (e.g., tributyl phosphate) that interfered with the performance of the RO system. To remove the organics, the wastewater is now pretreated by activated carbon columns. However, activated carbon accumulated mercury, which was present in the wastewater, so ion exchange columns were added to remove mercury before activated carbon treatment. The organics removal system includes three Duolite GT-73 ion exchange columns operating in parallel, and three activated carbon columns operating in series. Two ion exchange

Figure 7-1. F/H effluent treatment facility process flow sheet.



columns are in service and one is on standby (flooded status). Each column is 4 feet in diameter, 5 feet high, and contains 40 ft^3 of resin. The columns operate in a downflow mode. The wastewater is fed at 135 psi and the pressure drop is 15 psi. The ion exchange columns operate on the sodium cycle instead of the hydrogen cycle to avoid the need for downstream pH adjustment. The ion exchange columns are prewashed with NaOH in order to convert them from the hydrogen to the sodium cycle. Spent NaOH is directed to the evaporator. Regeneration of the ion exchange columns has not been required for about 4 years, since the system became operational. Headloss usually occurs because of biofouling. The headloss problem has diminished significantly, however, since the use of $Al(NO_3)_3$ was initiated.

The ion exchange capacity of the resins is reported to last for about 2 to 3 years. The effluent of the columns is monitored weekly for mercury. When the ion exchange capacity of a column is exhausted, it is taken out of service and buried on site, since the resin exceeds Toxicity Characteristic Leaching Procedure (TCLP) requirements.

Effluent from the ion exchange columns is directed to activated carbon columns. The granular activated carbon has a size 16 mesh and contains fines of 0.1% by volume. Each column is 16 feet tall, has a diameter of 10 feet, and contains 23,000 pounds of carbon. The activated carbon columns operate in the downflow mode. When there is a high pressure drop, the columns are pulsed with air and then are backwashed with water. The backwash water goes back to the head of the system. The activated carbon columns are backwashed every 2 weeks because of high headloss, believed to be due to biofouling.

The wastewater exiting the organic removal system enters a spiral wound RO system. The pH is reduced to a range between 5.5 and 6.5 ahead of the RO system, using dilute HNO_3. Each RO membrane represents an 8-in. diameter module and is 40 in. long. The RO membranes used are seawater-type, high-rejection membranes. Reportedly, they have the following decontamination (i.e., concentration) factors: (1) 20 for monovalent ions, such as Na^+, (2) 40 for divalent ions, such as Ca^{2+} and SO_4^{2-}, and (3) 60 for trivalent ions, such as PO_4^{3-}. The decontamination factor is defined as the ratio of concentration of ions in the feed over the concentration of ions in the product.

The RO system has two modules operating in parallel. The concentrate from these modules is directed to a third module, and the concentrate exiting the third module enters a fourth module. Oxalic acid and sodium metabisulfite are used to clean the RO membranes. The RO membranes are typically cleaned monthly, after they have treated 1.0 to 1.5 million gallons of wastewater. The wastewater from the RO system goes to a pH-adjustment system, where NaOH is added to adjust the pH in the range of 6 to 9.

Cation exchange columns are used at the end of the treatment train as a final polishing step. The wastewater first enters two cation exchange columns operating in parallel for additional mercury removal and then enters two cation exchange columns intended for the removal of cesium and strontium. These columns operate on the sodium cycle and are regenerated by $NaNO_3$ solution. The regenerant is directed to the evaporator feed tank.

Treated wastewater exiting the ion exchange polishing step goes into three 120,000-gal storage tanks. The following parameters are monitored: pH, specific conductivity, beta and gamma radiation, oil and grease, Pb, Cu, Zn, and Hg. Treated wastewater that does not meet the discharge limitations is retreated. Effluent meeting the discharge criteria is discharged to a surface receiving water. The evaporator bottoms go to a tank farm where they are solidified and buried.

7.1.2 ETF Feed Streams

Feed to the ETF is effluent from the SRS separation areas, evaporator condensate, and other waste streams, including contaminated cooling water, surface water runoff, and miscellaneous laboratory wastes. The normal sources of wastewater are evaporator overheads and effluent from the separation areas. The ETF is also designed to treat cooling water that may have accidentally become contaminated in the separation process. In addition, the ETF is designed to treat contaminated water that might result if a leak in a waste storage tank or transfer system should occur simultaneously with a rainstorm. Although the ETF is designed to handle an average flow of 288,000 gallons per day, it routinely handles a flow of 90,000 gallons per day because the volume of wastewater generated has decreased over the years.

Table 7-1 lists major nonradioactive constituents and Table 7-2 presents radioactive contaminants present in the wastewater.

7.1.3 ETF Discharge Limits

There are two sets of applicable discharge limits for the ETF. The first set of discharge limits is set by the state of South Carolina. These limits are generally related to water quality guidelines for conventional nonradioactive waste (see Table 7-1). The second set of discharge limits involves guidelines established by DOE for the discharge of radioactivity from the ETF (see Table 7-2).

7.1.4 Ion Exchange Role in the ETF

Two types of ion exchange columns are used in the ETF system: mercury removal ion exchange columns, and cesium and strontium removal ion exchange columns. The mercury removal ion exchange resin is Duolite GT-73 cation exchange resin, which has thiol functional groups. The cesium and strontium ion exchange resin is a macroporous sulfonic acid cation exchange resin. Each of these applications is discussed below.

Duolite GT-73 Resins

Three columns containing Duolite GT-73 resins operating in parallel are located between the filtration system and carbon columns. Two identical columns operating in parallel are located between the RO and the sulfonic acid resin columns. Duolite GT-73 resin has been reported to be very efficient in the removal of heavy metals, especially mercury (Ritter and Bibler, 1992). Duolite GT-73 is a macroporous, weakly-acidic polystyrene/ divinyl benzene cation resin with thiol functional groups that have a pronounced selectivity for mercury in any of its three common oxidation states. The following ion exchange reactions are postulated for the removal of Hg^{2+} and Hg_2^{2+} (Bibler et al., 1986):

$$R\text{-}S_2H_2 + Hg^{2+} \rightleftharpoons R\text{-}S_2Hg + 2H^+ \qquad [7\text{-}1]$$

$$R\text{-}S_2H_2 + Hg_2^{2+} \rightleftharpoons R\text{-}S_2Hg_2 + 2H^+ \qquad [7\text{-}2]$$

Two plausible mechanisms that address the sorption of Hg° have been proposed. The basis of the first mechanism is as follows: The solubilities of Hg° and HgO in air-free water are 60 ppb and 52 ppm, respectively. The solubility of Hg° in an aqueous solution with dissolved air (oxygen), however, increases by a factor of 700 compared to its solubility in air-free water, and the final solubility is nearly the same as that for HgO (Ritter and Bibler, 1992). These facts suggest that Hg° can be partially ionized by O_2 in an aqueous solution and thus be converted into a form that can be removed by the Duolite GT-73 resin. According to the second mechanism, sorption of Hg° by the Duolite GT-73 resin may also be explained by the van der Waals attraction between metallic mercury (Hg°) and the matrix of the resin, thereby interacting with the resin by physical absorption rather than ion exchange (Ritter and Bibler, 1992).

The Duolite GT-73 resin reportedly operates over a pH range of 1 to 13, a much broader range than for other commercially available mercury-selective resins. The Duolite GT-73 resin remains physically and chemically stable when exposed to ionizing radiation and is insoluble in most common solvents, but decomposes slowly in HNO_3 solution of greater than one molar concentration. The manufacturer's reported ion exchange capacity of the resin for Hg^{2+} is 1.4 meq/mL (Bibler et al., 1986).

Three alternatives have been studied at the ETF for handling the exhausted Duolite GT-73 ion exchange resins. These alternatives are (1) storage of mercury-containing resins as such, (2) storage of mercury containing resins incorporated into grout, and (3) recovery of mercury desorbed from the resin. Samples of Duolite GT-73 resin were saturated with mercury and analyzed by the EP toxicity test. The spent resin passed the EP toxicity test,

Table 7-1. Nonradioactive Contaminants and Discharge Limits (After Bibler and Wallace, 1987).

	Influent to ETF (ppm)		Influent to Ion Exchange (ppm)		Proposed Limits (ppm)	
Ion	Average	Maximum	Average	Maximum	Average	Maximum
NH’,	16	110	4.0×10^{-1}	2.8	20	—
Hg^{2+}	0.053	IO	1.3 x IO”	2.4×10^{-1}	4.5×10^{-1}	1.75×10^{-1}
Zn^{2+}	1.1	100	2.8×10^{-2}	2.5	1.48	2.61
Cr^{3}	0.031	240	7.8×10^{-4}	6.0	1.71	2.77
Cu^{2+}	0.14	18	3.5×10^{-3}	5.0×10^{-1}	1.30	1.89
Pb^{2+}	0.15	38	3.8×10^{-3}	9.5 x IO“	2.2×10^{-1}	4.5×10^{-1}
Mn^{2+}	0.18	21	4.5×10^{-3}	5.3×10^{-1}	—	—
NO,	1,015	22,400	25	560	—	—

Table 7-2. Radioactive Contaminants and Discharge Limits (After Bibler and Wallace, 1987).

	Influent to Ion Exchange		Release to Streams		DOE Guide
Radionuclide	**mCi/yr**	**mCi/mL**	**mCi/yr**	**mCi/mL**	**mCi/mL**
cs- 134,137	70	1.7×10^{-10}	0.7	1.7×10^{-12}	2.9×10^{-5}
Sr - 89, 90	9	2.2×10^{-11}	0.09	2.2×10^{-13}	3.3×10^{-6}
Co-60	5	1.2×10^{-10}	0.5	1.2×10^{-12}	3.0×10^{-5}
Other p-y	3.0	7.5×10^{-12}	3.0	7.5×10^{-12}	—
Total a	3.5 x IO”	8.7×10^{-3}	3.5×10^{-3}	8.7×10^{-15}	—

indicating that simple storage was a viable option. Similar resin samples were incorporated in Portland Type II grout and subjected to structural integrity tests and the Extraction Procedure (EP) toxicity test. These samples passed the structural integrity test but not the EP toxicity test. Because the EP toxicity test involved maintaining the sample at pH 5 with acetic acid and given the high concentration of calcium ions in grout, exchange of calcium ions for mercuric ions may have taken place. Thus, the storage of spent resin without incorporation into grout was preferred.

Although regeneration of the spent resin is possible, it is not deemed desirable at ETF. Mercury can be eluted from the resin using 3 M HCl or 2 M NaSCN, neither of which is chemically compatible with materials of construction or processes at SRS. Dissolution of the resin and reclamation of mercury by chemical means such as precipitation as the sulfide or reduction to the metal is an attractive alternative to storage, should recovery and removal become desirable.

Sulfonic Acid Cation Resins

A macroporous, strong acid cation exchange resin was chosen for removal of cesium and strontium. Several commercially available resins have demonstrated cesium and strontium removal capabilities coupled with ease of regeneration. Cesium and strontium in the regenerant can by a relatively small volume of neutral reagent be concentrated further and incorporated in concrete for final disposal. Spent resin can be decontaminated and discarded in an approved manner.

Several test runs were conducted to determine the performance of the sulfonic acid resin throughout several simulated feed, wash, and regeneration cycles. Results indicated that the effectiveness of the process was less than desirable after several cycles had been completed. A chromatographic effect was observed where concentrated bands of all metals present were detected in the effluent at unpredictable times during feed cycles. The frequency and concentrations of such eluted bands cannot be accurately predicted in the ETF due to the varying daily concentrations of influent to the facility. To prevent this behavior the ion exchange feed was first processed through the Duolite GT-73 columns for mercury removal, allowing the sulfonic acid columns to operate as designed for the removal of cesium and strontium.

7.2 Effluent Treatment Facility Economics

The treatment plant operates Friday through Sunday of each week. There are 5 operators during each shift, which lasts 12 hours, with an additional 0.5 hour turnaround. During the 1994 fiscal year, 22 million gallons of waste water were treated at a total cost of $18.8 million. This results in a unit cost of about $1/gallon. Figure 8-2 presents the ETF cost breakdown components.

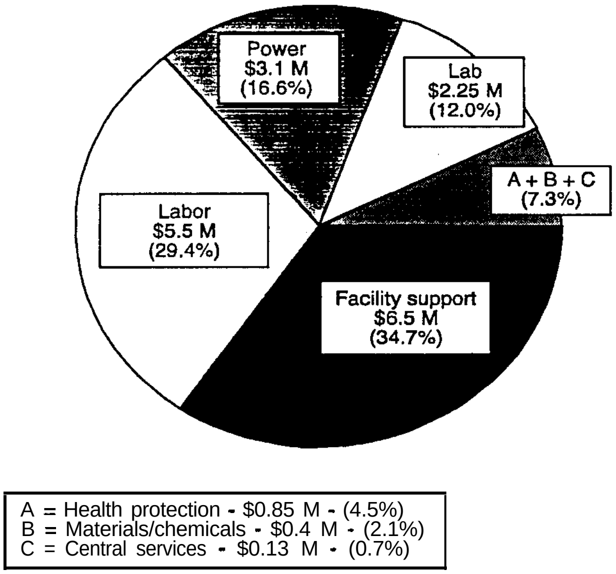


Figure 7-2. ETF facility O&M cost breakdown.

Chapter 8
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