# REUSE OF POWER PLANT DESULFURIZATION WASTE WATER



Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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by

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Grant R-802853-01-0 ROAP No. R21AZU-025 Program Element No. 1BB392

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY Office of Research and Development Washington, DC 20460

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#### ACKNOW LEDGMENTS

Sincere appreciation is acknowledged for the guidance and assistance provided by Dennis Cannon, the present EPA Project Officer, and by Alden Christianson and Guy R. Nelson, the prior Project Officers of this study program.

The authors are especially grateful to the late Lawrence J. Bornstein, who was the Project Manager for The Aerospace Corporation during most of this program. His tireless efforts in producing most of the survey data and evaluations and the major portion of this report contributed greatly to the accomplishment of this study.

#### CONCLUSIONS

The following conclusions were made as a result of an Aerospace Corporation study to determine the treatments and costs applicable to the reuse of liquor from nonregenerable flue gas desulfurization systems if there should be a necessity for a system purge to provide the capacity for the required fresh make-up water. (It should be noted that the determination of whether scrubbers should be purged was not made and was not an objective of this study.) These conclusions are based on the analysis and assessment of four different scrubber liquors, which were characterized in this study and which are believed to be representative of most but not all scrubber liquors. With these data as background and using existing criteria and guidelines, some postulated criteria, and an estimation of purge flow rates, the following conclusions are made regarding the potential reuse of purged scrubber liquors:

- a. Purged scrubber liquor must be treated if it is to be reused as power plant service water or if it is to be discharged.
- b. Treatment for service water usage in most cases can be accomplished by chemical precipitation (e.g., lime-soda softening, filtration, and pH control when necessary). This includes usages such as scrubber make-up, cooling tower make-up, and plant housekeeping. For an expected minority of cases, excessive chloride content will require additional treatment such as reverse osmosis.

- c. For discharge to surface waters, treatment would consist of a pretreatment and an additional treatment (e.g., lime-soda softening, filtration, and pH control plus reverse osmosis). This would result in costs approximately twice the cost of treatment for service water in most cases.
- d. Quantities of scrubber liquor in a 1000 Mw equivalent unit presumed for treatment for purposes of this study are 100 to 300 gpm nominally and 700 gpm maximum. Total treatment costs (capital and operating), based on a 30-year equipment life and 18 percent annualized capital charges, are as follows:

Flow rate of liquor to be treated	Lime-soda softening and filtration	Lime-soda softening and filtration pretreatment plus reverse osmosis
200 gpm	\$5.00/1000 gal	\$9.00/1000 gal
	or	or
	0.05 mill/kWh	0.11 mill/kWh
700 gpm	\$2.50/1000 gal	\$5.00/1000 gal
	or	or
	0.09 mill/kWh	0.22 mill/kWh

#### To convert:

- gpm to cu m/hr, multiply by 0.227.
- dollar/1000 gal to dollar/cu m, multiply by 0.264.

#### RECOMMENDATIONS

Analyses determined in this study of waste stream liquors and a review of related data given in Refs. 1 through 3 show that most lime and limestone scrubber liquors, including those produced during steady-state operating conditions, must be treated if they are to be reused after a scrubber system blowdown. If it is shown that a blowdown is required, it is recommended that the purged liquor be treated for reuse as power plant service water.

The potential liquor treatment requirements that were determined in this study were based on the chemical characterization of liquors from a limited number of power plants and postulated purge conditions. Therefore, it is recommended that additional studies be made to broaden the data base. These should include the characterization of liquors from additional power plant scrubbing systems, development of more comprehensive usage criteria, detailed analyses of potential purge conditions, and treatment demonstrations for those purge conditions, if any, that are shown to be necessary. Specific recommendations are as follows:

#### a. Analyses

1. An expanded data base regarding scrubber liquor chemical characterization should be determined or assembled. Any additional factors which were not part of this study, such as radioactivity, should be considered in this characterization.

- 2. Detailed analyses should be conducted on conditions that may require scrubber purge, including purge flow rates and purge cycles. These results should be confirmed by operational tests.
- 3. Investigations should be made of the techniques available that may prevent scrubber purge conditions from arising. These techniques should be tested on operational systems.
- 4. If scrubber purge conditions are determined to be unavoidable, the net effect of waste disposal should be determined, including the brine produced in water treatment systems.

#### b. Usage Criteria

- 1. Criteria should be established, consistent with results of the analyses recommended above, to define power plant service water quality.
- 2. Power plant effluent guidelines and standards should be expanded, consistent with the analyses recommended above, to relate to the potential discharge of treated liquors.

#### c. Demonstration

If it is shown that scrubber purge is unavoidable, a demonstration of purged liquor treatment is recommended. At this time, the following five treatment processes are recommended for consideration in the selection of hardware for demonstration:

- 1. Chemical precipitation (e.g., lime-soda softening)
- 2. Chemical precipitation plus reverse osmosis
- 3. Chemical precipitation plus ion exchange
- 4. Multistage flash evaporation
- 5. Brine concentration

#### SECTION 1

#### INTRODUCTION

#### 1.1 INTRODUCTION

The installation of nonregenerable flue gas desulfurization systems in coal-burning power plants using lime or limestone as the scrubber absorbent requires large quantities of water (Refs. 1 and 2). This water circulates through the scrubber loop as an alkaline slurry. The sulfur waste products that form are bled from the scrubber, and, in most systems where a settling tank or clarifier is used, the supernatant liquor is recirculated to the scrubber. Wastes produced by these systems are generally removed by disposing of the clarifier underflow, a filter cake, or a centrifuge cake. They are typically ponded or placed in a landfill after possible intermediate treatment for environmental protection. All supernate liquors resulting from the waste disposal processes are returned to the scrubber loop; hence, the current scrubber systems can be described as closed-loop operations. The only water lost is that which is evaporated with flue gases or occluded with the solid waste products. Fresh water is added to make up for these losses and is adequate to prevent the formation of scale that results from precipitation of solids at critical points within the system.

This study evaluates the potential reuse of scrubber liquor within water systems of the power plant, in the event that a purge is required to maintain adequate capacity for fresh make-up

water to the scrubber. The power plant water systems to be evaluated are those that may accept nonpotable water. These include cooling towers, housekeeping service, and scrubber make-up. Alternatively, these waters can be treated for discharge. In addition, those conditions that exist or may develop in the operation of flue gas scrubbing systems that may require a system purge are postulated. These conditions include variable sulfur content of the coal, variable boiler load factor, and sulfite sludge oxidation. In an evaluation of the reuse of scrubber liquor in other water systems, it is necessary to determine the relationship of the water quality of these liquors to the limiting requirements of the intended applications.

Currently, The Aerospace Corporation is conducting a study, "Disposal of By-Products From Nonregenerable Flue Gas Desulfurization Systems," under Environmental Protection Agency (EPA) Contract Number 68-02-1010 (Refs. 2 and 3). Data obtained in that study have shown that scrubber liquors are unacceptable for direct discharge and may not be acceptable for most other water systems within the power plant without prior water treatment.

This program was initiated because of the potential unacceptability of direct discharge of scrubber liquors and the need to determine the potential reuse of purged liquors as power plant service water. Secondary reasons are the national goal of zero discharge by 1985 in accordance with the Federal Water Pollution Control Act Amendments of 1972, and the requirements for the 1977 and 1983 discharge limitations based on the best practical control technology available and the best available technology economically achievable (Ref. 4). Program objectives and the study approach to characterize the problem and assess the technology applicable for water reuse are given in Sections 1.2 and 1.3, respectively.

#### 1.2 PROGRAM OBJECTIVES

The principal objectives of this study were to determine the requirement, if any, for treatment of nonregenerable flue gas desulfurization waters for reuse and to determine the water treatment processes and costs applicable for reuse of these waters.

#### 1.3 STUDY APPROACH

The study objectives were accomplished by performance of the following specific tasks:

- a. Determination of the characteristics of scrubber system liquors from four coal-burning power plants at the potential discharge points and quantification of the constituents affecting water quality.
- b. Identification of the scrubber systems with flow diagrams and corresponding liquor flow rates under varying scrubber operating conditions and estimation where possible of those conditions that may require system liquor blowdown.
- c. Assessment of the quality of liquor waste waters against appropriate water quality criteria.
- d. Survey of water treatment processes available and in development and assessment of the applicability of those processes deemed capable of reducing the concentration of constituents of concern in the waste waters to allow reuse within the power plant or to allow direct discharge.
- e. Recommendation of appropriate water treatment processes based upon technical and economic considerations.

Samples of flue gas desulfurization scrubber system liquors were obtained from four different scrubber systems (Table 1-1) using lime or limestone as the sulfur dioxide absorbents. The concentration of the trace elements and major species in the liquors of the potential discharge flow streams were determined by

conventional analytical techniques, and the results of these analyses were assessed against water quality criteria for the nonpotable reuse of the water within the power plant operations or for its discharge to surface waters.

Flow diagrams and rates were determined for the flow streams of the four scrubber systems. An extrapolation was made of the flow rates from each of these systems to an identical system of 1000 MW equivalent capacity.

A technical and economic review was conducted of the literature and industry to identify potentially acceptable water treatment processes. The economic assessment included initial investment, annual capital charges, and operating expenses for these processes.

## 1.4 ORGANIZATION OF THIS REPORT

Following this introduction, a summary of the total study is given in Section 2. Appropriate figures and tables are included to support the findings.

The technical discussion is given in Sections 3, 4, and 5. Significant features of each of these are as follows:

Section 3 discusses the water quality criteria selected for water reuse in the power plant as nonpotable service water or for discharge to surface waters.

Section 4 contains the flow diagrams, flow rates in the potential discharge flow streams, and water balances for the four scrubber systems. These data were extrapolated to power plant scrubbing systems using the same design and operating characteristics, but operating at 1000 MW capacity equivalent. This section also contains complete tabulated data and an assessment of the chemical characteristics of the scrubber liquors. An assessment is also made of the concentration of constituents at the potential discharge points

	Power plant			
Description of scrubber and coal	Tennessee Valley Authority (TVA) Shawnee Steam Plant, Paducah, Kentucky		Arizona Public Service Company Cholla Station, Joseph City, Arizona	Duquesne Light Company Phillips Station, South Heights, Pennsylvania
Scrubber				
Туре	Venturi and spray tower	Turbulent contact absorber (TCA)	Flooded disk scrubber (FDS) and absorption tower	Single- and dual-stage venturi
Equivalent capacity, MW	10 (EPA/TVA prototype)	10 (EPA/TVA prototype)	120 (full-scale)	125 each (four full– scale units)
Manufacturer	Chemical Construction Corporation	Universal Oil Products Company	Research Cottrell, Inc.	Chemical Construction Corporation
Absorbent	Lime	Limestone	Limestone and flyash	Lime
Coal		!		
Source	Eastern	Eastern	Western	Eastern
Sulfur content, percent	3.4 (avg)	3.4 (avg)	0.5	2

against water quality criteria for reuse as service water in other water systems in the power plant, and discharge to lakes and streams if the need should arise.

Section 5 summarizes the applicable water treatment processes and equipment described in the literature or in data available from industrial contractors. A technical assessment is made of the potentially applicable processes, and engineering cost estimates are made of the initial investment, annual capital charges, and operating costs.

Supporting data in the appendixes include a description of the analytical techniques used to determine the concentration levels of the constituents in the scrubber liquors, an evaluation of the accuracy and precision of the analyses, and the background data used in preparing the water treatment cost estimates.

#### SECTION 2

#### SUMMARY

#### 2.1 WATER CRITERIA

In the nonregenerable flue gas desulfurization scrubber operation, the scrubbing systems water is continuously recycled through a closed-loop system. Normally, there is no discharge of water from these systems except for the moisture discharged with the sludge and that which evaporates from the scrubber. Under off-design conditions or any other condition not generally employed in scrubbers at this time (Section 4.2), a certain amount of scrubber liquor may have to be purged and treated prior to its reuse. This assessment is based on a review of the chemical analyses of system liquors sampled from four different scrubbing systems (Section 2.3) and a comparison of these data with selected water use criteria.

The four systems from which liquors were analyzed do not necessarily represent a typical cross section of scrubbers installed or planned in the U.S. However, on the basis of other studies (Refs. 1 through 3), it appears that most system liquors will have characteristics within the ranges of those analyzed in this study. Some exceptions, such as the Mohave Station scrubber in Nevada and the General Motors scrubber in Parma, Ohio (both of which have high

concentrations of chloride), would require more extensive water treatment than the four stations represented in this study. The variations in scrubber liquor characteristics on a national overview basis should be the subject of a separate study; however, the conclusions reached in this report pertain to only those stations studied, which are believed to be representative of most nonregenerable scrubbing systems now operating or to be installed.

The potential reuse considered for treated scrubber liquors are power plant service water, scrubber reuse, and direct discharge to lakes and streams. Reuse as power plant service water or scrubber make-up was considered as a single category, and direct discharge as another. No specific criteria were found for power plant service water usage; therefore, the criteria postulated for this study was based on an informal survey of water requirements now practiced within the power industry. These criteria, listed in Table 2-1 as "nonpotable service water criteria" were used also for scrubber makeup on the basis of results obtained in The Aerospace Corporation study of scrubber waste disposal requirements (Ref. 3). For direct discharge, several criteria were available, e.g., the U.S. Public Health Service drinking water standards of 1962 (Ref. 5), federal and state water quality criteria documents (Refs. 6 and 7), EPA proposed criteria for public water supply intake dated October 1973 (Ref. 8), and the EPA effluent guidelines (Ref. 9). Of the public service and drinking water criteria available, the EPA proposed critera of October 1973 was selected as being the most appropriate for this assessment and is given in Table 2-1. The EPA effluent guidelines at this time are not broad enough to cover most of the major constituents of scrubber liquors, and therefore were not listed. They were used, however, in a comparative sense (Section 2.3).

An examination of Table 2-1 shows that the criteria for nonpotable service usage is much less stringent than the public service water criteria. Service water usage is concerned mostly

Table 2-1. WATER QUALITY CRITERIA AND RANGE OF CONCENTRATION OF CONSTITUENTS IN SCRUBBER LIQUORS STUDIED

	Concentration, mg/	unless otherwise	e indicated)
		Water criteria	
Constituents	Range of constituent concentrations at potential discharge points <sup>a</sup>	EPA-Proposed public water supply intake, October 1973	Nonpotable service waterb
Aluminum Antimony Arsenic Beryllium Boron	0.03 - 0.3 0.09 - 2.3 <0.004 - 0.3 <0.002 - 0.14 8.0 - 46.	- 0.1* 1.0*	1. 1. 0 2. *
Cadmium Calcium Chromium (total) Cobalt Copper	0.004 - 0.11 520 3000. 0.01 - 0.5 0.10 - 0.7 <0.002 - 0.2	0.01* 0.05* 1.0	1000.* 1. - 5.
Iron Lead Magnesium Manganese Mercury	0.02 - 8.1 0.01 - 0.4 3.0 - 2750. 0.09 - 2.5 0.0004 - 0.07	0.3* 0.05* - 0.05* 0.002*	10. 1. 1000.* 3. 0.5
Molybdenum Nickel Potassium Selenium Silicon	0.91 - 6.3 0.05 - 1.5 5.9 - 32. <0.001 - 2.2 0.2 - 3.3	- - 0.01*	- - - 3. 5.
Silver Sodium Tin Vanadium Zinc	0.005 - 0.6 14.0 - 2400. 3.1 - 3.5 <0.001 - 0.67 0.01 - 0.35	0.05* No limit <sup>c</sup> 5.	- - - - 10.
Carbonate Chloride Fluoride Sulfite Sulfate	<1.0 - <10. 420 4800. 0.07 - 10. 0.8 - 3500. 720 10,000.	250.* 0.7-1.2*8 250.*	5000. - 2500.*f
Phosphate Nitrogen (total) Chemical oxygen demand Total dissolved solids Total alkalinity (as CaCO <sub>3</sub> )	0.03 - 0.41 <0.001 - 0.002 60 390. 3200 15,000.d 41 150.		5. 30 (NO <sub>3</sub> ) - - -
Conductance mho/cm Turbidity, Jackson units	0.003 - 0.015 <3 <10.	No limit <sup>c</sup>	e -
рН	3.04 - 10.7	5-9*	5-10*

<sup>&</sup>lt;sup>a</sup>Samples obtained from: EPA/TVA, Shawnee, Steam Plant - venturi and spray tower; EPA/TVA Shawnee Steam Plant - turbulent contact absorber; Arizona Public Service Cholla Station - flooded disk scrubber and absorption tower; and Duquesne Light Phillips Station - single- and dual-stage venturi.

 $<sup>^{</sup>m b}{
m E}$  stimates based on discussions with power companies, water treatment processors, and data in the literature.

C''No limit" indicates that insufficient data existed for prescribing limits.

dIncludes all soluble species.

<sup>&</sup>lt;sup>e</sup>Salinity controlled by the presence of other ingredients.

 $<sup>^{</sup>m f}$ Subsaturation of CaSO $_4$  assumed.

g "USPHS Drinking Water Standards 1962," USPHS Publication No. 956.

hSee criteria for chloride and sulfate.

<sup>\*</sup>Scrubber liquor effluent from one or more power plants exceeds water criteria.

with nonscaling and noncorrosive properties, whereas the public service water criteria are concerned with health factors. Also, the demand for nonpotable service water in a power plant is always high, and the water treatment requirements for public service water usage are more extensive and expensive than that required for service water (Section 5.3). Throughout this report assessments are made for both types of uses. However, it is assumed that the treatment of scrubber liquors for reuse as public service water (i.e., drinking) would be employed only in rare cases. Therefore, the major emphasis in this study is placed on treatment of scrubber effluent for reuse as service water.

## 2.2 POWER PLANT SCRUBBING PROCESSES

As part of this study, a four-step analysis was made of the scrubbing process at each of the four scrubbers (Table 1-1). This analysis included:

- a. Examining the operating conditions occurring at the time the scrubber liquor samples were taken
- b. Identifying the water flow rates in the various flow streams of that scrubber system
- c. Projecting those flow rates to a scrubber of a size equivalent to that required for a 1000 MW power plant
- d. Estimating potential purge rates for purposes of this study.

Liquor samples were taken from the four scrubber systems of the coal-burning power plants identified in Table 1-1. These scrubbers ranged in equivalent capacity of 10 to 400 MW. The plants burned either eastern or western coals, and the flue gases were scrubbed with a lime or limestone slurry water that reacted with the sulfur dioxide. The process flow diagram for the EPA/TVA venturi and spray tower scrubber, which is designed for a 10 MW

equivalent capacity, using lime as the absorent, is shown in Figures 2-1 and 2-2 as an example case. The water balance for this system is shown in Figure 2-3 (Ref. 10). Following the scrubber is a clarifier and a vacuum filter. The separated liquor is recycled within the scrubbing system. At the times of sampling, an average of 3.4 percent sulfur coal was burned, 78 to 93 percent removal of the sulfur dioxide was obtained, and 306 cu m/hr (1350 gpm) of water was recycled into the scrubber.

The flow diagram illustrates the amount of water flowing in each major flow stream and its percentage as related to the total feed water to the scrubber. In this system, less than 1 percent of the feed water to the scrubber was lost with the sludge to the disposal pond and to the stack with the flue gases. Fresh water was introduced into the system with the lime slurry mix and by direct addition of fresh make-up water into the hold tank. The extrapolated values are shown in Figure 2-4 for a water balance for a 1000 MW scrubber system based on the same process used in the venturi and spray tower system. The water flow rates were scaled up from the test conditions that existed during sampling at the EPA/TVA facility. The calculations were based upon operating at 90 percent sulfur dioxide removal efficiency, using the identical scrubber design, having the same conditions in the scrubber and burning the same coal, and retaining the same scrubber liquid-to-flue gas ratio. For the 1000 MW capacity scrubber plant, it was estimated that 320 cu m/hr (1410 gpm) of water would be lost, of which 204 cu m/hr (900 gpm) would escape from the stack with the flue gases and 115 cu m/hr (510 gpm) would be occluded with the solids in the filter cake that was sent to the sludge pond for disposal. The rates of occluded water in the discharge of all four scrubbers were used to estimate potential purge rates (Section 2.4).

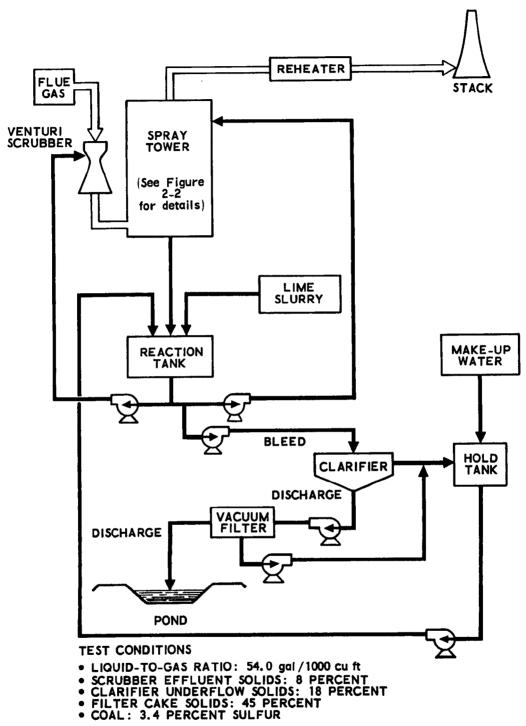


Figure 2-1. EPA/TVA Shawnee Steam Plant typical flow diagram for venturi and spray tower scrubber system: 8.34 MW equivalent operation

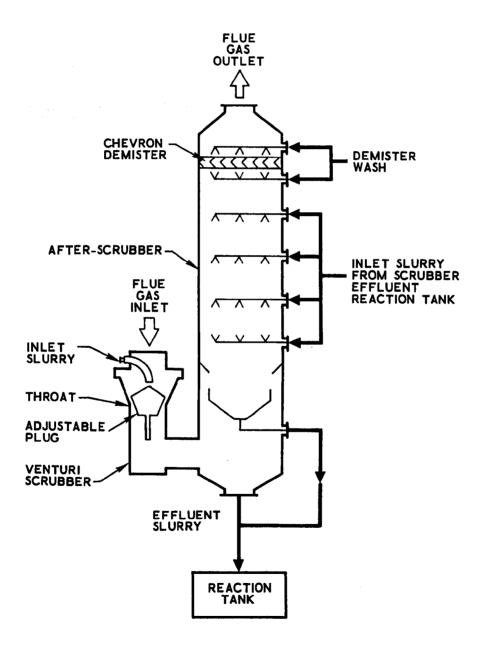
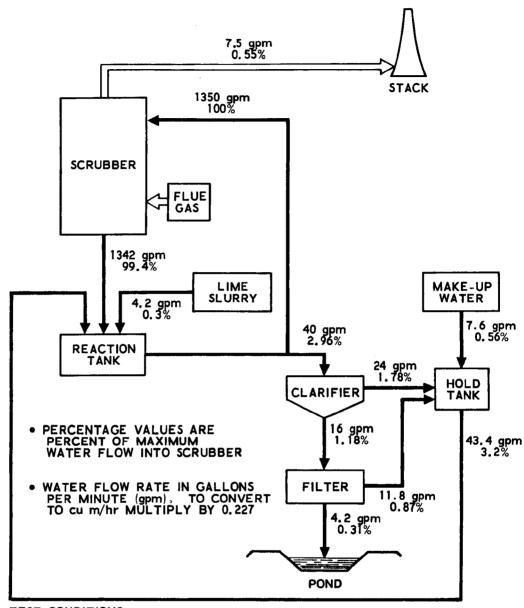


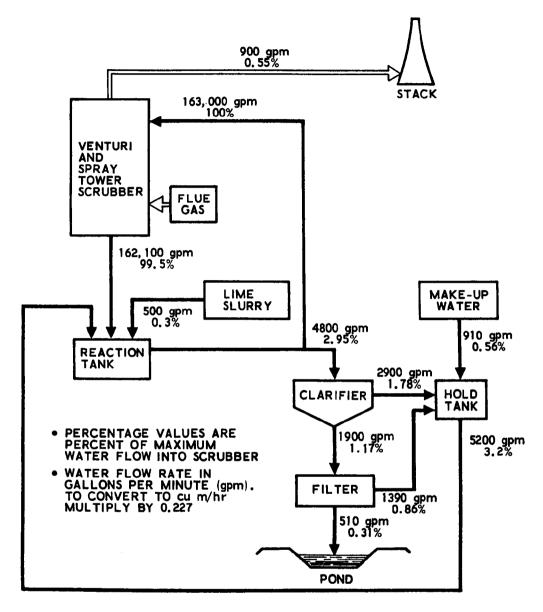
Figure 2-2. Schematic of EPA/TVA Shawnee Steam Plant venturi and spray tower scrubber



**TEST CONDITIONS** 

LIQUID-TO-GAS RATIO: 54.0 gal/1000 cu ft
SCRUBBER EFFLUENT SOLIDS: 8 PERCENT
CLARIFIER UNDERFLOW SOLIDS: 18 PERCENT
FILTER CAKE SOLIDS: 45 PERCENT
COAL: 3.4 PERCENT SULFUR

Figure 2-3. Water balance for EPA/TVA Shawnee Steam Plant venturi and spray tower scrubber system: 8.34 MW equivalent operation



#### **EXTRAPOLATED OPERATING CONDITIONS**

- LIQUID-TO-GAS RATIO: 54.0 gal/1000 cu ft
- SCRUBBER EFFLUENT SOLIDS: 8 PERCENT
- CLARIFIER UNDERFLOW SOLIDS: 18 PERCENT
- FILTER CAKE SOLIDS: 45 PERCENT
- COAL: 3.4 PERCENT SULFUR
- SO2 REMOVAL EFFICIENCY: 90 PERCENT

Figure 2-4. Water balance for venturi and spray tower scrubber system (extrapolation based on EPA/TVA Shawnee Steam Plant process): 1000 MW equivalent

Because each process is configured differently and has its own individual operating characteristics, the data obtained for these four scrubbers cannot be extrapolated directly to other systems.

# 2.3 SCRUBBER LIQUOR CHARACTERIZATION AND ASSESSMENT

Table 2-1 lists the constituent concentrations found in the scrubber liquor samples taken from the potential discharge points of the four scrubbers.

Variations in the concentration of the constituents are due in part to the different operating conditions that existed among plants. For example, the Arizona Public Service Cholla Station operates in a tightly closed scrubber loop situation resulting in high concentrations of chlorides and total dissolved solids in the bleed stream from the flooded disk scrubber slurry tank that is presently the discharge point for this system (Ref. 10). Conversely, the Duquesne-Phillips Station system has experienced operating conditions requiring high water use within the scrubbing system which diluted the concentration of the dissolved ingredients (Ref. 11). Variations in scrubber liquor composition at the potential discharge points were also caused by differences in the coal composition, in the absorbents, and in the scrubber process design and operating characteristics.

For the scrubber liquor to be reused in other systems within the power plant, it will be necessary to reduce the concentration of boron, magnesium, calcium, or sulfate, from one or more of the scrubber flow streams studied. An adjustment of the pH of the water would also be necessary for some of the flow streams. These reductions and adjustments of the characteristics of purged liquor would make the liquor applicable for reuse within the scrubber also.

The concentration of lead, mercury, selenium, chlorides, and sulfates and the pH in the scrubber liquor streams

from all four power plants exceed the EPA-proposed criteria for public water supplies. In addition, in one or more of the streams the concentration of arsenic, boron, cadmium, chromium (total), iron, manganese, and silver also exceed the criteria, but not simultaneously. Because these ingredients exceed the criteria, the scrubber liquor must be treated before it can be discharged.

The EPA effluent guidelines and standards (Ref. 9), though not as restrictive or as encompassing as public water supply criteria, require treatment of some of these liquors because of limitations on iron and pH level. However, this approach for direct discharge should be used with caution since the major constituents of the liquor are not specified.

The following section summarizes treatment technologies available for these purposes and discusses the relative complexities of treatment for reuse as service water and discharge to surface waters.

# 2.4 WATER TREATMENT TECHNOLOGY AND COSTS

A review was made of the literature, and technical meetings and discussions were held with water treatment processors and equipment manufacturers to determine the water treatment techniques applicable to the potential reuse or discharge of scrubber liquor. The results of this review are summarized in Table 2-2, which identifies the generic types of water treatment processes, the development status of each, and indicates whether or not the water would meet the water quality criteria.

It was found that a treatment process such as limesoda softening which reduces the concentration of all constituents, except soluble sodium and chloride salts, would be sufficiently effective that the water of the four liquors studied would be acceptable

Table 2-2. SUMMARY OF GENERIC TYPES OF WATER TREATMENT PROCESSES CAPABLE OF MEETING WATER QUALITY CRITERIA

Water treatment process	EPA-proposed public water supply intake, October 1973	Nonpotable service water	Status
Complete system			
Multistage evaporation	Yes	Yes	Operational
Tower distillation	Yes	Yes	Operational
Brine concentration	Yes	Yes	Operational
Spray drying	Yes	Yes	Operational
Vacuum freezing	Yes	Yes	Development
Solar distillation	Yes	Yes	Development
Rotating bipolar electrodes	No	No	Laboratory
Partial operation a			
Filtration or centrifugation	No	No	Operational
Ultrafiltration	No	No	Operational
Reverse osmosis	Yes	Yes	Operational
Ion exchange	Yes	Yes	Operational
Chemical precipitation (including lime-soda softening)	No	Yes	Operational
Electrodialysis	Yes	Yes	Development
Selective absorbent	No	No	Laboratory
Electrochemical; fluidized bed	No	No	Laboratory
Foam separation	No	No	Laboratory

aUsed with other operations to form a total water treatment system

(after pH adjustment, if necessary) for use as power plant service water (e.g., cooling tower makeup, heat exchangers, scrubber makeup, and housekeeping). In plants where a chloride concentration greater than 5000 mg/l is unacceptable, lime-soda softening would have to be followed by an additional process (e.g., reverse osmosis). This value was selected on the basis of an informal survey of the industry. Variations can be expected depending on the characteristics of any particular plant.

The use of scrubber liquor in a public water supply would require a complete treatment, e.g., lime-soda softening followed by reverse osmosis in all cases and, in some cases, pH adjustment. Therefore, treating the liquor for reuse as drinking water can require a treatment process and cost appreciably in excess of that required for reuse as service water.

Other existing treatment processes such as multistage flash evaporation, brine concentration, and softening-ion exchange could be used instead of softening and reverse osmosis, but would generally be less cost effective. Processes in development have not yet shown that they are cost effective.

A preliminary estimate was made of the amount of water that may have to be removed from the scrubber loop to provide the adequate volume for fresh water make-up requirements (Section 4.2). Two scrubber systems were considered: a venturi and spray tower system and a turbulent contact absorber system. The greatest amount of excess liquor that may have to be removed for maintenance of the water balance may occur in the case where gypsum is formed and the excess liquor is subsequently removed from the scrubber loop. The least amount may be in the case of a reduced load factor on the system. The quantity of water to be removed from a 1000 MW equivalent system appears to be in the range of 22.7 to 68.1 cu m/hr (100 to 300 gpm) but can possibly be as high as

160 cu m/hr (700 gpm). A detailed analysis of potential scrubber purge flow rates was not a subject of this study; however, an estimate was considered necessary because of the wide variations in treatment costs as a function of treatment system size. For this reason, costs were determined and plotted for flow rates up to 1000 gpm. Specific case values are presented for the lower nominal and the upper end of the estimated flow rate range, i.e., 200 and 700 gpm.

The total cost, including capital charges and operating expenses, for treating 45.4 and 160 cu m/hr (200 and 700 gpm) of scrubber liquor using a lime-soda process varies from 0.51 to 0.25 cents per gallon. This converts to a reverse order of approximately 0.05 to 0.09 mills per kWh at an average annual production of 4560 million kWh over 30 years. Likewise, when lime-soda pretreatment is combined with reverse osmosis, these values are approximately double, i.e., 0.9 to 0.5 cents per gallon and 0.1 to 0.2 mills per kWh, respectively. These costs are shown on Figures 2-5 and 2-6 where values are given for flow rates from 200 to 1000 gpm.

- 1974 DOLLARS
- 1000 MW POWER PLANT SCRUBBER
- COSTS BASED ON 30-YEAR ANNUALIZED COSTS, 4560 OPERATING HOURS PER YEAR, AND CAPITAL CHARGES OF 18%
- LAND COSTS NOT INCLUDED

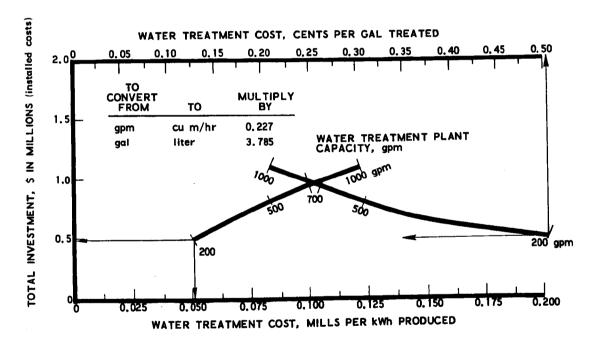


Figure 2-5. Estimated costs of lime-soda softening and filtration

- 1974 DOLLARS
- . 1000 MW POWER PLANT SCRUBBER
- COSTS BASED ON 30-YEAR ANNUALIZED COSTS, 4560 OPERATING HOURS PER YEAR, AND CAPITAL CHARGES OF 18%
- LAND COSTS NOT INCLUDED

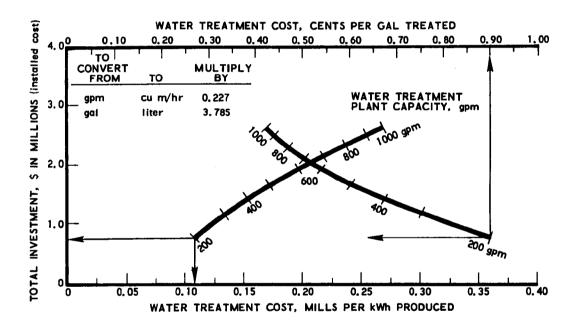


Figure 2-6. Estimated costs of lime-soda and filtration pretreatment plus reverse osmosis

# SECTION 3

### WATER QUALITY CRITERIA

The scrubber liquor is continuously recycled in the flue gas desulfurization scrubbing system. Currently, a bleed stream of scrubber slurry is withdrawn from the scrubber loop and is dewatered; the resultant solids are sent to a waste disposal pond. The supernate liquid (system liquors) and make-up water, which is added to replace the water lost with the waste product and by evaporation with the flue gases, are returned to the scrubber. If the scrubber liquors are to be reused within the power plant or discharged, they must meet the accepted water quality criteria for their intended use.

Large quantities of water are needed in the power plant operations for nonpotable uses (e.g., cooling water, scrubber make-up, housekeeping, and irrigation of the power plant vegetation). These uses can be divided into nonpotable water for use throughout the plant that will not cause scaling or corrosion of the equipment and irrigation water. After the identification of the specific water use, it is necessary to establish criteria to ensure that the water will be of sufficient quality for that use.

The October 1973 EPA-proposed criteria for public water supply intake (Ref. 8) is part of the data base for the 1985 goal of zero discharge of pollution into the nation's waters as defined by Public Law 92-500. These criteria were used to judge the quality of the scrubber liquor that might be discharged. A comparison of the

EPA criteria with the U.S. Public Health Service (USPHS) 1962 criteria (Ref. 5) shows a similarity except that the USPHS criteria have more stringent limitations on the concentration of total dissolved solids (TDS) (500 mg/l versus no limit) and arsenic (0.05 versus 0.10 mg/l). Conversely, the EPA criterion is tighter on the concentration of nitrates (10 versus 45 mg/l).

The service water and discharge water criteria are shown in Table 2-1. Because there are no published or approved power plant service water criteria, the service water values used were based upon the literature and discussing requirements with water treatment processors and power plant operating personnel. These values are goals assumed acceptable for service water use within most power plants; they are not absolute requirements. A specific power plant may have special requirements depending upon its operation and local restrictions. The EPA-proposed criteria for public water supply were used as the discharge criteria.

# **SECTION 4**

# SCRUBBER LIQUOR CHARACTERIZATION

# 4.1 POWER PLANT SCRUBBER LIQUOR SAMPLING

The data base for this study was prepared from samples taken from the four scrubbers listed in Table 4-1.

Table 4-1. POWER PLANTS SAMPLED

Power plant	Scrubber systems	Coal	Absorbent
TVA Shawnee Steam Plant	Venturi and spray tower	Eastern	Lime
TVA Shawnee Steam Plant	Turbulent con- tact absorber	Eastern	Limestone
Arizona Public Service Company Cholla Station	Flooded disk and absorption tower	Western	Limestone and fly ash
Duquesne Light Company Phillips Station	Single- and dual- stage venturi	Eastern	Lime

# 4.2 POTENTIAL SCRUBBER PURGE CONDITIONS

Power plant scrubbing systems are fundamentally identical although each installation is unique in detail design features.

Each scrubber vendor has developed hardware having basic system design differences; other differences also exist as a consequence of

coal type, fly ash collection facilities, and scrubber size. The similarities among scrubbing facilities are based primarily on the chemistry of scrubbing. For the lime or limestone systems, an alkaline slurry is recirculated between the scrubber and a reaction tank where the effluent from the scrubber reacts with the absorbent material. A bleed stream from the reaction tank carries off solid reaction products (and fly ash) and passes through a primary and often secondary dewatering system. A supernate liquor is returned to the system and, although clear, it is saturated with dissolved calcium sulfite and/or calcium sulfate salts.

Under normal conditions, no system bleed has been found necessary. Normal operating conditions are here considered as those conditions defined by design criteria and include characteristics of the boiler, coal, fly ash, existing hardware for retrofit systems, absorbent, disposal facilities, and any other consideration peculiar to that facility or design. The only water loss from these systems occurs by evaporation in the stack and from water lost to the disposal site by occlusion with the solids. In the operation of scrubber systems studied for this report and other systems now known to be operating, no system bleed is considered necessary for continuous operation. The fresh water used by the pump seals and demister spray provides enough make-up water to equal the loss of water by evaporation and solids disposal. The solids disposal includes enough dissolved solids in its occluded water to normally meet the bleed requirements necessary to limit dissolved solids build-up.

Several circumstances not now considered normal operating conditions may exist in the future that could affect the water balance of the system and create a need for a system purge. One such circumstance can arise when a scrubber is operated at a flue gas mass load level below some critical value created by low boiler loading, or alternatively under circumstances whereby lower sulfur coal is used than that for which the system was designed. Under these circumstances,

reduced solid quantities are formed in the reaction tank and a reduced bleed stream flow must be established so that a constant solids content can be maintained in the recirculation system of the scrubber. (The solids content of recirculating liquor is maintained so as to provide suitable nuclei in the scrubber onto which newly precipitated material may crystallize). The reduced bleed decreases the loss of water from the system. However, the need for fresh make-up water, which is dictated primarily by the requirement for demister water for scale prevention, is not reduced. Thus, when the fresh water requirement of the system is satisfied, an excess in system water would occur and a system purge would be required to maintain proper water balance. Of the power plants sampled in this study, one has experienced this condition while operating the scrubber at 33 percent of design load.

Another condition that could force a system bleed may arise under circumstances in which operational changes are made from that of the system design. For example, the oxidation of sulfite sludge to a sulfate sludge may evolve into a normal operating practice as a consequence of the greater efficiency in dewatering gypsum sludge and improved disposal practices. Under this circumstance, more sludge liquor would return to the scrubber because of the improved separation of liquid from the solids. The effect would be a reduction of water loss from the system. If this reduction reduces the make-up requirement below the fresh water requirement, the condition of excess water would result as described in the previous paragraph and a system bleed would be required to maintain water balance. This same condition may also exist if any of several improved dewatering methods are used.

As yet another circumstance, major repairs or hardware replacement are unavoidable, although not necessarily considered part of normal operation. If major maintenance can be prescheduled, it is often possible to divert the liquor from one system to another over a period of time. However, major repairs are often the result of more catastrophic circumstances, and the need for a quick blowdown may become an immediate requirement. Acceptable plans for such a contingency should be part of every plant's operation, and the reuse of these waters in other parts of the power plant is recognized as an alternative to be considered.

In each of the power plants sampled, reported values for total water balance are those for circumstances that are considered as normal and typical operating conditions, i.e., conditions within the range of design criteria and typical for the operation of that plant.\* Normal design criteria include maximum power output and a level of reduced power output that is usually undefined and depends on the flexibility of the system. Thus, the point at which fresh water requirements exceed make-up water requirements such that normal operation is affected must be determined empirically. From the power stations sampled, it can be estimated that this point is reached in the vicinity of about 50 percent of the maximum design parameter, i.e., 50 percent load factor or 50 percent reduction in sulfur content. The reduced flue gas mass loading that may accompany startup or shutdown of either boiler or scrubber causes a temporary excess liquor problem over such a short period of time that the capacity of a disposal pond is usually more than adequate to accept this excess water and, under normal conditions, to return it in the recirculation system.

In the one case in which the plant was operating at 33 percent of design load, a system purge was necessary. Reported values were corrected for this condition when extrapolating to full scale.

# 4.2.1 Shawnee Steam Plant Venturi and Spray Tower Scrubber System

This system is one of three parallel scrubber modules installed on a 150 MW coal-fire boiler at the TVA Shawnee Steam Plant, Paducah, Kentucky (Ref. 10). These modules were installed to provide a large, versatile prototype system as a test bed for wet scrubbing sulfur dioxide (SO<sub>2</sub>) and particulates from boiler flue gas. Each module has a 10 MW equivalent capacity; this is achieved by taking approximately 14.15 cu m/sec (30,000 acfm) of flue gas from the ductwork of Boiler No. 10 upstream of the electrostatic precipitators. This dual-stage scrubber, which is shown in Figure 4-1, consists of a venturi with an adjustable plug that permits control of the pressure drop in the first stage and a spray tower after-scrubber in the second stage. It was manufactured by the Chemical Construction Corporation (Chemico).

Flue gas entering the scrubber passes through the venturi and then upward through the spray tower countercurrent to the scrubbing liquors that are recirculated from the reaction tank. The effluent liquors return to the reaction tank where pH is adjusted with a slaked lime slurry. A bleed stream from the reaction tank is routed to a clarifier. The clarifier overflow is returned to the reaction tank; the underflow passes through a vacuum filter; and the filtrate is returned to the reaction tank. The filter cake is discharged to a disposal pond. A flow diagram is shown in Figure 4-2.

On three occasions, slurry samples were taken from three stations in the system: (a) the scrubber effluent to the reaction tank, (b) the clarifier underflow to the vacuum filter, and (c) the filtrate from the vacuum filter to the hold tank. The scrubber test conditions are presented in Table 4-2, and the analysis of the liquors from these sample points is presented in Table 4-3. Although the

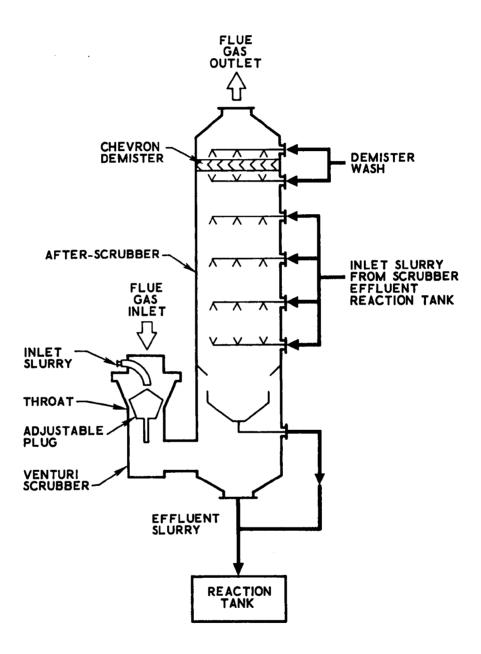


Figure 4-1. Schematic of EPA/TVA Shawnee venturi and spray tower scrubber

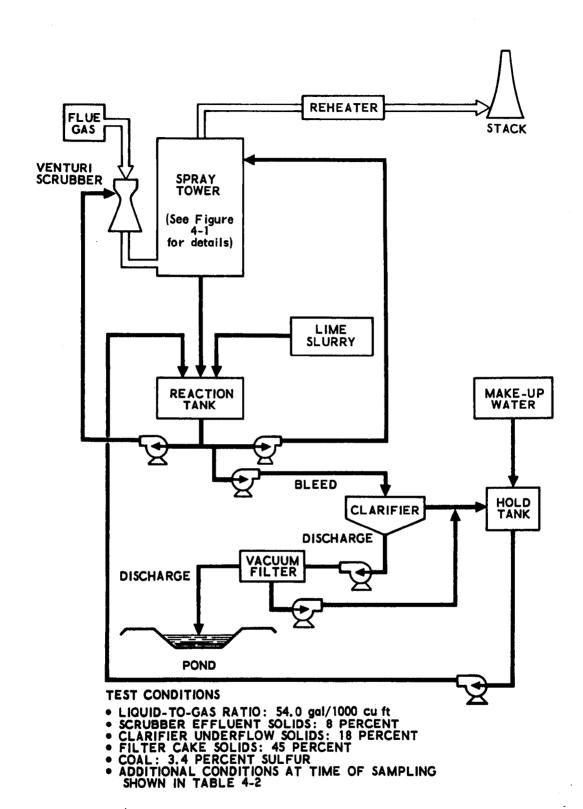


Figure 4-2. Typical flow diagram for EPA/TVA Shawnee venturi and spray tower scrubber system: 8.34 MW equivalent operation

Table 4-2. TEST CONDITIONS FOR EPA/TVA SHAWNEE VENTURI AND SPRAY TOWER SCRUBBER

	Sample date <sup>a</sup>				
Parameters	3/19/74	5/17/74	6/27/74		
Gas rate,					
cu m/sec acfm	11.8 25,000	11.8 25,000	11.8 25,000		
Equivalent megawatts	8.3	8.3	8.3		
SO <sub>2</sub> input, ppm	2,600	3,280	2,700		
SO <sub>2</sub> removal, percent	93	78	84		
pH control	8.0	8.0	8.0		
Dust input,					
gm/cu m gr/scf	8.0 3.5	8.0 3.5	8.0 3.5		
Scrubber, effluent solids, percent	8	8	8		
Liquid-to-gas ratio, gal/1000 cu ft	54.0	54.0	54.0		

<sup>&</sup>lt;sup>a</sup>Data base used in extrapolation of scrubber system to 1000 MW equivalent size scrubber and for determining water balance. Water balance at time of testing is shown in Figure 4-3, and values extrapolated to 1000 MW equivalent are shown in Figure 4-14.

Table 4-3. ANALYSES OF SCRUBBER LIQUORS FROM EPA/ TVA SHAWNEE VENTURI AND SPRAY TOWER SCRUBBER SYSTEM

Scrubber test conditions at time of sampling shown in Table 4.2. Concentration in milligrams per liter of filtered liquor (Whatman 40).

	In-process data Potential discharge point data								
Scrubber	Sample location								
liquor	Scrubber effluent Clarifier underflow Drum vacuum f				cuum filte	ilter filtrate			
constituents	Sample date								
	3/19/74	5/16/74	6/27/74	3/19/74	5/16/74	6/27/74	3/19/74	5/16/74	6/27/74
Aluminum (Al)	0.22	0.12	1.54	0.03	0.3	< 0.1	0.08	0.1	0.24
Antimony (Sb)	0.39	2.1	1.01	0.55	2.3	1,11	0.46	1.6	1.01
Arsenic (As)	0.15	0.15	0.04	0.30	0.03	0.02	0.15	0.01	0.02
Beryllium (Be) Boron (B)	0.05	0.05	<0.002 56	0.027	0.07	<0.002 46	0.026	0.05	<0.002 41
Cadmium (Cd)	0.02	0.04	0.12	0.03	0.004	0.11	0.03	0.006	0.10
Calcium (Ca)	980	2360	3000	800	2580	2820	660	2420	2520
Chromium (Cr) (total)	0.02	0.02	0.04	0.02	0.01	0.04	0.03	0.02	0.03
Cobalt (Co)		0.6	0.31		0.6	0.32		0.7	0.35
Copper (Cu)	0.08	0.03	0.01	0.07	0.07	<0.002	0.05	0.04	<0.002
Iron (Fe)	0.77	0.14	1.81	0.08	0.27	0.10	0.02	0.10	0.06
Lead (Pb)	0.03	0.12	0.33	0.06	0.13	0.39	0.01	0.13	0.33
Magnesium (Mg)	53	220	420	25	220	450	24	200	420
Manganese (Mn)		0.4			0.09	0.46		-0.2	0.84
Mercury (Hg)	0.10	<0.05	< 0.001	0.07	<0.05	<0.001	0.07	<0.05	<0.001
Molybdenum (Mo)			6.1			6.3			5,3 0,21
Nickel (Ni)	0.5	0.25	0.29	0.08	0.23 29	0.24 32	0.05	0.31	28
Potassium (K) Selenium (Se)	8.4 0.08	21	25 <0.02	0.09	1.9	<0.02	0.09	1.9	<0.02
Silicon (Si)	0.08	1.8	2.1	0.07	1.8	1.0	0.2	1.6	2.7
Silver (Ag)	0.09	0.01	0.03	0.06	0.01	0.03	0.06	0.01	0.02
Sodium (Na)	33	108	126	36	14	125	36	109	127
Tin (Sn)			3.5			3.5			3,1
Vanadium (V)				< 0.001					
Zinc (Zn)	0.09	0.02	0.18	0.01	0.02	0.11	0.01	0.02	0.08
Total carbonate	<10	<10	<10	<10	<10	<10	<10	<10	<10
Chloride (C1)	1230	4400	5400	1040	4200	4900	1050	4200	4800
Fluoride (F)	<0.3	1.5	0.2	1.4	4.5	4.0	1.4	3.0	3.3
Sulfite Sulfate	450 1000	3.0 1500	12 1800	2.2 1000	2.3 1350	0.8 1700	900	2.7 1250	0.9
						"	'		
Phosphate	<0.1	<0.1	<0.1	< 0.1	<0.1	<0.1	< 0.1	< 0, 1	<0.1
Total nitrogen	<0.001	<0.001	<0.001 149	<0.001 160	<0.001	<0.001 98	<0.001 85	<0.00	
Chemical oxygen demand Total dissolved solids	220 3500	8700	10800	3200	7800	10400	2800	8400	89 9400
Total alkalinity	54		63	49		82	57		76
Conductance, mho/cm Turbidity, Jackson	0.006	0.013	0.019	0.004	0.014	0.014	0.004	0.012	
units	<3	< 3	<3	<3	<3	<3	<10	<10	<10
pН	5.19	5.67	5,41	9.02	9.12	8.99	9.43	8.81	8.68

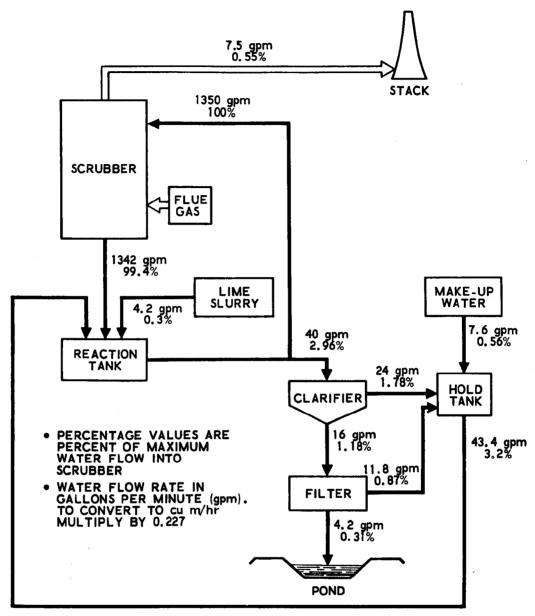
scrubber effluent is not a potential discharge point, it was included to identify the scrubber chemistry. Analysis of samples taken downstream of the reaction tank has shown that they are essentially equivalent in all cases and that they represent the water quality of the liquor at any potential discharge point.

The water balance for this system is presented in the simplified flow diagram in Figure 4-3. The actual water flow in gallons per minute is an integrated average for the equivalent power capacity specified on the three days for the nominal coal sulfur content of 3.4 percent and for a 78 to 93 percent efficiency in SO<sub>2</sub> removal from the flue gas. In each case, flow rates are given as water flow; slurry flows are greater because of the incorporation of solids in liquors in varying amounts at different points in the system. The percentages shown are based on the maximum water flow in the system, which in this case are represented by the recirculation liquor from the reaction tank to the scrubber.

# 4.2.2 EPA/TVA Shawnee Turbulent Contact Absorber (TCA) Scrubber System

This system is also one of the three parallel scrubber modules installed on Boiler No. 10 at the Shawnee Steam Plant. This module has the same design capacity as that of the system described in Section 4.2.1 (Ref. 10). The TCA scrubber (manufactured by Universal Oil Products) uses a fluidized bed of low density plastic spheres that are free to move between retaining grids (Figure 4-4). Three stages of grids are used to obtain sufficient surface for adequate scrubbing efficiency.

A system flow diagram is shown in Figure 4-5. Flue gas enters the scrubber from a side port, passes upward through the grids, contacts the levitated plastic spheres, and exits through chevron-shaped demisters. Scrubbing liquor from the reaction tank



- LIQUID-TO-GAS RATIO: 54.0 gal/1000 cu ft
   SCRUBBER EFFLUENT SOLIDS: 8 PERCENT
   CLARIFIER UNDERFLOW SOLIDS: 18 PERCENT
   FILTER CAKE SOLIDS: 45 PERCENT
   COAL: 3.4 PERCENT SULFUR
   ADDITIONAL CONDITIONS AT TIME OF SAMPLING SHOWN IN TABLE 4-2

Figure 4-3. Water balance for EPA/TVA Shawnee venturi and spray tower scrubber system: 8.34 MW equivalent operation

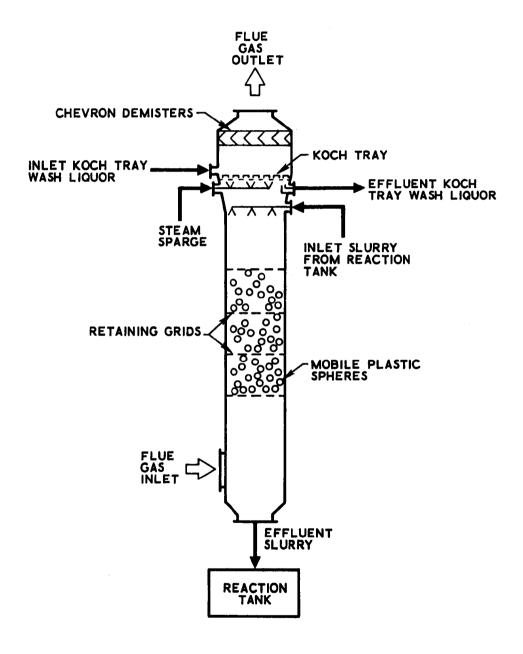
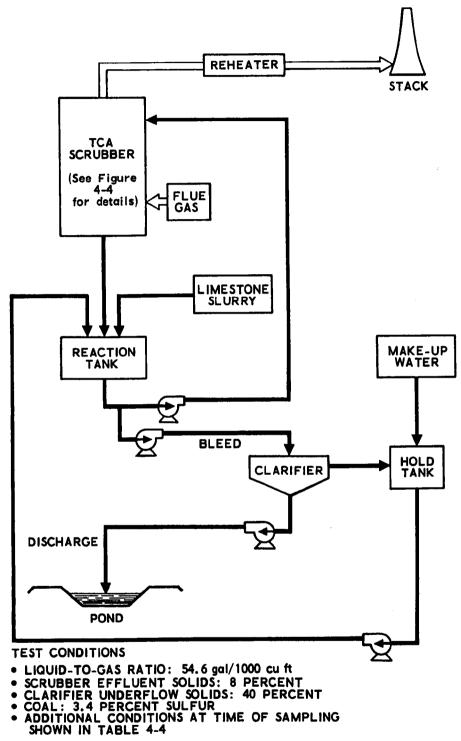


Figure 4-4. Schematic of EPA/TVA TCA scrubber



Typical flow diagram for EPA/TVA Shawnee Figure 4-5. TCA scrubber system: 6.8 MW equivalent operation

is sprayed against the rising flow of flue gas, percolates downward through the scrubbing stages, and exits to the reaction tank. The pH is adjusted with a limestone slurry that is also fed to the reaction tank. A bleed stream from the reaction tank is passed through a clarifier. The overflow returns to the reaction tank, and the underflow is pumped to a disposal pond. No secondary dewatering is done in this system.

On two occasions slurry samples were taken from the scrubber effluent and clarifier underflow. Only the clarifier underflow represents the potential discharge points. The test conditions of the scrubber on these days are presented in Table 4-4, and the results of the liquor analysis from these sample points is presented in Table 4-5.

The water balance for this system is presented in the simplified flow diagram in Figure 4-6. The water flow is given in gallons per minute, and the percentages are based on maximum flow to the scrubber. The reported flow rates are for the equivalent power capacity treated as specified, for the nominal coal sulfur content of 3.4 percent, and for about an 86 percent SO<sub>2</sub> removal efficiency.

# 4.2.3 Arizona Public Service Company Cholla Power Station -- Flooded Disk Scrubber (FDS) and Packed Absorption Tower Scrubber System

This system consists of two parallel dual-stage scrubbers installed on a 115 MW coal-fired boiler at the Cholla Station,
Joseph City, Arizona (Ref. 11). Each scrubber is designed for 60
MW equivalent power generation capacity. The flooded disk and
absorption tower scrubbers (Figure 4-7), (manufactured by Research
Cottrell, Inc.) were designed to handle fly ash and remove SO<sub>2</sub> from
the flue gas. The FDS is a variable throat, flooded disk, venturitype scrubber used principally to remove the fly ash entrained in the

Table 4-4. TEST CONDITIONS FOR EPA/TVA SHAWNEE TCA SCRUBBER

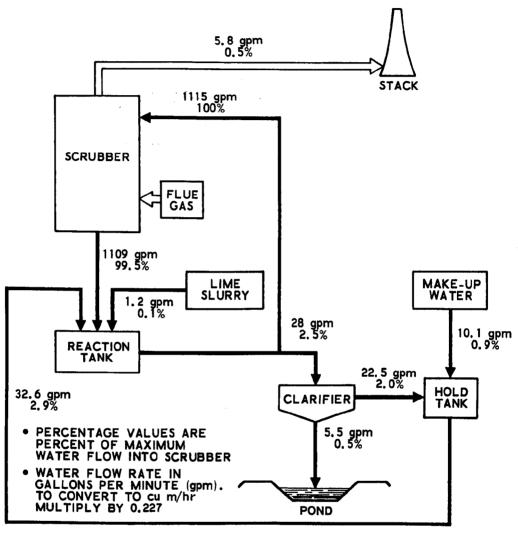
	Sample date			
Parameters	11/27/73	6/15/74 <sup>a</sup>		
Gas rate,				
cu m/sec acím	9.7 20,500	9.7 20,500		
Equivalent megawatts	6.8	6.8		
SO <sub>2</sub> input, ppm	2,700	2,400		
SO <sub>2</sub> removal, percent	83	86		
pH control	5.9	5.5		
Dust input				
gm/cu m gr/scf	8.0 3.5	8.0 3.5		
Scrubber effluent solids, percent	16.0	8.0		
Liquid-to-gas ratio, gal/1000 cu ft	54.6	54.6		

<sup>&</sup>lt;sup>a</sup>Data base used in extrapolation of scrubber system to 1000 MW equivalent size scrubber and for determining water balance. Represents stable test conditions. Water balance at time of testing is shown in Figure 4-6, and values extrapolated to 1000 MW equivalent are shown in Figure 4-15.

Table 4-5. ANALYSES OF SCRUBBER LIQUORS FROM EPA/ TVA SHAWNEE TCA SCRUBBER SYSTEM

Scrubber test conditions at time of sampling shown in Table 4-4. Concentration in milligrams per liter of filtered liquor (Whatman 40).

į	In-proc	ess data	Potential discha	arge point data			
	Sample location						
C	Scrubbe	r effluent	Clarifier underflow				
Scrubber liquor	Sample date						
constituents	11/27/73	6/15/74	11/27/73	6/15/74			
Aluminum (Al)		2.7		0.6			
Antimony (Sb)		2.0		1.4			
Arsenic (As)	0.2	0.4	0.3	0.1			
Beryllium (Be)	0.01	0.07	0.004	0.05			
Boron (B)							
Cadmium (Cd)	0.04	0.005	0.004	0.004			
Calcium (Ca)	1800	840	1	520			
Chromium (Cr) (total)	0.04	0.16	0.5	0.09			
Cobalt (Co)	0.04	0.16	1 0.5	0.10			
Copper (Cu)	0.05	0.10		0.01			
Copper (Cu)	0.05	0.02		""			
Iron (Fe)		0.35		0.02			
Lead (Pb)	0.06	0.35	0.12	0.23			
Magnesium (Mg)	900	2800	600	2750			
Manganese (Mn)							
Mercury (Hg)		<0.5	0.05	<0.05			
Molybdenum (Mo)							
Nickel (Ni)	0.16	0.44	0.50	0.33			
Potassium (K)	6.3	1	5.9				
Selenium (Se)	0.2	1	0, 2				
Silicon (Si)							
·							
Silver (Ag)		0.008		0.005			
Sodium (Na)	63						
Tin (Sn)							
Vanadium (V)							
Zinc (Zn)	0.84	0.03	0.35	0.02			
Total carbonate							
Chloride (Cl)	3400	3300	1900	2300			
Fluoride (F)	2,3	2.3		6.5			
Sulfite		1400		80			
Sulfate	2000	9500		10000			
Phosphate	<0.1	<0.1	<0.1	<0.1			
Total nitrogen	<0.005	<0.005	<0.005	<0.005			
Chemical oxygen demand							
Total dissolved solids	12000	17800	11000	15000			
Total alkalinity			150				
Conductance, mho/cm		0.027		0.015			
Turbidity, Jackson	< 3	< 3	< 3	< 3			
units		``	``				
рН	5, 90	4.64	9.50	7.96			



- LIQUID-TO-GAS RATIO: 54.6 gal/1000 cu ft
   SCRUBBER EFFLUENT SOLIDS: 8 PERCENT
   CLARIFIER UNDERFLOW SOLIDS: 40 PERCENT
   COAL: 3.4 PERCENT SULFUR
   ADDITIONAL CONDITIONS AT TIME OF SAMPLING SHOWN IN TABLE 4-4

Figure 4-6. Water balance for EPA/TVA Shawnee TCA scrubber system: 6.8 MW equivalent operation

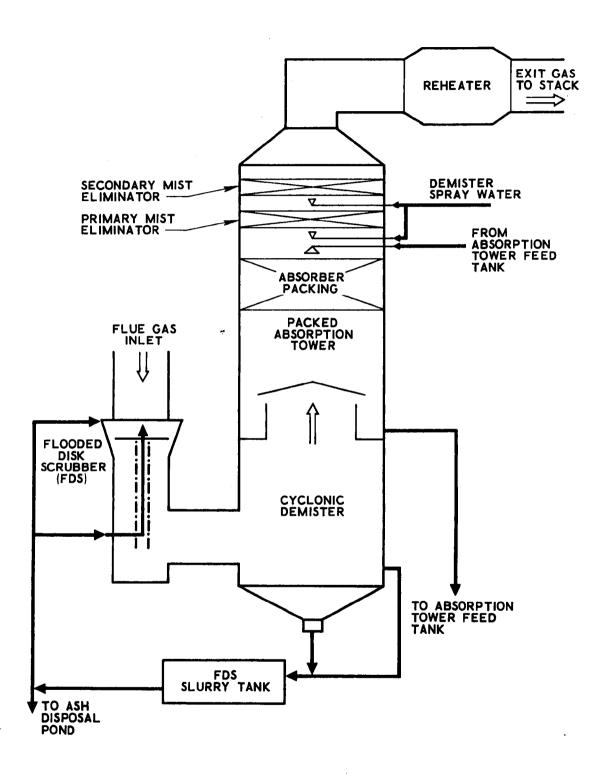


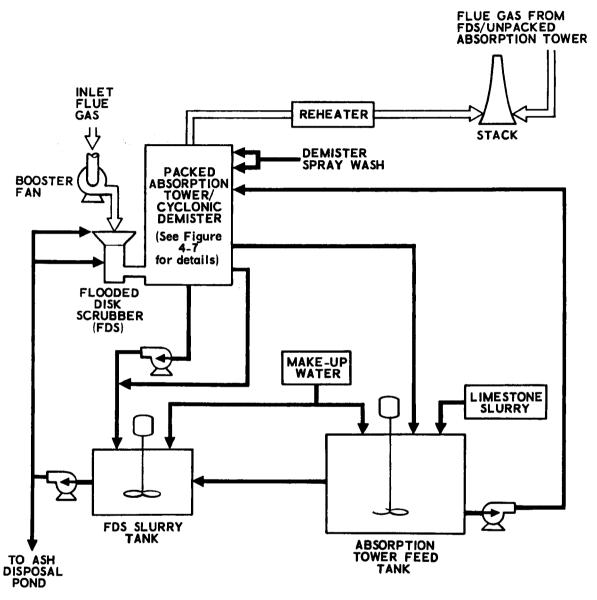
Figure 4-7. Schematic of Arizona Cholla Station FDS and packed absorption tower scrubber

flue gas after passing through the upstream mechanical collectors that remove 80 percent of the fly ash.

A flow diagram is shown in Figure 4-8. A forced draft booster fan forces flue gas into the FDS and then into the base of the absorption tower. Recirculating limestone slurry is pumped from the FDS slurry tank into the FDS scrubber tangentially above the throat and at the disk. The scrubber slurry is carried with the flue gas through the cyclonic demister and then returns to the FDS slurry tank after having removed the fly ash and 15 to 30 percent of the SO2. The flue gas rises through the packed absorption tower countercurrent to limestone slurry recirculated from the absorption tower feed tank. Of the two parallel absorption towers, one is operated as a packed tower and the other as a spray tower. The slurry returns to the absorption tower feed tank after scrubbing approximately 40 to 60 percent of the remaining SO, from the flue gas. Adjustment of pH is made by the addition of a limestone slurry to the absorption tower feed tank. A crossfeed between the absorption tower feed tank to the FDS slurry tank provides a bleed for the absorption tower scrubbing liquors and a supply of absorbent for the FDS liquors. The scrubber system bleed is made from the FDS slurry tank and is used without dewatering to slough the mechanically collected fly ash to a disposal pond.

On two occasions, slurry samples were taken from the FDS slurry tank and the absorption tower feed tank. Only the output of the FDS slurry tank can be considered a potential water discharge point. The operating conditions existing in the scrubber at the time of sampling are presented in Table 4-6, and the results of the chemical analyses are presented in Table 4-7.

The water balance for this system is presented in the simplified flow diagram in Figure 4-9. The water flow is given in



- LIQUID-TO-GAS RATIO: 70.9 gal/1000 cu ft
  FDS SLURRY TANK EFFLUENT SOLIDS: 15 PERCENT
  COAL: 0.5 PERCENT SULFUR
  ADDITIONAL CONDITIONS AT TIME OF SAMPLING SHOWN IN TABLE 4-6

Figure 4-8. Typical flow diagram for Arizona Public Service Cholla FDS and packed absorption tower scrubber system: 115 MW equivalent operation

Table 4-6. OPERATING CONDITIONS FOR ARIZONA PUBLIC SERVICE CHOLLA FDS AND ABSORPTION TOWER SCRUBBER SYSTEM

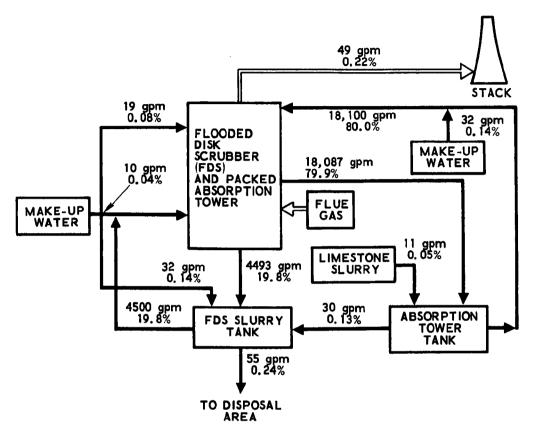
	Sample date <sup>a</sup>			
Parameters	4/1/74	11/7/74		
Gas rate,				
cu m/sec acfm	151 320,000	151 320,000		
Equivalent megawatts	115	115		
SO <sub>2</sub> input, ppm	360	360		
SO <sub>2</sub> removal, percent	75	75		
pH control	6.5	6.5		
Dust input				
gm/cu m gr/scf	0.41 0.18	0.41 0.18		
Absorption tower effluent solids, percent	15	15		
Liquid-to-gas ratio, gal/1000 cu ft	70.9	70.9		

a Data base used in extrapolation of scrubber system to 1000 MW equivalent size scrubber and for determining water balance. Water balance at time of testing is shown in Figure 4-9, and values extrapolated to 1000 MW equivalent are shown in Figure 4-16.

Table 4-7. ANALYSES OF SCRUBBER LIQUORS FROM ARIZONA PUBLIC SERVICE CHOLLA FDS AND ABSORPTION TOWER SCRUBBER SYSTEM

Scrubber test conditions at time of sampling shown in Table 4-6. Concentration in milligrams per liter of filtered liquor (Whatman 40).

	In-proces	s data	Potential discha	arge data point		
Scrubber		Sample	location			
liquor	Absorption to	ower tank	FDS tank			
constituents	Sample date					
	4/1/74	11/7/74	4/1/74	11/7/74		
Aluminum (Al) Antimony (Sb) Arsenic (As) Beryllium (Be) Boron (B)	0.06 0.03 <0.004 0.08	2.1 0.16 0.02 <0.003 3.8	2 0.09 <0.004 0.14	0.22 0.04 8.0		
Cadmium (Cd) Calcium (Ca) Chromium (Cr) (total) Cobalt (Co) Copper (Cu)	0.007 580 0.02 0.05 0.03	0.012 390 0.004 <0.01 0.01	0.011 680 0.14 0.17 0.20	0.044 770 0.024 0.1 0.16		
Iron (Fe) Lead (Pb) Magnesium (Mg) Manganese (Mn) Mercury (Hg)	0.17 0.02 7' 0.30 0.007	0.13 0.15 9 0.48 <0.5	0.42 0.01 3 0.34 0.07	8.1 0.37 4 2.5 <0.05		
Molybdenum (Mo) Nickel (Ni) Potassium (K) Selenium (Se) Silicon (Si)	1.0	0.09 0.06 7.5 <0.033	1.5 16 2.2 3.3	0.91 0.30 28 <0.001		
Silver (Ag) Sodium (Na) Tin (Sn) Vanadium (V) Zinc (Zn)	0.01 800  0.02	<0.007 370  0.07 0.04	0.03 2250  0.11	0.05 1650  0.67 0.47		
Total carbonate Chloride (Cl) Fluoride (F) Sulfite Sulfate	<1 620 2.4 1.0 2200	<1 760 1.0 21 1360	<1 1700 0.7 0.9 4000	<1 4200 1.5 3500 3750		
Phosphate Total nitrogen Chemical oxygen demand Total dissolved solids Total alkalinity	<0.1 <0.005 105 4300 52	<0.1 <0.005 90 3300 130	0.41 0.002 340 8700	<0.5 <0.005 390 14000		
Conductance, mho/cm Turbidity, Jackson units	0.0053 <5	0.00299 <5	0.0112 <5	0.014 <5		
pН	6.59	6.80	3.04	3.38		



- LIQUID-TO-GAS RATIO: 70.9 gai/1000 cu ft
- FDS SLURRY TANK EFFLUENT SOLIDS: 15 PERCENT
- COAL: 0.5 PERCENT SULFUR
- ADDITIONAL CONDITIONS AT TIME OF SAMPLING SHOWN IN TABLE 4-6
- PERCENTAGE VALUES ARE PERCENT OF MAXIMUM WATER FLOW INTO SCRUBBER
- WATER FLOW RATE IN GALLONS PER MINUTE (gpm). TO CONVERT TO cu m/hr MULTIPLY BY 0.227

Figure 4-9. Water balance for Arizona Public Service Cholla FDS and packed absorption tower scrubber system: 115 MW equivalent operation

gallons per minute, and the percentages are based on the maximum combined water flow to the two stages of scrubbing.

# 4.2.4 <u>Duquesne Light Company Phillips Station -- Single-</u> and Dual-Stage Venturi Scrubber System

This system, which is installed on the coal-fired boilers at the Phillips Station, South Heights, Pennsylvania, is a full-scale system designed to treat 500 MW of power generating capacity in four parallel modules (Ref. 12). Since each module is designed to handle approximately 125 MW, the full plant capacity of 387 MW is expected to be handled with three modules; one would be a spare. Three modules (Figure 4-10) are single-stage venturi scrubbers designed primarily for particulate removal; the fourth (Figure 4-11) consists of a dual-stage venturi scrubber designed to remove fly ash in the first stage and SO<sub>2</sub> in the second stage. All four modules were manufactured by Chemico. An SO<sub>2</sub> removal efficiency of about 60 percent is obtained in the single-stage venturi scrubbers when a lime slurry is used as the absorbent; the efficiency is about 90 percent for the dual-stage unit. A schematic of the design of the single-stage venturi scrubber is shown in Figure 4-12.

Flue gases pass through mechanical and electrostatic dust collectors located in series with each boiler, then the gases are diverted into a common manifold with lines leading to each of the three single-stage scrubbers and the first stage of the dual-stage scrubber. The hot flue gas enters the first stage of the dual-stage scrubber or the single-stage scrubber and impinges upon the upper cone where half of the scrubber liquor is introduced (Figure 4-12). The other half of the scrubber liquor enters through the tangential nozzles at a point above the adjustable throat dampers. The flue gas and scrubbing liquor make contact in the throat section of the scrubber where the particulates and some SO<sub>2</sub> are removed. The gas and liquor continue

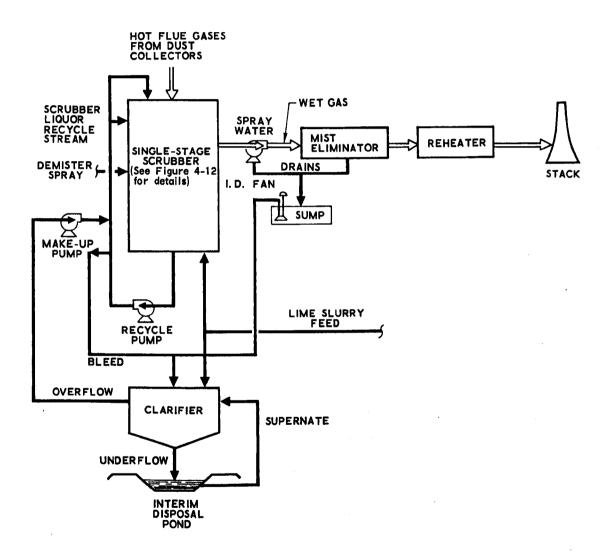


Figure 4-10. Typical flow diagram for Duquesne Phillips single-stage scrubber system

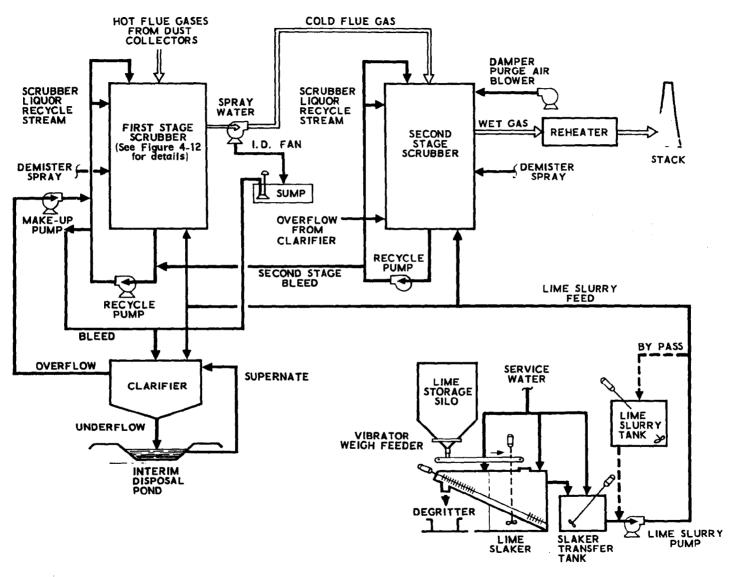


Figure 4-11. Typical flow diagram for Duquesne Phillips Station dual-stage scrubber system

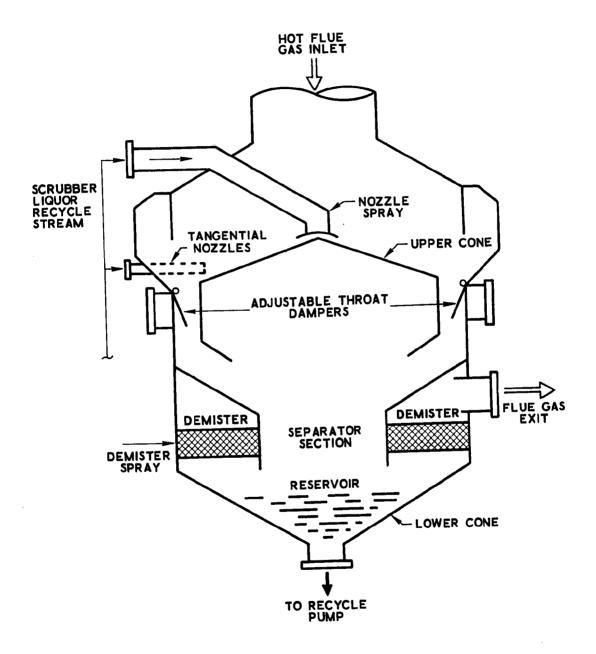


Figure 4-12. Schematic of Duquesne Phillips Station singlestage scrubber

downward to the separator section where the flue gas enters a demister, leaves the scrubber through a wet induced draft (ID) fan, and enters the second stage of the dual-stage train, or through mist eliminators in the three single-stage scrubbing trains.

Scrubbing liquor leaves the scrubber to be either recirculated or pumped to the clarifier. The overflow from the clarifier is recycled to the scrubber, and the underflow is sent to one of three interim disposal ponds. Lime slurried with fresh water is added in each scrubber and in the clarifier. The pump and fan spray waters also provide make-up water.

On two occasions slurry samples were taken from the clarifier and scrubber and once from the pond. The conditions that existed in the scrubber at the time of sampling are given in Table 4-8. The results of the liquor analysis from these sample points are presented in Table 4-9. Clarifier underflow and pond supernate represent potential discharge points in this system.

The water balance for this system is presented in the simplified flow diagram in Figure 4-13 representing water flow under operating conditions corrected for water imbalance caused by variances from system design. The water flow is given in gallons per minute, and the percentages are based on the maximum water flow in the system represented by the water flow to the scrubber.

# 4.3 EXTRAPOLATION OF PROCESS FLOWS

# 4.3.1 Scale-Up of Four Systems Studied

The actual flows of process liquors as presented in Figures 4-3, 4-6, 4-9, and 4-13 were used to calculate the process flow expected for 1000 MW facilities operating at 90 percent SO<sub>2</sub> removal efficiency, using the identical scrubber design, operating conditions, and coal as those on which the data base was established. In all cases, scale-up of flow rates was presumed to be proportional

Table 4-8. OPERATING CONDITIONS FOR DUQUESNE PHILLIPS STATION: SINGLE- AND DUAL-STAGE VENTURI SCRUBBER SYSTEMS

	Sample date <sup>a</sup>			
Parameters	10/4/73 <sup>b</sup>	6/17/74 <sup>c</sup>		
Gas rate,				
cu m/sec acfm	274 580,000	236 500,000		
Equivalent megawatts	145	120		
SO <sub>2</sub> input, ppm	1,400	1,400		
SO <sub>2</sub> removal, percent	60	70		
pH control	6.0	6.0		
Dust input				
gm/cu m gr/scf	0.57 0.25	0.57 0.25		
Venturi effluent solids, percent	5	5		
Liquid-to-gas ratio, gal/1000 cu ft	29.9	29.9		

<sup>&</sup>lt;sup>a</sup>Data base used in extrapolation of scrubber system to 1000 MW equivalent size scrubber and for determining water balance. Water balance at time of testing is shown in Figure 4-13, and values extrapolated to 1000 MW equivalent are shown in Figure 4-17.

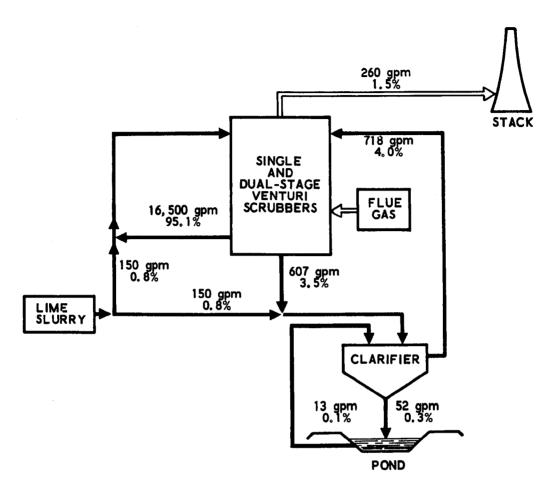
bTwo single-stage scrubbers.

<sup>&</sup>lt;sup>c</sup>Two single-stage and one dual-stage scrubbers.

Table 4-9. ANALYSES OF SCRUBBER LIQUORS FROM DUQUESNE PHILLIPS STATION: SINGLE-AND DUAL-STAGE VENTURI SCRUBBER SYSTEMS

Scrubber test conditions at time of sampling shown in Table 4-8. Concentration in milligrams per liter of filtered liquor (Whatman 40).

			<u> </u>		
,	In-proc	ess data	<del></del>	point data	
	<u></u>	Sample location			
	Scrubbe	r effluent	Clarifier	underflow	Pond supernate
Scrubber liquor			Sample date		
constituents	10/4/73	6/17/74	10/4/73	6/17/74	6/17/74
Aluminum (Al)					
Antimony (Sb)					
Arsenic (As)	0.085	0.06		<0.004	<0.004
Beryllium (Be) Boron (B)	0.012	0.002	0.012	0.003	0.002
201011 (2)			]		
Cadmium (Cd)	0.022		0.023		
Calcium (Ca)	1300	660	1400	600	600
Chromium (Cr) (total) Cobalt (Co)	0.037		0.040		
Copper (Cu)	0.06		0.07	-:	
Copper (Su)	0.00		0.07		
Iron (Fe)			0.026		
Lead (Pb)	0.08	0.5	0.18	0.4	0.4
Magnesium (Mg) Manganese (Mn)	220		410		[
Mercury (Hg)	0.09	0.0004	0,05	<0.002	0.0004
, ( , g,					
Molybdenum (Mo)					
Nickel (Ni)	20				
Potassium (K) Selenium (Se)	20 0.8	10 0.33	0.8	26 0.028	22
Silicon (Si)	0.0	0.55	1 0.8	0.028	0.095
,		ĺ		ļ	
Silver (Ag)	0.02				
Sodium (Na)	1680	440	2400	320	344
Tin (Sn) Vanadium (V)					
Zinc (Zn)	0.12	<u> </u>	0.09	<u> </u>	
_			,		
Total carbonate	<1	<1	<1	<1	<1
Chloride (Cl)	1800	540	2700	470	420
Fluoride (F) Sulfite	4.8 <1	8 1.7	2.6 <1	10 20	7 4.8
Sulfate	4500	2700	6450	720	1000
<b>.</b>					
Phosphate	<0.05	<0.05	<0.05	<0.05	<0.03
Total nitrogen Chemical oxygen demand	<0.005	<0.005 65	<0.005	<0.005 60	<0.005
Total dissolved solids	9400	4600	14000	4200	4000
Total alkalinity	61	78			41
Conducto					
Conductance, mho/cm	0.0063 < 3	0.0033	0.01	0.0034	0.0030
Turbidity, Jackson units	<u> </u>	< 3	< 3	< 3	< 3
pH	9.20	8.92	7.11	10.70	10.44



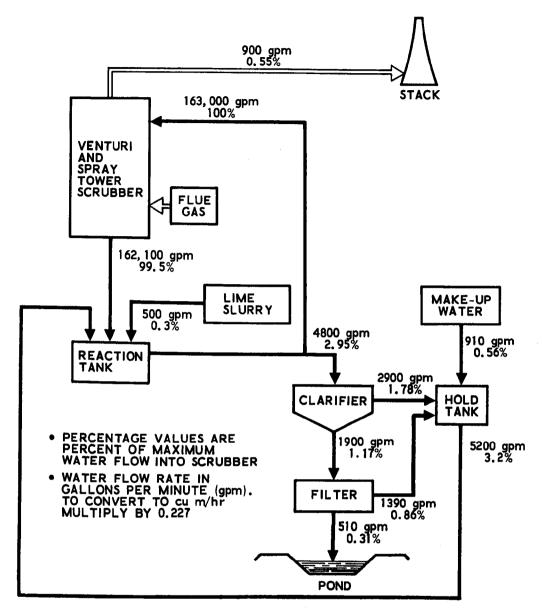
- LIQUID-TO-GAS RATIO: 29.9 gai/1000 cu ft
- SCRUBBER EFFLUENT SOLIDS: 5 PERCENT
- CLARIFIER UNDERFLOW SOLIDS: 38 PERCENT
- COAL: 2 PERCENT SULFUR
- ADDITIONAL CONDITIONS AT TIME OF SAMPLING SHOWN IN TABLE 4-8
- PERCENTAGE VALUES ARE PERCENT OF MAXIMUM WATER FLOW INTO SCRUBBER
- WATER FLOW RATE IN GALLONS PER MINUTE (gpm). TO CONVERT TO cu m/hr MULTIPLY BY 0.227

Figure 4-13. Water balance for Duquesne Phillips Station singleand dual-stage venturi scrubber systems: 120 MW equivalent operation

to the flue gas flow rates; therefore, the power generated would be a direct scale-up when identical coal was used.

The scale-up of the scrubbing system based on the two EPA/TVA Shawnee Steam Plant prototype facilities represents the greatest size scale-up of the four facilities examined. However, it was assumed that individual scrubber modules of several hundred megawatt capacity equivalence would be constructed for a large power generating plant of this design rather than a single 1000 MW unit. Thus, the scale-up factor would probably be within the range of 10 to 30 times rather than a factor of two orders of magnitude. Accordingly, it was assumed that the relative flow rates would be unaffected by the number of parallel units required to handle the full plant capacity. The scale-up of a scrubber system based on an EPA/ TVA Shawnee venturi and spray tower or TCA type scrubber system was determined on a linear proportional basis whereby the scrubber liquid-to-gas ratio was held unchanged from those of the sampling conditions. The results of these calculations are presented in the simplified schematic flow diagrams in Figures 4-14 and 4-15.

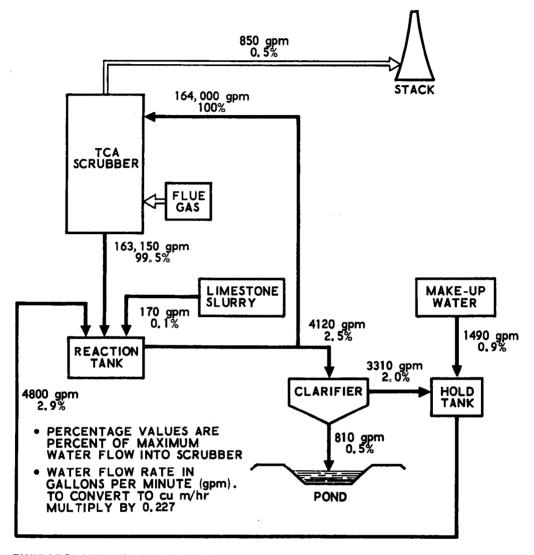
For the Arizona Public Service Cholla Station scrubbing system, full-scale scrubbers exist; thus, the scale-up to 1000 MW equivalent power generating capacity was done on the presumption that additional like-units would be added in parallel. During sampling periods, the SO<sub>2</sub> removal efficiency of this system was 75 percent although a scrubber module with a packed absorption tower removes 90 percent of the SO<sub>2</sub> (the absorption tower performing as a spray tower is 60 percent efficient in SO<sub>2</sub> removal). In performing the scale-up of this design to 90 percent removal efficiency, it was assumed that all scrubbers would operate at the flow rates required for a packed absorption tower. The results of these calculations are presented in the flow diagram in Figure 4-16.



# EXTRAPOLATED OPERATING CONDITIONS

- LIQUID-TO-GAS RATIO: 54.0 gai/1000 cu ft
- SCRUBBER EFFLUENT SOLIDS: 8 PERCENT
- CLARIFIER UNDERFLOW SOLIDS: 18 PERCENT
- FILTER CAKE SOLIDS: 45 PERCENT
- COAL: 3.4 PERCENT SULFUR
- SO2 REMOVAL EFFICIENCY: 90 PERCENT
- TEST CONDITIONS USED AS BASIS FOR EXTRAPOLATION SHOWN IN TABLE 4-2

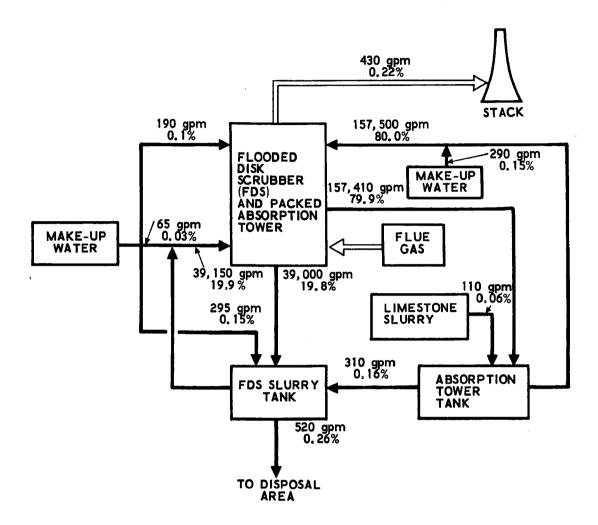
Figure 4-14. Water balance for venturi and spray tower scrubber system (extrapolation based on EPA/TVA Shawnee type of process): 1000 MW equivalent operation



#### EXTRAPOLATED OPERATING CONDITIONS

- LIQUID-TO-GAS RATIO: 54.6 gal/1000 cu ft
- SCRUBBER EFFLUENT SOLIDS: 8 PERCENT
- CLARIFIER UNDERFLOW SOLIDS: 40 PERCENT
- COAL: 3.4 PERCENT SULFUR
- SO2 REMOVAL EFFICIENCY: 90 PERCENT
- TEST CONDITIONS USED AS BASIS FOR EXTRAPOLATION SHOWN IN TABLE 4-4

Figure 4-15. Water balance for TCA scrubber system (extrapolation based on EPA/TVA Shawnee type of process): 1000 MW equivalent operation



#### EXTRAPOLATED OPERATING CONDITIONS

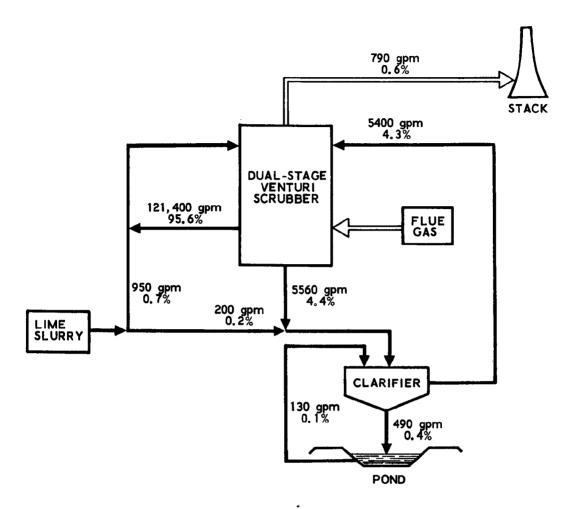
- LIQUID-TO-GAS RATIO: 70.9 gal/1000 cu ft
- COAL: 0.5 PERCENT SULFUR
- 50, REMOVAL EFFICIENCY: 90 PERCENT
- FDS SLURRY TANK EFFLUENT: 15 PERCENT
- OPERATING CONDITIONS USED AS BASIS FOR EXTRAPOLATION SHOWN IN TABLE 4-6
- PERCENTAGE VALUES ARE PERCENT OF MAXIMUM WATER FLOW INTO SCRUBBER
- WATER FLOW RATE IN GALLONS PER MINUTE (gpm). TO CONVERT TO cu m/hr MULTIPLY BY 0.227

Figure 4-16. Water balance for FDS and absorption tower scrubber system (extrapolation based on Arizona Public Service Cholla Station process): 1000 MW equivalent operation

The Duquesne Phillips Station scrubbing system is designed for about 400 MW operating capacity; thus, scaling up this system to 1000 MW equivalent would require only about a 2.5 increase in scrubbing capacity. However, at the time of sampling, flue gases from only 120 MW generations capacity boilers were being treated, but the full scrubber design capacity of three 125 MW equivalent scrubbers was being used. Also at that time, the flue gas velocity through the collectors was such that fly ash carry-over was four times that normally experienced. This higher solids content resulted in an increase in particulate loading which saturated the system's design solids capacity. To scale up this sytem to 1000 MW at 90 percent SO2 removal efficiency and to compensate for the higher solids loading, it was presumed that dual-stage venturi scrubbers would be required and deficiencies would be corrected. As in the other cases, the scrubber liquid-to-gas ratio was assumed to be unchanged from those of the test conditions. The results of these calculations are presented in the simplified flow diagram in Figure 4-17.

# 4.3.2 Summary

Table 4-10 summarizes and compares the water requirements for the four scrubber systems studied and extrapolated in size to an equivalent capacity of 1000 MW. Several observations can be made from these comparisons relative to water use in SO<sub>2</sub> scrubbing systems. The maximum water flow into the scrubber varies among the different types of scrubber systems and appears to be unrelated to the sulfur content of the coal, fly ash content, or the percentage of the scrubber's design capacity being used. Since the scrubber liquor requirement appears to be solely a function of scrubber system design, no extrapolation of water use from a given system to other systems or other sulfur content coals is possible



#### EXTRAPOLATED OPERATING CONDITIONS

- LIQUID-TO-GAS RATIO: 29.9 gai/1000 cu ft
- SCRUBBER EFFLUENT SOLIDS: 5 PERCENT
- CLARIFIER UNDERFLOW SOLIDS: 38 PERCENT
- COAL: 2 PERCENT SULFUR
- SO, REMOVAL EFFICIENCY: 90 PERCENT
- OPERATING CONDITIONS USED AS BASIS FOR EXTRAPOLATION SHOWN IN TABLE 4-8
- PERCENTAGE VALUES ARE PERCENT OF MAXIMUM WATER FLOW INTO SCRUBBER
- WATER FLOW RATE IN GALLONS PER MINUTE (gpm). TO COVERT TO cu m/hr MULTIPLY BY 0.227

Figure 4-17. Water balance for dual-stage venturi scrubber system (extrapolation based on Duquesne Phillips Station type of process): 1000 MW equivalent operation

Table 4-10. SUMMARY AND COMPARISON OF WATER BALANCE PROJECTIONS FOR 1000 MW EQUIVALENT SCRUBBERS

# Values based on 90 percent $SO_2$ removal

Scrubber location, type, and absorbent	TVA Sh venturi spray,	and	TVA Sha TCA, li	iwnee, mestone	Arizona ( FDS and a tower, lin and fly as	bsorption nestone	Duquesne dual-stag lime		
Water balance shown in	Figure 4-14		Figure 4-15		Figure 4-16		Figure 4-17		
Extrapolation base	8.3 MW equiv., 83% loading, 85% SO <sub>2</sub> removal		6.8 MW equiv., 68% loading, 86% SO <sub>2</sub> removal		115 MW equiv., 100% loading, 75% SO <sub>2</sub> removal		120 MW equiv., 33% loading, 65% SO <sub>2</sub> removal		
Sulfur in coal, percent	3.4		3.	3.4		0.5		2.0	
Flow points	Water flow, <sup>a</sup> gpm	Percent of total flow	Water flow, <sup>a</sup> gpm	Percent of total flow	Water flow, <sup>a</sup> gpm	Percent of total flow	Water flow, <sup>a</sup> gpm	Percent of total flow	
Scrubberb									
Input	163,000	100	164,000	100	196,840	100	127,750	100	
Output	162,100	99.5	163,150	99.5	196,410	99.8	126.960	99.4	
Bleed	4,800	2.95	4,120	2.5	520	0.26	5,560	4.4	
Clarifier									
Overflow	2,900	1.78	3,310	2.0	No	) ot	5,400	4.3	
Underflow	1,900	1.17	810	0.5	Applicable		490	0.4	
Filter									
Filtrate	1,390	0.86	No.	l ht	l No	į ot	Ne	l ot	
Filter cake	510	0.31		cable	Applicable		Applicable		
Water losses									
Stack	900	0.55	850	0.5	430	0.22	790	0.6	
Pond	510	0.31	810	0.5	520	0.26	360	0.3	
Water input									
With absorbent	500	0.30	170	0.1	110	0.06	1,150	0.9	
Make-up	910	0.56	1,490	0.9	840	0.43		]	

<sup>&</sup>lt;sup>a</sup>To convert gpm to cu m/hr multiply by 0.227.

<sup>&</sup>lt;sup>b</sup>Values of Arizona Cholla are for FDS slurry tank rather than scrubber.

from these data. Moreover, based on the operating procedures at the time of sampling, it was presumed that the liquid-to-gas ratios within a scrubber would be maintained constant so as to obtain the desired sulfur removal efficiency. Thus, an extrapolation to power plant load factors other than those observed during sampling would be expected to be a reasonably linear function. No other variables or conditions appear to affect the scrubber water requirements.

Table 4-11 summarizes the flows of the liquor bleed streams. In the bleed stream from the scrubber, the larger streams come from the higher sulfur bearing coals; however, a direct correlation is impossible because of the fly ash content variation in the solids and the total solids content in the slurry. Comparison of water loss to the pond is also impossible because of the different sludge disposal designs among the plants.

An analysis was made to establish a scaling factor that could be used to correlate the ratio of water loss to the pond (based on a 1000 MW equivalent scrubber capacity) as a function of the sulfur content of the coal being burned. However, to establish this factor two normalizing assumptions were made:

- a. The sludge from the scrubber would be dewatered to a solids content of 45 percent solids by weight.
- b. All available supernate from the dewatering process would be returned to the scrubber system.

On the basis of these two assumptions, it was found that for the four scrubber systems studied the ratio of F/S is between 150 to 224 with an average of 187, where F is the water loss to the disposal site in gallons per minute (to convert to cu m/hr multiply by 0.227) and S is the percent sulfur in the coal.

In a given system, a reduction in sulfur content with all other system parameters held constant will have the effect of . reducing the quantity of solid waste and the waste water associated

# Table 4-11. SUMMARY OF SCRUBBER BLEED STREAM FLOW PROJECTIONS FOR 1000 MW EQUIVALENT SCRUBBERS

# Values based on 90 percent SO<sub>2</sub> removal

Scrubber location, type, and absorbent	TVA Shawnee, venturi and spray tower, lime	TVA Shawnee, TCA, limestone	Arizona Cholla, FDS and absorption tower, limestone and fly ash	Duquesne Phillips, dual-stage venturi, lime
Water balance shown in	Figure 4-14	Figure 4-15	Figure 4-16	Figure 4-17
Coal type and sulfur content, percent	Eastern 3.4	Eastern 3.4	Western 0.5	Eastern 2.0
Scrubber capacity, MW	10	10	120	Four units of 125 each
Extrapolation base, MW	8.3	6.8	115	120
Sulfite and sulfate in total solids, percent	50	50	40 <sup>a</sup>	40 <sup>a</sup>
Scrubber <sup>b</sup>				
Bleed stream, gpm <sup>c</sup>	4800	4120	520	5560
Solids, percent	8	8	15	5
Clarifier				
Underflow, gpm	1900	810	Not	490
Solids, percent	18 <sup>d</sup>	40	Applicable	38
Filter				
Water loss in cake, gpm	510			
Solids in cake, percent	45	Not Applicable	Not Applicable	Not Applicable
Filtrate, gpm	1390			
Solids, percent	45			
Pond				}
Supernate, gpm	Not Applicable	Not Applicable	Not Applicable	130
Solids, percent				<1

<sup>&</sup>lt;sup>a</sup>Adjusted to 90 percent SO<sub>2</sub> removal efficiency.

<sup>&</sup>lt;sup>b</sup>Values for Arizona Cholla are for FDS slurry tank rather than scrubber.

 $<sup>^{\</sup>mathrm{c}}$  Water flow rate in gallons per minute; to convert gpm to cu m/hr multiply by 0.227.

 $<sup>^{</sup>m d}$ Clarifier was undersized resulting in shorter residence time and lower solids content.

with the solids. The reduced loss of waste water to the disposal site will reduce the volume of make-up water required to balance the system. However, if this reduction is sufficiently large so as to be inadequate to satisfy minimum fresh water requirements, a system imbalance may occur. In this case, when minimum fresh water requirements are met, make-up water will then exceed water losses by evaporation or to the pond and excess system water will result. Two potential environmentally acceptable solutions exist: (a) increase the relative quantity of waste water being disposed with solids, or (b) treat a portion of the return water from the dewatering treatment circuit to satisfy the fresh water requirement. In many cases, the need for fresh water can be reduced by blending untreated return water with fresh water, but there is a limit to the extent that blended water can satisfy the demister or pump seal fresh water requirement. This limit is a system design parameter for each plant and must be found by experience.

The make-up water requirement for each system is dependent primarily upon the water balance from pond losses and stack losses. However, in watertight systems, the water balance requirement for make-up water may be exceeded by the fresh water requirements of the demister and pump seals. In these cases, the limit to the degree of dewatering may be dictated by this fresh water requirement, and there may exist only a slight accommodation for reducing the sulfur content without major system design changes. Since stack losses are dependent upon atmospheric conditions and design variables, adjustments in this value are not easily made; therefore, it is not an adjustable parameter.

In addition to a change in sulfur content as it affects the water balance, an identical effect is experienced with a decrease in flue gas mass loading to the scrubber. In a case of reduced load factor, as before, a reduction in sulfur waste products causes a reduction in waste water and in make-up water to meet water balance requirements. As before, if this reduction exceeds the fresh water requirements of the system, an identical water balance problem arises.

# 4.4 CHEMICAL CONDITIONS AFFECTING COMPOSITION OF SCRUBBER LIQUORS AND WATER IMBALANCE

In each case of water imbalance previously identified, excess system water occurs only when fresh water requirements exceed make-up water requirements and can take place whenever a critical reduction in water losses occurs. Other system variations beside those identified here are possible, but the point at which excess system water is produced can not be determined without detailed study of the system design or by experimental determination. It could not be determined from these data whether sulfur removal efficiency or other specific design parameters could produce independently the conditions necessary for excess system water.

The following sections (4.4.1 and 4.4.2) provide the results of an overview of fundamental scrubber chemistry and the potential for water imbalance.

# 4.4.1 <u>Saturation Concentrations and Solubility of</u> Ingredients

An evaluation of the scrubber liquor chemical analysis (shown in Tables 4-3, 4-5, 4-7, and 4-9) indicates that the scrubber systems operate at saturation concentrations of calcium and sulfate ions amounting to several thousand milligrams per liter. In addition, sodium and chloride ions were found to be present in high concentrations, but they are not controlled by saturation conditions.

The analytical data for the liquor samples are consistent with the assumption of saturation with gypsum (CaSO<sub>4</sub> ·  $2H_2O$ ).

However, it should not be inferred that the concentrations of calcium or sulfate will not vary among the liquor samples, nor will the solubility of calcium sulfate (as expressed by the product of the sulfate and calcium concentrations) remain constant. In addition to the effect of temperature, the solubility of calcium sulfate is affected by the presence of other ions (e.g., sodium, magnesium, or chloride). Although the quantitative relationship is somewhat complicated, in general the solubility of calcium sulfate will increase by the summation of all molar ionic concentrations after each has been multiplied by the square of its ionic charge. Therefore, magnesium ions have a fourfold greater effect than equimolar concentrations of either sodium or chloride ions. An approximate correlation may be observed between the solubility of calcium sulfate and the total dissolved solids (TDS) of the sample. For example, each of the three data sets for the EPA/TVA Shawnee-venturi system shows a fivefold increase in the product of the calcium and sulfate concentrations which corresponds to a threefold increase in TDS. Similar relationships exist in each of the other scrubbing systems.

The chemistry of other chemical constituents including the trace elements in the system are controlled by their saturation concentrations in the presence of calcium, sulfate, and hydroxyl ions. Trace elements, including toxic species, tend to be limited by their equilibrium concentration with the calcium and sulfate ions at low values of pH and with the hydroxyl ions at high values of pH. Most of these elements are controlled in the scrubber liquor at concentration levels below 1 mg/l, and many are controlled at about 0.05 mg/l.

Control of highly soluble species is dependent upon maintaining steady-state conditions whereby the system's rate of loss (as soluble species in occluded water associated with solid waste) balances the rate of intake (either by absorption from flue gas or from

process ingredients). The tighter the closed loop, the higher the specie concentrations become. The most direct effect of these species is their contribution to the TDS. In each case, sodium, calcium, sulfate, magnesium, and chloride ions constitute the measurable dissolved solids content in the liquors. High TDS values increase the ionic strength of the liquor which in turn increases the saturation concentrations of chemically controlled soluble species in the system.

The concentration of soluble species in the scrubber liquors is dependent upon two system variables: the pH of the system liquors, and the tightness of the water balance within the system. The latter will affect the TDS, and the calcium sulfate chemistry control will be affected by both.

In addition to these system variables, a reduction in the coal's sulfur content will increase the soluble species in the scrubber. In this case, the rate of production of sulfur by-products is reduced. As a consequence, the scrubbing of other salts and acids from the flue gas is proportionately greater and will result in higher soluble salt contents. The resulting increase in ionic strength will also increase the soluble saturation concentration of calcium sulfate. In some systems, the increase of soluble calcium sulfate will increase the demister scaling problem. In all cases, an independent reduction in sulfur content will increase the level of dissolved solids in the liquor relative to higher sulfur operation.

# 4.4.2 Water Imbalance

A reduction in boiler load factor decreases the flue gas mass flow but does not affect the water quality of the liquor. In this case, absorption of all species from the flue gas (or from fly ash carried in the flue gas) is reduced in direct proportion to the reduction in flue gas mass flow. The rate of production of sulfur by-products

is reduced proportionately to all other system rates; thus, no change is effected in the concentration of soluble species in the liquor. In both the cases of reduced load factor and reduced sulfur content, it has been assumed that the reduced need for make-up water to satisfy water balance remains sufficient to satisfy the minimum requirement for fresh water make-up.

The chemical analysis of system liquors reveals that the chemical constituents within these liquors exist at essentially identical concentrations at all potential system purge points. Minor variations exist as a consequence of the design choice of make-up water introduction or absorbent introduction into the system, but these variations do not affect the general water quality of the liquor. The exception to this generalization exists between scrubber effluent and points past the introduction of the absorbent. The scrubber effluent has a slightly lower pH than the system downstream of the reaction tank and concentrations of species controlled by the hydroxyl ion tend to be somewhat higher. Since scrubber effluent is not a potential point of system purge, it need not be considered for water quality acceptance.

# 4.5 ASSESSMENT

Table 2-1 shows the range of concentration of the constituents found in the scrubber liquors at the potential discharge points, the criteria assumed for the quality of nonpotable service water for usage in the power plant, and a tabulation of the October 1973 EPA proposed criteria for public water supply intake. It presents the total range of values of the ingredients found in the liquors at the potential purge points among the four systems studied. This range of constituent values depends upon the composition of the coal and absorbents used, the scrubber design, and system operating characteristics. The values in the table are given in milligrams

per liter; however, the potential discharge rate in pounds per day can be calculated from the following equation:

DR = 0.012 cf

where

DR = discharge rate of the ingredient in lb/day (to convert lb/day to kg/day multiply by 0.4536)

c = concentration of the constituent in mg/l

f = flow rate of the water in the scrubber system
flow streams in gpm

For example, a given constituent at 0.004 mg/ $\ell$  at a flow rate of 400 gpm would mean about 0.009 kg/day (0.019 lb/day) of material potentially would be discharged.

An assessment was made of the potential water uses and the constituents of concern for each use; the results are summarized in Table 4-12. There is a need for large quantities of nonpotable water for general operations within the power plant (listed under "Service water" in Table 4-12) and for other applications that require water free of constituents that would corrode, scale, or foul the equipment. Although the concentration of many constituents does not present a problem for scrubber liquors to satisfy these needs, it is necessary to reduce the concentration levels of the chloride, sulfate, magnesium, and calcium present from one or more of the liquor streams studied.

A treatment process such as lime-soda softening will reduce the sulfate, magnesium, and calcium concentrations to preclude scaling of the equipment. In addition, the concentrations of arsenic (As), boron (B), cadmium (Cd), iron (Fe), lead (Pb), selenium (Se), mercury (Hg), copper (Cu), zinc (Zn), nickel (Ni),

Table 4-12. POTENTIAL WATER USES AND CONSTITUENTS OF CONCERN

Water use	Constituents of concern		
Service water Scrubber make-up	Calcium, magnesium, and sulfate		
Air conditioning equipment			
Pump seals  Cooling tower make-up  Evaporative coolers  Housekeeping	Calcium, chloride, magnesium, sulfate, and total dissolved solids		
Discharge	Arsenic, boron, cadmium, chlo- ride, chromium (total), fluoride, iron, lead, manganese, mercury, selenium, silver, and sulfate		

cobalt (Co), and manganese (Mn) will also be reduced by this process. In existing or new plants where brackish water is acceptable for service water use this process would be adequate. In cases where brackish water is unacceptable, the lime-soda softening process would have to be followed by an additional process such as reverse osmosis. Furthermore, a high chloride content water requires that the equipment in contact with this water be constructed from, or coated with, salt water resistant materials. Although it is within the current state of the art to build chemical process equipment to withstand the corrosive effects of high chloride content water, the equipment costs will be increased. Chlorides can be removed from the scrubber liquor by the use of reverse osmosis, ion exchange, or evaporation and condensation techniques. These techniques, in addition to other concepts such as electrodialysis and vacuum freezing vapor compression, are being tested in many parts of the world as methods for converting sea water to potable water.

If the scrubber liquor is to be discharged to surface or ground waters and is to meet the October 1973 EPA-proposed criteria for public water supplies, the concentration of the following constituents will have to be reduced for some of the cases studied: As, B, Cd, chromium (Cr) (total), fluoride, iron, Mn, and silver (Ag). In addition, it was found that Pb, Hg, Se, chlorides, and sulfates in the scrubber liquor from all four power plants exceeded the criteria. The amount of reduction of the constituents will depend upon the specific composition of the scrubber liquor. For example, analyses of the individual power plant scrubber liquors showed that the Arizona Public Service Cholla Station scrubber at the time of sampling was operating in a tightly closed scrubber loop condition resulting in higher than acceptable concentration levels in the discharge stream from the

FDS tank for all of the aforementioned ingredients, except As. The EPA/TVA Shawnee TCA scrubber system exceeded the limits for As, Cr (total), Pb, Hg, Se, Ag, chlorides, and sulfates. The EPA/TVA Shawnee venturi and spray tower scrubber system exceeded the limits for As, B, Cd, Cr (total), Pb, Mn, Hg, Se, Ag, chlorides, and sulfates in the discharge from the clarifier underflow or from the drum vacuum filter filtrate on one or more of the sampling dates. Conversely, the Duquesne Phillips Station system was experiencing operating conditions requiring high water flow rates through the system which diluted the concentration of the dissolved ingredients. The result was that the liquor from the clarifier underflow exceeded the proposed EPA criteria only for Cd, Pb, Hg, Se, chlorides, and sulfates; these results may not represent the normal concentrations to be expected in this scrubber liquor.

#### SECTION 5

#### WATER TREATMENT STUDIES

### 5.1 LITERATURE AND INDUSTRY REVIEW

The domestic and foreign literature was reviewed, and technical meetings and discussions were held with representatives from water treatment processors, consulting firms, equipment manufacturers, research laboratories, and governmental agencies conducting research and development testing in the field of water treatment. This review was conducted to determine what data are available on processes and types of equipment for use in reducing the concentration levels of the sludge liquor constituents (Refs. 13 through 50). The results indicated that there are many pieces of equipment available designed to accomplish a specific water treatment and that numerous laboratories, agencies, and companies are currently engaged in expanding the field of water chemistry and treatment operations. However, most of this work is being directed toward the treatment of brine or fresh water for public use or a specific industrial process, and for sanitary waste disposal; only a limited amount of work has been done in industrial water reuse.

Generic types of water treatment processes and an indication of their current status is given in Table 5-1. Also included is an assessment, which is based upon the data gathered in the technical review, about the possibility of the treated water meeting the established water quality criteria for reuse or discharge. A selection of the systems considered and applicable for scrubber liquor treatment is given in Section 5.2.

Table 5-1. SUMMARY OF GENERIC TYPES OF WATER TREATMENT PROCESSES CAPABLE OF MEETING WATER QUALITY CRITERIA

Water treatment process	EPA-proposed public water supply intake, October 1973	Nonpotable service water	Status
Complete system			
Multistage evaporation	Yes	Yes	Operational
Tower distillation	Yes	Yes	Operational
Brine concentration	Yes	Yes	Operational
Spray drying	Yes	Yes	Operational
Vacuum freezing	Yes	Yes	Development
Solar distillation	Yes	Yes	Development
Rotating bipolar electrodes	No	No	Laboratory
Partial operation <sup>a</sup>			
Filtration or centrifugation	No	No	Operational
Ultrafiltration	No	No	Operational
Reverse osmosis	Yes	Yes	Operational
Ion exchange	Yes	Yes	Operational
Chemical precipitation (including lime-soda softening)	No	Yes	Operational
Electrodialysis	Yes	Yes	Development
Selective absorbent	No	No	Laboratory
Electrochemical; fluidized bed	No	No	Laboratory
Foam separation	No	No	Laboratory

<sup>&</sup>lt;sup>a</sup>Used with other operations to form a total water treatment system

# 5.1.1 Multistage Evaporation

Many concepts and designs of single- and multistage evaporators are available and have been used in the chemical process industry for many years to concentrate the solids in a liquid mixture by evaporation of the liquid material (Ref. 13). Multistage evaporation uses the concept of a series of evaporators with decreasing pressure from one stage to the next; the vapor from one stage is fed into the heating chamber for the following stage. This evaporation and condensation concept can produce a condensate of high purity water that meets the requirements for discharge to bodies of water, for potable water, or for direct use as boiler feed water. Multistage evaporation was one of the first techniques used for desalting sea water for drinking water and is still being used. An efficient multistage evaporator design using flash evaporation was evaluated in this study (see Section 5.2.4).

### 5.1.2 Tower Distillation

Tower distillation could be used for water purification, and the distillate would be of potable or boiler feed quality (Ref. 13). However, unless there are special circumstances (e.g., a supply of excess heat or steam available and a need for potable water) this is not a cost-effective approach for obtaining discharge or service water. The cost for distilled water is higher than condensate water from a multistage flash evaporator.

# 5.1.3 Brine Concentration

Brine concentration uses a type of falling film evaporator wherein the feed brine falls in a film inside a tube bundle, and a portion of this film is then vaporized (Refs. 14 and 15). There is also a vapor-compression thermodynamic cycle in which the vapor is compressed and introduced to the shell side of the tube bundle. The

temperature differential between the vapor and the brine film causes the vapor to condense as pure water. The concentrated brine solution is withdrawn to a disposal pond. The condensate meets the discharge or power plant reuse water quality criteria. The results of a technical and economic evaluation on the potential use of a brine concentrator for treating the scrubber liquor are given in Section 5.2.5.

### 5.1.4 Spray Drying

Spray dryers are similar to flash evaporators. A material is sprayed into a vacuum chamber, the liquid is evaporated, and the particulate matter is collected in the base of the dryer. This equipment is generally used for removing moisture from solid particles that are considered the product rather than vice versa (Ref. 13). Consequently, this specific process was not examined as a potential water treatment operation although the condensate would be a high-quality water. However, a combination of a modified multistage evaporation and spray drying called multistage flash evaporation was evaluated (see Section 5.2.4).

# 5.1.5 Vacuum Freezing

In the vacuum freezing vapor-compression process, latent heat of fusion is given up when precooled feed water is introduced into a chamber under low pressure. The feed water is pumped into the system through a deaerator and then through heat exchangers where it is cooled to the freezing temperature by cold brine and cold product water leaving the system. The deaerated and cooled feed water is subsequently pumped into the freezer where a simultaneous boiling-freezing process occurs. The low pressure causes the water to boil and part of it vaporizes. The vapor extracts heat of vaporization from the remaining feed water, part of which then freezes. The ice-brine slurry is transferred from the freezer to a washer to remove adhering brine and in turn is sent to a melter. This process is

reported to be in a development stage for use in desalting sea water (Refs. 16 and 17). However, an investigation into the adaptability of this process for producing discharge or service water from desulfurization slurry liquor indicated that additional developmental tests must be made before using this technique.

### 5.1.6 Filtration or Centrifugation

Filtration or centrifugation, which is a mechanical separation process that can remove particles from a feed water source, is ineffective on dissolved ingredients (Refs. 18 through 20). Consequently, this process must be considered for use only in conjunction with other processes capable of removing the dissolved constituents from the water.

# 5.1.7 <u>Ultrafiltration</u>

Ultrafiltration or microfiltration uses membranes of pore size ranging from 0.001 to 10 microns to achieve separation of impurities in waste water on the basis of molecular size only. This filtration process removes smaller particles from the liquor to be treated than normal filtration or centrifugation, but it does not reduce the concentration levels of dissolved constituents such as the chloride salts. Although ultrafiltration processes are operational, the application is for removal of suspended solids, coliform bacteria, and similar particle type contaminants in sewage waste water.

# 5.1.8 Reverse Osmosis

Osmosis occurs when pure water and a salt solution are on opposite sides of a semipermeable membrane and pure water diffuses through the membrane diluting the salt solution (Refs. 16, 17, and 21 through 26). The osmotic process can be reversed by applying pressure [>30 kg/sq cm (>420 psi)] to the salt solution.

This process has been successfully used for desalting sea water and can be used to treat scrubber liquors for discharge or reuse. The results of an economic evaluation of this technique following a pretreatment of lime-soda softening are discussed in Section 5.2.2.

### 5.1.9 Ion Exchange

Demineralization or ion exchange is based on the removal of the impurities from water by means of synthetic resins that have an affinity for dissolved or ionized salts. The exact types of resins to be used will depend upon the specific constituents to be removed (Refs. 16, 17, and 26 through 29). An economic analysis was made of the ion exchange process in conjunction with the lime-soda softening process (see Section 5.2.3). Work is under way by many researchers to develop resins that will selectively remove specific ions and trace metals from water solutions. Five examples for heavy metal removal are:

- a. Chelex-100 resin is reported to concentrate cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), and zinc (Zn) in preference to calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na). A pH controlled solution of 5 to 6 is required.
- b. Amberlite EX 318 resin at a pH of >4 selectively concentrates Cd, Co, Cu, iron (Fe), mercury (Hg), Ni, Pb, vanadium (V), and Zn.
- c. Titanium arsenate selectively removes Cd, Co, Cu, Mn, Ni, Pb, tin (Sn), and Zn.
- d. Permutit S 1005 resin at a pH of 5 to 9 is reported to remove Cd, Co, Cu, Mn, molybdenum (Mo), Ni, Pb, V and Zn from a water solution.
- e. Rohm and Haas EX 243 is being used to remove boron (B) from a magnesium chloride brine solution.

#### 5.1.10 Selective Absorbent

Laboratory work is progressing on identifying absorbents that have an affinity for specific ions or heavy metals (Refs. 29 through 31). An example is tannery hair chemically treated to form the sulfhydryl and used as packing in a column. Silver (Ag), Cd, Cu, Hg, and Zn will be absorbed from a water solution passed through the column.

Activated carbon is widely used for removing organic impurities from waste water, and work is under way to determine if activated carbon can be used effectively for removing inorganic substances. Manganese is reported to be removed from water by the spray aeration of the water to oxidize the manganese and form a precipitate; this is followed by filtration and absorption with activated carbon. However, the use of selective absorbents has not progressed sufficiently for it to be considered an economically available process for treating scrubber liquor.

# 5.1.11 Chemical Precipitation (including lime-soda softening)

Chemical precipitation is an all encompassing term for reacting ingredients together to form a chemical compound that will precipitate from the water solution (Refs. 32 through 43). A commonly used example of chemical precipitation is the reaction of lime and soda ash with calcium and magnesium salts to reduce the hardness of water. Section 5.2.1 presents the results of an evaluation of using a lime-soda softening operation for treating scrubber liquors. All chemical precipitation processes require a separation operation to remove the precipitates from the liquid.

Considerable research is also under way to develop chemical reactions that will selectively remove heavy metals from a water solution. For example, in tests at the Central Contra Costa County, California, Sanitary District Treatment Plant it was shown

that a process using the addition of calcium hydroxide to water to attain a pH of 11.5 followed by settling, recarbonation with carbon dioxide to lower the pH to a range of 9.5 to 10.5 and subsequently filtration, reduces the concentration of Ag, barium (Ba), Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in the water. In a similar process, the Orange County Water District, Santa Ana, California, is using a treatment process consisting of operations such as coagulation with ferric sulfate and a lime-soda softening to reduce the concentration of heavy metals in their sewage water reuse treatment plant.

At the EPA Water Supply Research Laboratory, National Environmental Research Center, Cincinnati, Ohio, laboratory tests have confirmed the reduction in concentration of arsenic (As), Ba, Hg, and selenium (Se) as the result of coagulation with ferric sulfate and a lime softening operation at a pH of 11.

Some other chemical reactions include:

- a. Thioacetamide in water at a pH of 1 is reported to precipitate Cd, Cu, and Pb, and at a pH of 8 to precipitate Cr, Mo, titanium (Ti) and Zn.
- b. Metal sulfides such as CdS<sub>2</sub> at a pH of 2.5 will precipitate Co, Cr, Cu, Mo, Ni, and V from water.
- c. Chelation with ammonium pyrrolidine dithiocarbonate at a pH of 4.5 to 6 is reported to remove Cd, Co, Cu, Mn, Mo, Ni, Pb, and Zn.
- d. Dibromo-oxime (dibromo-hydroxy-quinoline) with acetone in brine water at a pH of 5 to 8 is reported to precipitate Co, Cr, Cu, Mn, Pb, and Zn.
- e. The addition of aluminum sulfate will precipitate As, Cr, Cu, Pb, Se, and Zn from a water solution at a pH of 6.8 to 7.
- f. Calcium hydroxide at a pH of 9.5 will cause precipitation of Co, Cr, Cu, Mn, Ni, Pb, and Zn from water, and dolomite limestone of 40 to 70 percent calcium hydroxide and 30 to 60 percent magnesium hydroxide added to water will precipitate Pb and Sn.

- g. Coagulation with ferric sulfate at a pH of 9 to 11 will remove As from the water, and at a pH of 6 to 9 Se will be removed. At a pH of about 7 to 8 and followed by air injection, filtration, and magnetic attraction of the ions, it is reported that antimony (Sb), Cr, Cu, Fe, Hg, Ni, and Pb can be removed from water.
- h. Starch xanthate mixed with a cationic polymer (such as polyvinylbenzyl trimethyl-ammonium chloride) into a water solution containing heavy metals is reported to precipitate both the polymer and the heavy metals as a cohesive floc. This process will remove Ag, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn.

### 5.1.12 Electrochemical; Fluidized Bed

Laboratory tests are being made on a method of removing trace heavy metals from a water-lime solution with a pH of 7 to 8 by applying a low voltage direct current field across a fluidized bed of conductive particles. The metallic impurities plate out on the tin granules that are used as the collector particles. Arsenic, Cd, Cr, Cu, Hg, and Zn were reported to be reduced in concentration by this operation. This process will not remove the chlorides from the water; a reverse osmosis or other process must be used in conjunction with this method (Ref. 44).

#### 5.1.13 Rotating Bipolar Electrodes

A process is being studied in the laboratory in which bipolar electrodes are rotated in a central chamber containing water. The cations in the water are attracted toward the negatively charged surface and will flow into a side chamber and be attracted by a stationary electrode. The anions are similarly attracted into a side chamber on the opposite side of the central chamber. This process may have application for the purification of a small side stream, but more laboratory and development work will be required before the technique becomes operational for use in treating scrubber liquors. (Ref. 45).

# 5.1.14 Electrodialysis

Electrodialysis uses electric current to drive charged ions through one or more ion-permeable membranes. The passage of current through the solution causes an increase in the concentration of one species on one side of the membrane and a corresponding reduction on the other side. It is necessary to ensure the feed water does not contain suspended particles or they will clog the pores of the membrane; therefore, removal of suspended solids is accomplished by a separation pretreatment. Tests, which were conducted with sea water, have shown that a potable water can be obtained. However, further work is necessary to develop this concept before it can be considered fully operational for use with scrubber water (Refs. 46 through 48).

# 5.1.15 Foam Separation

A process has been tested in the laboratory in which it is reported that sodium hydroxyphenyl butylbenzyl sulfonate as a surface active agent is mixed with water and then flowed countercurrent in a tower with nitrogen gas with a pH of 5.5 to 8 to remove Co, Cr, and Ni from the water. A subsequent separation operation is needed with this process (Ref. 29).

# 5.1.16 Solar Distillation

Techniques and equipment to utilize solar energy to supply heat to evaporate water and subsequently condense the vapor as pure water is being investigated. One solar still concept being tested is a large covered pond which uses solar energy for heating and evaporating the water in the pond. The vaporized water condenses on the underside of the pond roof and runs off through troughs to a collection basin. This technique shows promise for hot, dry areas such as the southwestern U.S., but it has obvious limitations in the colder climates and locations with many days of cloud cover. With

the current U.S. energy shortage, more effort is being expended by government agencies and private research laboratories to develop practical concepts to harness solar energy. However, additional research and testing is still needed before a concept employing solar energy is considered usable for treating scrubber liquor in all areas of the U.S. (Ref. 49).

# 5.1.17 Analysis of Review

An analysis of the numerous water treatment processes, techniques, and equipment reveals that a lime-soda softening process and a separation operation to remove the precipitates will reduce the concentration of As, B, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Pb, Se, Zn, and sulfates in the scrubber liquors; however, the process will not reduce the concentration of certain soluble ingredients (i.e., sodium and chloride salts). This process is currently operational and will not require a breakthrough or advancement in the state of the art.

In plants where brackish water is acceptable for service water, the lime-soda softening would be adequate. However, in plants where brackish water is unacceptable, an additional operation such as reverse osmosis or ion exchange will be necessary. A pH adjustment may be required in some cases. An evaporation/condensation process will also produce acceptable water. Adaptations of this latter process for treating scrubber liquor are the multistage flash evaporator and the brine concentrator techniques; either would produce a condensate capable of being reused in the power plant or discharged.

It is recommended that before a full-scale plant for treating scrubber liquors is installed, pilot plant testing be performed on the specific scrubber liquor to be treated to acquire specific data to properly size the equipment and to check out its operation. This study reviewed the literature and held technical discussions with power plant operators and organizations active in water treatment processing and equipment manufacturing. No work was done in the laboratory to treat any of the scrubber liquors.

# 5.2 SELECTED WATER TREATMENT PROCESSES

Processes adaptable for treating scrubber water to reduce the concentration of ingredients were identified in Section 5.1. As indicated, many processes are available that could reduce the concentration of one or more of the constituents; however, their development status ranges from those still in laboratory testing to those that are in full-scale operation (Refs. 13 through 49). In reviewing the different processes, five appear to have been developed to the degree that they can be considered an off-the-shelf process and readily adaptable for use in treating the scrubber system bleed streams. Table 5-2 lists these processes and their capability for meeting the water quality criteria. Each of these is discussed in the following Sections.

# 5.2.1 <u>Lime-Soda Softening Process</u>

The concept of using currently available processes to treat scrubber liquors at the potential discharge point is fulfilled by this process if the plant is designed to accept brackish water (defined for this study as water having 5000 mg/l or greater of chloride). In this process lime (CaO) and soda ash (Na<sub>2</sub>CO<sub>3</sub>) are reacted with the major species in the liquor to precipitate the Ca and Mg together with the heavy metals. The pH is adjusted with carbon dioxide and the solution is filtered or centrifuged with the precipitates being sent to the disposal site and the product water fed to the reverse osmosis or ion exchange operation for chloride removal if the power plant cannot accept brackish water for service water.

Table 5-2. CAPABILITY OF WATER TREATMENT PROCESSES TO MEET REQUIREMENTS

	Criteria			
***		Nonpotable service water <sup>a</sup>		
Water treatment process (in decreasing order of cost effectiveness)	EPA-proposed public water supply intakeOctober 1973	Brackish water acceptable	Brackish water not acceptable	
Lime-soda softening	No	Yes	No	
Lime-soda softening plus reverse osmosis	Yes	Not applicable	Yes	
Lime-soda softening plus ion exchange	Yes	Not applicable	Yes	
Multistage flash evaporation	Yes	Not applicable	Yes	
Brine concentration	Yes	Not applicable	Yes	

<sup>&</sup>lt;sup>a</sup>Brackish water for this study is defined as water having 5000 mg/l or more of chloride.

The literature indicates that the lime-soda softening process can reduce the concentration of the Ca and Mg salts to less than 1000 mg/l. Data showed that about an 80 to 90 percent reduction in concentration of As, Cd, Mn, Pb, and Se has been achieved by this process and, depending upon the source of the data analyzed, it was reported that 30 to 90 percent of hexavalent chromium can be removed. Boron will also be reduced in concentration during the softening process; insoluble calcium and magnesium borate salts are formed and subsequently removed with other precipitates.

The pH of the liquor at the potential discharge points ranges from 3 to 10.7 for the four scrubbing systems studied and exceeds the criteria of 5 to 10 (Table 2-1). If the pH of the water is low at the time of bleed to the water treatment plant, the pH will be increased by adding lime. After precipitation and prior to filtration or centrifugation there is a pH adjustment with carbon dioxide, if necessary, to lower the pH.

# 5.2.2 Pretreatment Process (Lime-Soda Softening) Plus Reverse Osmosis

The use of reverse osmosis to treat the product water from the lime-soda softening pretreatment process will remove sodium chloride salts and other undesirable constituents and will result in a high-quality product readily capable of meeting both the service water and the EPA-proposed public water supply intake criteria.

The three basic designs for commercial reverse osmosis modules are as follows:

- a. The tubular type that uses small diameter (about 1/2-in.-diameter) porous or perforated tubes. The reverse osmosis membrane is installed on either the internal or external side of the tube and bundles of the tubes are joined to a feed water header system.
- b. The hollow fiber type that uses many capilliary tubes in a bundle configuration.
- c. The spiral wound type that uses a flat sheet of membrane to cover each side of a flat sheet of porous water-conducting material. The membrane is sealed on the two long sides and one end to form an envelope. The other side of the membrane and porous water-conducting material is sealed to a perforated tube that receives the product water.

All three types are designed to operate at pressures of about 30 to 45 kg/sq cm (430 to 640 psi) and are being used commercially.

Reverse osmosis was initially developed to produce potable water from brackish supplies, but because multivalent ions such as Ca, Mg, and sulfate are as readily rejected as are the monovalent ions (e.g., C1), this concept has been adapted for boiler feed water and treatment of waste waters for reuse. The literature implies that the reverse osmosis treatment would be the only operation needed to treat the scrubber water for either reuse or discharge. However, reverse osmosis equipment manufacturers and system users recommended that because of the high concentration of the major species in the scrubber water, a lime-soda softening process should precede the reverse osmosis operation. The pretreatment would reduce the concentration of the major species to a level compatible with current operational practices and experience, eliminate any objectional colloidal matter present in the scrubber liquor, and prevent precipitation of large deposits of the Ca and Mg sulfate salts on the membrane surface. Furthermore, this high concentration would have a greater tendency to cause an increase in equipment downtime for cleaning and repair and a predicted shorter membrane life. A higher reverse omosis investment as well as higher operating costs could result than if pretreatment were used followed by reverse osmosis to remove the final traces of the cations and anions.

The percent water loss from the pretreatment and reverse osmosis system was estimated to be about 25 to 30 percent of the feed water to the water treatment facility. This water would contain extremely high concentrations of the undesirable ingredients (e.g., As, Hg, Pb, and Se) and should be disposed of with the waste products from the scrubber.

# 5.2.3 Pretreatment Process (Lime-Soda Softening) Plus Ion Exchange

A review of the literature and technical discussions held with ion exchange manufacturers indicated that the use of the ion exchange process by itself would not be an economical approach as a scrubber liquor water treatment process. The manufacturers recommend that a pretreatment operation to reduce the high concentration of constituents be undertaken before flowing the water over the ion exchange resins. Otherwise, there would be excessive equipment down time for flushing and clean up of the resin beds. However, by using a pretreatment consisting of lime-soda softening and filtration or centrifugation, the constituent concentration levels will be reduced to values that can be handled by an ion exchange process to produce a product capable of meeting the EPA-proposed public water supply intake criteria.

Numerous resins of various chemical compositions are available or are being tested for general water treatment and for specific element removal. These resins are, by definition, insoluble solids containing fixed cations and anions capable of reversible exchange with mobile ions of the opposite sign in the solutions with which they are brought into contact. Ion exchange was used for years in water softening and limited impurity removal; however, industry is now developing newer resins for different applications. For example, Rohm and Haas has developed a deionization process for use in desalination work. The process is based upon the use of weak electrolyte ion exchange resins for treating brackish waters of 500 to 5000 ppm total dissolved solids. The process consists of three units in series: the alkalization unit, dealkalization unit, and carbonation unit. The influent to the first unit is passed through a bed of weak base anion exchange resin in which the anionic constituents are converted to the

bicarbonate salts of Na, Ca, and Mg. In the second unit, which contains a weak acid cation exchange resin, the bicarbonate salts are converted to carbonic acid. The third unit, which also contains a weak base anion exchange resin but in the free base form, absorbs the carbonic acid from the effluent of the second unit. After the exhaustion cycle is complete, the first unit is regenerated to the free base form while the second unit is converted back to the hydrogen form. Since the third unit is already in the bicarbonate form, the flow pattern is simply reversed for the next cycle. The third unit becomes the alkalization unit and the first unit becomes the carbonation unit. An adaptation of this process could be used to remove the chlorides from the scrubber liquor.

Other ion exchange resin beds must also be incorporated into the overall process to remove specific trace metals that may be in excessive concentration. Specific resins are available for selective heavy metal removal. For example, Rohm and Haas' Amberlite EX 318 resin is used to concentrate Cd, Co, Cu, Fe, Hg, Ni, Pb, V, and Zn, and EX 243 is used to remove B. Other manufacturers market resins also capable of removing trace elements.

There is a water loss incurred in conjunction with the operation of an ion exchange process. The amount is a function of the degree of backwashing and rinsing during the regeneration cycle and can be determined precisely only by conducting pilot plant tests using the exact liquor and with the specific manufacturer's resin. However, it is estimated that the degree of loss would be 25 to 30 percent of the feed water to the treatment facility.

# 5.2.4 Multistage Flash Evaporation

Multistage flash evaporation involves the process of progressively heating and flash evaporating the scrubber liquor in a series of stages under progressively lower pressures. Each stage of the evaporator is configured with a heat exchanger for preheating the incoming liquid and a vacuum chamber for flash evaporation. The vapor is used for preheating the liquid and is condensed in this operation. The condensate or product water from each stage is collected for reuse in the power plant or discharged. A portion of the residual concentrated scrubber water is mixed with influent liquor for recycling through the evaporator; the remaining portion is transported to a disposal area. The product from this operation is of high quality and suitable for boiler feed water or for drinking water as evidenced by the fact that this process has been widely used as an acceptable technique for producing potable water from sea water.

There is a loss of water with the concentrated slurry mix. The exact quantity of water lost is a function of the specific design of the evaporator and the equipment operating characteristics. For example, equipment that is operated to achieve a total dissolved solids (TDS) content in the discharge concentrate of 100,000 ppm, using a 10,000 ppm TDS feed water and <50 ppm TDS product condensate, has a water loss of 10 to 12 percent of the water fed to the evaporator.

### 5.2.5 Brine Concentration

A brine concentrator using the concept of a falling film evaporator can produce a product that can meet the reuse or discharge water quality criteria. This type of concentrator flows the feed water in a film inside a tube bundle, and a portion of this film is vaporized. A vapor compression thermodynamic cycle is part of the system in which the vapor is compressed and introduced to the shell side of the tube bundle. The temperature differential between the vapor and the water film causes the vapor to condense as pure water. The concentrated brine solution is subsequently withdrawn for disposal. It is.

estimated that with a feed water of about 10,000 ppm total dissolved solids, a discharge concentrate of 100,000 ppm, and a product of <50 ppm, there would be a loss of about 10 percent of the feed water.

#### 5.3 ESTIMATED WATER TREATMENT COSTS

In order to make a comparison of the economics of the five selected water treatment processes discussed in Section 5.2, engineering cost estimates were prepared for each process. Both capital and operating costs were considered, and all costs were based on 1974 dollars (Ref. 50 through 62). The results of the cost estimates are shown in Figures 5-1 through 5-5. The capital costs for each process were based on average annual charges of 18 percent of the original investment over a 30-year life including straight line depreciation, parts replacement, insurance, taxes, and cost of capital. Operating costs were based on 4560 operating hours per year (30 year average) and included labor, maintenance, repair, and operating power charges. Two types of coal were assumed to be burned:

- a. Type 1 coal has a thermal content of 29,700 joules/gm (12,500 Btu/lb) and is burned at the rate of 0.38 kg (0.84 lb) of coal to produce 1 kWh of electricity.
- b. Type 2 coal has a thermal content of 18,600 joules/gm (8,000 Btu/lb) and is burned at the rate of 0.42 kg (0.92 lb) of coal per kWh produced.

The capital and operating cost comparisons for water treatment contained in Sections 5.3.1 through 5.3.5 are based on a flow rate variation of 200 to 700 gpm.

- PRETREATMENT PROCESS USED: LIME-SODA SOFTENING
- 1974 DOLLARS
- 1000 MW POWER PLANT SCRUBBER
- . LAND COSTS NOT INCLUDED
- TO CONVERT gpm TO cu m/hr MULTIPLY BY 0.227

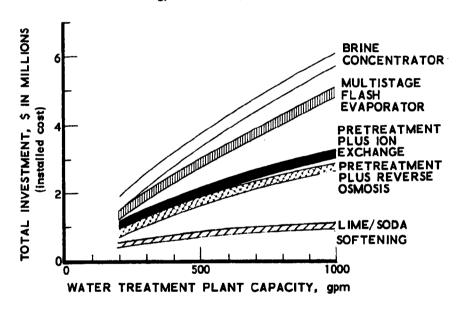


Figure 5-1. Estimated capital investment

- PRETREATMENT PROCESS USED: LIME-SODA SOFTENING
  1974 DOLLARS
  1000 MW POWER PLANT SCRUBBER
  COSTS BASED ON 30-YEAR ANNUALIZED COSTS, 4560 OPERATING
  HOURS PER YEAR AVERAGE OVER 30 YEARS

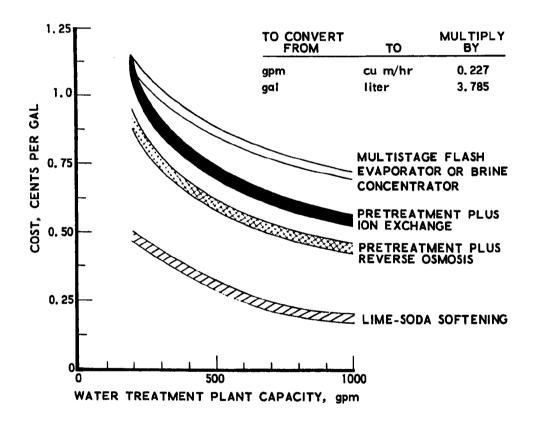
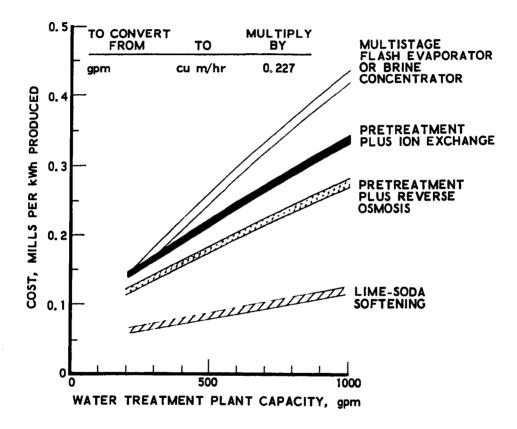


Figure 5-2. Estimated water treatment costs per gallon

- PRETREATMENT PROCESS USED: LIME-SODA SOFTENING

- 1974 DOLLARS
  1000 MW POWER PLANT SCRUBBER
  COSTS BASED ON 30-YEAR ANNUALIZED COSTS, 4560 OPERATING
  HOURS PER YEAR, AVERAGE OVER 30 YEARS



Estimated water treatment costs per kilowatt hour Figure 5-3. for power output of 1000 MW

- PRETREATMENT PROCESS USED: LIME-SODA SOFTENING
- 1974 DOLLARS
- 1000 MW POWER PLANT SCRUBBER
- COAL: TYPE No. 1 -- 12,500 Btu/lb, 0.84 lb/kWh

TYPE No. 2 -- 8,000 Btu/lb, 0.92 lb/kWh

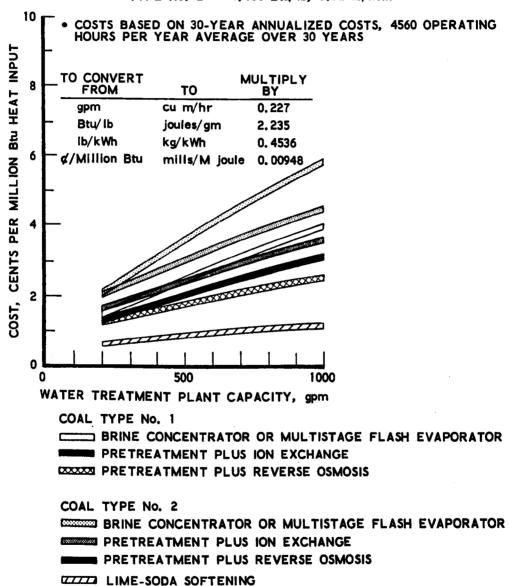


Figure 5-4. Estimated water treatment costs per million Btu heat input for power output of 1000 MW

- PRETREATMENT PROCESS USED: LIME-SODA SOFTENING
- 1974 DOLLARS
- 1000 MW POWER PLANT SCRUBBER
- COAL: TYPE No. 1 -- 12,500 Btu/lb, 0.84 lb/kWh

TYPE No. 2 -- 8,000 Btu/lb, 0.92 b/kWh

• COSTS BASED ON 30-YEAR ANNUALIZED COSTS, 4560 OPERATING HOURS PER YEAR AVERAGE OVER 30 YEARS

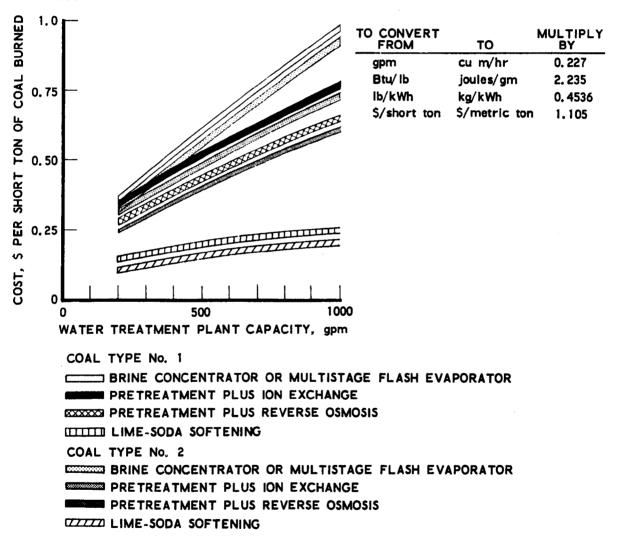


Figure 5-5. Estimated water treatment costs per ton of coal burned for power output of 1000 MW

# 5.3.1 <u>Lime-Soda Softening</u>

Capital investment charges vary from \$0.47M to \$0.9M, and total average treatment costs over 30 years, including annualized capital charges and operating costs, vary from 0.51 cents per gallon to 0.25 cents per gallon over the same range. These costs convert to the following:

- a. From 0.053 to 0.092 mills per kWh produced. The power was assumed to be produced at an average annual rate of 4560 million kWh.
- b. From 0.0047 to 0.0081 mills per megajoule (0.51 to 0.88 centers per million Btu) heat input from Type 1 coal and from 0.0067 to 0.0116 mills per megajoule (0.73 to 1.26 cents per million Btu) heat input for Type 2 coal.
- c. From 0.14 to 0.24 dollars per metric ton (0.13 to 0.22 dollars per short ton) of coal burned for Type 1 coal and 0.13 to 0.22 dollars per metric ton (0.12 to 0.20 dollars per short ton) of coal burned to Type 2 coal.

#### 5.3.2 Lime-Soda Pretreatment Plus Reverse Osmosis

The capital investment varies from 3/4 to 2 million dollars. Athough currently used membranes have a service life of about 3 years (depending upon the specific operating conditions and quality of the feed water), industry sources are predicting a membrane life of 5 to 6 years for membranes now being evaluated; therefore, membrane life was assumed to be 5 years. Labor expenses were assumed to be \$200,000 per year.

The average water treatment costs for the lime-soda softening pretreatment plus reverse osmosis over a 30-year period, range from 0.90 to 0.51 cents per galloon. These costs convert to:

a. From 0.11 to 0.22 mills per kWh produced. Power was assumed to be produced at an average annual rate of 4560 million kWh.

- b. From 0.011 to 0.019 mills per megajoule (1.2 to 2.0 cents per million Btu) heat input for Type 1 coal and from 0.014 to 0.027 mills per meagjoule (1.5 to 2.9 cents per million Btu) heat input for Type 2 coal. (See Section 5.3 for a definition of Type 1 and 2 coals.)
- c. From 0.31 to 0.57 dollars per metric ton (0.28 to 0.52 dollars per short ton) of coal burned for Type 1 coal and 0.28 to 0.53 dollars per metric ton (0.25 to 0.48 dollars per short ton) of coal burned for Type 2 coal.

### 5.3.3 Lime-Soda Softening Plus Ion Exchange

The initial investment ranges from \$1.1 to 2.5 million. The resin life was estimated to be 5 years. The estimated average water treatment costs over a period of 30 years for the flow rate range assumed above are as follows:

- a. From 1.1 to 0.62 cents per gallon of water treated.
- b. From 0.14 to 0.27 mills per kWh produced. Power was assumed to be produced at a constant average annual rate of 4560 million kWh.
- c. From 0.011 to 0.023 mills per megajoule (1.2 to 2.5 cents per million Btu) heat input for Type 1 coal and from 0.019 to 0.034 mills per megajoule (2.0 to 3.6 cents per million Btu) for Type 2 coal. (See Section 5.2.2.2 for a definition of Type 1 and 2 coals.)
- d. From 0.39 to 0.67 dollars per metric ton (0.35 to 0.61 dollars per short ton) of coal burned for Type 1 coal and 0.35 to 0.63 dollars per metric ton (0.32 to 0.57 dollars per short ton) of coal burned for Type 2 coal.

These costs are about 20 to 30 percent higher than the pretreatment process plus reverse osmosis operation that will provide water of comparable quality.

In reviewing the quality of the water produced and the investment and treatment costs, it appears as if the lower cost pretreatment and reverse osmosis operation is a more cost-effective

approach than pretreatment and an ion exchange operation to provide water of sufficient quality for reuse or discharge.

# 5.3.4 Multistage Flash Evaporator

The estimated investment for a multistage flash evaporation facility ranges from about \$1.4 to 3.7 million (Figure 5-1). These values are 60 to 90 percent more than for comparable quality water obtained from the pretreatment process plus a reverse osmosis operation, and the average water treatment costs are estimated to be 1-1/4 to 1-2/3 times higher (Figures 5-2 through 5-5).

Consequently, it does not appear to be cost effective to use a multistage flash evaporator to treat scrubber water when the lime-soda softening and reverse osmosis process will provide the quality of water needed at a lower cost.

#### 5.3.5 Brine Concentrator

Brine concentrators have been operational only a relatively short time compared to other available water treatment processes. The estimated initial investment and water treatment costs are compared to the other processes in Figures 5-1 to 5-5. The economic analysis was made on the same basis as previously described, except that the labor was reduced to only a part-time operator on the recommendation of the manufacturer, thus, the labor was estimated at \$50,000 per year. It is expected that in the future the brine concentrator costs can be reduced. However, at the present time this process is technically compatible with the requirement to produce a product with reduced concentrations of ingredients to meet the water quality criteria, but it does not appear to be as cost effective to employ this process for low cost, off-the-shelf water treatment for scrubber liquor when other processes such as lime-soda softening and reverse osmosis could accomplish the same function at a lower cost.

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#### APPENDIX A

# DESCRIPTION OF CHEMICAL ANALYSIS TECHNIQUES

#### A.1 INTRODUCTION

This appendix describes the analytical techniques (Refs. 63 and 64) used to determine the concentration of constituents in the scrubber liquors. The constituents are divided into (a) major chemical species (calcium, sodium, sulfate, and chloride), (b) trace metal species, and (c) additional chemical species. Other water quality tests are also described.

Consideration was given to the constituent's range of concentration and to the corresponding costs of the analyses to obtain data having high precision or high accuracy. Although the basis for selecting the proper analytical technique was minimizing any interference from other species, the presence of chemical species interfering with a particular analysis was fully acknowledged. Only when the interference was considered significant were corrections applied.

# A.2 MAJOR CHEMICAL SPECIES

#### A. 2. 1 Calcium Determination

The method selected from among several has an accuracy of 4 percent and was one in which calcium oxalate was precipitated

<sup>&</sup>quot;Precision is defined as the relationship between a measured value and the statistical mean of measured values, and accuracy is the relationship between the true value and the measured value.

and filtered from the solution, the filter cake was redissolved in HCl, and the solution was titrated against KMnO<sub>4</sub> to a characteristic purple end point. Correction was then made for excess permanganate at the characteristic end point.

Alternative techniques using a specific ion electrode and atomic absorption spectrophotometry were eliminated because they had lower accuracies resulting from interferences, primarily from the sulfate ions.

# A. 2. 2 Sodium Determination

Atomic absorption spectrophotometry was selected in preference to a method that determines sodium gravimetrically by separating the calcium salts from the sodium salts in the scrubber liquors by fractional precipitation. The selected technique uses a Perkin-Elmer 303 instrument with a graphite furnace at 3302Å wavelength. For every test the liquor concentration required multiple dilutions to achieve a level suitable for optimum analytical determination. Any errors in results tend to be high because of the effects of interference and the high concentration of sodium in the scrubber liquors; however, the errors are less than 10 percent.

#### A. 2. 3 Sulfate Determination

Standard nephelometry techniques are used for this task. A barium sulfate precipitate was formed by the reaction of the sulfate ion with a barium chloranilate reagent. The resulting turbidity was determined by a spectrophotometer and compared to a curve from standard sulfate solutions. Although multiple dilutions are necessary to bring the concentration to a range of optimum reliability, the resulting error is less than 10 percent.

#### A.2.4 Chloride Determination

A solid-state electrode was used to determine the electrode potential of chloride ions in scrubber liquors. The results were compared against a standard curve. This method has a precision of about 1 percent and an accuracy greater than 5 percent.

# A.3 TRACE METAL SPECIES

Since most trace metal species are highly sensitive to atomic absorption spectrophotometry, this technique was used. A Perkin-Elmer 303 instrument, with deuterium background corrector, and a graphite tube heater, for increased sensitivity, were used to determine soluble concentrations for the following elements: aluminum, antimony, boron, beryllium, cadmium, chromium, copper, cobalt, iron, magnesium, manganese, molybdenum, nickel, lead, silicon, silver, tin, vanadium, and zinc. Precision and accuracy are dependent upon the specific element, its relative concentration, and the extent of interference. The precision and accuracy of the measurements of concentrations of all elements that exceed water quality reuse criteria ranged between 5 and 20 percent.

Mercury was also determined using this technique; however, the mercury is reduced to the elemental state with stannous chloride and the absorption produced from the resulting mercury vapor is measured. This method has a precision of about 20 percent and an accuracy probably greater than 50 percent.

Arsenic was determined by the Gutzeit method that reacts arsine with mercurous bromide to produce  $Hg_3As$ ; the unknown is compared colorimetrically against standards. For this application this technique has a precision of about 25 percent and an accuracy probably greater than 50 percent.

A fluorimetric technique that has a sensitivity down to micrograms per liter was used to determine selenium. It has a precision of about 10 percent and is accurate to 100 percent.

#### A.4 ADDITIONAL CHEMICAL SPECIES

If these species existed in sufficiently high concentration, they would affect the water quality of the liquors; however, most of them were present in trace quantity and their importance in defining water quality was considered insignificant. Therefore, precise or complete analyses were not considered of particular value to this program. The concentration of many of them is controlled by interaction with one or more of the major species. Their expected concentration was determined using an Aerospace Corporation developed computer program (part of the work for a related EPA contract) that calculates the maximum concentration of each minor species in chemical equilibrium with the major species in the system. The experimental determinations were always in agreement with the expected concentration values.

# A.4.1 Carbonate Determination

Total carbonate was determined gravimetrically by the absorption of CO<sub>2</sub> evolved from an acidified sample. This technique does not have high sensitivity and could not detect concentrations in scrubber liquors at values less than 10 mg/l carbonate. (The expected value determined by the Aerospace computer program was typically less than 1 mg/l for all samples analyzed.)

#### A.4.2 Sulfite Determination

Total sulfite was determined using a specific ion electrode and no significant interferences were observed. The oxidation of the sulfite ion to sulfate in the scrubber liquor was found to be a very rapid reaction. Liquor protected from the atmosphere will typically reveal concentrations of several hundred milligrams per liter of the sulfite ion; however, a brief atmospheric exposure will cause oxidation and reduce these concentrations by one or more orders of magnitude.

The reported sulfite measurements were for samples analyzed immediately upon arrival in the laboratory. No specific action was taken to inhibit oxidation other than to ensure that the samples were transported from the power plant scrubber to the analytical laboratory in sealed containers. The exposure to air during sampling, filtering, and measuring, however, resulted in the sulfite values reported. It is presumed that these concentrations would probably more closely represent the oxidation state of liquor in the event of their potential discharge.

# A.4.3 Phosphate Determination

The phosphate analysis was determined by spectrophotometry methods, using ammonium molybdate to form the molybdenum blue complex. Total range of phosphate content varied from 0.5 mg/l in an acid liquor (pH = 4.3) to 0.01 mg/l in a base liquor (pH = 10.4).

# A.4.4 Nitrogen Determination

Total nitrogen was determined by the Kjeldahl method which converts organic nitrogen components to ammonia. The ammonia is then distilled and the amount determined by titration. This method has a precision of about 10 percent, and accuracy at the levels of the concentrations determined is about 25 percent.

# A.4.5 Fluoride Determination

The fluoride ion was determined by the specific ion electrode using a Beckman Model 76 digital pH meter. There are no significant interferences in the scrubber liquors. This method has a precision of about 5 percent; an accuracy of 20 percent is attainable at the low levels measured.

#### A.5 OTHER WATER QUALITY TESTS

#### A. 5. 1 Chemical Oxygen Demand

Chemical oxygen demand was determined by reacting the organics and sulfites present with potassium dichromate and measuring the reduced chromium by spectrophotometry. While a precision of 25 percent is attainable, accuracy depends on the sample history (i.e., degree of exposure to atmospheric oxygen) and is about 100 percent for routine analysis.

# A.5.2 Total Alkalinity

Total alkalinity is determined by titrating a 25 ml sample with standard acid to a pH of 4.0. The Beckman Model 76 digital pH meter is used as the indicating instrument. Total alkalinity is expressed as milligrams per liter calcium carbonate, but is actually a determination of the buffering capacity of the liquor due to a number of weak acid species (i.e., carbonate, sulfite, borate, arsenite, selenite, and silicate). Precision is about 5 percent and accuracy is estimated to be 25 percent.

#### A. 5. 3 Total Dissolved Solids Determination

The total dissolved solids are determined gravimetrically by evaporating a 10 to 25 ml sample overnight in a tared weighing bottle under vacuum at 120°F. Since two of the major constituents (calcium and sodium sulfates) form stable hydrated salts and are very hygroscopic in the anhydrous state, prolonged drying and minimal exposure of the dried residue are mandatory. The precision is about 2 percent, and the accuracy is about 5 percent.

#### A. 5.4 Total Conductance Determination

This measurement, which was made with a General Radio Impedance Bridge Type 1650A, gives an estimate of the total

ionic strength of the liquor. Precision is about 1 percent, and accuracy is estimated to be about 2 percent.

# A.5.5 pH Determination

This parameter is measured with a Beckman Model 76 digital pH meter to a precision of 0.2 percent and an accuracy of 1 percent.

# A.5.6 Turbidity Determination

Turbidity measurements were made by nephelometry in which light absorption is compared to standards that were prepared using a formazin mixture that is a mixture of hydrazine sulfate and hexamethylene tetramine in a water solution. Most scrubber liquor samples were obtained as slurries and were virtually opaque. Chemical analyses were performed on filtered samples, and turbidity values were also obtained on these filtered samples. Only a few samples were obtained as filtrate; their results are reported as received rather than after filtering.

#### APPENDIX B

#### COSTING BACKGROUND DATA

# B.1 INTRODUCTION

This appendix describes the methodologies used in preparing the cost estimates for the various water treatment processes analyzed in this study. The rationale used for both capital and operating costs is presented.

# B. 2 CAPITAL AND OPERATING COSTS

The cost data obtained from the various sources listed in the reference section were converted, in all cases, to equivalent 1974 dollars. This conversion was made by use of an appropriate economic indicator such as the Plant Cost Index published monthly in Chemical Engineering. The estimated capital and operating costs for each water treatment process are included with the description of each process and are based on treating 200 to 1000 gpm. Total annualized costs were compiled as the total of annualized capital costs and operating costs.

# B. 2. 1 Capital Cost Estimates

The capital costs for the various water treatment processes were based on an equipment operational life of 30 years. The annualized capital charges were estimated on this basis and include elements such as insurance, cost of capital, depreciation, replacements, and taxes. Certain specific equipment items, such as reverse

osmosis membranes, identified as having a service life less than 30 years were depreciated on an accelerated schedule, e.g., five years. The itemized approach for computing annualized capital charges is shown in Table B-1. It should be noted that the cost of land was not included in the capital cost estimates.

The estimated capital costs for various water treatment processes can be illustrated by the approach used on lime-soda ash softening. From data obtained from the references, installed costs were generated for the clarifier-reactant tank, the chemical storage hopper and feed system, the filter, two surge tanks, five pumps (plus five spares), piping for the complete facility, and building and site improvements. The pumps and piping were assumed to be fabricated with stainless steel because of the corrosive nature of the water being handled. These costs were derived as a function of flow rate. An additional 10 percent was added for interest expense during construction. The average annualized capital charges were computed on the total of these amounts at the rate of 18 percent, as described in Table B-1. This same procedure was used in arriving at the capital cost estimates for the other water treatment processes.

#### B. 2. 2 Operating Cost Estimates

The operating cost estimates were computed on the basis of 4560 hours per year (190 days) as an average over 30 years. Again, using the lime-soda treatment as an example, the chemical costs, utility power, materials, operating labor, and maintenance labor were computed as a function of flow rate. An overhead rate of 20 percent was applied to the total of these costs. As stated above, annualized capital and operating costs were combined to obtain total annual costs.

Table B-1. AVERAGE ANNUALIZED CAPITAL CHARGES (30-YEAR LIFE - 1974 DOLLARS)

# Straight line depreciation is assumed

Cost elements		Percentage of capital investment	
Depreciation based on 30-year life			3,33
Replacements items: 20% of depreciation			0.67
Insurance			0.50
		Subtotal	4.50
Cost of	capital:		
•	50% debt @ 11% 11% (0.5)		5.50
•	50% equity @15% 15% (0.5)		7.50
Taxes			
•	Assume Federal tax to be the same as equity		7.50
•	Other taxes at 80% of Federal		6.00
1		Subtotal	26.50
On a 30 year basis, the average annual capital charge on initial investment is			
$4.50 + \frac{26.50}{2} = 17.75\%$		Total	17.75

# B. 3 WATER TREATMENT COST CURVES

The cost curves presented in Section 5.2 of this report were based on the operation of a scrubber at a 1000 MW station. The cost parameters are plotted as a function of flow rate for each of the five processes considered to be readily adaptable to treating scrubber bleed water.

### B. 3. 1 Capital Investment

The data plotted in the curves shown in Figure 5-1 represent the costs for materials and labor to install the water treatment processing equipment, including contractors' fees, engineering design, construction supervision, and interest expenses during construction at a rate of 8 percent annually. These curves do not include land costs, start-up costs, or brine disposal. The cost estimates were prepared by contacting manufacturers, the treatment industry, and government experts, as well as conducting a thorough literature search.

#### B. 3. 2 Treatment Costs per Gallon

The estimated water treatment costs per gallon (Figure 5-2) were prepared for each process by combining the annual capital and operating costs as a function of the total annual flow rate. The annualized capital charges were calculated as described in Section B. 2.1. The annual operating costs were estimated as described in Section B. 2.2.

# B. 3. 3 Treatment Costs per Kilowatt Hour

The process treatment costs per kilowatt hour (Figure 5-3) were computed from the total annual costs consisting of annualized capital charges as described in Section B. 2. 1, plus annual operating costs, for 4560 operating hours per year. The average annual energy output was assumed to be  $4.56 \times 10^9$  kWh.

# B. 3.4 <u>Treatment Costs per Million BTU</u> Heat Input

Water treatment costs as a function of Btu input (Figure 5-4) were computed from the total annual costs for each treatment process and the weight and Btu content of the two types of coal considered. The coal quantities computed were based on a 1000 MW output and 4560 average operating hours per year.

# B. 3. 5 Water Treatment Costs per Ton of Coal

The total annual costs for each water treatment process were computed as a function of weight of coal burned. Consideration was given to the characteristics of type 1 and 2 coal for a 1000 MW station. The same average annual operating period of 4560 hours was used for this calculation as for the other operating curves.

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)				
1. REPORT NO. 2. EPA-600/2-76-024	3. RECIPIENT'S ACCESSION NO.			
4. TITLE AND SUBTITLE Reuse of Power Plant Desu Ifurization Waste Water	5. REPORT DATE February 1976 6. PERFORMING ORGANIZATION CODE			
R. C. Rossi, and J. Rossoff	8. PERFORMING ORGANIZATION REPORT NO.			
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation 2350 East El Segundo Boulevard El Segundo, California 90245	10. PROGRAM ELEMENT NO.  1BB392; ROAP R21AZU-025  11. CONTRACT/GRANT NO.  Grant R-802853-01-0			
EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Final; 1/74-4/75  14. SPONSORING AGENCY CODE			

15. SUPPLEMENTARY NOTES For technical details contact Fred Roberts, EPA, Environmental Research Laboratory, 200 SW 35th St., Corvallis, Oregon 97330

from nonregenerable flue gas desulfurization systems by applying available water treatment processes. Although scrubbers normally operate in a closed-loop mode, this study investigated liquor reuse if a scrubber purge became necessary as a result of off-design or other operating conditions. Chemical characterizations were performed on liquors from four different scrubbers; these were assessed for use as power plant service water or for direct discharge. Treatment is required for either use; but, in most cases (for economic reasons), treatment for discharge is not recommended. Chemical precipitation (e.g., lime-soda softening, filtration, and pH control) is adequate for most service water usage cases. Cases involving high chloride content in the purge liquor would require an additional treatment such as reverse osmosis, as would all cases for direct discharge. The applicabilities of available treatment systems are given, in addition to scrubber flow diagrams, water balance, and treatment costs for a range of liquor flow rates.

17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DE	SCRIPTORS	b.IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group		
Air Pollution Waste Water Liquids Regeneration (Engineering) Reclamation	Water Treatment Electric Power Plants Flue Gases Desulfurization Scrubbers Chemical Analysis	Air Pollution Control Stationary Sources Reuse	13B 10B 21B 07A		
13. DISTRIBUTION STATEMENT  Unlimited		19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified	21. NO. OF PAGES  136  22. PRICE		