Upper Colorado River Basin 13(a) Assessment:

COSTS OF WASTEWATER DISPOSAL IN COAL GASIFICATION AND OIL SHALE PROCESSING

A report to the

Executive Director's Office
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CONVERSION FACTORS

Conversion of American to International System (SI) Units

	Multiply	By	To Obtain
ACCELERATION	foot/second^2	3.048×10^{-1}	meter/second^2
	free fall, standard	9.807	meter/second^2
AREA	acre	4.047×10^{3}	meter^2
	feet^2	9.290×10^{-2}	meter^2
ENERGY	Btu (mean)	1.056×10^{3}	joule
	calorie (mean)	4.190	joule
	kilowatt-hours	3.60×10^{6}	joule
ENERGY/AREA-TIME	Btu/foot^2 hour	3.152×10^{-1}	watt/meter^2
	Btu/foot^2 minute	1.891×10^{2}	watt/meter^2
	Btu/foot^2 second	1.135×10^{4}	watt/meter^2
	calorie/cm^2 minute	6.973×10^{2}	watt/meter^2
FORCE	dyne	1.00×10^{-5}	newton
	kilogram force (Kg_f)	9.807	newton
	pound force (lb_f, avoirdupois)	4.448	newton
LENGTH	foot	3.048×10^{-1}	meter
	mile	1.609×10^{3}	meter
MASS	pound (avoirdupois)	4.536×10^{-1}	kilogram
	ton (metric)	1.00×10^{3}	kilogram
	ton (short, 2000 lb)	9.072×10^{2}	kilogram
MASS/TIME	pound/hour	1.260×10^{-4}	kilogram/second
	pound/minute	7.560×10^{-3}	kilogram/second
	ton (short)/hour	2.520×10^{-1}	kilogram/second
	ton (short)/day	1.050×10^{-2}	kilogram/second
MASS/VOLUME	gram/centimeter^3	1.00×10^{3}	kilogram/meter^3
	pound/foot^3	1.602×10^{1}	kilogram/meter^3
	pound/gallon (U.S. liquid)	1.198×10^{2}	kilogram/meter^3
MISCELLANEOUS	Btu/hr-ft^2-°F	5.674	joules/sec-m^2-°C
	Btu/kw-hr	2.929×10^{-1}	joules/kw-sec
	Btu/lb	2.324×10^{3}	joule/kg
	Btu/lb-°F	4.184×10^{3}	joule/kg-°C
	gal/10^6 Btu	3.585×10^{-12}	meter^3/joule
	kilocalorie/kilogram	4.184×10^{3}	joule/kg
POWER	Btu/hour	2.939×10^{-1}	watt
	Btu/minute	1.757×10^{1}	watt
	Btu/second	1.054×10^{3}	watt
	calorie/hour	1.162×10^{-3}	watt
	calorie/minute	6.973×10^{-2}	watt
	calorie/second	4.184	watt
	horsepower	7.457×10^{2}	watt
PRESSURE	atmosphere	1.013×10^{5}	pascal (= newton/m^2)
	foot of water (39.2°F)	2.989×10^{3}	pascal
	psi (lb_f/in^2)	6.895×10^{3}	pascal
	lb_f/foot^2	4.788×10^{1}	pascal
SPEED	foot/minute	5.08×10^{-3}	meter/second
	foot/second	3.048×10^{-1}	meter/second
	mile/hour	4.470×10^{-1}	meter/second
TEMPERATURE	°F	0.556 (°F + 459.7)	°K

(continued)

CONVERSION FACTORS (continued)

	Multiply	By	To Obtain
VOLUME	acre foot	1.590×10^{-1}	meter^3
	barrel (oil, 42 gal)	1.233×10^{3}	meter^3
	foot^3	2.832×10^{-2}	meter^3
	gallon (U.S. liquid)	3.785×10^{-3}	meter^3
VOLUME/TIME	ft^3/min	4.719×10^{-4}	meter^3/second
	ft^3/sec	2.832×10^{-2}	meter^3/second
	gal (U.S. liquid)/day	4.381×10^{-8}	meter^3/second
	gal (U.S. liquid)/min	6.309×10^{-5}	meter^3/second

Other Conversion Factors

The following table is based on a density of water of 62.3 pounds per cubic foot. This is the density of water at 68°F (20°C) and corresponds to 8.33 pounds of water per gallon.

acres	4.36×10^{4}	square feet
acres	1.56×10^{-3}	square miles
acre-feet	4.36×10^{4}	cubic feet
acre-feet	3.26×10^{5}	gallons
acre-feet/year	1.38×10^{-3}	cubic feet/second
acre-feet/year	3.91×10^{-5}	cubic meters/second
acre-feet/year	6.20×10^{-1}	gallons/minute
acre-feet/year	8.93×10^{-4}	million gallons/day
barrels, oil	4.2×10	gallons
Btu	2.52×10^{2}	calories
Btu	3.93×10^{-4}	horsepower-hours
cubic feet	2.30×10^{-5}	acre-feet
cubic feet	7.48	gallons
cubic feet of water	6.23×10^{1}	pounds of water
cubic feet/second	4.49×10^{2}	gallons/minute
cubic feet/second	6.46×10^{-1}	million gallons/day
gallons	3.07×10^{-6}	acre-feet
gallons	2.38×10^{-2}	barrels, oil
gallons	1.34×10^{-1}	cubic feet
gallons of water	8.33	pounds of water
gallons/minute	1.61	acre-feet/year
gallons/minute	2.23×10^{-3}	cubic feet/second
gallons/minute	1.44×10^{-3}	million gallons/day
gallons of water/minute	5.00×10^{-1}	thousand pounds of water/hr
horsepower	6.11×10^{4}	Btu/day
horsepower	2.55×10^{3}	Btu/hour
kilowatt-hours	3.41×10^{3}	Btu
milligrams/liter	1	parts/million
million gallons/day	1.12×10^{3}	acre-feet/year
million gallons/day	1.55	cubic feet/second
million gallons/day	6.94×10^{2}	gallons/minute
million gallons of water/day	3.47×10^{2}	thousand pounds of water/hr
pounds of water	1.20×10^{-1}	gallons of water
pounds of water	1.60×10^{-2}	cubic feet of water
pound moles of gas	3.80×10^{2}	standard cubic feet of gas
square feet	2.30×10^{-5}	acres
temperature, °C	1.8	32 - °F
temperature, °F-32	5.56×10^{-1}	°C
thousand pounds/hour	1.2×10	tons/day
thousand pounds/hour	4.38×10^{3}	tons/year
thousand pounds of water/hour	2.00	gallons of water/minute
thousand pounds of water/hour	2.88×10^{-3}	millions gals of water/day
tons (short)	2×10^{3}	pounds
tons (short)	9.07×10^{-1}	metric tons
tons/day	8.33×10^{-2}	thousand pounds/hour
tons/year	2.28×10^{-4}	thousand pounds/hour
watts	3.41	Btu/hour

1. INTRODUCTION AND CONCLUSIONS

The Department of Natural Resources of the State of Colorado is, under agreement with the U.S. Water Resources Council, assessing aspects of development of a fuel industry in the Upper Colorado River Basin. To assist, Water Purification Associates has studied the monetary costs of disposal of the wastewaters produced by coal gasification and oil shale retorting. The study is divided into three sections:

Coal Gasification
Surface Retorting of Oil Shale
Modified In Situ Retorting of Oil Shale

The conclusions are tabulated below and a very brief summary is presented as Tables 1-1, 1-2, and 1-3.

1.1. Conclusions - Coal Gasification

Coal conversion plants producing gas generate two different major types of wastewater streams that are difficult to treat and/or dispose of. The first type are blowdown streams from boiler feedwater treatment and cooling towers that are highly concentrated in salt. These streams are of a relatively high volume and are expensive to dispose of because the salts are leachable and may contaminate underground waters unless contained properly. Return to the river is not an acceptable disposal option in the Upper Colorado River Basin.

The second important wastewater is the wastewater stream condensed out of the product fuel process lines. The water is derived from the hydrogenation of oxygen in the coal, from moisture in the coal, and from unreacted steam put through the coal conversion reactor. The condensate flow rates are relatively large, show a wide variation, and may contain large quantities of ammonia, carbon dioxide, phenols and other organics. In most conversion processes the condensate wastewater is so contaminated that its release to the environment in any form is unacceptable. Apart from the prohibitive cost of evaporation ponds for disposing of such a large wastewater stream, ammonia and volatile organic matter will cause serious air pollution if this water is stored. Another option is to use treated condensate as makeup to a cooling tower because a circulating cooling system can accept considerably more organic material and ammonia than would be permissible for discharge to a river. However, the cooling tower blowdown then becomes the principal discharge point for the whole plant and the water will contain, in addition to the usual concentrated salts, residues of organic matter originating

TABLE 1-1 SUMMARY OF WASTEWATER STREAMS AND TREATMENT COSTS FOR COAL GASIFICATION

Waste Stream	Flow Rate (AF/yr)	Quality Before Treatment	Disposal Options	Approximate Cost (¢/million Btu)
Runoff	< 200, very variable	good, with possibly oily contamination	1) removal of oil and reuse in cooling system	not estimated
Boiler feedwater preparation waste	320, with variations of twofold to one-fifth	2.0 to 2.5% dissolved inorganic solids	1) with coal ash* 2) lined evaporation pond 3) vapor compression and then lined evaporation pond	negligible 0.12-1.2 0.14-2.1
Foul process condensate	2,250, with variations of twofold to one-fifth	high level of ammonia, BOD, COD, & phenols	1) sequential treatment for use in cooling tower ** a) ammonia stripping and recovery b) solvent extraction c) biological oxidation	 not estimated*** 1.25-5.0 0.35-1.4
Cooling tower blowdown	350, with variations of twofold to one-fifth	dependent upon the gasification process****	1) with coal ash* 2) with coal ash after reduction of organic contamination 3) lined evaporation pond 4) vapor compression and then lined evaporation pond	negligible 0.05-6.0 0.35-1.4 0.4-2.4
Domestic wastes at plant	45	low TDS, BOD = 200-250 mg/l	1) secondary treatment and low-quality in-plant use or revegetation	0.03

*If ground water is protected.

**It is anticipated that foul process condensate will be treated only as much as is necessary in order to make it acceptable for make-up to a cooling tower (when diluted with additional river water).

***In most plants, the cost of treatment would be offset by the value of the ammonia recovered.

****The reason for this is that the kind of gasification process controls the quality of the make-up water in the cooling tower (i.e., the foul process condensate produced varies from process to process). Bad quality blowdown would be expected to have the following concentrations of constituents (in mg/l): phenols (8-20), BOD (2,000-5,000), COD (7,000-17,000), ammonia (less than 20), and TDS (2,000-6,000+).

TABLE 1-2 SUMMARY OF WASTEWATER STREAMS AND TREATMENT COSTS FOR SURFACE RETORTING OF OIL SHALE

Waste Stream	Flow Rate (AF/yr)	Quality Before Treatment	Disposal Options	Approximate Cost (¢/million Btu)
Runoff	very variable	in plant area, good with possibly oily contamination; in processed shale area, poor	1) removal of oil and reuse in cooling system	not estimated
			2) moisturize spent shale	negligible
Boiler feedwater preparation waste	2-90 (Paraho) 120-220 (TOSCO II)	2.0 to 2.5% dissolved inorganic solids	1) moisturize spent shale*	negligible
			2) lined evaporation pond	< 0.1 (Paraho) 0.3-0.5 (TOSCO II)
			3) vapor compression-lined evaporation pond	< 0.3 (Paraho) 0.4-1.1 (TOSCO II)
Retorting & upgrading wastewaters	430 (TOSCO II) 565-710 (Paraho)	high in ammonia, H_2S, CO_2, and organic matter; low in phenols	1) sequential treatment for use in cooling tower**	
			a) ammonia stripping and recovery	not estimated***
			b) biological oxidation	0.8-3.1
Cooling tower blowdown	420-1,240	better than that in coal gasification****	1) moisturize shale*	negligible
	100-300*****		1) lined evaporation pond	0.2-0.6
			2) vapor compression lined evaporation pond	0.3-1.5
Sour water stripper	420	COD ~ 500-1,500 mg/l; phenols ~80-150 mg/l	1) dust control	< 0.2
Domestic wastes at plant	24	low TDS, BOD = 200-250 mg/l	1) secondary treatment and low-quality in-plant use or revegetation	0.01

*This is the most probable means of disposal for the TOSCO II process. Thus, the other disposal options would likely be employed only for a Paraho type process.

**It is assumed that these waste streams are treated only enough to render them suitable for use as make-up to a cooling tower. It is further assumed that no more than about 15 percent of the cooling tower make-up comes from this source.

***In most plants, the cost of treatment would be offset by the value of the ammonia recovered.

****By way of comparison, see table 1-1. The reason for the improved quality is that the phenol content of retorting and upgrading waste streams is much lower than that for foul process condensate from coal gasification. Furthermore, the dilution of retorting and upgrading streams in the cooling tower make-up is much greater.

*****If not spent for shale moisturization, the volume of blowdown would be decreased by increasing the cycles of concentration in the cooling tower.

TABLE 1-3 SUMMARY OF WASTEWATER STREAMS AND TREATMENT COSTS FOR MODIFIED IN-SITU RETORTING OF OIL SHALE

Waste Stream	Flow Rate (AF/yr)	Quality Before Treatment	Disposal Options	Approximate Cost (c/million Btu)
Mine drainage water				
treatment for plant use*	2,970	TSD = 900-1,350 mg/l; high flouride and boron concentrations	1) in-plant uses	0.7-0.9
treatment of excess**	3,460-15,130	same as above	1) discharge to river	2.0-9.0
Boiler feedwater treatment blowdown***	24	1-2% TDS	1) low-quality water needs	negligible
Retort water	2,670	foul water with high concentration of ammonia, BOD, and COD	1) treatment for make-up to cooling tower****	2.2
Cooling tower blowdown	110-260*****	lower organics and higher TDS than for coal gasification	1) shale disposal, mine uses	negligible
Domestic wastes at plant	70	low TDS, BOD = 200-250 mg/l	1) secondary treatment and low-quality in-plant uses or revegetation	0.04
Runoff and leachate	200 (plant) 420 (shale disposal)	good fair to good	1) low-quality water needs	not estimated

*The portion of the mine drainage water to be used in the plant would have to be treated first. Electrodialysis or reverse osmosis are the probable treatment processes, with separate removal of boron by ion exchange for that part of the water needed for domestic, potable uses. The cost of this treatment is estimated to be about 0.7c-0.8c/million Btu. The quality of the waste concentrate from these steps would be about 5,500-8,000 mg/l of TDS and its volume about 440 acre-feet per year. The concentrate could be disposed of at a negligible cost by using it for dust control or shale disposal. If the volume of concentrate was too large, vapor compression with disposal to an evaporation pond could be used at an estimated cost of 0.1c/million Btu.

**Electrodialysis or reverse osmosis, with separate removal of boron by ion exchange, would be required in order to produce an effluent dischargeable to a river. The concentrate resulting from these steps would then have to be disposed of. This probably would be done by first reducing its volume with a vapor-compression evaporator, with final disposal to an evaporation pond. The estimated costs cover all of these treatment and disposal steps.

***Even after the mine drainage is treated for general plant use, "polishing" demineralization (by ion exchange) would be required for the water used in the boiler (to produce steam for injection into the retort). The disposal of the blowdown from this step is the item reflected by this entry.

****Quality of the foul retort water is highly uncertain at this time. Therefore, estimated treatment costs are very problematic. Treatment would entail stripping of ammonia and acid gases, removal of organics (probably through biological oxidation, although resin adsorption may prove viable), and reduction of bicarbonate levels through acidification or lime softening. The treated waste stream would be used as make-up to the cooling tower.

*****If the blowdown exceeds that which can be employed for shale disposal and mine uses, then its volume could first be reduced to no more than about 110 acre-feet per year by increasing the cycles of concentration in the cooling tower. Following this, vapor compression with disposal to a lined evaporation pond could be used, at an estimated cost of 0.2c/million Btu.

in the coal reactor. This wastewater must be disposed of in an environmentally acceptable manner.

There are a number of ways that the wastewater stream can be disposed of besides impoundment in evaporation ponds. One is to dispose of the wastewater by using it for dust control. However, the wastewater must be treated to remove any leachable contaminants, thus wastewaters containing highly concentrated salts will not be used for this purpose, but treated condensate may be used if ammonia and phenols are removed to sufficiently low levels. Not enough data is available to determine the proper limits for disposal. Another method of disposal is to wet down the coal ash with the concentrated blowdowns. The cost of disposal is negligible for this case if the coal ash site is prepared to prevent groundwater contamination from coal and ash leachates. We have not considered the cost that may be necessary to upgrade the ash site if salty water is used to wet the ash. Sufficient data is not available to determine the level of salts and organic matter in the wastewaters that may be unacceptable for disposal.

Contaminated rain run-off from the plant site, mining area and waste storage area is collected and impounded. Oil will be separated and the impounded water mixed with other waters as makeup to the circulating cooling system. We have not considered the costs of collecting, impounding and monitoring contaminated run-off.

The flow rates and costs of treatment and disposal are given below for a 250×10^6 scf/day coal conversion plant producing either pipeline gas, or medium or low Btu gas. The flow rates that are given are the operating on-stream flow rates. The costs are based upon a stream factor of 90 percent. As a basis of comparison, the cost of pipeline gas is estimated to be about $\$3\text{-}4/10^6$ Btu of product output.

Three waste streams are identified:

a) <u>Run-off from Rain</u>

<u>Quantity</u>: Very variable, maximum 125 gal/min (= 200 acre-ft/yr) based on 15 inches/yr rain on 160 acres.

<u>Quality</u>: Depends on housekeeping, may have oil, otherwise most probably good quality. Quality from coal pile depends on pyrite content of coal.

Disposal: Will be collected and impounded properly. Can be fed to cooling system or used for other low quality in-plant uses. No treatment except for oil separation. Costs not estimated.

b) Waste from Boiler Feedwater Preparation

Quantity: 200 gal/min (= 320 acre-ft/yr) with variations of two-fold to one-fifth.

Quality: 2 to 2.5% total dissolved solids; no organic contamination.

Disposal: (1) Not useful within the plant. May be mixed with coal ash at negligible cost if groundwater protected.

(2) Disposal in a lined evaporation pond averages $4.6/1000 gals (= $1500/acre-ft). A standard size plant requires about 110 acres with variations of two-fold to one-fifth. The cost is 0.6¢/10^6 Btu product output with the same variation.

(3) Blowdown might first be treated by a vapor compression evaporator and then disposed of in a much smaller pond. A vapor compression evaporator costs $5.6 to $10/1000 gals after taking credit for clean water recovered. The evaporation pond following a forced evaporator need be less than 10 acres. The total cost of vapor compression and natural evaporation is 0.7¢/10^6 Btu with variations of approximately three-fold to one-fifth.

c) Cooling Tower Blowdown

Note: Organically contaminated condensate, effluent from the gasifier, is assumed treated to such a quality that, when diluted with additional river water as needed, the mixture is satisfactory for makeup to a cooling tower. An example of a water acceptable in a cooling system is given on Table 2-10. Necessary treatments ahead of the cooling system are described in Section 2.7 and costs given. These treatments are taken to be essential for plant operation, as distinct from environmental protection, and not summarized here.

Quantity: 220 gal/min (= 350 acre-ft/yr) with variations of two-fold to one-half.

<u>Quality</u>: This is strongly dependent on the gasification process as this controls the quality of the cooling system makeup. A range of bad quality blowdown is shown on Table 2-12. Some gasification processes will have less organic contamination.

<u>Disposal</u>: Most plans call for disposal of this water with coal ash at zero treatment cost. If, for a chosen process, the organic content is unacceptable, it can be reduced by:

(1) Adding biotreatment to the makeup at a cost of \$2.4 to \$5.6/1000 gals (= \$780 - \$1830/acre-ft) blowdown or 0.3¢/10^6 Btu with variations of approximately five-fold to one-half.

(2) Adding resin adsorption to the makeup at a cost of \$9-21/1000 gals (= \$2930 - \$6850/acre-ft) blowdown, or 1.2¢/10^6 Btu with variations of approximately five-fold to one-half.

(3) Adding resin adsorption to the blowdown at a cost of about \$3/1000 gals (= \$980/acre-ft), or 0.4¢/10^6 Btu with variations of two-fold to one-half.

(4) Adding activated carbon adsorption to the blowdown at a cost very dependent on water quality and ranging from \$1 to over \$12/1000 gals (= \$330 - \$3900/acre-ft), or 0.1¢/10^6 Btu with variations of approximately 25-fold to one-half.

(5) Adding wet oxidation to the blowdown at a cost of about \$6/1000 gals (= \$1960/acre-ft), or 0.8¢/10^6 Btu with variations of two-fold to one-half.

Unfortunately, the quality effluent from these treatments cannot be defined. Resin adsorption is not an established technology. If it works, it will be placed in the blowdown at about \$3/1000 gals (Item (3) above). The second choice is biotreatment and its use depends on the biodegradability of the waste. The cost is probably higher than resin adsorption and the quality may be better or worse. Both activated carbon and wet oxidation are expected to give the best quality effluent. Wet oxidation, at \$6/1000 gals (= \$1960/acre-ft), will be used when activated carbon would cost more than this, otherwise carbon would be used.

If dissolved salts are unacceptable, evaporation ponds or forced evaporators must be used as described for boiler feed water waste above. This water is close to saturation in calcium carbonate and calcium sulfate and processes that do not tolerate precipitation, such as reverse osmosis, cannot be used.

(1) If the blowdown is disposed of in lined evaporation ponds, the cost is 0.7¢/10^6 Btu with variations of two-fold to one-half.

(2) If the blowdown is first treated by vapor compression and then disposed of in evaporation ponds, the cost is 0.8¢/10^6 Btu with variations of approximately three-fold to one-half.

d) Treatment of Foul Process Condensate for Internal Plant Reuse

Note: The following are conclusions drawn from the treatment of foul process condensate for use in the cooling system. This is not a wastewater stream intended for disposal.

Quantity: 1400 gal/min (= 2250 acre-ft/yr) with a range of about two-fold to one-half.

Quality: High levels of ammonia, BOD, COD and phenols. See tabulated examples in Appendix.

Treatment: Sequential treatment will be used to fit the water for makeup to the cooling system. Not all waters require all the following treatments:

(1) Solvent extraction for gross removal of phenols at a cost of about \$3/1000 gals (= \$980/acre-ft), or 2.5¢/10^6 Btu with a variation of about two-fold to one-half.

(2) Stripping and recovery of ammonia. In most plants this treatment is covered by the value of recovered ammonia.

(3) Biological oxidation at a cost of about \$0.80/1000 gals (= \$260/acre-ft), or 0.7¢/10^6 Btu with a variation of about two-fold to one-half.

e) Domestic Wastes from Plant

Quantity: 28 gpm (= 45 acre-ft/yr)

Quality: Typical domestic wastewater with a low TDS and a BOD of 200-250 mg/l after primary treatment.

Disposal: Secondary treatment by packaged activated sludge unit at a cost of \$1.95/1000 gals (= \$640/acre-ft), or 0.03¢/10^6 Btu, and then used for revegetation or low quality water needs.

1.2 Conclusions - Surface Retorting of Oil Shale

Two different water management schemes have been identified for an oil shale conversion complex in which surface retorting occurs. One scheme is characteristic of that used for an oil shale process in which the spent shale is disposed of in a manner similar to that proposed for Tosco II. The processed shale is moisturized, transported to the disposal site and compacted. The compacted shale has an in-place moisture content of about 13 percent after compaction. The shale is moisturized with all of the wastewaters generated in the plant and then some. This scheme obviously does not encourage reuse of the wastewaters. The only treatment that would be required would be to remove odorous, volatile substances, which is standard practice and is done as part of the normal upgrading operation. The cost of disposal for this type of management scheme is negligible.

The second scheme is characteristic of that used for an oil shale process in which the spent shale is disposed of in a manner similar to that proposed for Paraho. The Paraho design involves lining a valley with a thin impermeable layer of compacted spent shale which is wetted down. The remainder of the spent shale is deposited into the lined basin and is compacted, but not wetted down except for controlling dust. Less than one percent of the spent shale would be wetted down. However, the revegetation water requirements are larger for Paraho because of the higher residual carbon in the spent shale. The retorting and upgrading wastewaters will have to be treated for recycle and reuse within the plant. It cannot be used directly for revegetation because of its poor quality. With minimum treatment it could be disposed of in evaporation ponds, but this is wasteful of water. We will assume that the wastewater will be treated for use in a cooling tower, in a manner similar to that for a coal gasification plant. The only costs that will be presented are for the Paraho process and are based upon the results presented in Section 3. The flow rates and costs will be based on an oil shale complex designed to produce 50,000 barrels/day of synthetic crude plus any by products not utilized as plant fuel. They will also be normalized with respect to the heating value of the synthetic crude, which is 2.9×10^{11} Btu/day for the 50,000 barrel/day synthetic crude plant. A typical price for shale oil is \$15/barrel, or about \$2.50/10^6 Btu.

a) Run-off

Quantity: Very variable, depending on site.

Quality: In plant area, will contain residual oil. Near processed shale disposal area, will be of very poor quality, contains both organics and inorganics.

Disposal: Will be collected and impounded properly. Can be fed to cooling system or used to moisturize spent shale. Costs not estimated.

b) Boiler Feedwater Makeup Treatment Blowdown

Quantity: In range 1 to 60 gpm (2 - 90 acre-ft/yr) for Paraho, depending upon whether crude shale is upgraded. Approximately 120 to 220 gpm (≈ 190 to 350 acre-ft/yr) for Tosco II.

Quality: 2 to 2.5% total dissolved solids with no organic contamination.

Disposal: (1) Will probably be used to moisturize spent shale at negligible cost.

(2) Disposal in a lined evaporation pond should not exceed 0.1¢/10^6 Btu product output for Paraho, and is in range 0.3 - 0.5¢/10^6 Btu for Tosco II. Area of ponds will not exceed 35 acres for Paraho, and will be in range of 60 to 120 acres for Tosco II.

(3) Blowdown might first be treated by vapor compression evaporation and then disposed of in much smaller ponds. Cost will not exceed 0.3¢/10^6 Btu for Paraho, and will be in range 0.4 - 1.1¢/10^6 Btu for Tosco II after taking credit for the clean water recovered. The evaporation pond following the forced evaporation will require less than 12 acres.

c) Cooling Tower Blowdown

It is assumed that no more than about 15 percent of the makeup to the cooling tower comes from using retorting and upgrading foul wastewaters. These wastewaters are treated and diluted with water from the river to a quality that is suitable for makeup to the cooling tower (as described in Section 2.6). These treatments are taken to be essential for plant operation.

Quantity: Estimated to be in the range of 260 to 770 gpm (= 420 - 1240 acre ft/yr), if used to moisturize shale, and in range 100 - 300 gpm (= 160 - 480 acre-ft/yr) if disposed of in evaporation ponds.

Quality: Will be of better quality than the blowdown quality shown on Table 2-12 for the gasification processes because the phenol content in the retorting and upgrading wastewaters are much lower and the dilution water from the river is much larger.

Disposal: (1) Will probably be used to moisturize spent shale at negligible cost.

(2) Disposal in a lined evaporation pond will be in range 0.2 - 0.6¢/10^6 Btu. Area of ponds will be in range 55-165 acres.

(3) Blowdown might first be treated by vapor compression evaporation and then disposed of in much smaller ponds. Cost will be in range 0.3 - 1.5¢/10^6 Btu with pond area not exceeding 15 acres.

d) Sour Water Stripper Wastewater

Quantity: Estimated to be about 260 gpm (= 420 acre-ft/yr).

Quality: COD in range 500-1500 mg/l, phenols in range 80-150 mg/l and ammonia in range 25-50 mg/l.

Disposal: For dust control within the plant after treatment by flotation and biological oxidation at a cost of $0.80 - 1.20/1000 gals or less than 0.2¢/10^6 Btu of synthetic crude.

e) Domestic Wastes from Plant

Quantity: 15 gpm (= 24 acre-ft/yr)

Quality: Typical domestic wastewater with a low TDS and a BOD of 200-250 mg/l after primary treatment.

Disposal: Secondary treatment by packaged activated sludge unit at a cost of $1.95/1000 gals ($640/acre-ft), or 0.01¢/10^6 Btu, and then used for revegetation or low quality water needs.

1.3 Conclusions - Modified In Situ Retorting of Oil Shale

Two major water treatment and disposal problems present themselves in the modified in situ retorting of oil shale in the Piceance Creek Basin of Colorado. The first is the treatment of large quantities of brackish mine drainage water of up to 16 x 10^6 gal/day (= 18,000 acre-ft/yr) for discharge to a surface stream and for use in the plant. Associated with this treatment is the disposal of large quantities of concentrated waste equal to about 15 percent of the water to be treated. The second major problem is the treatment for internal plant use of large quantities of foul retort water generated in the process, which are about equal in volume to the shale oil output of the plant. For a 57,000 barrel/day plant, the retort water would amount to 2.4 x 10^6 gal/day or 2,700 acre-ft/yr.

The difficulties in assessing the treatment and disposal costs at this time stem from the fact that detailed information on the quantity and, particularly the quality, of the mine and retort waters is not known with any degree of certainty. All estimates which are given must therefore be used with great caution as they can only be considered educated guesses in a number of instances. This is emphasized by the fact that water balances and mine water flows differ markedly between different development plans. An illustrative plant water balance, and mine and plant water flow treatment sheets are prepared for estimating purposes. Illustrative mine and retort water qualities are suggested on the basis of the most recent available data. The plant design, all flow rates and costs are based on the production of 57,000 barrels/day of shale oil and 300 MW of byproduct electric power in the central portion of the Piceance Creek Basin of Colorado. A typical price for shale oil might be \$15/barrel, or \$2.50/10^6 Btu.

a) Excess Mine Drainage Water

Quantity:	2,150-9,400 gpm (= 3460 - 15,130 acre-ft/yr) or even higher. Very dependent on site.
Quality:	900-1,350 mg/l total dissolved solids consisting principally of bicarbonate, sodium and sulfate. High fluoride and boron concentrations; taken to be 10-15 mg/l and 2-4 mg/l, respectively. Organic contamination unknown.
Disposal:	Treatment by electrodialysis or reverse osmosis to potable quality for stream discharge. Separate removal of boron by ion exchange. Disposal of concentrate from membrane process by forced evaporation in a vapor compression

evaporator. Total treatment cost, including boron removal, ranges between $0.80/1000 gal (= $260/acre-ft) and $1.25/1000 gal ($400/acre-ft). Concentrate disposal costs average about $1/1000 gal ($330/acre-ft) of mine water treated. The total average cost of disposal and treatment is $2/1000 gal ($650/acre-ft), or in the range of 2.0 to 9.0¢/10^6 Btu.

b) Runoff and Leachates

Quantity: 125 gpm (200 acre-ft/yr) runoff from plant and mine area and 260 gpm (420 acre-ft/yr) of leachate from mined-out shale disposal area.

Quality: Plant runoff most probably of good quality. Leachate from mined-out shale disposal area probably has an inorganics level lower than the levels in local waters and an organics level possibly higher, but quality is uncertain at this time. It is likely to be of fair to good quality.

Disposal: Collected and used for revegetation, shale disposal, dust control and other low quality water needs. No treatment.

c) Mine Water Treatment Concentrate

Quantity: 275 gpm (= 440 acre-ft/yr).

Quality: Same as mine drainage water concentrate. Total dissolved solids of 5,500 to 8,000 mg/l. Mostly inorganic salts, organic contamination expected to be low, but concentrations unknown at this time.

Disposal: Utilize for mine uses, dust control and shale disposal. No treatment needed. If water is in excess of plant needs and disposal is required, this would be done by forced evaporation in same type vapor compression system used for concentrate from excess mine drainage water treatment. Disposal cost would be about $1/1000 gal (= $330/acre-ft) of mine water treated, or 0.1¢/10^6 Btu of product output.

d) Boiler Feedwater Treatment Blowdown

Quantity: 15 gpm (24 acre-ft/yr).

Quality: 1 to 2% total dissolved solids; no organic contamination.

Disposal: Use for low quality needs such as shale disposal; no treatment. If disposal is required, evaporate along with excess mine drainage concentrate. Additional cost may be neglected in comparison with other disposal costs.

e) Cooling Tower Blowdown

It is assumed that upgraded foul retort water is used in the cooling tower. Treatment is assumed to yield a water with relatively low organics contamination, but bicarbonate level may be moderate. Acidification or lime softening of the water may be required.

Quantity: 70-160 gpm (= 110 - 260 acre-ft/yr).

Quality: Lower organics concentration, but possibly somewhat higher total dissolved solids than shown in Table 2-12.

Disposal: Use for dust control, shale disposal and mine uses. If water is in excess of plant needs and disposal is required, higher cycles of concentration would be used in cooling tower to give lower blowdown quantity of 70 gpm. Disposal would be done by forced evaporation in same type vapor compression system used for concentrate from excess mine drainage water treatment. Disposal cost would range between $5.85 and $6.85/100 gal (= $1910 - 2230/acre-ft) of blowdown, or 0.2¢/10^6 Btu.

f) Domestic Wastes from Plant

Quantity: 45 gpm (≈ 70 acre-ft/yr).

Quality: Typical domestic wastewater with a low TDS and a BOD of 200-250 mg/l after primary treatment.

Disposal: Secondary treatment by packaged activated sludge unit at a cost of $1.95/1000 gal ($630/acre-ft), or 0.04¢/10^6 Btu, and then use for revegetation, or low quality water needs.

g) Mine Water Treatment for Plant Use

This is discussed under mine water treatment concentrate (Section 4.4.1).

Quantity: 1645 gpm (= 2970 acre-ft/yr).

Quality: Same as excess mine drainage water.

Treatment: Treated to same quality as water for surface discharge and by same means (electrodialysis or reverse osmosis) but without boron removal, except for 70 gpm used to meet potable and domestic requirements. Cost of treatment will range between \$0.75/1000 gal (= \$240/acre-ft) and \$0.95/1000 gal (= \$310/acre-ft), or 0.7¢/10^6 Btu to 0.8¢/10^6 Btu.

h) Retort Water for Internal Reuse

Quantity: 1660 gpm (= 2670 acre-ft/yr).

Quality: Quality not determinable at this time, but is assumed to be a foul water with a high concentration of ammonia, a BOD about 5,000 mg/l and a COD about 8,500 mg/l; see Table 4-8.

Treatment: An illustrative treatment is oil separation, followed by ammonia stripping and acid gas removal, followed by oxygen activated sludge treatment. Treated water should have a relatively low BOD, probably in the hundreds of mg/l, a low level of ammonia and possibly a moderate level of bicarbonate. Acidification or lime softening may also be required in connection with use of the water for evaporative cooling. The treatment cost is estimated at \$2.8/1000 gal (= \$910/acre-ft), or 2.2¢/10^6 Btu, although so little is known of the retort water quality that this figure must be considered a crude estimate at best.

2. WASTEWATER STREAMS IN COAL GASIFICATION

2.1 Three Wastewater Streams

Although each individual gasification plant (i.e. each process using a specific coal at a specific site) requires careful analysis to determine the water treatment scheme best suited for its needs, a very large number of optimum schemes will fall within the general approach depicted in Figure 2-1. As shown, there are three major wastewater streams. First, source water is treated to process quality; usually this quality is boiler feed water quality. This produces a wastewater stream highly concentrated in salt. Second, wastewater out of the process is usually so contaminated that it cannot be directly returned to the environment without extensive treatment. Figure 2-1 shows that it is treated and delivered to the cooling tower where it is partially consumed by evaporation. Additional makeup to the cooling tower comes from source water. The cooling tower is blown down to prevent scale formation in the cooling system. The third principal wastewater stream is surface run-off from the plant site. Domestic wastes, a minor stream, will also be considered.

The wastewaters are not usually returned to the river. In the Colorado River Basin the "Regulations for Implementation of the Colorado River Salinity Standards through the NPDES Permit Program" are directed towards zero discharge. However, the granting of NPDES permits is done on a case-by-case basis and generalizations regarding discharge cannot be made. Other possibilities, shown on Figure 2-1, are to (1) mix the wastewater with coal ash or other solid residues, (2) spray the wastewater to control dust on mine roads or (3) to evaporate the wastewater. We will return to the discussion of disposal for each waste stream separately. First, however, we begin by quantifying the waste streams.

2.2 Run-off

Run-off is not a difficult problem in the Colorado River Basin area as long as it is collected and impounded properly. The quantity depends very much on the site. A large quantity would, for example, be 15 inches of rain/year falling on 0.25 square miles (= 160 acres = 7×10^6 ft^2). Nearly all of this rainfall would be collected and would amount to 200 acre-ft/yr (= 62×10^3 lb/hr = 125 gal/min), which is not a large stream. As a minimum, runoff from

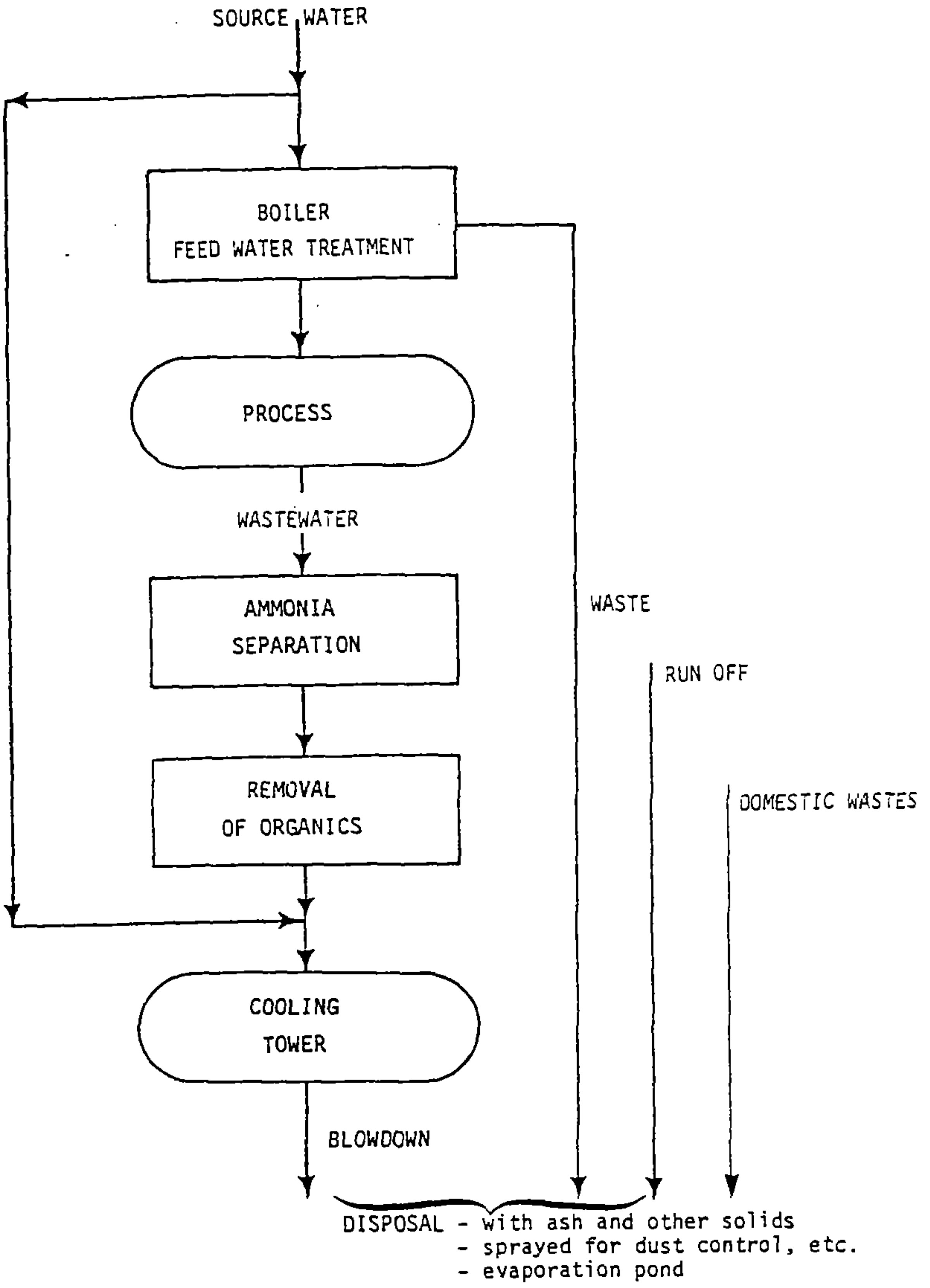


Figure 2-1. Major parts of a water management scheme in a coal conversion plant.

active areas, such as the plant site, mining area and waste storage areas, from any precipitation event less than or equal to a 10-year, 24-hour event, would have to be contained. If discharged, its quality would be monitored and the runoff treated to meet effluent limitations. The quality of the run-off will depend on the cleanliness of the plant. In the usual case, oil will be separated and impounded water mixed with other waters as makeup to the circulating cooling system. Run-off will not exceed 5% of the average cooling water makeup.

Although run-off from piles of eastern high pyrite coals is usually very acid and high in iron and sulfate[1], this is not necessarily true for low pyrite western coals. Run-off from the Neal Generating Station in Iowa, using a Wyoming coal, is expected to be alkaline and low in total dissolved solids[2]. The need to segregate coal pile runoff will depend on the coal. Consideration should also be given to groundwater contamination and the permeability of the coal pile storage area. In any event all that is necessary is to surround the coal pile with a ditch in which rain run-off accumulates and from which it evaporates. This is done, for example, at the steam-electric generating station in Hayden, Colorado and at other stations in the West.

The costs of impounding the runoff and monitoring its quantity and quality for discharge have not been estimated.

On Figure 2-2 is shown a simplified example of one possible water management scheme for a Lurgi process plant in New Mexico producing 250 x 10^6 scf/day of pipeline gas. The flow rates are shown in gallons per minute and acre-ft/yr and are the full operating rates. This figure will serve as background to the following discussion on various process water streams.

2.3 Waste from Boiler Feed Water Preparation

2.3.1 Quantities of Boiler Feed Water. Coal gasification consumes water as a source of hydrogen. To make 250 x 10^6 scf/day of pipeline gas, which is over 90% methane (CH_4), theoretically requires hydrogen in an amount equivalent to 790 x 10^3 lb/hr water (= 1580 gal/min = 2550 acre-ft/yr, Reference 3). Not all processes require that this water be added as steam. Conceptual designs for Bigas process plants include pumping the coal up to gasifier pressure in a slurry in water. The water is evaporated inside the gasifier system. This means that this part of the water does not have to be deionized; salts dissolved in the water mostly end up with the coal ash.

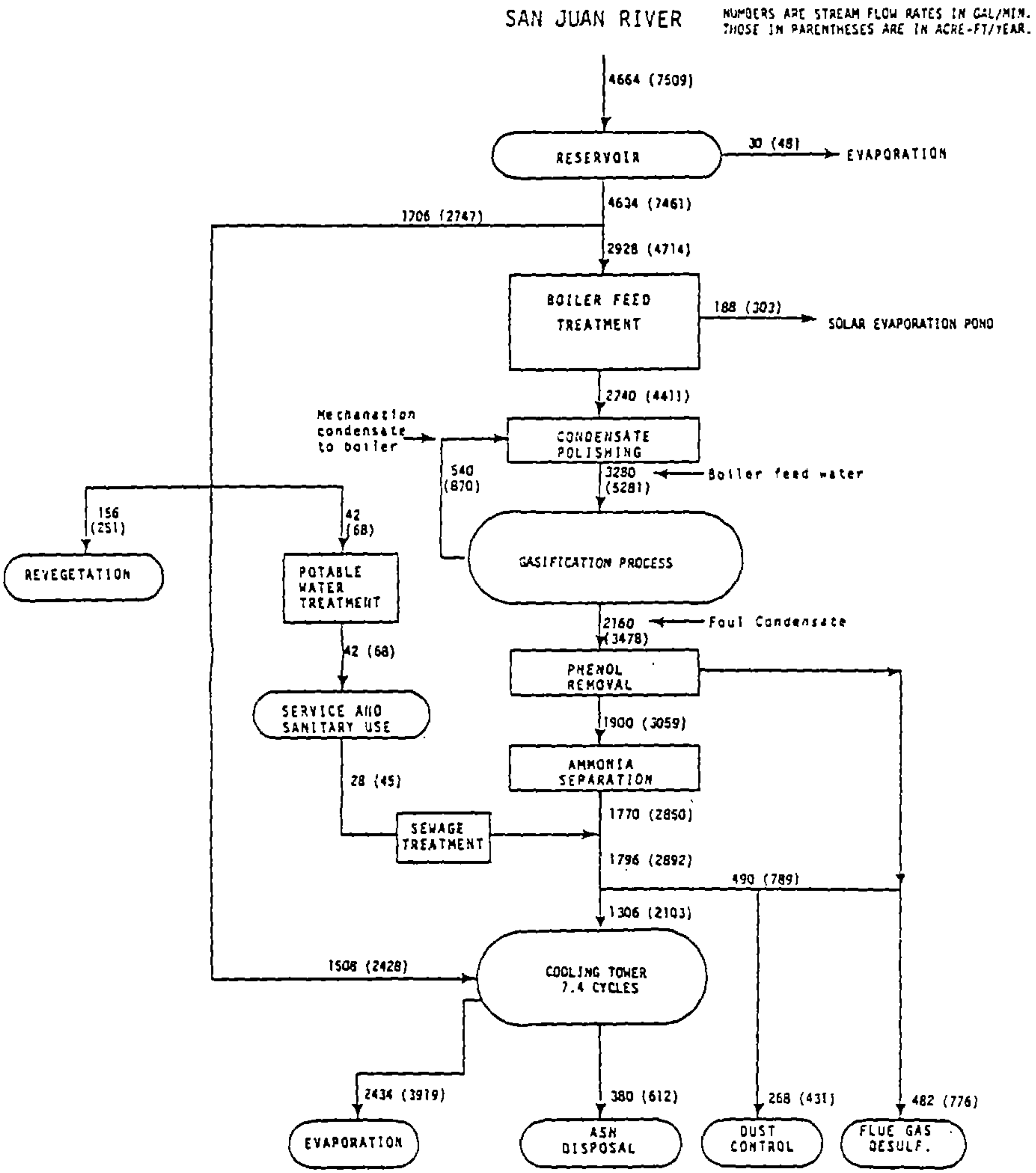


Figure 2-2. Example of water management scheme for a Lurgi process plant producing 250 x 10^6 scf/day pipeline gas in New Mexico.

In plants taking all the water as steam, all of the water must be treated by ion exchange or reverse osmosis. The quantity required is usually more than 790 x 10^3 lb/hr because excess steam is added to the gasifier to control the temperature. This is most noticeable in a low temperature gasifier such as the Lurgi process. In the standard Lurgi gasifiers, 45 to 50 percent of the steam is decomposed. More steam is decomposed in the shift reactor, but not all. When the Lurgi gasifier is run in a slagging mode (the ash melts), all the steam added to the gasifier decomposes[4].

Water in the coal does not enter into reaction. For many gasification processes the coal is dried, but even when it is not, as for the Lurgi process, a moist coal results only in an increased quantity of wastewater, not in a reduced steam requirement.

Requirements for boiler feed water in coal gasification plants have been collected on Table 2-1[3,4,5]. In medium-Btu or low-Btu gas the chemicals are carbon monoxide and hydrogen, rather than methane, and as less hydrogen is used, the water requirements fall at the lower end of the scale. If details are lacking, a figure of 100 lb water/10^6 Btu product (= 3.7 x 10^{-5} acre-ft/10^6 Btu = 12 gal/10^6 Btu) can be used for estimating, but it will not necessarily be accurate. The requirements are large. By way of reference a 1000 MWe steam electric generating station requires boiler makeup of 45 to 80 x 10^3 lb water/hr (= 145 to 260 acre-ft/yr = 90 to 160 gal/min).

2.3.2 Quantities, Quality and Disposal of Ion Exchange Regenerant Waste.

The volume of wastewater resulting from the preparation of boiler feed water (which is deionized, degassed water) depends on the quality of the source water and on the preparation method used. We have studied three methods of producing boiler feed water: (1) co-current regenerated ion exchange, (2) counter-current regenerated ion exchange and (3) reverse osmosis[6]. In this section we will discuss the two ion exchange procedures. Reverse osmosis will be discussed in the next sub-section.

Co-current regenerated ion exchange is the usual treatment used in this country. Wastewater volumes vary from 8 to 15% of the product water volume and the wastewater concentration is about 2% total dissolved solids.

Counter-current regeneration of the ion exchange beds means that regenerant is pumped upwards through the beds necessitating some mechanism to prevent the beds from lifting. Counter-current regeneration results in a lower use of

TABLE 2-1. BOILER FEED WATER REQUIREMENTS FOR VARIOUS GASIFICATION PROCESSES PRODUCING 250 x 10^6 SCF/DAY GAS

Process	Product Gas	10^3 lb/hr	lb/10^6 Btu Product Gas
Lurgi	Pipeline[+]	1400-1700	140-170
Synthane	Pipeline	∿ 1200	∿ 120
CO_2 Acceptor	Pipeline	∿ 1000	∿ 100
Hygas	Pipeline	∿ 1000	∿ 100
Bigas	Pipeline	∿ 700	∿ 70
Stirred Bed	Medium Btu[++]		∿ 100
Winkler	Medium Btu		∿ 100
Molten-Salt	Medium Btu		∿ 100
Koppers	Medium Btu		16-22
Winkler	Low Btu[+++]		∿ 44

[+] Heating value range: 920-1000 Btu/scf

[++] Heating value range: 250-550 Btu/scf

[+++] Heating value range: 100-250 Btu/scf

Source: Refs. 3,4 and 5.

regenerant chemicals and, in all the cases we have studied, in lower cost. Although not a standard procedure today, we expect counter-current regeneration to become popular. The waste streams for any given job are smaller for counter-current regeneration than those for co-current regeneration. However, the difference between the quality of the feed waters is much more than the difference between regeneration procedures on the same water. The most accurate statement of the wastewater is that it is between 6 and 12% of the product water and the concentration is about 2.0 to 2.5% total dissolved solids.

Using counter-current regeneration, a study has been made for a Lurgi process plant (see Figure 2-2) making 250 x 10^6 scf/day of pipeline gas drawing water from the San Juan River and requiring 2930 gal/min (= 4730 acre-ft/yr = 1465 x 10^3 lb/hr) of makeup water[6]. The quality of the San Juan River water and the specifications for the boiler feed water are given on Table 2-2. The cheapest ion exchange system found is shown on Figure 2-3. The capital and operating cost estimate for this system is shown on Table 2-3. The cost for boiler feed water treatment is 1.2¢/10^6 Btu compared to the cost of pipeline gas of about $3-4/$10^6$Btu. Details of the waste from this system are shown on Table 2-4. The low volume of waste in this plant comes partly from the fact that the source water is of good quality and partly from the fact that excellent operation has been assumed.

Ion exchange waste streams in coal gasification plants will average 10 lb wastewater/10^6 Btu product gas with variations of twofold to one fifth. For a 250 scf/day pipeline gas plant, this is 100 x 10^3 lb wastewater/hr (= 200 gal/min = 320 acre-ft/yr).

Given the saltiness of ion exchange waste, there are no convenient disposal treatments other than evaporation, of which there are only two useful possibilities. On the one hand the water can be sprayed out for dust control and evaporated in an uncontrolled manner, at negligible cost. However, it is highly unlikely that the use of ion exchange wastewater for dust control would be allowed because of the concerns of runoff and groundwater contamination. Alternately the water can be impounded and evaporated at costs discussed in Section 2.4. A forced evaporator, with recovery of distillate, may be used if technically possible, as discussed in Section 2.4. The particular example shown on Table 2-4 is probably so high in calcium and sulfate that scale formation will make forced evaporation impractical. For this particular waste, probable disposal would be to a 55 acre lined pond costing $2.37 x 10^6 or about $3.65/1000 gal (= $1190/acre-ft) of waste, or 0.3¢/10^6 Btu of product output for a plant operating at a capacity of 90 percent.

TABLE 2-2. SPECIFICATIONS FOR BOILER FEED WATER TREATMENT SYSTEMS FOR LURGI PLANT IN NEW MEXICO

Raw Water Composition

	mg/l	mg/l as $CaCO_3$
Ca	55	137
Mg	9	37
Na	33	73
HCO_3	143	117
SO_4	113	117
Cl	9	13
SiO_2	12	
TDS	374	
pH	7.8	

Specifications for Boiler Feedwater

Design flow rate = 2930 gal/min = 1465×10^3 lb/hr

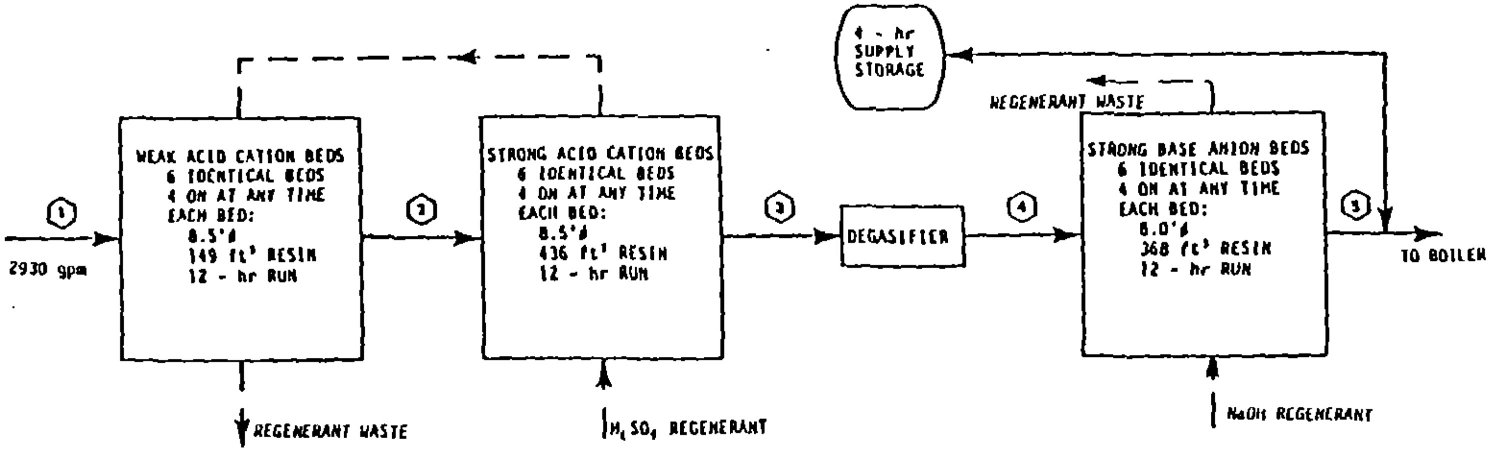
Na < 0.300 mg/l (as $CaCO_3$)

Si < 0.02 mg/l (as SiO_2)

Conductivity < 1.5 micromho/cm

Treatment systems include three 200,000 gal storage tanks (4 hr supply)

Source: Ref. 6



WATER ANALYSIS
(in mg/l as $CaCO_3$ except for Si)

	① Raw water	② Weak acid effluent	③ Strong acid effluent	④ Degasifier effluent	⑤ Strong base effluent
Ca	137.0	57	0.0	0.0	0.0
Mg	37.0		0.0	0.0	0.0
Na	73.0	73.0	0.28	0.28	0.28
HCO_3	117.0	0.0	0.0	0.0	0.0
SO_4	117.0	117.0	117.0	117.0	0.0
Cl	13.0	13.0	13.0	13.0	0.0
Si (as S_1O_2)	12.0	12.0	12.0	12.0	<0.02
CO_2	3.3	120.0	120.0	5.0	0.0

Figure 2-3. Counter-current regeneration ion exchange system for boiler feed water at a Lurgi plant in New Mexico.

TABLE 2-3. COST ESTIMATES (IN THOUSANDS OF DOLLARS) FOR BOILER FEED WATER TREATMENT AT LURGI PLANT IN NEW MEXICO

Capital cost*	2,790
Annual operating costs:**	
Acid	173.2
Caustic	236.3
Labor	116.8
Resin replacement	35.7
	562
Amortization @ 15% of capital	419
Total annual cost:	981
$/1000 gal**	0.71
¢/10^6 Btu product	1.2

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*Budget estimate 1978 Gulf Coast

**Based on stream factor of 90%

Source: Ref. 6

TABLE 2-4. WASTE FROM BOILER FEED WATER TREATMENT AT LURGI PLANT IN NEW MEXICO

Approximate Waste Composition

	mg/l	mg/l as $CaCO_3$	mole/l
Ca	1080	2688	54
Mg	177	726	14.5
Na	3276	7142	142
CO_3	134	223	4.5
SO_4	9390	9766	196
Cl	181	255	5.1
Si	235		
pH	$\sim$ 11.5		

Waste volume: 106,400 gal/12-hour service run = 148 gal/min ≈ 74 x 10^3 lb/hr
= 240 acre-ft/yr = 5.4% of product water.

Source: Ref. 6

2.3.3 Quantities, Qualities and Disposal of Reverse Osmosis Waste.

An alternative to the use of ion exchange for boiler feed water preparation is reverse osmosis used in conjunction with a polishing mixed-bed ion exchanger. The reverse osmosis-ion exchange system gives a completely different waste than does ion exchange by itself. In a typical situation very few regenerant chemicals are used and the waste contains two streams. The first, and major one, is about 4 times the concentration of the source water and one-third the volume of the product water. The second stream, from the "polishing" ion exchange, contains 1 to 2% total dissolved solids and has a volume of 0.5 to 1% of the product water.

Reverse osmosis is more expensive than ion exchange for large throughputs, but cheaper for small throughputs[6]. This means that reverse osmosis may be preferred for plants which are about one-fifth the "standard" size plants of 250×10^6 scf/day"; i.e., for plants below an output of about 2×10^9 Btu/hr. For larger plants reverse osmosis will be used when it results in savings in waste disposal.

If allowed, the reverse osmosis waste from the larger plants may be suitable for return to the river. While the concentration of salts is up to 4 times greater than in the river, the amount of dissolved material is nearly the same as that which was in the water withdrawn from the river because no chemicals are added during the treatment. Thus if returning salts to the river is acceptable, reverse osmosis should be considered for boiler feed water treatment and the costs of an evaporation pond avoided. The cost of reverse osmosis is decreasing relative to ion exchange and it may become as cheap as ion exchange for large plants when the cost of waste disposal is taken into account. However, in the Colorado River Basin, because of the regulations directed towards zero discharge of brackish water, it would seem unlikely that discharge of concentrated reverse osmosis wastewater would be allowed.

2.4 Cost of Evaporation

Evaporation has been mentioned above as the probably procedure for disposal of ion exchange regenerant waste. Evaporation may also be considered for disposal of other wastes such as cooling tower blowdown and so a separate section on the cost of evaporation is inserted here. Throughout the Upper Colorado River Basin, evaporation is greater than precipitation. Some average, net, evaporation rates are:

	in/yr
Colorado	35
Wyoming	40
New Mexico	53
Southern Utah	60

There is a range of 35 to 60 in/yr. For orientation, the approximate area needed to evaporate a few different flow rates at a net evaporation rate of 35 in/yr (= 4.15×10^{-5} gals/(ft^2)(min) = 2.07×10^{-2} lbs/ft^2)(hr) = 6.68×10^{-5} acre-ft/(ft^2)(yr) is:

Flow		Approximate Area to Evaporate	
Gal/min	10^3 lb/hr	10^6 ft^2	Acres
100	50	2.4	55
200	100	7.2	111
500	250	12.0	276

Uncontrolled evaporation by spraying water with ash or for the purpose of dust control has a modest cost, dependent on the distance over which the water is pumped and the charge for using the land. Impoundment means an additional cost because it requires dikes, scooping a pond and, most particularly, lining. This is used extensively at coal fired power plants in the Western United States. Lined ponds cost about \$1/ft^2 (\$43,000/acre) with the actual cost being very dependent on location and proximity to the source of clay for lining. Polymer liners will be used where clay is too expensive. A financial charge of 8%/yr for 20 years gives an annual charge of about 10%/yr or \$0.10/(ft^2)(yr). Thus, evaporation pond charges are approximately \$4.60/1000 gals evaporated (= \$0.55/1000 lb evaporated = \$1500/acre-ft).

If very large ponds are required, they become distant from the plant and the cost of pumping and of acquiring the land will go up. One alternative is to first use forced evaporation to reduce the quantity of wastewater treated and then use a smaller evaporation pond for final disposal. In many modern coal fired steam-electric power plants in the Western United States vapor compression evaporation is used to treat cooling tower blowdown. A vapor compression evaporator is used when the waste stream is large and dilute so that scale formation is not a problem. The blowdown from the vapor compression evaporators is discharged to lined evaporation ponds while the distillate is used as makeup to the boilers. A cost estimate for a forced evaporation vapor-compression evaporator is:

Minimum capital cost	\$4,500/(1000 gals)(day)
Maximum capital cost (allowing for slurry formation)	\$9,000/(1000 gals)(day)
Amortization and maintenance (20% of capital cost)	\$3.0 - 6.0/1000 gals
Electricity @ 85 kw-hr/1000 gal @ 3¢/kw-hr	\$2.6/1000 gals
Labor and chemicals	\$1.0 - 2.5/1000 gals
TOTAL AMORTIZATION AND OPERATING COSTS:	\$6.6 - 11.1/1000 gals (\$2,333 - 3,620/acre-ft)

or, for the example shown in Figure 2-2, the costs are 1.5-2.5¢/10^6 Btu product output. When using a forced evaporator, there is a credit of about \$1/1000 gals for the distilled water recovered.

If large, lined ponds are not environmentally acceptable, then an additional cost of \$2 to 6/1000 gals must be incurred to use forced evaporation to the maximum extent. However, the volume of dry salt remaining is not altered by the choice of evaporator.

2.5 Quantities and Qualities of Process Condensate

All processes to convert coal to other gas cause the release of a wastewater stream which is condensed out of the product fuel process lines. This water is derived from the hydrogenation of oxygen in the coal, from moisture in the coal and from unreacted steam put through the coal conversion reactor. Some quantities of process condensate are shown on Table 2-5. There is a lot of variation. A middle of the range value of 70 lb/10^6 Btu product gives, for a 250 x 10^6 scf/day pipeline gas plant, a flow of 700 x 10^3 lb/hr (= 1,400 gals/min = 2,250 acre-ft/yr). This is a large stream to treat.

The water contains coal reaction products, coal decomposition products, coal pyrolysis products and varying amounts of soluble inorganic products from

TABLE 2-5. QUANTITIES OF FOUL PROCESS CONDENSATE FOR VARIOUS GASIFICATION PROCESSES PRODUCING 250 × 10^6 SCF/DAY GAS

Process	Product Gas	10^3 lb/hr	lb/10^6 Btu Product Gas
Lurgi*	Pipeline	1000-1900	100-190
Synthane	Pipeline	680-710	69-72
Hygas	Pipeline	∿ 300	30
Bigas	Pipeline	900-1300	91-131
Stirred Bed	Medium Btu		∿ 90
Winkler	Medium Btu		∿ 63
Molten-salt	Medium Btu		∿ 61
Koppers	Medium Btu		∿ 17
Winkler	Low Btu		∿ 30

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*Variation is controlled by moisture in the coal

Source: Refs. 3,4 and 5

coal ash and gangue. Sample analyses are shown in Appendices A and B. The concentration of pollutants depends on the coal type and on the process. If we take chemical oxygen demand, COD, as the first measure of pollutant level, the Synthane and Lurgi processes using subbituminous coals and the Hygas process using a lignite have the dirtiest water. Less polluted is the Hygas wastewater when a bituminous coal is used. Least polluted is the condensate from the entrained flow Koppers gasifier.

The level of contamination, to a first approximation, decreases when the coal rank increases and when the reactor temperature increases. However, reactor residence time and configuration also enter into the picture. A great deal of variation in Synthane wastewater has been obtained by changing the point of injection of steam and oxygen[7].

For all except the highest temperature gasifiers, process condensate is much the most troublesome wastewater in the plant. As can be seen from the analyses in the appendix, the water is usually foul. It contains large quantities of ammonia and carbon dioxide. In gasifying western, low sulfur coals, the wastewater will, fortunately, be low in hydrogen sulfide.

Condensate can be high in phenols and high in other oxygen demand. Since phenol exerts about 2 lb biochemical oxygen demand per 1 lb phenol, or 2.4 lb chemical oxygen demand per 1 lb phenol, it can be calculated that phenols represent in the range of half of the BOD and below one quarter of the COD. The organic matter, in addition to phenol, contains fatty acids and other compounds which are mostly biodegradable[8,9].

In most processes foul condensate wastewater is so contaminated that its release to the environment in any form is unacceptable. Apart from the prohibitive cost of evaporation ponds for so large a flow, ammonia and volatile organic matter will cause serious air pollution if this water is stored. Therefore, release of untreated condensate wastewater is, for the purposes of this study, taken not to be a permitted option. Rather, the water must first be treated for removal of ammonia and organic matter. In all but a few plants ,where treatment of condensate wastewater is required, the treatment will be such as to fit the water for makeup to a cooling system instead of for disposal to a river. This is because a circulating cooling system can accept considerably more organic material and ammonia than effluent guidelines, under PL92-500, are apt to permit for discharge to a river. Furthermore, treated process condensate, being derived from steam, usually contains less scale-forming inorganic contamination (hardness and alkalinity) than river water. It thus can be more suitable for use in a cooling system than is river water.

In the following sections we will first explain how water quality affects the operation of a cooling tower and circulating cooling system, and show that a cooling tower is a water treatment. Secondly we will mention the treatments necessary to fit waste condensate for cooling system makeup. Finally we consider the cost-quality relationships in disposal of the cooling tower blowdown.

2.6 A Cooling Tower as a Water Treatment

The problems inherent in control of a circulating cooling system can best be summarized by quoting from Reference 3:

> A wet cooling tower is an evaporator, and salts dissolved in the makeup water concentrate, often to the point of precipitation. The precipitate tends to adhere to heat transfer surfaces forming a hard scale..... Not only may the makeup water contain silt, but the circulating water in its passage through the tower scrubs dust out of the air. Circulating water thus contains an ever-increasing amount of suspended matter, which will settle out in stagnant spots in the pipes and heat exchangers.... The well-oxygenated circulating water is very corrosive to heat transfer surfaces....Circulating cooling water is warm and well-oxygenated and is an ideal habitat for microbial growth. The water is seldom sterile when fed to the system and, in any case, receives a steady supply of air-borne growth. Untreated cooling systems are subject to fungal rot of the wooden parts of the tower, bacterial corrosion of iron and bacterial production of sulfide, growth of algae in the sun-lit portions of the tower, and suspended sloughed-off growth that can lodge in the system and block the flow. Biocidal chemicals must be added to control growth.

Scaling is prevented by controlling the concentration of species which form slightly soluble salts, particularly salts whose solubility decreases with an increase in temperature so that precipitation tends to be on the surface of the condenser, where hard, adherent scale is formed. The most common scales are calcium carbonate and calcium sulfate with additional problems from silica, magnesium silicates and calcium phosphates. The species that must be controlled are Ca^{++}, Mg^{++}, SiO_2, $CO_3^{=}$ and PO_4^{3-}.

Concentration of dissolved salts in circulating cooling water is usually controlled by blowing down. There is always some drift of water droplets from a cooling tower, which can be considered to be a blowdown. When the circulating cooling water is very concentrated the drift may damage foliage and land upon which it settles. For high concentration cooling systems, the best modern drift eliminators will be used. Blowdown cannot acceptably be prevented by allowing a high drift.

Most makeup waters contain carbon dioxide in excess of the concentration in equilibrium with the atmosphere. Quite high alkalinities occur, nearly all as bicarbonate (HCO_3^-). In the cooling tower there is a tendency for CO_2 to be driven off converting some of the alkalinity to carbonate ($CO_3^=$) and causing precipitation. This is common and is usually prevented by adding sulfuric acid which replaces some of the alkalinity with equivalent sulfate.
Scale by calcium sulfate is sometimes prevented by softening the makeup water. Lime and soda ash are added to precipitate calcium. This has the added advantage of removing some carbonate alkalinity as well. If desired, the softener can be operated to precipitate magnesium as hydroxide. Silica quite readily adsorbs onto the surface of magnesium hydroxide and is partly removed with the magnesium, which is advantageous.

Gasification wastewater can be useful as makeup water to the cooling system because it is usually lower in non-volatile dissolved solids than river water.

Suspended solids, if not sufficiently controlled by blowdown, can be and have been controlled by a side stream clarifier or filter.

Corrosion is controlled by operating at as high a pH as is acceptable (just at the point of scale formation) and by dosing the circulating water with anti-corrosion chemicals. The best anti-corrosion chemical is hexavalent chromium. Fortunately, it is not the only anti-corrosion chemical and it is not essential in alkaline waters. Mixtures of such chemicals as hydroxyethilidene diphosphonate, sodium molybdate, benzotriazole and sodium gluconate have been demonstrated to be adequate[14 to 17]. If chromium is used, it must be removed from the blowdown as its return to a river is not permitted under present water quality standards. Removal of chromium from blowdown is part of the cost of using chromium and need not be considered in this study.

When treated wastewater is added to the cooling system, the control of biological growth can become a serious problem, since the water contains nutrients. Relevant experience has been obtained in the petroleum industy and it has been shown that, within limits, organic contamination is permissable in cooling water makeup.

It has been conclusively demonstrated that refinery phenolic wastewaters can be used in a cooling tower and that bio-oxidation of phenol will occur with very high removal efficiencies. This has been practiced at the Sun Oil refinery in Toledo, Ohio[11], at the Mobil Oil refinery in East Chicago[12] and at other refineries according to a brief note by Maguire of Betz Laboratories[13]. Table 2-6 brings together some of the pertinent information.

It must be remembered that "phenol" in a refinery sour water probably contains a higher fraction of C_6H_5OH than will be found in the coal conversion wastewater, so the analogy is less than perfect. Mohler and Clere[11] identified several species of bacilli and cocci in their tower; five species utilized 200 ppm phenol and two of the five grew in 1000 ppm phenol/mineral salts medium. The bacteria were mesophilic with optimum growth in the range 60-100°F. Hart[12] reports that his towers operated at 80-86°F.

Necessary conditions for successful bio-oxidation are low sulfide[11] (below 2 ppm is suggested[13]), and only slow, small excursions in pH[11]. References 11 and 12 report a pH range of 7.8 to about 8.3. Hydrogen sulfide is lower in this water than in stripped refinery sour water.

Chlorination to prevent slime was used at Mobil[12], but had to be carefully controlled to maintain bioxidation. Maguire[13] reports similarly and suggests the use of acrolein or other non-oxidizing biocide to prevent the formation of toxic chlorinated phenols. We recommend not using chlorine for coal conversion wastewaters because of the possible release of chlorinated aromatic compounds. Most of the suppliers of proprietary chemical mixtures can supply biocides other than chlorine and control of slime will not be a problem.

Corrosion of steel has been low at both Mobil and Sun Oil. Low corrosion is also experienced when treated sewage is used in a cooling tower[18].

Before setting quality limits on the organic contamination of water used in cooling system makeup, an example can be considered. The Lurgi process plant designed by El Paso to make 250 x 10^6 scf/day pipeline gas in New Mexico will require cooling water makeup of about 1,500 x 10^3 lb/hr (= 3,000 gal/min = 4,830 acre-ft/yr) 50% of which will be treated process condensate. The quality of treated process condensate is not precisely known, but two estimates

TABLE 2-6 EXPERIENCE WITH BIO-OXIDATION OF PHENOLIC REFINERY WASTEWATER IN A COOLING TOWER

	Sun Oil Refinery[1]	Mobil Oil Refinery[2]	Summary[3]
Makeup concentration of phenol(ppm)	13 to 70	~ 14(a)	33 to 110
Fraction removed (%)	>99.4%	92-97% avg	> 90%
Tower loading:			
gpm/ft^2	3.3 to 3.4		
lb phenol/day	102 to 840	100	
$lb\ phenol/(ft^3)(day)$	~ 68(a)		

Notes:

(a) Estimated from information in the publication.

1) Ref. 11

2) Ref. 12

3) Ref. 13

have been made[19,20]. They are reproduced on Tables 2-7 and 2-8. When treated condensate is diluted with an equal volume of San Juan River water, a probable composition of the mixture is that shown on Table 2-9. With the addition of some acid and some anti-scale chemicals, this water can be concentrated eightfold and circulated at a pH of about 7.5 without scale formation[6]. It has been assumed by the designers, and we agree, that the organic contamination is not bad and that the tower will operate.

Of all the plant designs we have seen or made, this plant has the highest organic contamination in the makeup water. We have used this to suggest upper limits of permissable concentrations in makeup. The limits shown on Table 2-10 apply to the mixed makeup; they are high and will require good control by the operators, but they are not necessarily the maximum. Treatment to this quality is, for this report, regarded as necessary, in-plant, treatment. Treatment to a better quality is, for this report, regarded as treatment for environmental protection and is discussed later. Please recognize that the limits are rather arbitrary. In particular the limit on ammonia requires discussion.

Ammonia is driven off in a cooling tower. Ammonia does not concentrate in a cooling tower and will be reduced in concentration if a large enough fraction (approximately more than 85%) of the makeup water is evaporated rather than blown down. This is easily calculated from vapor pressure data and has been demonstrated[10]. The most important limit to the permissable concentration in the makeup water is the formation of noxious fumes. Our calculations show that the odor threshold for ammonia in the cooling tower plume will not be exceeded with ammonia concentrations of up to 500 mg/l. Therefore, the limit of 100 mg/l, shown on Table 2-10, should be no problem. Removal of ammonia below the limit shown on Table 2-10 may be required to avoid air pollution, but the costs of doing this are specifically excluded from this contract.

Because of ammonia, copper should not be used as a material of construction and chlorination, which is not planned, will be reduced in efficacy.

2.7 Wastewater Treatment for Internal Plant Reuse

In this section we briefly discuss the water treatments used to improve process condensate to the quality shown on Table 2-10, with emphasis on the

TABLE 2-7. PHENOSOLVAN PLANT PERFORMANCE

SASOL FACILITY

(For combined clean and contaminated gas liquor stream)

COMPONENT	UNTREATED CONDENSATE Concentration, ppm
Phenols	3,250-4,000
Sodium	53
Ammonia (free)	10,600
Ammonia (Fixed)	150-200
Suspended Tar & Oil	5,000
CN	6
Total S	228
Fatty Acids as $C_2H_4O_2$	600
CO_2	0.7%

COMPONENT	TREATED CONDENSATE Concentration, ppm
Phenols (Steam volatile)	1
Phenols (Bound)	60-160
Fatty Acids as $C_2H_4O_2$	560
Ammonia as Nitrogen	215
Hydrogen Sulfide	12
CN	1
Fluoride	56 gm/l
Chloride	25
Calcium (As Ca)	18
Iron (As Fe)	1 mg/l
Orthophosphate	2.5
Total Dissolved Solids	875
Suspended Solids	21
COD	1,126
pH	8.4

Source: Ref. 19

TABLE 2-8. TREATED CONDENSATE (CALCULATED) FROM PHENOSOLVAN PROCESS

	mg/l
Mono-hydric phenols	27
Poly-hydric phenols	432
Other organics	1,834
BOD	2,151

Basis:

Assumed composition of crude phenol:

- 85% mono-hydric phenol
- 15% poly-hydric phenol
- 5% other organics

Assumed extraction recoveries:

- 99.5% for mono-hydric phenols
- 60.0% for poly-hydric phenols
- 15.0% for other organics

BOD_5 factors:

mono-hydric phenols = 1.7
poly-hydric phenols = 1.9
other organics = 0.7

Source: Ref. 20

TABLE 2-9. PROBABLE COMPOSITION OF MAKEUP TO COOLING TOWER IN LURGI PLANT (50% from river & 50% treated process condensate effluent)

	mg/l
Phenols	100
BOD	1,000
COD	2,000
Ammonia as N	100
Total P	1
HCO_3	80
Ca	37
Mg	5
Na	22
Cl	17
SO_4	69

TABLE 2-10. SUGGESTED LIMITS ON THE CONTAMINATION OF MAKEUP WATER FOR A COOLING TOWER

	mg/l
Phenols	100
BOD	1000
COD	$>$2000
Ammonia as N	100
H_2S	2

additional costs incurred in obtaining a still higher quality. The treatment procedures are:

stripping ammonia and carbon dioxide
solvent extraction
biological oxidation
adsorption

Stripping

Ammonia is derived from nitrogen in the coal. Except for the very few gasifiers run so hot that ammonia is not formed, it is produced in large quantities whether or not organic molecules are produced. Because of its very high solubility, ammonia is removed from the gas stream in the condensate. The condensate is circulated, if necessary, to scrub all the ammonia out of the gas.

The wastewater is steam stripped and the ammonia either recovered from the stripper overhead gases, or incinerated. It is usual to keep the stripper between 20 and 40 trays (100 to 300 ppm bottoms NH_3) at a steam rate of about 0.9 lbs steam per gal wastewater (about \$2.7/1000 gals for steam at $\$3/10^6$ Btu). Ammonia recovery is capital and/or energy intensive depending on the process selected, but can be economical at high ammonia throughputs. A 2,000 gpm 14,000 ppm N wastewater stream, which might be obtained from a Lurgi commercial scale plant, can economically yield about 190 ton/day anhydrous ammonia. An 85 ft high 12 ft diameter \$300,000 (uninstalled) stripper would remove 99% of the ammonia producing a treated effluent containing 180 ppm NH_3. The total installed cost would be approximately 3.75 times the uninstalled cost. This ammonia concentration is suitable for a downstream biological purification step, and will not cause problems in the cooling tower circuit. Should a concentration of 500 ppm ammonia prove acceptable, the stripper column can be reduced in height and, therefore, in cost by about 8%. This is a saving in <u>installed</u> cost of about \$90,000 for which the charges amount to about 1.4¢/1000 gals, or 0.1¢/10^6 Btu product output at an amortization rate of 15 percent per year.

If the stripped ammonia is incinerated, stripper and steam costs are essentially the total cost of ammonia separation. If ammonia is recovered, additional plant, steam and cooling water are required. The USS Engineers and Consultants PHOSAM-W process, which produces anhydrous ammonia, appears to be the most economical of the processes we have studied. A PHOSAM-W plant for the exemplary Lurgi stream would require about $\$10^7$ of equipment (installed), consume 1.6 lb steam per gal wastewater treated, and have a cooling water consumption (by evaporation) of 0.1 gal per gal wastewater treated. Cooling water consumption can be reduced by 60% by using air coolers, but at additional capital cost. The total operating cost is $\$7.4 \times 10^6$ per year, or \$7.80/1000 gals of feed water, or 9.4¢/10^6 Btu product output[6]. Credit for ammonia sales cover the cost of this treatment.

The same column can yield a product water having about 14 ppm ammonia if the stripping steam rate is doubled at an additional cost of about \$2.7/1000 gals. As stated in the preceding section, we have not studied this aspect. The additional cost of \$2.7/1000 gals is a maximum. It may be cheaper to use a larger column and less steam or to follow stripping with biological nitrification.

Solvent Extraction

In solvent extraction a solvent is intimately mixed with the wastewater in contacting devices in which the phenols are transferred to the solvent phase. The mixture then enters settling vessels to separate the solvent and water streams. Several stages are required to achieve adequate phenol removal. As a typical example, two trains of six mixer settler stages each plus solvent recovery equipment costing $\$14.6 \times 10^6$ (installed) are required to remove 99% of the phenol from a 2,000 gpm, 6,000 ppm phenol wastewater stream[6]. Such a stream could be obtained from a Lurgi commercial scale gasification plant. The cost in capital investment and maintenance amounts to $\$2.93 \times 10^6$ per year, or \$2.80/1000 gals treated[6]. Costs are not dependent on influent concentration, but costs can be decreased by reducing the removal efficiency. The lowest acceptable removal efficiency, as determined by both water reuse and environmental constraints, is not known.

At 80% efficiency only one or two theoretical stages are required, and the number of stages is not strongly dependent on the distribution coefficient of the solvent. At 99% efficiency, six to seven theoretical stages are required, although these can be reduced either by increasing the amount of solvent used, or by using a solvent with a higher distribution coefficient. As the solvent distribution coefficient is increased, the number of stages and/or the amount of solvent for a given removal efficiency can be decreased.

However, there exists a minimum solvent rate for adequate mixing and the benefits of using improved solvents diminish with increasing distribution coefficients.

The optimum solvent rate for the Lurgi example is 30 lb solvent/100 lb wastewater. Suitable solvents will usually be recovered for recycle by distilling them from the extracted phenols. Assuming a value for the latent heat of vaporization of the solvent of 133 Btu/lb (for n-butyl acetate) and a 20% reflux in the solvent still, the energy consumed is 4,800 Btu/100 lb wastewater = 0.4×10^6 Btu/1000 gals. At a cost of \$3/10^6 Btu, the energy cost is \$1.20/1000 gals. In addition, the charges for cooling water, solvent makeup and electricity are about \$0.60/1000 gals so that the total utility and chemical costs do not exceed about \$1.80/1000 gals. Thus, the total operating cost of solvent extraction, including amortization and maintenance, is about \$5.00/1000 gals.,[6] or 6¢/10^6 Btu product output.

Solvent extraction is not a cheap process, although the costs are partly offset by the value of the recovered phenol. Since the quality of the recovered phenol is unknown and probably not high, its value is probably limited to its fuel value, about 4¢/lb. The phenol recovered from 6,000 ppm has a value of about \$2.0/1000 gals, or 2.4¢/10^6 Btu, as compared to the total cost of solvent extraction of 6¢/10^6 Btu. Thus, the value of recovered phenol is important.

Solvent extraction is not a required treatment. It will be used when it pays to use it, which will be when the phenol concentration is high. Furthermore, solvent extraction is not suitable for obtaining very low concentration effluent water. The examples shown on Tables 2-7 and 2-8 for Phenosolvan plant effluent are examples of water treated by solvent extraction. They probably represent the best water reasonably obtainable by solvent extraction. The water is, in our opinion, just good enough to feed to a cooling tower when diluted with an equal volume of river water.

Biological Oxidation

Every test reported shows that most of the organic material in coal gasification wastewater is biodegradable. Biological oxidation is a suitable treatment. In Reference 4 we calculated the cost of air activated sludge biological treatment and of high purity oxygen activated sludge treatment. The air activated sludge plants were sized "on the assumption that the biodegradability of coal conversion wastewaters is identical with that of coke wastewater".

Since then, good measurements of the biokinetics have been made on a Synthane wastewater[22,23] and an H-Coal wastewater[21]. We find that the aeration basins needed are four to eight times larger than would have been predicted from the kinetics of coke oven liquor[6]. The high purity oxygen activated sludge plants will also have to be about two times larger than previously thought and the oxygen consumption estimate is higher.

The cost of biological oxidation is in the range of 10-20¢/lb BOD removed, with the high cost corresponding to air activated sludge and the lower cost corresponding to oxygen activated sludge[6]. A cost of 15¢/lb BOD removed can be converted to give:

BOD Removed (mg/l)	$/1000 Gallons
20,000	25
15,000	19
10,000	12
5,000	6

In considering solvent extraction, we mentioned that the cost, for large throughputs, is not much dependent on the concentration of phenol, but that credit for phenol recovered is proportional to the concentration. This means that solvent extraction is preferred at high concentrations and biological oxidation at low concentrations. The cost curves cross in the approximate range of 2000 mg phenol/l and 6,000-10,000 mg BOD/l. Throughput also matters, but for large gasification plants, we can expect to have wastewater streams for which solvent extraction appears preferrable to biological oxidation for gross removal of contaminants. We must, therefore, consider the cost of biological treatment when it is used to follow a solvent extraction treatment for the purpose of improving the quality of the water effluent from solvent extraction.

For low concentrations, below about 2,000 mg BOD/l, the rate of removal of BOD is not a good correlator of cost. The best expression is $/1000 gals. For municipal plants, Culp, Wesner and Culp have reported[24] 20¢/1000 gals for operating costs plus capital costs which we estimate as 20-30¢/1000 gals. We use industrial, not municipal, costs of capital. This was in 1974 with an EPA index of 200. Today the EPA index is about 300, so total costs are in the range 60-80¢/1000 gals. We have designed and estimated some second stages for biotreatment and agree with a cost of 80¢/1000 gals, or 1¢/10^6 Btu product output.

For the added cost of about 80¢/1000 gals, we can hope to change the effluent from a solvent extraction treatment from approximately the analyses of Tables 2-7 and 2-8 to about 50-100 mg/l BOD and 10-20 mg/l phenol. It must be remembered that, in a cooling tower, we concentrate the phenol and BOD, but also destroy about 50% of the feed BOD and 98% of the feed phenol. Whether or not a biological treatment is worthwhile after a solvent extraction will be discussed later.

Adsorption

If adsorption is used, the wastewater is passed through a resin which adsorbs the phenol. Such a resin is expensive. The 2,000 gpm Lurgi wastewater stream would require dual train resin beds costing about $\$4.8 \times 10^6$; of this, $\$1.8 \times 10^6$ is for the instrumented vessel bed, and $\$3.0 \times 10^6$ is for the resin which has an expected lifetime of five years[6]. Capital amortization and resin replacement costs amount to about \$1.70 per 10^3 gals treated[6]. The resin has to be regenerated--about every eight hours in the example quoted. The cost of regeneration is dependent on the solvent regenerant costs. In the Lurgi plant example, with 6,000 mg/l phenol, the resin will hold 5 lb phenol/ft^3 and will require 1.5 ft^3 resin to regenerate. The solvent will be distilled from the phenol, as for solvent extraction. The distillation energy for methanol, assuming 80% reflux in the still, is about

$$1.8 \times \frac{470\ \text{Btu}}{\text{lb solvent}} \times \frac{80\ \text{lb solvent}}{5\ \text{lb phenol}} \times \frac{50\ \text{lb phenol}}{1000\ \text{gals}} = 0.7 \times 10^6\ \text{Btu/1000 gals}$$

At $\$3/10^6$ Btu, this is \$2.0/1000 gals. Solvent losses (1%) amount to a further \$0.6/1000 gals. If acetone is used as solvent, energy costs are halved, but the cost of lost solvent nearly trebled, to give the same cost for solvent regeneration. Total costs for resin adsorption will again not be less than \$4.50/1000 gals.,[6]. If credit is taken for phenol recovery, the net operating cost will be about \$2.50/1000 gals or $3¢/10^6$ Btu product output.

For our particular Lurgi plant examples (2,000 gpm at 6,000 mg phenol/l) the cost of solvent extraction is similar to that of resin adsorption. The phenol is recovered in both cases. A study by C. F. Braun[25] on a different water stream (1,000 gpm at 15,800 mg phenol/l) found solvent extraction cheaper than adsorption. No absolute costs are given, only the difference.

Adsorption is not as established a procedure as solvent extraction and the following remarks, based on a few designs of our own, are tenative.

1) The cost of solvent extraction is highly dependent on effluent quality, but the cost of adsorption is essentially independent of fractional removal. Therefore, it is best to design for over 99% removal.

2) It is probable, but not proved, that for the same percent removal of phenol, adsorption gives a higher removal of COD than solvent extraction.

3) The cost of adsorption is lower when the influent phenol concentration is lower, but the cost of extraction is not dependent on influent concentration.

Adsorption is a suitable procedure for improving the water quality beyond the minimum needed for feed to cooling tower. A study has been made on the exemplary Lurgi plant effluent, assuming 80% phenol removal by solvent extraction, followed by as high a removal as can be obtained in practice by adsorption. The feed to adsorption is 1,200 mg phenol/l at 2,000 gal/min. The design effluent from adsorption is 12 mg phenol/l (99% removal) but this is meaningless in fact because we do not know what will really be adsorbed. The total capital cost of phenol removal by combined solvent extraction and resin adsorption[6] is about \$10 x 10^6. The total operating cost is \$3.92 x 10^6/yr or \$3.75/10^3 gals.,[6]. If credit is taken for phenol recovery, the net operating cost is \$1.80/1000 gals, or 2.2¢/10^6 Btu, which is about \$0.70/1000 gals lower than either solvent extraction or resin adsorption alone.

2.8 Quantities, Qualities and Disposal of Cooling Tower Blowdown

In the preceding two sections we have shown that a cooling tower can accept water that is importantly more contaminated than would be permissible for discharge to a river. For this reason foul condensate water leaving the process will be treated, using the methods discussed, to a quality required for makeup to the cooling system, and not to a quality required for return to the river. The consequence of this flow path, however, is that cooling tower blowdown becomes the principal discharge point for the whole plant and the water will contain, in addition to the usual somewhat concentrated salts, residues of organic matter originating in the coal reactor. Disposal of cooling system blowdown is not as straightforward as, for example, in electric generating plants. It is this problem which is faced in this section.

2.8.1 Quantity and Quality

A cooling system is both a concentrating device and a form of treatment, as discussed above in Section 2.6. Additional treatments can be placed either on the makeup or in the blowdown and the quantities and qualities fed to the treatments will depend on the location. Cost estimating must begin with a measure of the flow rates. Furthermore, since the cooling tower is a concentrating device, quality and quantity will alter together and cannot be separated.

The water evaporated for cooling is very much a matter of plant design. Table 2-11 shows the calculation for a 65% efficient gasification plant with 25% of the unrecovered heat dissipated by evaporative cooling. The evaporation rate is 100 lb/10^6 Btu. In a series of detailed studies[5] we have considered the individual cooling loads in a variety of coal conversion plants, and determined the degree to which wet cooling, dry cooling or wet/dry cooling should be used as a function of the availability and cost of water in the Western United States. We found that the dissipation of 25% of the unrecovered heat by evaporative cooling is not excessive, but not minimum, in the Colorado River basin. The balance of the unrecovered heat is dissipated directly, as up a stack, or through air cooled heat exchangers. This conclusion is borne out by all available commercial plant designs.

As was discussed in Section 2.6, the cooling system must be blown down to prevent the formation of scale. Acidification of suspending or anti-scaling agents, and, occasionally, softening to remove calcium, all help to minimize blowdown. In current steam-electric power plant practice in the West, a concentration in the circulating water of fivefold (called "five cycles of concentration") is low; tenfold is beginning to be found economical and higher concentrations are being planned. In the example on Table 2-11 we found that a thirteenfold concentration would yield just enough blowdown to dispose of with the coal ash. If this were chosen, then the circulating water would be treated to prevent scaling at thirteenfold concentration.

For a typical plant we will take 10% of the makeup as blowdown and 100 lb evaporated/10^6 Btu product giving 11 lb blowdown/10^6 Btu and 111 lb makeup/10^6 Btu. A plant making 250 x 10^6 scf/day pipeline gas would produce 109 x 10^3 lb/hr cooling system blowdown (= 218 gals/min = 351 acre-ft/yr). This is similar in quantity to the ion exchange waste.

TABLE 2-11. APPROXIMATE MATERIAL AND ENERGY INFORMATION ON A 65% EFFICIENT COAL GASIFICATION PLANT

Product:	10^6 Btu as gas
Coal:	1.54×10^6 Btu Approximately 154 lb coal
Unrecovered energy:	0.54×10^6 Btu
Fraction lost to cooling water:	25%
Evaporation rate:	1400 Btu dissipated per pound of water evaporated. 96 lb water evaporated
Coal ash:	Approximately 15 lb ash
Water lost with coal ash:	35% moisture in wet colids 8 lbs water
Concentration in cooling tower:	13 fold
Makeup to cooling tower:	104 lb water

On Table 2-5 it was shown that the flow rate of dirty condensate was very variable with process and, for some processes, with moisture in the coal. In addition, some of the dirty condensate will be taken for purposes other than cooling system makeup. One possible use is makeup to a flue gas desulfurization system if the plant boilers are coal fired rather than gas fired. For this purpose additional removal of organic material is probably not required. Because it is low in salt, treated condensate is suitable for spraying on roads to control dust. For this purpose good organic removal helps. Still in most plants most of the process condensate will be used in the cooling system and will be treated just enough to permit this use. This level of treatment is for this report, an internal treatment that must be done for adequate plant operation rather than for environmental control. The cooling blowdown will contain concentrates derived from process condensate and if these are unacceptable then additional treatment of condensate (before mixing into the cooling system feed) or of cooling system blowdown is required.

Approximately 20-50% of the makeup to the cooling system may be treated condensate, with 30-70 lb condensate/10^6 Btu requiring at least enough treatment for use in the cooling tower. Based on the above discussions, the condensate may require additional treatment for the safe disposal of the blowdown with 30-70 lb condensate treated for every 11 lb of blowdown.

If treated condensate had twice the organic concentrations shown on Table 2-9; if this water were 20-50% of the tower makeup; if the tower concentrated tenfold, except for ammonia; and if 50% of the feed BOD and 98% of the feed phenol were removed in the tower, then the concentration of the blowdown might be as shown on Table 2-12. The blowdown contains appreciable organic contamination. Blowdown from many gasification processes will have less organic contamination. This table will be used for discussion of the cost of blowdown treatment. Please remember that it is largely conjecture[30].

The total dissolved solids shown on Table 2-12 depend mostly on the quality of the river water taken into the plant. Furthermore, the blowdown is likely to be supersaturated in scale forming salts so treatments intolerant of precipitation, such as reverse osmosis or electrodialysis, are unlikely to be suitable for desalting this water.

We will discuss treatment and its cost, but first disposal must be mentioned.

TABLE 2-12. ESTIMATE OF CONCENTRATIONS IN COOLING SYSTEM BLOWDOWN

	mg/l
Phenols	8 - 20
BOD	2,000 - 5,000
COD	7,000 - 17,000
Ammonia	< 20
Total Dissolved Solids	2,000 - 6,000+

2.8.2 Disposal

As indicated on Figure 2-1, most plans do not include disposal of blowdown to the river. Current and proposed regulations in the Colorado River Basin are directed towards zero discharge. The Lurgi designs of El Paso[32] and Wesco[33] do not have any effluent discharges. The usual plant will use blowdown to wet down the coal ash for disposal and will try to control the cooling system to ensure that the plant stays in balance. For the example shown in Figure 2-2, the cooling tower was operated in such a way as to use all of the blowdown for ash disposal.

For the purposes of this study, we do not count the ultimate disposal procedure relevant. If, for any chosen disposal procedure, the blowdown is too dirty or too salty, then additional treatment is needed.

2.8.3 Treatments and Costs

Because cooling tower blowdown is supersaturated, the most probable procedure for salt removal is evaporation. If forced evaporation is used, the organic matter will distill with the water and if this is not good enough, it must be removed, probably before the evaporator. Impoundment and natural evaporation is also possible. The flow rate of blowdown is the same as the flow rate of ion exchange waste and the discussion for ion exchange waste applies. Here again, if organic contamination of the pond residue is unacceptable, then organic removal is required. At this time we do not know what level of organic contamination is unacceptable.

Consider the organic removal possibilities, one-by-one, basing the discussion on 1000 gals of blowdown.

Biological treatment will probably be functional in the blowdown stream. However, there will be present biocides to control slime in the cooling system and these may interfere or render smooth operation difficult. It is possible, but not probable, that the high salt concentration will interfere. More important is the fact that biological treatment removes BOD and not COD. In an activated sludge process, non-biodegradable contamination is removed by adsorption onto the sludge. Probably this will happen much less in the cooling tower and the ratio COD/BOD will be higher in the blowdown than in the makeup. Consequently, biological treatment should probably be placed in the makeup. If this were done 3000 to 7000 gals would have to be treated per 1000 gals of blowdown at a cost of $2.4 to $5.6/1000 gals blowdown (= $782 to $1826/acre-ft). We can say little about the quality of the effluent water, but we expect it to be medium good.

Our information and costs for Resin Adsorption are based on phenol, not COD. If it works on the blowdown, it will cost about $2.0/1000 gals (= $652/acre-ft), but we cannot predict the quality. It will be used in the makeup only if it gives an improved quality over biological oxidation. Whether it will or not is unknown at this time.

Carbon Adsorption may, tentatively, be expected to give a good quality effluent. Based on 1973 costs from Hutchins[28,29], we found 11¢/lb COD removed[4]. Today's costs are nearer 15¢/lb COD. This translates as

COD Removed (mg/l)	$/1000 gals
10,000	12.5
5,000	6.2
1,000	1.2
500	0.6

Culp and Shuckrow, for very large municipal plants with low COD loadings, found $0.6/1000 gals (= $196/acre-ft).

The cost of the use of carbon is so dependent on the COD that we cannot safely predict it. Carbon will only be used if the costs are less than alternatives.

Wet Oxidation is likely to be a reliable general purpose treatment[31], but the cost will be more than $6/1000 gals ($1956/acre-ft). Wet oxidation can take the place of carbon adsorbtion for high concentrations.

In sum, in plants having the maximum organic content in the cooling tower blowdown, a great improvement in quality can be obtained by biological treatment of the makeup at a cost of $2.4 to $5.6/1000 gals of blowdown. A better quality probably can be obtained by carbon adsorption or wet oxidative treatment of the blowdown at more than $6/1000 gals of blowdown. Salt removal will be by forced evaporation at an additional cost of $6-11/1000 gals. Impoundment with, or without any of the above treatments, costs about $4.60/1000 gals.

2.9 Domestic Wastes from Plant

A discussion on the quality and treatment of wastewaters from potable and domestic usage is found in Section 4.5. The quantity of wastewater is relatively small, about 28 gpm (= 45 acre-ft/yr).

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3. WASTEWATER STREAMS IN THE SURFACE RETORTING OF OIL SHALE

3.1 Water Management

In this section we will discuss the wastewater streams associated with the mining and surface retorting of oil shale and the methods of treating and managing these waters. The data that will be presented was derived primarily from three oil shale retorting processes; Paraho Direct and Indirect heated retorts[1] and Tosco II[2], and combinations of each[3]. The water management schemes for these processes are representative of the water management schemes of the various other surface retorting technologies. The role that water plays in the production of synthetic crude from oil shale is presented in Reference 4, together with a description of various retorting processes and calculations of the water requirements for large oil shale mine-plant complexes. References 5-8 also present the water related impacts of shale oil conversion.

In an integrated oil shale mine-plant complex, there is a net consumption of water. All surface processing operations involve mining, crushing, retorting and upgrading to produce a synthetic crude oil for refining. Water is required for dust control in the mine, for crushing and for other dust control operations in transporting the crushed shale to the retort. When shale is retorted, large quantities of water are evolved, partly due to the surface moisture of the shale, partly from the thermal decomposition of the carbonate materials and, in direct retorting, partly from the water produced in combustion. However, in indirect retorting, the water in the combustion product is generally lost up the stack. Some processes require large amounts of cooling in retorting, while others require little or no cooling, the actual amount depending on how the retort operates. Cooling water is required, however, in dissipating waste heat that has been generated in the plant. Steam will be consumed for process cooling and in distillation or stripping columns. Finally, water may be required for the disposal and revegetation of the spent shale piles.

From the point of view of water management, the type of retort and the method of disposal of the spent shale are quite important. The Tosco II and Paraho retorting processes represent two different limits with respect to water treatment and water management schemes and the quantity of water consumed in disposing of and revegetating the spent shale.

The processed shale from the Tosco II retort is a fine black sandy material with about 60 percent of the particles passing through a 200 mesh screen

(0.003 inch opening)[2]. In the proposed Tosco II design[2] the processed shale is moisturized with wastewater, transported to the disposal site and compacted to a density of about 90 pounds of dry spent shale per cubic foot. The compacted shale will have an in-place moisture content of about 13 percent. The addition of the water leads to cementation of the shale after compaction, producing a substance which apparently freezes in the moisture that was added and which is effectively impermeable and resists percolation so that soluble salts cannot be leached out. The water added to the spent shale contains the dirty water from the retorting and upgrading operations, blowdown water from ion exchange treatment, blowdown water from the cooling tower and other blowdown and wastewaters. Treatment is required to remove odorous, volatile components from the dirty process water before being used to moisturize the spent shale. All of the wastewaters generated in the mine-plant complex are not sufficient to provide the proper moisture content for disposal and additional water from the river must be added. In addition, river water is provided for revegetation. As a result, the water management scheme for the Tosco II process is not premised upon the treatment, recycling, and reuse of wastewaters within the plant, since all of the wastewater and more is required to moisturize the spent shale for disposal. The only major treatment that would be required is to remove odorous, volatile substances, such as ammonia and hydrogen sulfide. This is standard practice in refineries and is done as part of the normal upgrading operation. After compaction, additional water will be used to control fugitive dust and to establish vegetative cover.

In the Paraho processes, the spent shale consists of lumps about 3/8 to 1 1/2 inch in size[9]. The Paraho design for the disposal of the spent shale[9] involves lining a valley with a heavy compacted impervious layer of retorted shale. As a result of adding about 20 percent by weight of water to the spent shale and then compacting it, the shale cements up and the layer is made impermeable. The remainder of the retorted shale is deposited into the lined basin and is compacted but not wetted down except for controlling dust and for vegetation. Less than one percent of the total volume of spent shale would be wetted down, substantially reducing the water requirements for spent shale disposal for the Paraho process in comparison to the Tosco II process. However, the water requirements for revegetating the spent shale from the Paraho Indirect retort are larger than those from the Paraho Direct retort and the Tosco II retort because of the higher residual carbon in the former. Moreover, since the wastewaters evolved during the retorting and upgrading operations in the Paraho process are much larger than the water requirements for disposing of the spent shale, they will have to be treated for recycle and reuse within the plant or disposed of in evaporation ponds. The wastewater cannot be used directly for revegetation because its quality must be similar to the quality of river water. Since the latter is wasteful of water, we will assume that the wastewaters will be treated for use in a cooling tower, in a manner similar to that for a coal gasification plant as described in Section 2. The process wastewaters evolved in retorting range from about 10 to 25 percent of the water requirements for cooling in the Paraho process.

Figures 3-1 and 3-2 show the major parts of the two water management schemes discussed above for an oil shale conversion complex in which the source water is river water. In Figure 3-1, which would be characteristic of that used for an oil shale process in which the spent shale is disposed of in a manner similar to that for Tosco II, the retorting and upgrading wastewaters are treated to remove odorous, volatile substances and then, with other plant wastewaters, completely used to moisturize the spent shale. In the scheme shown in Figure 3-2, which is characteristic of a process in which the spent shale is disposed of in a manner similar to that for Paraho, the retorting and upgrading wastewaters are treated for cooling tower makeup, similar to the scheme presented in Section 2 (see Figure 2-1) for coal gasification. If the source water is brackish or high in suspended solids, it must be treated for service use within the mine-plant complex. The service water is generally of potable water quality. Figures 3-3 and 3-4 show the major water streams for a Tosco II plant producing 50,000 barrels/day of synthetic crude (upgraded shale oil) and for a Paraho Direct plant producing 50,000 barrels/day of synthetic crude, respectively. These detailed designs were made recently by Water Purification Associates and are different in some respects than the designs reported in Ref. 4. As a result there may be some discrepancies in flow rates between the values shown on Figures 3-3 and 3-4 and the values found in Ref. 4 and also repeated in this section.

It should be noted that in the proposed White River oil shale design[3], although 85 percent of the oil shale will be processed in Paraho retorts and

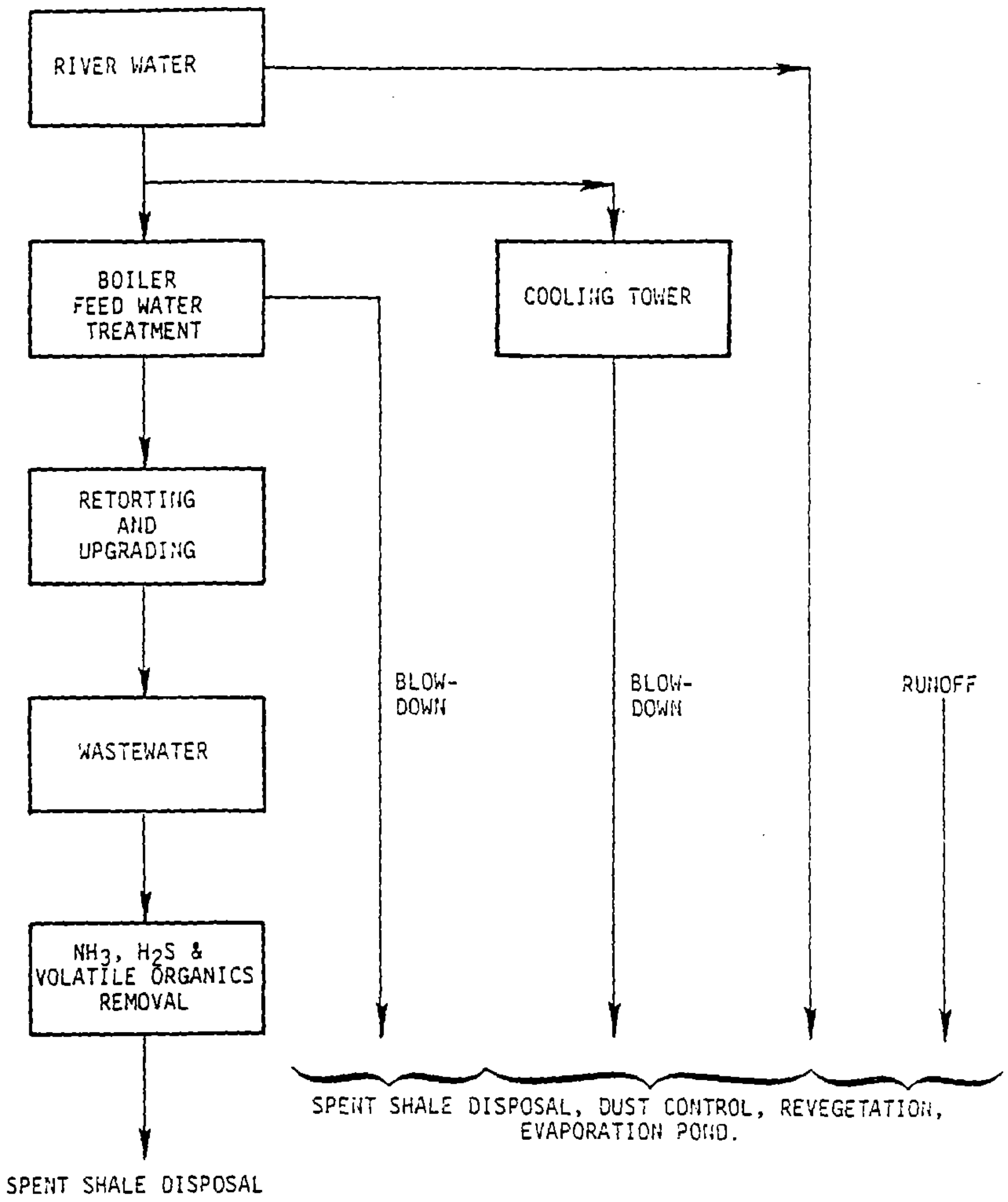

Figure 3-1. Major parts of a water management scheme in a shale oil conversion complex. Typical of process in which the spent shale is disposed of in a manner similar to that for TOSCO II.

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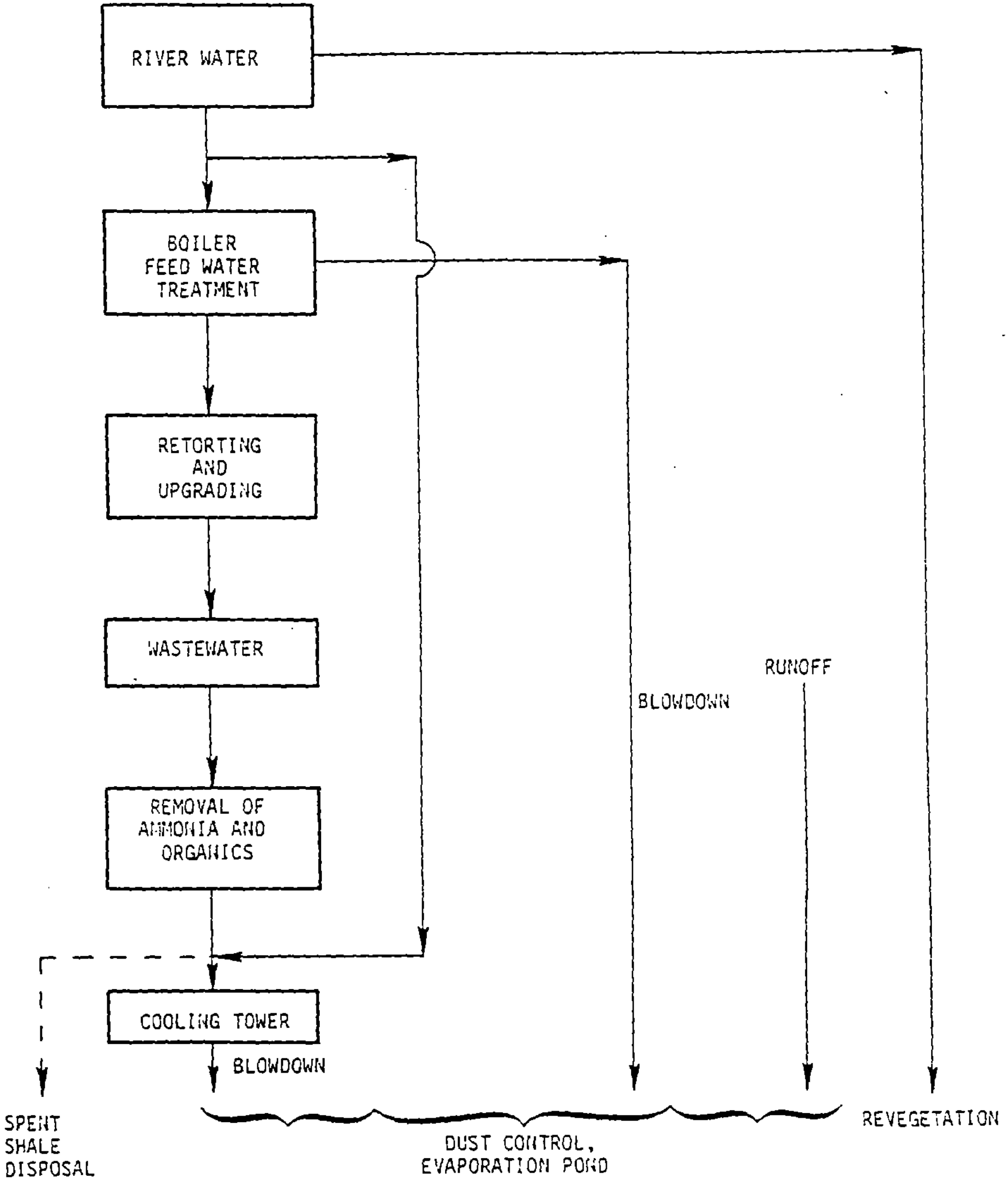


Figure 3.2. Major parts of a water management scheme in a shale oil conversion complex. Typical of process in which the spent shale is disposed of in a manner similar to that for Paraho.

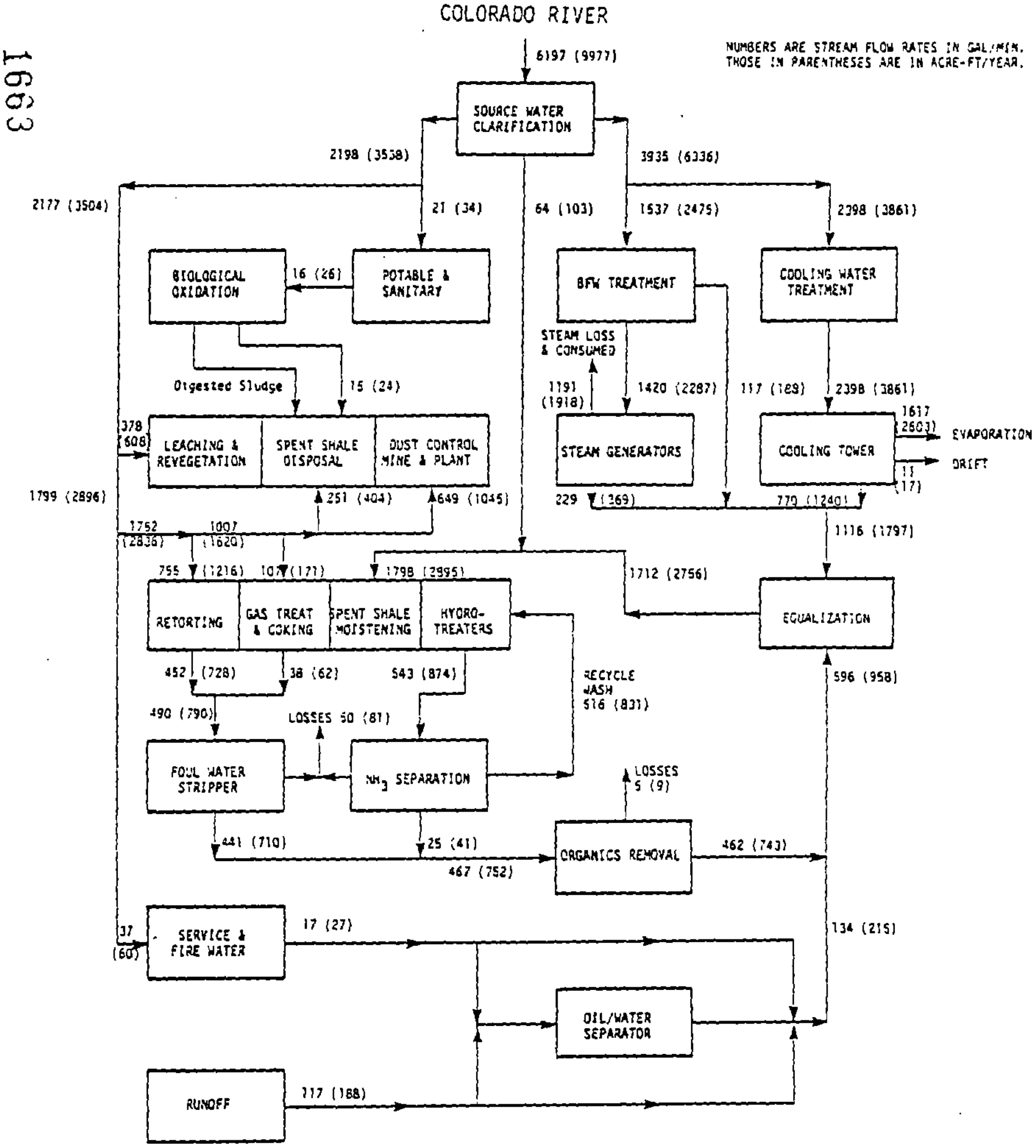
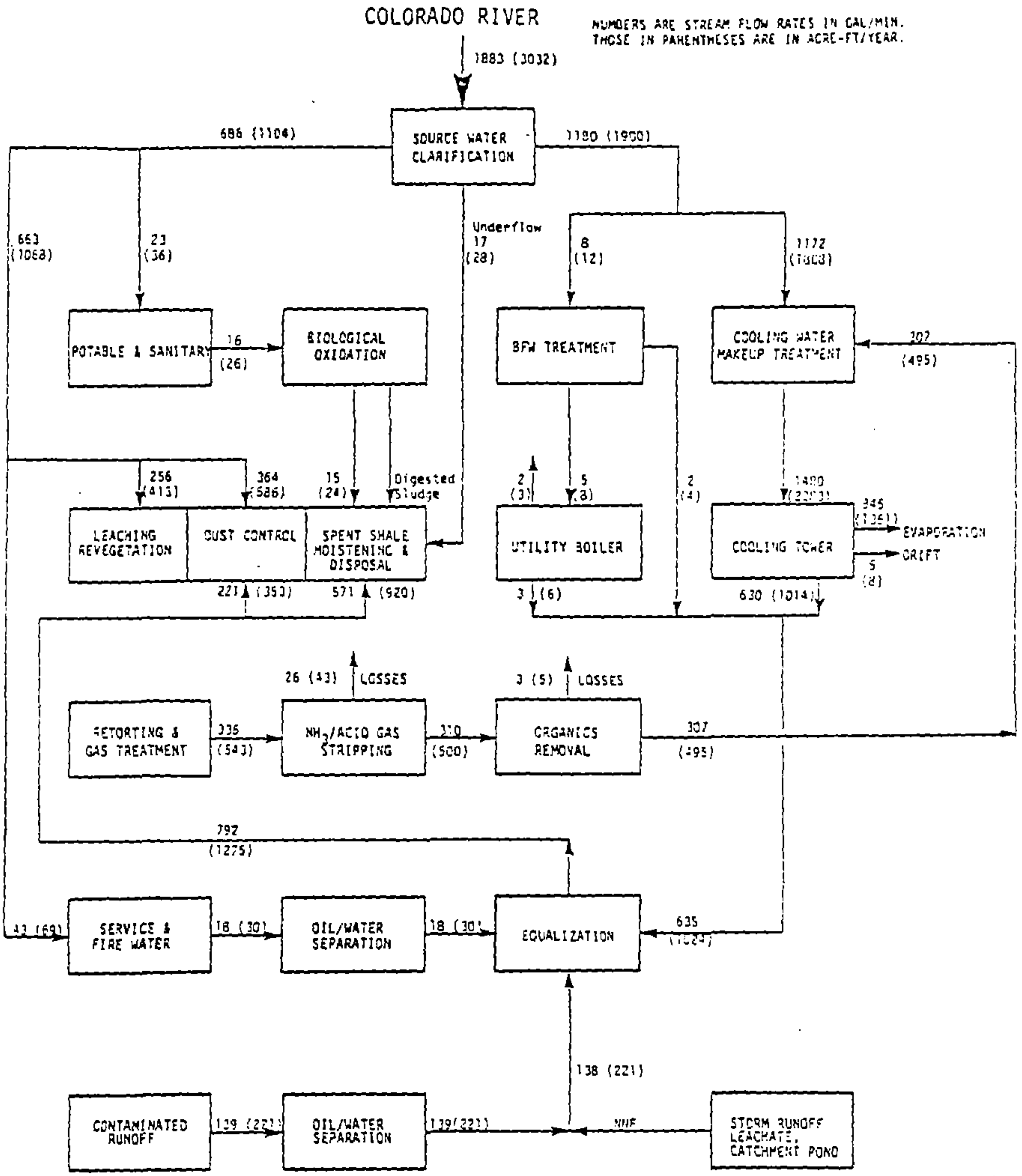


Figure 3-3. Major water streams for TOSCO II process producing 50,000 barrels/day of synthetic crude.



NUMBERS ARE STREAM FLOW RATES IN GAL/MIN.
THOSE IN PARENTHESES ARE IN ACRE-FT/YEAR.

Figure 3-4. Major water streams for Paraho Direct heated process producing 50,000 barrels/day of synthetic crude from 30 gal/ton shale. Recirculating streams are not shown.

only 15 percent processed in Tosco II retorts, the water management scheme is similar to that for the Tosco II design[2]. This is ascribed to the fact that the processed spent shale will contain about 9 percent moisture by weight, requiring all of the process and cooling wastewaters for moisturizing as well as additional makeup from the White River itself. In fact over 60 percent of the water required for moisturizing the spent shale for disposal would be fresh water from the White River.

The wastewaters that will be discussed include runoff, boiler feedwater makeup treatment blowdown, cooling tower blowdown, retorting and upgrading wastewaters, and domestic wastes from the plant. We have assumed that there is no excess mine drainage water produced during the surface retorting process. If there is, the treatment or handling of these excess groundwaters can be carried out in a manner described in Section 4.2. The wastewater quantities for the Tosco II process will be estimated although the costs of wastewater treatment are considered to be zero since all of the wastewater is used for spent shale disposal. The various treatment options have been discussed in Section 2 and will not be repeated.

The water quantities presented in this section will be based upon a 50,000 barrel/day plant. There are, however, different interpretations of the meaning of this size plant in terms of the product output. In the Paraho design[2] the nominal output is expressed in terms of the crude shale oil production, while the Tosco design[2,10] expresses the output as the sum of the upgraded liquid fuels. In order to have a uniform basis for comparing different retorting procedures and different grades of oil shale, a standard size oil shale complex will be one that is designed to produce 50,000 barrels/day of synthetic crude plus any byproducts not utilized as plant fuel. The total heating value of the basic product fuel is 2.9 x 10^{11} Btu/day[4]. The sized shale feed rate in the Paraho Direct and Indirect processes to produce 50,000 barrels/day of synthetic crude is 87,350 and 100,000 tons/day of 30 gal/ton shale, respectively, while in the Tosco II process the sized shale feed rate is 73,350 tons/day of 35 gal/ton shale The water quantities will be specified for both the "50,000 barrels/day design" and a plant producing 50,000 barrels/day of synthetic crude, where synthetic crude for Paraho means pumpable crude shale oil and for Tosco II means partially upgraded shale oil.

3.2 Runoff

Runoff is not a difficult problem as long as it is collected and impounded properly. For oil shale conversion complexes, storm runoff and leachate from the processed shale area will be collected and used primarily to control dust on the processed shale disposal pile, or to moisturize the spent shale. In the plant area the runoff will contain residual oil which must be separated from the water before the water can be used in the moisturizer or for dust control or as makeup to the cooling tower. The quantity of runoff is very site dependent.

3.3 High Total Dissolved Solids Wastewaters

There are a number of wastewater streams that contain a large quantity of total dissolved solids. The primary ones are the blowdown stream from boiler feedwater makeup treatment by ion exchange and the blowdown from the cooling tower.

3.3.1 Boiler Feedwater Makeup Treatment Blowdown. In the Tosco II process steam is used primarily in the upgrading operation[2]. Steam levels of 60 psi and 400 psi have been proposed, which in general are lower than the pressure requirements for the steam generated in coal gasification plants and which, as a result, does not require as much treatment. Because of the relatively low pressure steam only zeolite softening, and not complete demineralization, has been proposed for boiler feedwater makeup treatment. The high pressure steam passes through turbines and drives rotating machinery. The condensate is recycled. Low pressure steam is consumed for process heating and in stripping columns. Approximately 1450 gpm (= 2330 acre-ft/yr) of boiler makeup is required for the 50,000 barrel/day Tosco design[2,5], or about 1510 gpm (= 2470 acre-ft/yr) of steam is required for a plant producing 50,000 barrel/day of synthetic crude. In the proposed Tosco design[2], the blowdown from the zeolite softener is sent to the processed shale moisturizer.

Our estimate of 7 gpm (= 12 acre-ft/yr) for boiler makeup for a Paraho Direct plant producing 50,000 barrels/day of synthetic crude is given on Figure 3-4. This makeup is very small because there is no upgrading in the Paraho design. However, in the design for the proposed White River Oil Shale Project[3] which uses a combination of Paraho Indirect and Direct heated retorts and a Tosco II retort, but with a lower grade shale of 28 gal/ton, the boiler makeup requirements are much larger. In the White River design approximately 85 percent by weight of the oil shale will be processed in Paraho retorts and only 15 percent will be processed in a Tosco II retort. A Paraho Direct retort will process 71 percent of the oil shale with the other 14 percent used in a Paraho Indirect retort. The steam is used primarily for upgrading with steam levels of 50, 150 and 600 psg. Approximately 370 gpm (= 600 acre-ft/yr) of boiler makeup is required for the 50,000 barrel/day White River design or 420 gpm (= 680 acre-ft/yr) for a plant producing 50,000 barrels/day of synthetic crude. In the proposed design the blowdown from the ion exchange units are fed to a storage tank and then used to moisturize the spent shale.

As is pointed out in Section 2.3.2, the blowdown streams are from 8 to 15 percent of the product water volume and the wastewater concentration is about 2 to 2.5 percent total dissolved solids.

3.3.2 Cooling Tower Blowdown. Although some retorting processes require little or no water for cooling, as for example the Paraho direct process, cooling water is required to dissipate waste heat generated primarily in the upgrading operation. Estimates of the overall conversion efficiency, the unrecovered heat removed by wet cooling, and the total water evaporated in an oil shale complex for cooling, including that for retorting, is given in Table 3.1. The values are taken from Reference 4 and are based on heat balance calculations made from the Paraho[1] and Tosco II[2] designs.

TABLE 3.1 UNRECOVERED HEAT RECOVERED BY WET COOLING, OVERALL CONVERSION EFFICIENCY AND WATER EVAPORATED IN AN OIL SHALE PLANT PRODUCING 50,000 BARREL/DAY SYNTHETIC CRUDE

	Overall Conversion Efficiency (%)	Fraction of Unrecovered Heat to Evaporate Water (%)	Water Evaporated for Cooling (gpm)
Paraho Direct	71	28	2320
Paraho Indirect	57	19	2660
Tosco II	68	18	1700

The complete water management flow diagram for the Tosco II process, shown in Figure 3-3, gives evaporation and drift losses equal to 1530 gpm (= 247 acre-ft/yr) for the 50,000 barrel/day design or 1630 gpm (= 2620 acre-ft/yr) for a mine-plant complex producing 50,000 barrel/day of synthetic crude, as compared to the value of 1700 gpm shown in Table 3.1. These values are consistent with those found in Reference 5. The evaporation and drift losses for the Paraho Direct process are shown in Figure 3-4; approximately 740 gpm (= 1190 acre-ft/yr) will be consumed in the 50,000 barrels/day Paraho Direct design and 850 gpm (= 1370 acre-ft/yr) will be consumed in a plant producing 50,000 barrels/day of synthetic crude. In the White River design[3,5], which should also be characteristic of the Paraho Direct retort process, the water evaporated for cooling is 900 gpm (= 1450 acre-ft/yr) for 50,000 barrel/day of shale oil or about 1030 gpm (= 1660 acre-ft/yr) for a plant producing 50,000 barrel/day of synthetic crude. The value of 1030 gpm for White River is consistent with the value of 850 gpm shown in Figure 3-4 for the Paraho Direct process because the White River design requires additional energy for upgrading, whereas the Paraho Direct design does not. The value of 2320 gpm shown in Table 3-1 was calculated for a design that assumed that the retort gas is compressed prior to gas purification as compared to the design shown in Figure 3-4 in which the gas is compressed at the gas turbines and is not cooled. Thus, the higher value shown in Table 3-1 is due to the cooling of the retort gas. We have taken a range of a factor of three for the water consumed in cooling for the Paraho Direct process. In both the Tosco and White River designs, the blowdown from the cooling tower eventually ends up in moisturizing the spent shale.

In both the proposed Tosco II and White River designs, as well as the Paraho Direct design shown in Figure 3-4, approximately 3 to 5 cycles of concentration was used in the cooling tower. It is not necessary to go to higher cycles of concentration in these cases because the blowdown is to be used for spent shale disposal.

The blowdown from the cooling towers for the Tosco II design is 720 gpm (= 940 acre-ft/yr) or 770 gpm (= 1240 acre-ft/gpm) for a mine-plant complex producing 50,000 barrel/day of synthetic crude, while for the White River design the blowdown is 230 gpm (= 370 acre-ft/gpm) or 260 gpm (= 420 acre-ft/yr) for a plant producing 50,000 barrels/day of synthetic crude. For the Paraho design shown in Figure 3-4, the blowdown is 630 gpm (= 1010 acre-ft/yr) for a plant producing 50,000 barrel/day of synthetic crude. The total dissolved salt concentration would range from 2000 to 10,000 ppm, depending on the cycles of concentration and the TDS of the source water.

3.4 Retorting and Upgrading Wastewaters

As was previously pointed out for oil shale processes which dispose of the spent shale in a manner similar to that for Tosco II, all of the retorting and upgrading wastewaters are treated to remove odorous, volatile substances as part of the normal upgrading operations and then used to moisturize the spent shale. The cost of wastewater treatment for this case is negligible. However, for processes which dispose of the spent shale in a manner similar to that for Paraho, the retorting and upgrading wastewaters should be treated for reuse within the plant rather than, for example, evaporating the waters in lined evaporation ponds, which is wasteful of water. One use of the wastewater is as cooling tower makeup similar to that for coal gasification. The waters evolved in retorting and that used for upgrading are approximately 20 percent of the cooling water makeup in the Paraho Direct process and approximately 12 percent in the Paraho Indirect process[4], as compared to a range of 20 to 50 percent for coal gasification (i.e. for coal gasification the process condensate is about 20 to 50 percent of the cooling water makeup).

Limited data is available on the quality of the retort waters. Table 3-2, taken from Reference 6, shows the range of concentration of the major constituents present in the retort water from the Paraho direct process. The retort water consists of the water separated from the crude shale oil and the water condensed from the retort gases. Little data is available on the quality of the upgraded wastewater. An analysis of the Tosco II retort water is given in Table 3-3 and represents a composite from data in References 2 and 11 (also see Reference 4). Both retort waters are high in ammonia and are quite dirty. The Tosco II water has a very low phenol content with the organic acids primarily carboxylic acids which are highly biodegradable[11]. The approximate composition of the combined retorting and upgrading wastewaters for the Tosco II process is given in Table 3-4. The major components are mineral salts, phenols, amines, organic acids and neutral oils.

The quantities of water evolved in retorting and the combined foul water out of retorting and upgrading is given in Table 3-5[4]. The quantity of upgraded water is relatively constant for all three processes ranging from 167 gpm for Paraho Direct to 191 gpm for Paraho Indirect.

TABLE 3-2 ANALYSIS OF PARAHO DIRECT PROCESS RETORT WASTEWATER

Constituents	Concentration Range (mg/l)
Ammonia Nitrogen	2,000 - 20,000
Organic Carbon	10,000 - 29,000
Carbonates	2,000 - 24,000
Bicarbonates	5,000 - 26,000
BOD	5,000 - 12,000
COD	17,000 - 20,000

Source: Ref. 6

TABLE 3-3 ANALYSIS OF RETORT WATER FROM TOSCO II PROCESS

Carboxylic acid (mg/l)	1,000 - 2,000
Phenols	50
Ammonia (nitrogen as ammonia, mg/l)	15,800
Sulfur	4,000
pH	∿ 8 - 9

Source: Refs. 2,4 and 11

TABLE 3-4 APPROXIMATE COMPOSITION OF TOSCO II COMBINED PROCESS RETORTING AND UPGRADING WASTEWATER

Component	Concentration in Water (mg/l) Added to Spent Shale
Ca^{+2}	280
Mg^{+2}	100
Na^{+1}	670
NH_4^{+1}	16
Zn^{+2}	5
As^{+5}	.015-0.3
Cr^{+6}	2
CO_3^{-2}	360
HCO_3^{-1}	100
SO_4^{-2}	850
$S_2O_3^{-2}$	90
PO_4^{-3}	5
Cl^{-1}	570
CN^{-1}	5
Phenols	315
Amines	410
Organic Acids	1,330
Neutral Oils	960
TOTALS (Rounded)	6,100

In addition to above, elements present in trace quantities (less than 1 mg/l) are Pb, Ce, Ag, Mo, Zr, Sr, Rb, Br, Se, Cu, Ni, Co, Fe, Mn, V, Ti, K, P, Al, F, B. Li.

Source: Ref. 6

TABLE 3-5 QUANTITIES OF PROCESS WATER STREAMS FOR OIL SHALE PLANTS PRODUCING 50,000 BARRELS/DAY OF SYNTHETIC CRUDE

	Water Out of Retorting (gpm)	Combined Foul Water Out of Retorting and Upgrading (gpm)
Paraho Direct	272+	439
Paraho Indirect	159++	350
Tosco II	83	266

+86% in retort gas, 24% in crude shale oil

++48% process condensate, 24% in retort product gas, 28% in crude shale oil.

Source: Ref. 4

TABLE 3-6 QUALITY OF SOUR WATER STRIPPER BOTTOMS

pH	8.5 - 9.5
COD	500 - 1500 mg/l
Oil & Grease	50 - 100 mg/l
Phenols	80 - 150 mg/l
Ammonia	25 - 50

Source: Ref. 3

The wastewaters contain large quantities of ammonia and carbon dioxide, hydrogen sulfide, and organic matter which are mostly biodegradable. However, the waters are low in phenol content, unlike the coal gasification foul condensate, which is high in phenol. Thus, insofar as treatment of the wastewater to cooling water makeup quality is concerned, it would be very similar to the treatment of foul condensate. (See Section 2.7). Ammonia, hydrogen sulfide and carbon dioxide are removed by steam stripping and ammonia and sulfur recovered in ammonia separation and sulfur recovery units. Biological oxidation will remove the organics from the stripped wastewaters. The costs of these treatments are estimated in Section 2.7.

3.5 Sour Water Stripper Wastewater

In the White River design the wastewater from the sour water strippers is estimated to have a quality shown in Table 3-6, with a flow rate of 225 gpm (= 360 acre-ft/yr) for the 50,000 barrel/day White River design or a flow rate of about 260 gpm (= 420 acre-ft/yr) for a plant producing 50,000 barrel/day of synthetic crude. The water appears to be highly biodegradable. The water is then treated by flotation to remove oil and then a biological oxidation system to remove the organics. It is then used for dust control within the plant . The BOD is estimated to be in the range 300-1000 mg/l. The cost of biological oxidation falls in the range 80-120¢/1000 gals (See Section 2.7) with the concentration of the product water less than 20 mg/l of BOD with phenols less than 1 mg/l.

3.6 Domestic Wastes from Plant

A discussion on the quality and treatment of wastewater from potable and domestic usage is found in Section 4.5. The quantity of wastewater is relatively small, about 15 gpm (= 24 acre-ft/yr) for both the Tosco II and Paraho Direct designs shown in Figures 3-3 and 3-4.

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4. WASTEWATER STREAMS IN MODIFIED IN SITU RETORTING OF OIL SHALE

4.1 Water Management

The specification of the water management for modified in situ (MIS) retorting of oil shale depends primarily upon (i) the site, (ii) the retorting procedure, (iii) the product and byproducts, and (iv) the disposition of the mined-out shale.

The site affects the water management principally through the groundwater inflow to the mine and retort - a factor which is dependent on local geohydrological conditions. The average shale grade, which is site dependent, also has some influence on the water needs and retort water produced. The amount of water or steam injection into the retort, along with the steam pressure, is determined by the retorting procedure. These factors in turn directly affect the quantity and quality of the retort water produced.

The product affects the water management through the rate of output and through the product quality, as for example whether a pumpable shale oil or an upgraded high quality synthetic crude is the product. The byproducts are similarly important, in particular whether and how cleaned retort off-gas is burned to generate electricity for possible transmission off site. The mined-out raw shale may simply be disposed or it may be surface retorted. The option selected has a strong bearing on the water management scheme.

In order that we may define the water treatment and disposal costs for modified in situ retorting of oil shale, it is first necessary to specify the processing criteria for the plant. Little concrete information is available at this time on modified in situ processing because of its early stage of development. Our criteria and water management outline must be derived from the development plans outlined by two groups[1-5]. These two groups are now only at the early stages of commercial ventures for the modified in situ production of shale oil in the Piceance Creek Basin of Colorado. The C-b Shale Oil Venture of Occidental (Oxy) and Ashland Oil is the most advanced of the two programs, with tests already carried out on three smaller retorts of about 1,000 square feet in cross section and from 72 to 114 feet high and two full-size retorts about 300 feet high and 15,000 square feet in cross section. Testing is presently being started on a third full-size retort. The Rio Blanco Project is only now shaft sinking and mining experimental retorts, with rubblizing and burning of the first of five small retorts not scheduled to begin until October, 1979.

In Table 4-1 products and plant parameters projected in both programs for commercial phase operation[1,4] are compared. It should be noted that the Rio Blanco program assumes the likelihood of surface retorting of the mined-out shale to produce an additional 19,000 barrels/day of shale oil, whereas Oxy considers surface retorting an option to be examined at a later date. The Rio Blanco parameters shown are derived from their development plan for the case where the mined-out shale is not surface retorted. The similarity between the parameters of Table 4-1 is striking. Both programs envisage producing a pumpable shale oil and not an upgraded product suitable as a refinery feedstock, as was envisaged in the surface retorting programs discussed in Section 3. Perhaps the principal difference in the plans from a water management point of view is in how the electricity would be generated from the retort off-gas. Oxy assumes the likelihood of using a combined cycle gas turbine system, while Rio Blanco assumes the likelihood of using an open cycle gas turbine system, which, though less efficient, is also less water consumptive since no evaporative cooling is employed.

Table 4-2 compares the plant water balances from the same development plans[1,4] and supplemental modifications[2,3,5]. It is important to emphasize that many of the flow rates shown in both balances had to be deduced or derived from limited data or information, as explained in the footnotes to the table. It should also be emphasized that these figures represent the latest "draft" values of the developers and must be expected to change as more test data becomes available and as plant designs become more specific. What is, however, most striking about Table 4-2 are the marked differences in the assumed water dispositions and water needs between the two plants, despite the similarities of the plant parameters and products evidenced in Table 4-1.

Also shown in Table 4-2 are the mine drainage waters projected for the C-a and C-b sites. These sites are both near the center of the Piceance Creek Basin where significant groundwater is expected. This groundwater is normally discussed in terms of lower and upper aquifers separated by the mahogany zone of oil shale. The occurence of mine drainage waters is not uniform throughout the basin. The aquifers are in the form of bowls with the greatest depth near the center of the basin. Developments on the south end of the basin near

TABLE 4-1. COMPARISON OF COMMERCIAL PHASE PRODUCT AND PLANT PARAMETERS FOR MODIFIED IN SITU RETORTING

	Oxy(a)	Rio Blanco(b)
Shale Oil (pumpable)	57,000 bbls/day(c)	57,000 bbls/day
Sulfur	92 tons/day	100 tons/day
Low-Btu Gas	1.57×10^9 SCF/day	1.30×10^9 SCF/day(d)
Electricity	300-400 MW(e)	230 MW(f)
Mined-out Shale	41,000 tons/day	40,000 tons/day
Injected Retorting Gas	Air/Steam(g)	Air/Steam
Manpower	1,600	1,550

(a) Ref. 1.
(b) Ref. 4, MIS retorting only.
(c) All days refer to stream days.
(d) Assuming 60 Btu/SCF.
(e) Combined cycle generation.
(f) Open cycle generation.
(g) 30% steam by volume from data in Fig. III-J, Ref. 1, (848×10^3 lb steam/hr; 10^9 SCF air/day).

TABLE 4-2. COMPARISON OF COMMERCIAL PHASE WATER BALANCES FOR MODIFIED IN SITU RETORTING TO PRODUCE 57,000 BBLS/DAY OF SHALE OIL AND BYPRODUCT ELECTRIC POWER[a]

Oxy[b]		Rio Blanco[c]	
IN TO PLANT	gpm	IN TO PLANT	gpm
MIS Retort Water	770[d]	MIS Retort Water	1,400
Mine Water	7,000[e]	Mine Water	275[e]
-	-	Runoff Water	790
-	-	Boiler Water of Combustion	530
	7,770		2,995
OUT OR CONSUMED		OUT OR CONSUMED	
Steam into Retort	1,700[d]	Steam into Retort	810[f]
Cooling Tower Evapor.	3,370	Cooling Tower Evaporation	115[g]
Shale Disp./Dust Contr.	750	Shale Disposal/Dust Control	660[h]
Spray Irrigation	1,000	Spray Irrigation	680[h]
Process Uses	310	Miscellaneous Uses	100[i]
Evaporation & Potable	40	Evaporation	20
Mine Uses	300	Power Generation Flue Gas Loss	610
Construction Use	300	-	-
	7,770		2,995
Mine Drainage Water	4,000-10,000[j]	Mine Drainage Water	11,250[k]

(a) See Table 4-1 for values.
(b) Data from Ref. 3; Table p. 196, Vol. 2, Ref. 2; Fig. III-J, Ref. 1.
(c) Data from Fig. 6-6-3, Ref. 5; "Water Balance" & Table 3-3-5, p. 3-3-31, Vol. 2, Ref. 4.
(d) Assumed to be the same as in Fig. III-J, Ref. 1.
(e) Quantity required for balance taken to be excess mine water.
(f) Assumed equal to 1,880 evaporated - (610 flue gas loss + 330 cooling tower evaporation + 130 misc. loss) = 810 gpm. Evaporated quantity given in Fig. 6-6-3, Ref. 5 & other values given in water balance on p. 3-3-31, Vol. 2, Ref. 4.
(g) Estimated to be 35% of cooling tower loss of 330 gpm (footnote (f)) from figures given for circulating cooling water in Table 3-3-5, Vol. 2, Ref. 4.
(h) Assumed to be same value for unretorted as for retorted shale.
(i) Estimated at 75% (57,000/76,000) of misc. loss of 130 gpm (footnote (f)).
(j) Projected maximum.
(k) Personal communication (July 1978) from C-b Oil Shale Venture indicates higher upper limit possible.

the rim have little or no groundwater. The oil shale mine drainage waters are thus quite site specific. Indeed, the C-b tract may yield even higher flow rates than shown in Table 4-2 based on its location (see footnote (j)). Clearly very wide differences in quantity among sites is to be expected. Moreover, as we shall discuss below, the quality may also vary significantly and may not resemble the aquifer water, depending upon whether or not the mine water has passed through and been exposed to rubblized shale.

For purposes of estimating water treatment costs in modified in situ oil shale processing, we have developed the composite water balance given in Table 4-3. We have chosen a product output of 57,000 bbls/day of pumpable shale oil, rather than an upgraded product as in Section 3, in order that we may be consistent with the developers' projected plans. In the earlier stages of commercial development, it is probable that the product would be the one assumed. On the other hand, as commercial development progress, shale oil upgrading may be expected to be integrated into the plants. This would, however, not be likely to take place until some considerable time in the future, so that the assumption of shale oil production with off-site upgrading is quite reasonable and provides the best basis for comparison. In any case, upgrading requirements could be backed out from the discussion of Section 3. The assumption of electric power production is also consistent with the developers' plans, although the combined cycle system assumed parallels the direction Occidental has chosen as likely. The reason for our choice is that it is a more efficient process than generation by an open cycle gas turbine system with only a relatively small increase in water consumption. At the same time, it enables the use of the cooling tower as an integral part of the water treatment system for which retort wastewater can be used as makeup, so that upstream removal of ammonia and organics need not be as efficient (and, therefore, as expensive) as it would need to be if the retort water were to be treated for discharge to a river.

The estimated water balance of Table 4-3 assumes that all plant and process waters are recycled or reused, and that any water requirements over and above the process generated retort water and runoff waters are met from mine drainage groundwater. This is consistent with the estimates made by both prospective developers of modified in situ processing in the Piceance Creek Basin. We recognize that this need not always be the case, but it is

TABLE 4-3. ESTIMATED WATER BALANCE WITH MINE WATER INPUT FOR MODIFIED IN SITU RETORTING TO PRODUCE 57,000 BBLS/DAY OF SHALE OIL AND 300 MW OF ELECTRIC POWER[a]

IN TO PLANT	gpm
MIS Retort Water	1,660[b]
Mine Water	1,845[c]
Plant & Mine Area Runoff	125[d]
Shale Disposal Area Runoff	260[e]
	3,890
OUT OR CONSUMED	
Steam into Retort	1,700[f]
Cooling Tower Evaporation	850[g]
Shale Disposal, Dust Control & Reveget.	670[h]
Process Uses	310[i]
Evaporation & Potable	50[j]
Mine Uses (Including Dust Control)	210[k]
Miscellaneous Uses	100
	3,890
Excess Mine Drainage Water to be reinjected and/or Treated for Disposal[l]	2,150-9,400

(a) Generated by combined cycle system.
(b) One part retort water to one part shale oil by volume.
(c) Quantity required for balance.
(d) Quantity estimated in Section 2.2.
(e) Estimated on 5 in/yr of runoff and drainage over 1,000 acres.
(f) Assumed to be the same as in Fig. III-J, Ref. 1. See also footnote (g) Table 4-1.
(g) One-fourth of electricity (75 MW) assumed to be generated by steam turbines. Approximately 150 MW of heat will therefore be dissipated in evaporative cooling tower at about 1400 Btu transferred/lb of water evaporated. This yields an evaporation rate of 730 gpm. An additional 120 gpm is assumed to be evaporated for auxiliary cooling (see Rio Blanco estimate, Table 4-2). Evaporation is about 1/4 of value in Table 4-2 because gas is compressed after and not before gas purification, thereby obviating a large cooling load.
(h) Estimated at 100 lb water/10^3 lb disposed shale, which is equal to 10% by weight of 40,000 tons/day of disposed shale (cf. Table 7.11, Ref. 6).
(i) From Oxy water balance, Table 4-2.
(j) Consumption of 25 gpm for 1,500 people (see p. 207, Ref. 6) plus 25 gpm for evaporation (see p. 209, Ref. 6 and Ref. 3).
(k) Mine use at 32 lb water/10^3 lb mined out shale (see p. 195, Ref. 6).
(l) Calculated from minimum and maximum values of mine drainage water given in Table 4-2 and mine water usage shown.

a reasonable assumption for a large portion of the Piceance Creek Basin of Colorado. In addition, we have shown in Table 4-3 a net output of mine drainage water in an amount consistent with the expected drainage waters from the C-a and C-b oil shale sites. The treatment or handling of excess groundwater, a situation which could also occur with mines for surface retorting, will be discussed in the next section.

Figure 4.1 shows the major parts of a water management scheme for a modified in situ oil shale plant with a product mix and water balance characterized by Table 4-3. Two important features in the water management are that the foul retort water produced is in excess of the water requirement for the cooling tower, and the mine drainage water, which provides the water for the plant, exceeds the plant needs. Figure 4.2 is a simplified diagram of the treatment path for the mine drainage water, where the water in excess of the plant needs must be treated for disposal.

For the water management scheme of Figure 4.1 and the water balance of Table 4-3, we have shown in Figure 4.3 a simplified water treatment flow diagram for a modified in situ plant producing 57,000 bbls/day of shale oil and 300 MW of electricity by a combined cycle system. Note that the streams do not balance around the retorting and gas cleaning section in part because water is generated in the retorting and water appears as hydrogen in the retort off-gas. It cannot be emphasized too strongly that the treatment flow diagram is simply illustrative, with its purpose to place the treatment procedures in perspective with regard to sequence and quantities handled. In the sections which follow, we shall we shall discuss each of the individual waste streams.

4.2 Excess Mine Drainage Water

In the preceding section we have provided some estimates of the quantities of excess mine drainage water that may be expected in the modified in situ processing of oil shale in the Piceance Creek Basin. It has generally been assumed that the quality of the mine drainage water will closely resemble the water in the aquifer that is drawn down (Ref. 4 (Vol. 3) and Ref. 7). This can be expected to be true so long as the groundwater does not contact or is not stored in contact with freshly rubblized raw shale. If the water does contact freshly exposed shale, contaminants, particularly organic acid salts, may be leached out. The extent of the leaching may be dependent on the water volume, contact time with the raw shale, suspended shale solids in the water and other factors. Because sufficient data is not available at this time, we have to assume that the mine drainage water is characterized by the aquifer water. Information on this important point is needed.

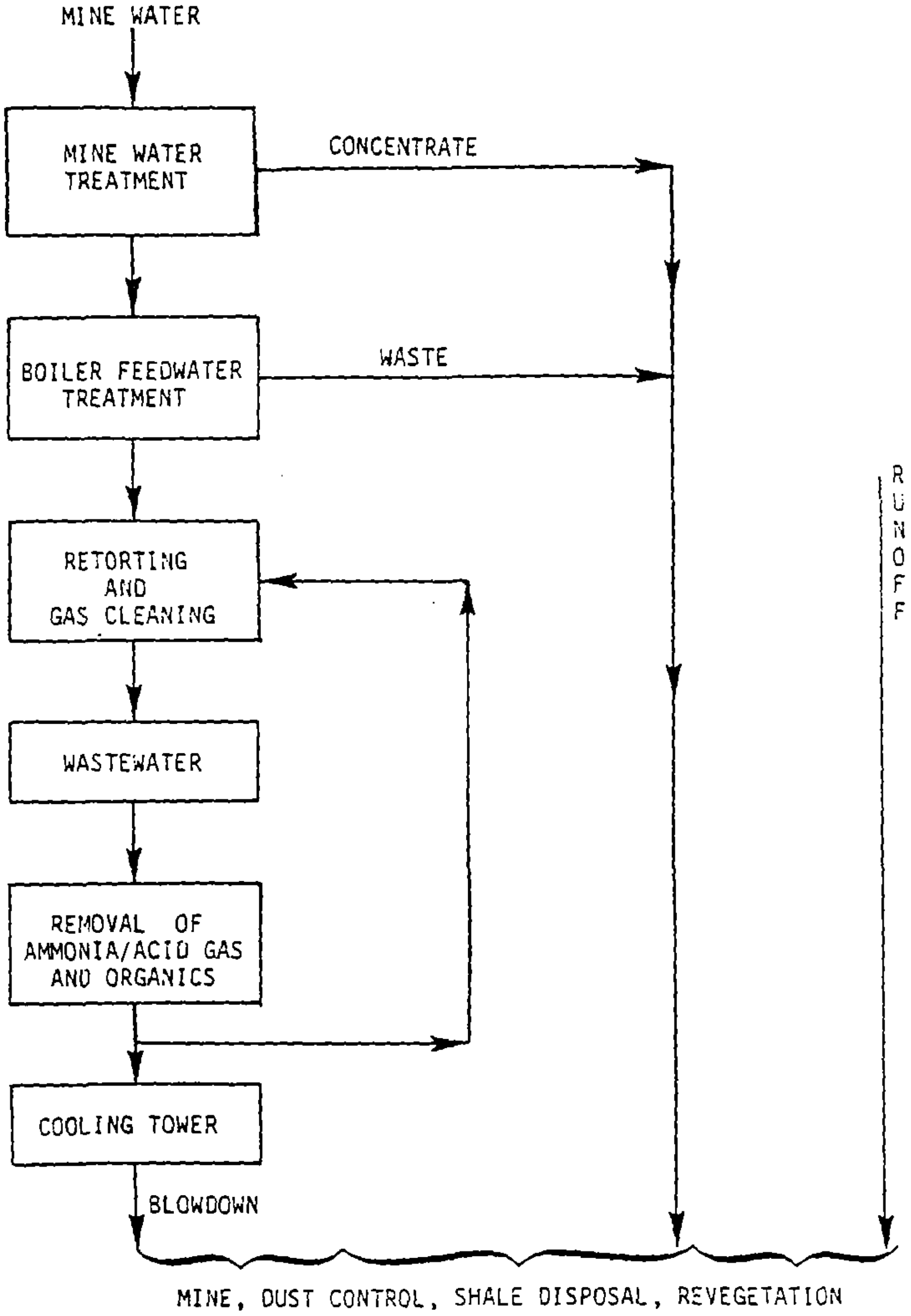

Figure 4.1. Major parts of a water management scheme in a modified in situ oil shale plant with byproduct electricity production by a combined cycle system.

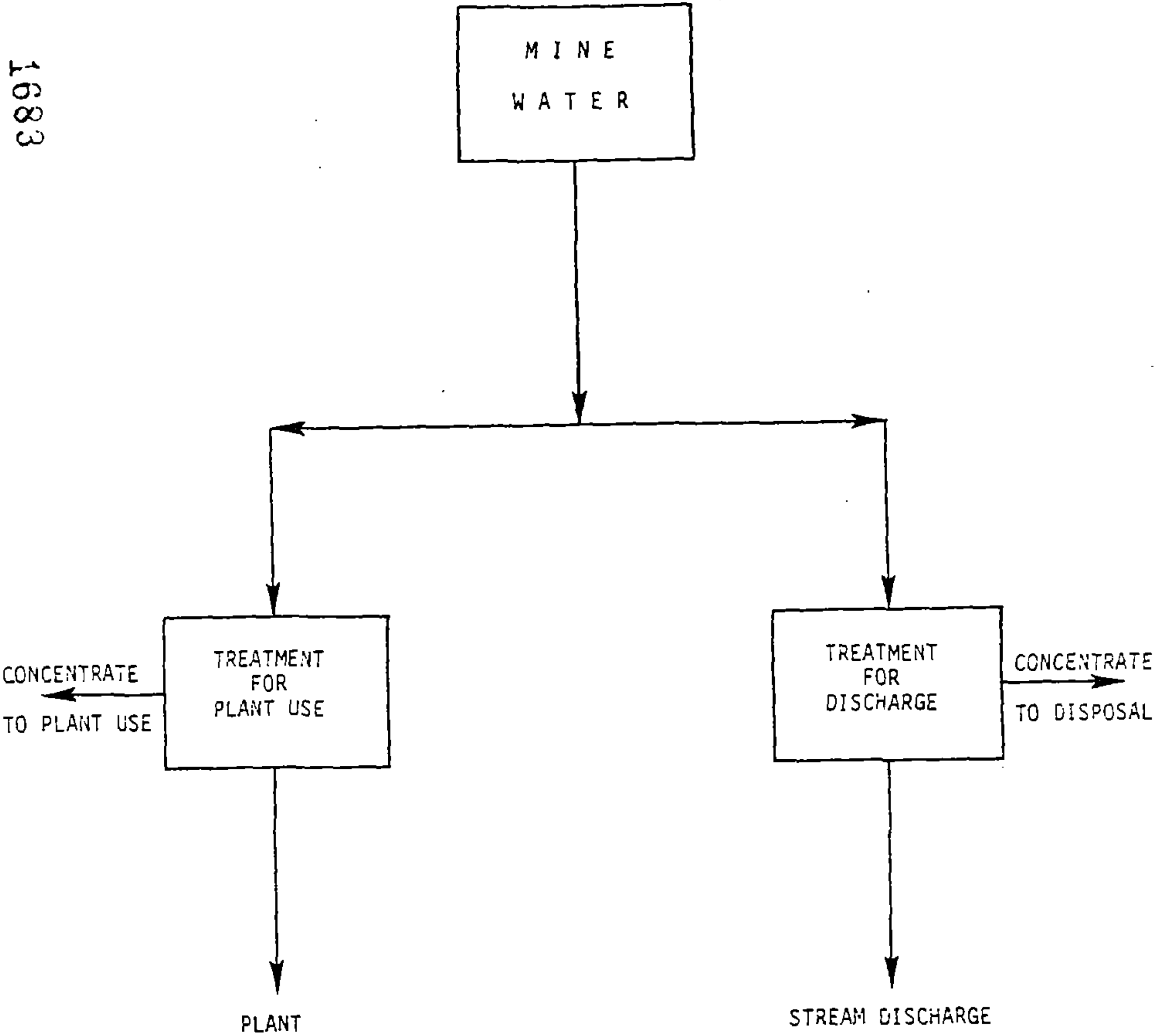

Figure 4.2. Water treatment flow diagram for oil shale mine drainage water.

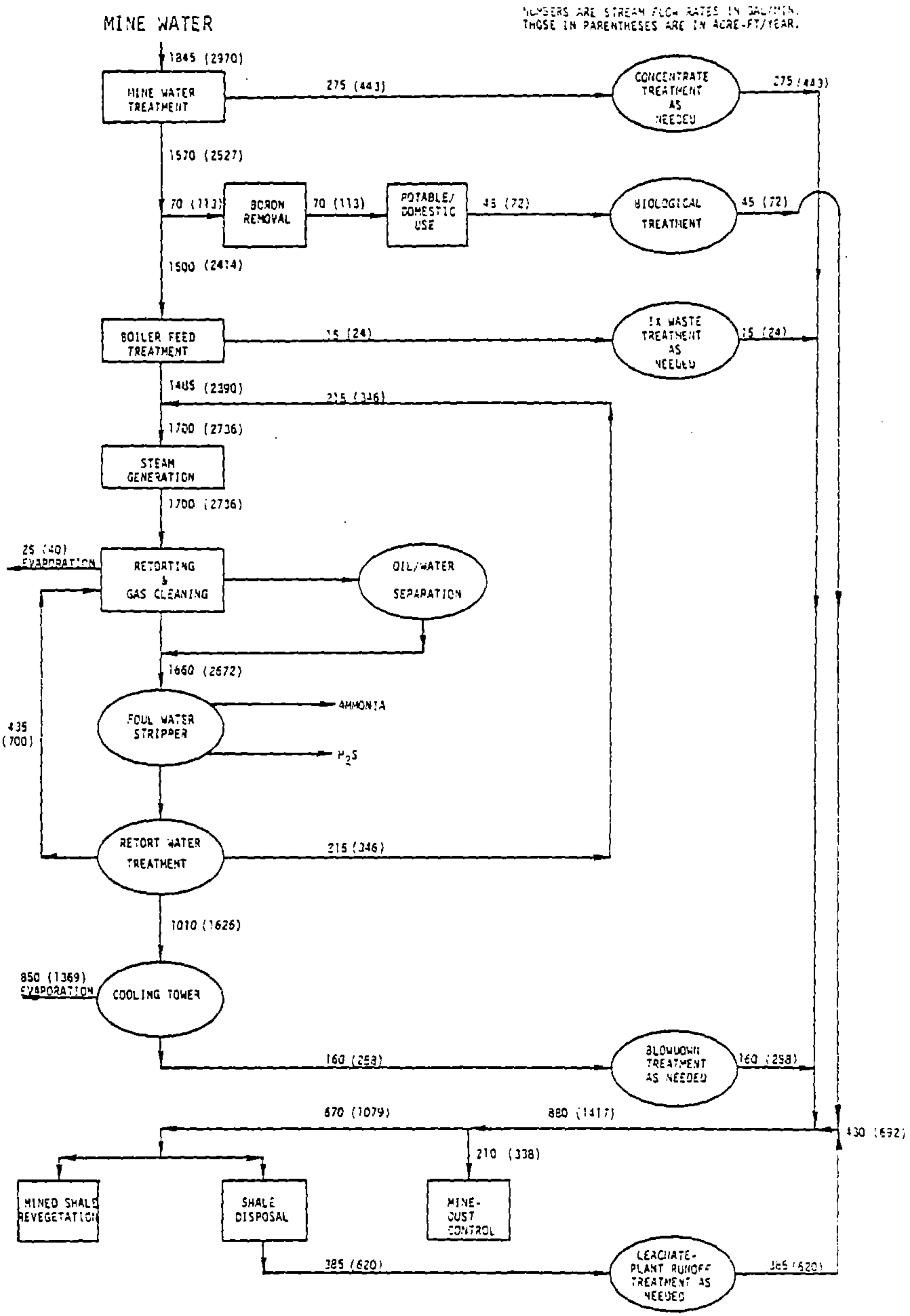
NUMBERS ARE STREAM FLOW RATES IN GAL/MIN. THOSE IN PARENTHESES ARE IN ACRE-FT/YEAR.

Figure 4.3. Illustrative water treatment flow diagram for a 57,000 barrel/day modified in situ shale oil plant producing 300 MW of byproduct electricity and using a mine water supply.

Table 4-4 shows ranges of the latest water quality data for the upper and lower aquifers in the Piceance Creek Basin published by the U.S.G.S.[8]. The wide spread between the high and low values is evident. For the lower aquifer we have shown in the same table mean values determined by Rio Blanco from a large number of analyses of water under the C-a site. Their ranges, which are not shown, are similarly as broad as those of the U.S.G.S.

TABLE 4-4. TYPICAL WATER QUALITY FOR AQUIFIERS IN PICEANCE CREEK BASIN, COLORADO

Constituent	Concentration (mg/l unless noted)		
	Upper Mine Aquifer		Lower Mine Aquifer
	U.S.G.S. Range[8]	Rio Blanco Mean[9]	U.S.G.S. Range[8]
Bicarbonate	350-2100	482	265-4300
Boron	<0.16-11	0.3	.05-12
Calcium	5.4-52	35	4-28
Carbonate	0-53	0.9	0-360
Chloride	4.1-151	12	1-700
Fluoride	3.1-19	0.4	6.5-45
Magnesium	4.2-54	52	1.9-29
Silica	10-19	26	2-19
Sodium	200-780	212	143-2320
Sulfate	< 5-370	325	< 4-350
Total Dissolved Solids	750-1800	905	356-5747
pH (units)	8.3-8.9	6.8	8.3-9.3

There are two principal means by which excess mine water can be disposed. One disposal method is by reinjection into an aquifer and the other by discharge to a surface stream. Although reinjection might require little or no treatment of the water, it is concluded in Ref. 2 (Vol. 2, p. 203) that it does not appear to be an attractive method for disposing of large volumes of water for a sustained period. The reasons given there are that a relatively large number of wells would be required in locations far from the mine, miles of buried pipeline would be needed to deliver the water, maintenance would be difficult, and leakage of highly saline water through fracture springs might result. For these reasons we shall not consider reinjection further.

Discharge of mine drainage water to a surface stream will necessitate treatment of the water. At the present time, NPDES permit limits for surface discharge have not been defined. Recently proposed State of Colorado permit limits for discharge into Piceance Creek from the C-b oil shale tract are shown in Table 4-5. The discharge limits shown in the left column of Table 4-5 were obtained from the C-b Shale Oil Venture[10] during the early phases of this program and were used in defining the water treatment schemes and estimating their costs for excess mine drainage water. The total dissolved solids level is met relatively easily, but the limits on fluoride, boron, phenol and ammonia could require relatively expensive treatment, depending upon the levels present in the mine water. The discharge limits shown in the right column of Table 4-5 were obtained during review of the draft of this report from the Colorado Department of Health[17]. They are the latest proposed NPDES limits and are still undergoing review. The limits on fluoride, boron, and phenol have been relaxed from the earlier limits. From what is known at this time of the mine water quantity and quality, and of the discharge quality requirements, any generalized estimates of treatment costs can at best be educated guesses. Great care must, therefore, be exercised when using any of the costs derived below.

In Table 4-6 we have shown assumed ranges of contaminants in the mine drainage water pumped to the surface. The ranges are based on the assumption that the mine water will be principally a mixture of upper aquifer water and water from the upper portion of the lower aquifer of the Piceance Creek Basin. The ranges are based on the data shown in Table 4-4 and the U.S.G.S. data of Ref. 11. The TDS, fluoride and boron levels are roughly consistent with the planning values adopted by Occidental Oil (Ref. 2, Vol. 2, p. 189), although we have assumed a somewhat higher mean boron level based on personal discussions

TABLE 4-5. PROPOSED NPDES PERMIT LIMITS FOR DISCHARGE TO PICEANCE CREEK FROM C-b OIL SHALE TRACT(a)

	Reference 10		Reference 17	
	30 Day Average	Daily Maximum	30 Day Average	Daily Maximum
TSS (mg/l)	30	45	30	45
TDS (mg/l)	680	1020	1200	1800
Total Fluoride (mg/l)	2	3	-	9.0
Total Boron (mg/l)	1.0	1.5	-	3.5
Total NH_3-N	1.6 lb/10^6 gal in Piceance Cr.(b)		-	1.3
Total Phenol	8.3×10^{-3} lb/10^6 gal in Pi.Cr.(c)		-	0.2
Total Residual Cl (mg/l)	0.5	-		0.02
Oil and Grease (mg/l)	-	10(d)	-	10(d)
pH (units)	-	6-9	-	6-9

(a) Based on a 10:1 dilution factor.
(b) Approximately 0.2 mg/l. Also 0.19 mg/l per 10 cfs flow in Piceance Creek.
(c) Approximately 1 ug/l.
(d) With no visible oil sheen.

TABLE 4-6. ASSUMED WATER QUALITY RANGES FOR MINE DRAINAGE WATER IN PICEANCE CREEK BASIN

Constituent	Concentration (mg/l)
Bicarbonate	500-750
Boron	2-4
Calcium	25-50
Chloride	10-20
Fluoride	10-15
Magnesium	30-60
Sodium	200-300
Sulfate	275-350
Total Dissolved Solids	900-1350
pH (units)	∿ 8.5

with Occidental[3]. We shall further assume that after treatment the water quality level is consistent with that of Table 4-5, with the possible exception of organics contamination. It may be noted that no value has been specified for the organic contaminants in the mine water because there is simply no way of knowing at this time what they might be.

For the relatively low TDS mine water with fluoride contamination, two processes prevent themselves as the most appropriate for obtaining a high purity product: electrodialysis and reverse osmosis[11,12]. However, electrodialysis will only separate those molecules which are in ionic form in solution. Boron, for example, requires that the solution pH be about 8.5 to 9 to become ionic. In general electrodialysis also does not have a capability for separating soluble organic molecules. Reverse osmosis, on the other hand, has a moderate capability for separating soluble organic molecules, but a very poor capability for separating boron from acidic waters. It is only at a quite high pH (∿ 9.5-10) that a 75% rejection of boron is attained. Fluoride rejection is typically about 90%. Both of the processes require a moderate to good level of prefiltration to remove suspended solids which will be contained in the mine water. The mine water is alkaline and electrodialysis would require pretreatment with sulfuric acid to prevent scaling on the membranes. Acid addition or chelating agents would also be required for the reverse osmosis system to prevent precipitation of salts. We emphasize that both of the systems would provide a product with a lower total dissolved solids than required for discharge. As a rule, reverse osmosis would give the lowest TDS product with a typical value for the mine water considered of from 100-200 mg/l, while the electrodialysis product might range from 200-400 mg/l. These values are illustrative only and are controlled by the system economics. If total dissolved solids content were the only discharge requirement to be met, then a significant reduction in treatment cost could be achieved by treating only part of the water and blending it with untreated water from which only the suspended solids have been removed. However, for the contaminant levels shown in Table 4-6, it is not likely that the discharge limits specified in Table 4-5 could be met with blending. Of course, specific pollutant removal might still be practiced which would enable blending. This decision is also an economic one.

In Figure 4.4 we have shown a single water treatment flow diagram, which illustrates a water treatment scheme for each of the two systems discussed above. We have shown both pretreatment and postreatment operations as may be needed. Implicit in the treatment schemes of Figure 4.4 is that the fluoride is reduced down to a level that meets discharge standards, but that boron passes through unchanged. We would emphasize that fluoride removal may not be achievable economically by the once-through systems illustrated. In that case the likely scheme would be to treat only part of the mine water by one of the membrane processes and blend the clean product water with the untreated but filtered mine water. The blended product would then be passed through a specific adsorption system for fluoride removal (e.g., activated alumina or bone char). For either electrodialysis or reverse osmosis, boron removal is assumed to be accomplished by passing the treated water through a specific ion exchanger (e.g., Rohm & Haas' Amberlite IRA-743). As indicated in the figure, it might also be necessary to add a carbon adsorption or resin adsorption polishing unit if organics removal were also required. This is more likely to be required with electrodialysis than reverse osmosis.

We have costed out both membrane processes without disposal of the concentrated solution and without boron removal and find the costs for the two systems to be quite close. Our estimates are based on a 15% annual amortization of capital. In Table 4-7 are shown the estimated electrodialysis costs in $/1000 gal as a function of the mine water throughput and total dissolved solids in the water. Electricity costs are taken to be 3¢/kwh. The O&M costs constitute about two-thirds of the total cost.

TABLE 4-7. COST OF MINE WATER TREATMENT BY ELECTRODIALYSIS
(in $/1000 gal)

Flow Rate (gpm)	Initial TDS (mg/l) 900	Initial TDS (mg/l) 1350
2,150	0.75	0.88
9,400	0.66	0.74

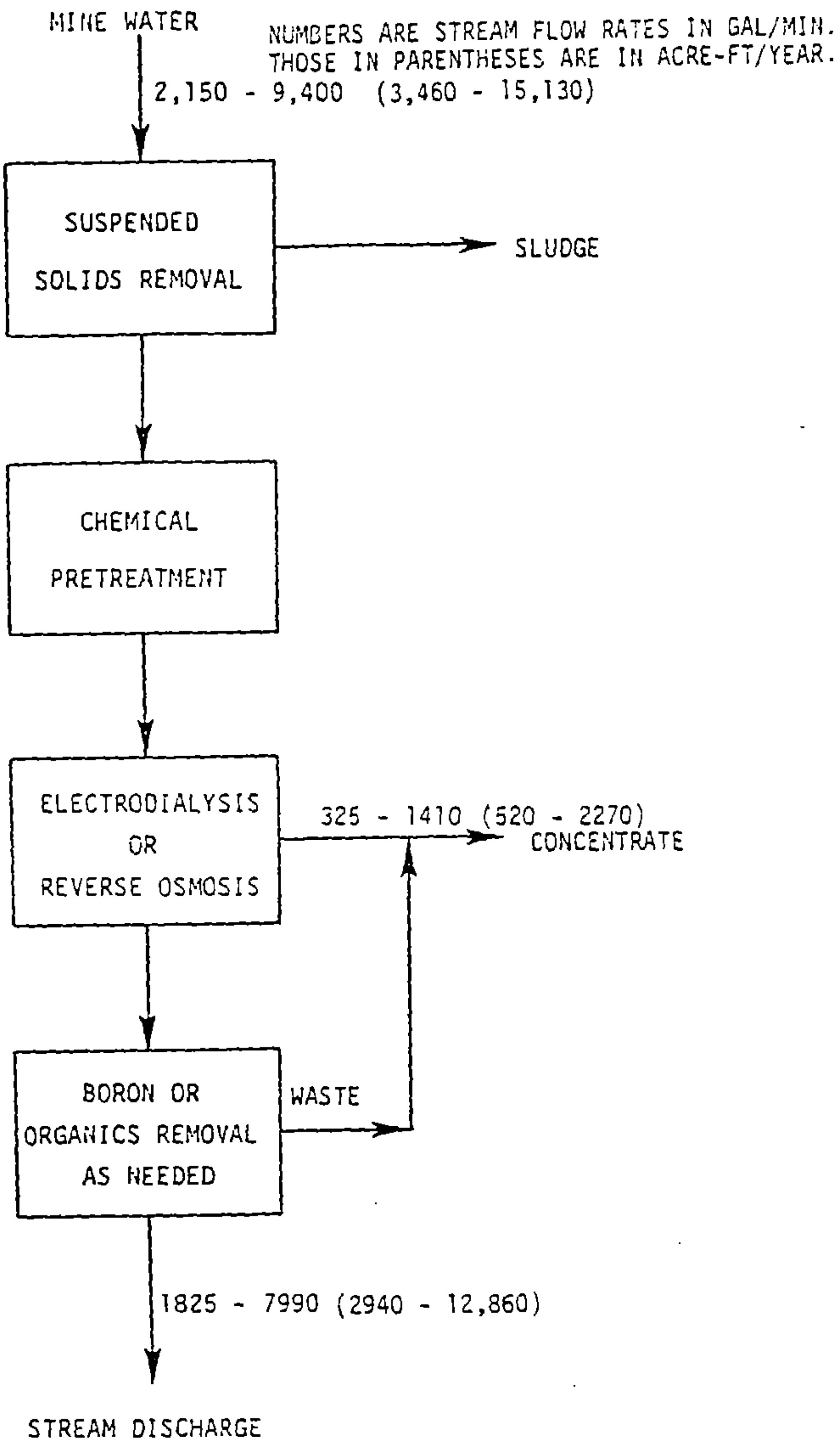

Figure 4.4. Two water treatment schemes for upgrading excess mine drainage water to surface discharge quality.

We have also estimated the reverse osmosis costs for the conditions of Table 4-7 and find a cost of $0.94/1000 gal (= $306/acre-ft) for the lower flow rate and about $0.67/1000 gal (= $218/acre-ft) for the higher rate. The cost is essentially independent of concentration for the differences in initial TDS considered, and is about equally divided between O&M and debt service.

The selection of one system over the other clearly cannot be made on costs alone since they appear to be so close. In favor of electrodialysis is that it is a well tested and reliable system with units now operating with capacities of 4 to 5 mgd. Another important factor is that modified in situ operations envisage generating electricity on site so that d.c. power could be produced directly. This could result in an important reduction in the capital cost of the system since the need for rectifiers is eliminated. It might be noted that the original commercial development of electrodialysis was for the treatment of mine drainage water from a gold mine in South Africa. In favor of reverse osmosis is that if organics are present, the system has a moderate capability for organics rejection. It also can yield a product water with a lower dissolved solids content than electrodialysis. However, large scale installations of the type required are only now being installed and long term operating experience is not as yet available.

We have assumed in our treatment schemes that boron removal will be carried out separately by means of selective ion exchange. Using Rohm & Haas' Amberlite IRA-743 resin, which has a high selectivity for boron, we find that the treatment cost ranges from $0.13/1000 gal (= $42/acre-ft) to $0.30/1000 gal (= $98/acre-ft). The lower figure corresponds to the higher flow rate of 9,400 gpm (= 15,130 acre-ft/yr) and the higher one to the lower rate of 2,150 gpm (= 3,460 acre-ft/yr). The cost of the ion exchange treatment at the high flow rate is more than 70% capital cost and at the low flow rate more than 85%. The regenerant waste is small and may be assumed to be disposed with the concentrate from either the reverse osmosis or electrodialysis systems.

A cost not so far discussed is that for the concentrate disposal. If we assume an 85% recovery and 90% separation of the dissolved solids, then the waste stream has about 6 times the concentration of the mine water and about one-seventh its volume. The cost of disposal of this stream is a major part of the treatment cost. From 0.26 x 10^6 gal/day to 2.0 x 10^6 gal/day of waste must be disposed. For the large and relatively dilute waste streams considered here, we suggest that it would be appropriate to use a vapor-compression evaporator to concentrate for disposal. The costs for such a system are discussed in Section 2.4. Because of the relatively large volumes, we shall take the lower cost estimated there of $6.6/1000 gal (= $2150/acre-ft) of waste treated. This cost is taken to be largely independent of the flow rate because of the modular character of the units. The recovery of fresh water is greater than 95% so that less than 5% of the feed to the evaporator would have to be disposed in a lined pond. At most this would add an additional $0.23/1000 gal (= $75/acre-ft) for the pond disposal costs, using the charges derived in Section 2.4. Balanced against this is a credit of about $1/1000 gal (= $326/acre-ft)for the distilled water recovered. This gives a total cost for disposal of the membrane system concentrate of $0.87/1000 gal (= $284/acre-ft) with credit for the distilled water recovery and $1.22/1000 gal (= $400/acre-ft) without the credit. We may take an average of $1/1000 gal as a suitable figure for estimation purposes.

In summary, we find that the total treatment cost, including boron removal, ranges between about $0.80/1000 gal (= $261/acre-ft) and $1.25/1000 gal (= $408/acre-ft) or an average of about $1/1000 gal over the range of flow rates and concentrations considered. The disposal costs also average about $1/1000 gal for a total average cost of $2/1000 gal (= $650/acre-ft) for mine water treatment and disposal. These costs could be significant if 13.5 x 10^6 gal/day of water must be treated. For a 3 x 10^{11} Btu/day output of shale oil, this would amount to a treatment cost of 9¢/10^6 Btu of product. The cost would be correspondingly reduced for lesser degrees of mine water treatment and would be about 4 times less for the lower flow rate of 3.1 x 10^6 gal/day considered here.

4.3 Runoff and Leachates

As discussed in Sections 2.2 and 3.2, rain runoff from the plant area is not an important or difficult problem. This water is generally of good quality and can be collected for use, as is indicated in Figure 4.3.

In modified in situ complexes, the mined out raw shale cannot be compacted into an impermeable cement so that some leaching from the disposal area will result from precipitation and snow melt. All developers plan to contain the leachate and runoff, generally by ditches around the piles which conduct the water to a dam area. Little is known about the composition of such leachates but it is likely that the level of inorganics would be lower than the levels in the local waters, while the organics level could possibly be higher. However, as with mine drainage water, the leachate composition is not known at this time and it will, moreover, undoubtedly depend on local conditions. It is likely, as indicated in Figure 4.3, that this runoff would be used for disposal purposes or other low quality water needs and would not require any special treatment. This assumption is made here.

4.4 High TDS Wastewaters

4.4.1 Mine Water Treatment Concentrate

We assume that the mine water is treated for use in the plant in the same way that it is treated for surface discharge. The exception to this is that boron is not removed except in the relatively small amount of water which goes to potable and domestic use (see Figure 4.3). This means that the cost of treating this water will range between about $0.75/1000 gal (= $245/acre-ft) and $0.95/1000 gal (= $310/acre-ft), depending upon the contaminant concentration and membrane process used, as discussed in Section 4.2.

The concentrate from the membrane system amounts to 275 gpm for an 85% recovery. The water will have a TDS of from 5,500 to 8,000 mg/l, consisting mostly of inorganic salts, and is quite suitable for a variety of disposal, dust control and mine uses. So long as there is a need for this water, we suggest that treatment is not necessary. However, should the water be in excess of plant requirements, then we assume it would be disposed in the same way as the concentrate from the treatment of the excess mine drainage water. The reason for this is that the disposal system would already be designed for this type of waste and, therefore, it would be most economical simply to expand the capacity to accomodate the additional waste. The disposal cost would be the same as derived in the preceding section, that is, about $1/1000 gal (= $326/acre-ft) of mine water treated.

4.4.2 Boiler Feedwater Treatment Blowdown

In the modified in situ processing of oil shale, steam is used principally in the retorting process. It is introduced into the retort to increase the shale oil recovery, moderate the retort temperature and improve the off-gas quality and shale oil characteristics. The pressure at which the steam is introduced depends on the details of the retorting procedure. However, in Ref. 1 a pressure of 450 psig is indicated and we shall assume this value. As discussed in Section 3.3.1, the generation of steam at this pressure requires a high quality feed water. We assume that ion exchange "polishing" demineralization will be required for the 1500 gpm of water fed to the boilers.

The waste stream from the ion exchange treatment is small and should be no more than 1 percent of the product water with 1 to 2 percent total dissolved solids (see Section 2.3.3). This stream may be used for low quality needs as shown in Figure 4.3, or if disposal is required, this could be done by evaporation along with the excess mine drainage water concentrate. The additional cost is sufficiently small that we may neglect it for our purposes here.

4.4.3 Cooling Tower Blowdown

As discussed earlier and shown in Figure 4.3, approximately 850 gpm is evaporated in the cooling tower. Since the cooling tower blowdown can be used for disposal and other low quality purposes, it is not necessary to go to high cycles of concentration. We have chosen about 6.5 cycles, with the value dictated by the ability to use the blowdown water for plant needs. In the illustrative example this gives a blowdown stream of about 160 gpm. Should treatment be required, if, for example, the plant needs prove to be less, then disposal by evaporation is the proper method. This could be accomplished in part by higher cycles of concentration than used in the example here (see Section 2.8.1), with the reduced blowdown disposed by forced evaporation in the same manner as the excess mine drainage water concentrate. We would expect that under the worst conditions, where all the blowdown had to be disposed, that by increasing the cycles of concentration no more than 70 gpm would have to be evaporated in the vapor compression system. As discussed in Section 4.2, this disposal cost would range between about \$5.85 and \$6.85/1000 gal (= \$1910 to \$2230/acre-ft) of blowdown.

4.5 Domestic Wastes From Plant

The wastewater from potable and domestic usage after primary screening is a low TDS, low BOD water which can be treated to acceptable quality for revegetation, disposal and mine uses by standard activated sludge treatment. The quantity of water to be handled is relatively small, amounting to about 45 gpm or 65,000 gal/day. Standard, packaged extended aeration plants can be purchased for handling this waste and we have obtained quotations for such a plant. The installed cost would run about $150,000 or, when amortized out at 15% annually, about $0.95/1000 gal. To this cost must be added labor costs of about 0.5 man years per year. At a burdened labor rate of $20/hr, this amounts to an additional $0.85/1000 gal. Electricity, chemicals and maintenance add about another $0.15/1000 gal. The resulting total cost for the secondary treatment is $1.95/1000 gal (= $636/acre-ft). The reason for this relatively high value for treating water with a BOD in the 200 to 250 mg/l range is the relatively small quantity. After secondary treatment the water could be used for revegetation and other low quality needs.

4.6 Retort Water for Internal Reuse

In the modified in situ retorting of oil shale with steam injection, it is estimated that an equal volume of water is coproduced with the shale oil[14]. For a 57,000 barrel/day shale oil plant, this corresponds to a production of about 1660 gpm of retort water. The quality of this foul in situ retort water is quite variable and has a strong dependence not only on site and method of processing, but also on time[14]. Apart from the difficulty of defining a "representative" in situ retort water, it has been shown that even the chemical characterization of a given water is quite difficult[15]. For the most part, all of the waters have high concentrations of ammonia and high concentrations of BOD, often in the presence of toxic materials. However, these waters also have very high ratios of alkalinity to ammonia, resulting from infiltrated ground water or from the leaching of sodium carbonate and bicarbonate. In addition, they may have high COD-to-BOD ratios.

Despite the fact that there really is no "representative" water for modified in situ retorting, for a "properly" operated in situ retort, where large quantities of water relative to oil are not produced, the simulated in situ retort water produced in the Laramie Energy Research Center's 150-ton retort may be used for characterization without the water necessarily being representative. An analysis of this water[17] is given in Table 4-8.

TABLE 4-8. ANALYSIS OF LERC SIMULATED IN SITU RETORT WATER

Constituent	Concentration (mg/l)
Ammonia nitrogen	10,150
Organic carbon	4,980
Alkalinity	38,000
BOD	5,325
COD	8,800
pH (units)	8.6

Figure 4.5 shows, as an example, a water treatment scheme for processing a modified in situ retort water of a quality illustrated in Table 4-8 to a level suitable for use in a cooling tower and for other process needs. We emphasize that this is but one possible approach and many alternatives are possible. Moreover, as noted below, the specific process use may require some additional treatment as, for example, acidification, softening, etc.

The retort condensate is screened to remove coarse particulate matter and then taken to standard (e.g., API) gravity separators/decantors for recovery of the shale oil. The recovered oil would normally be treated in secondary heater/treaters for final water removal. The water streams from the primary and secondary separators are then combined with the quench water condensed upstream of the gas purification section. This combined stream is here referred to as the retort water.

The first major treatment step is removal of ammonia and acid gases, and this will always be done by stripping. The normal procedure would be to strip the NH_3, CO_2 and H_2S simultaneously. In some processes the ammonia is held back by appropriate reflux and wash, and the acid gases stripped preferentially. The ammonia is then obtained in relatively pure form in a second stripping column. The proposed normal stripping is, in any case, used in recovering ammonia in the PHOSAM W process. In this process, ammonia is separated from the stripped acid gases by absorption in ammonium phosphate solution.

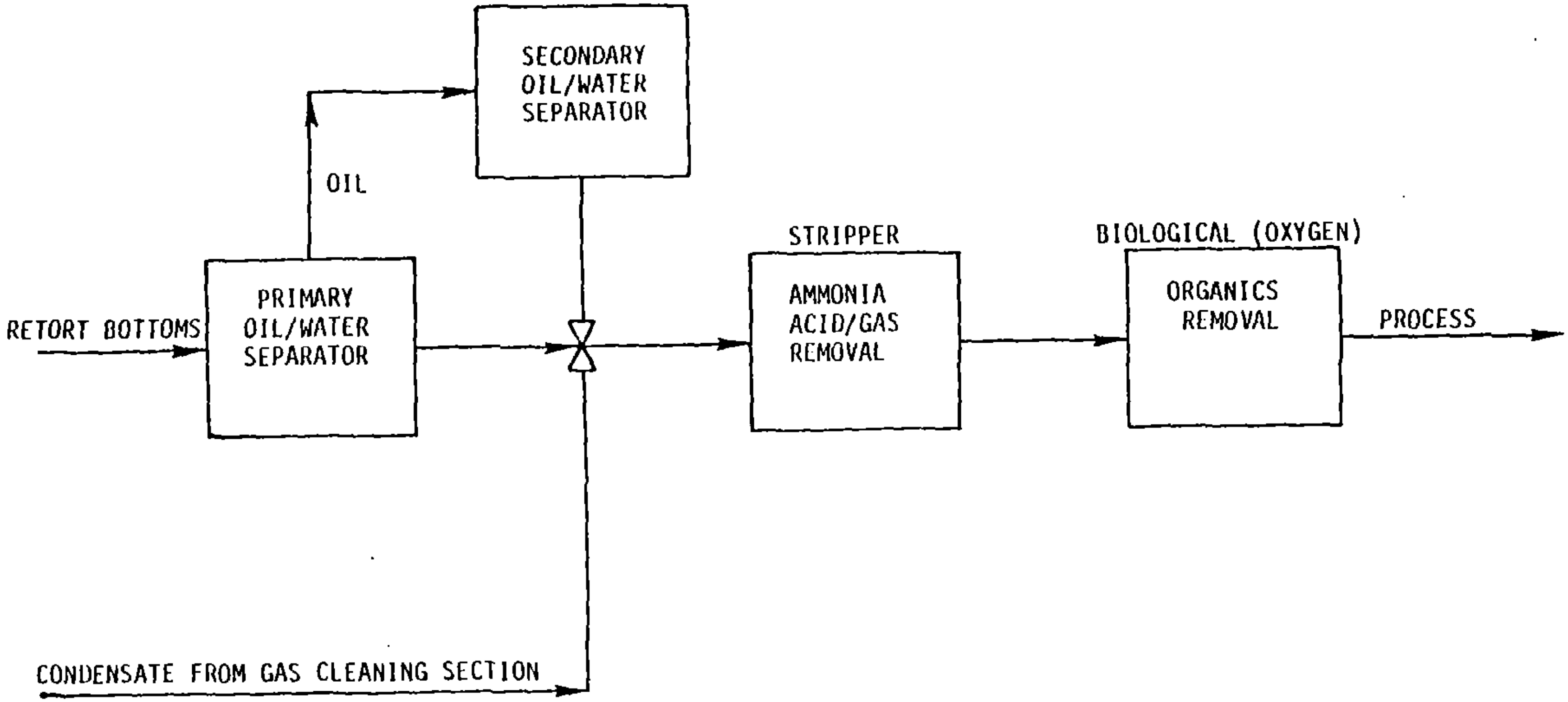

Figure 4.5. Water treatment scheme for oil shale retort water.

The next major treatment step is removal of organics. Here we have selected biological oxidation in preference to adsorption. Certainly, biological treatment will be more economical than carbon adsorption at the high BOD and COD levels. However, resin adsorption may prove to be a viable process, particularly for those waters containing high COD/BOD ratios. Insufficient information is available on resin adsorption characteristics for modified in situ oil shale waters to compare costs. The design and costing of the biological unit has to be based on kinetic data obtained using coal conversion wastewaters since this data is not available for in situ retort waters. In our example we selected an oxygen system since indications are that costs will be lower for the high (> 1000 mg/l) BOD waters. Also, oxygen systems operate more stably and some measure of control over stripped volatile vapors is available.

The bicarbonate levels may be high enough to require either acidification or lime softening prior to use in the cooling tower. Such treatment is standard and may be considered as part of the cooling water system.

In Section 2.7 the cost of biological treatment for the BOD removal that would be required for the water of Table 4-8 is \$2.3/1000 gal (= \$750/acre-ft). From our ammonia stripping studies (Ref. 6, Section 2) we conclude that after taking a credit of \$120/ton for the approximately 100 tons of ammonia recovered per day the stripping cost for the retort water would be, at most, \$0.40/1000 gal (= \$130/acre-ft). Primary and secondary oil-water separation may be estimated at \$0.15/1000 gal (= \$49/acre-ft), although this is only used for about half the water. Adding these costs together the cost of treating the retort water for reuse is \$2.8/1000 gal (= \$913/acre-ft). It cannot, however, be emphasized too strongly that this is for an assumed retort water for which data upon which to base an accurate design is not available at this time.

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APPENDIX A

ANALYSIS OF FOUL PROCESS CONDENSATE, WESTERN COALS.

The following compilation is extended from:

> Goldstein, D. J. and Yung, D., "Water Conservation And Pollution Control In Coal Conversion Processes," EPA report 600/7-77-065, January 1977, NTIS Catalog No.PB 269-568/2WE;

the original references are included.

(mg/l unless noted)

Process	Synthane	Synthane	Synthane	Hygas	Hygas	Hygas	Lurgi (ref. 3)			
							Rosebud, Montana, Subbituminous			
Coal	Wyoming Subbit.	N. Dakota Lignite	Montana Rosebud	Montana Lignite	Montana Lignite	Montana Lignite	Coarse Graded		Fine Graded Coal	
Ref. or Note	2	2	1	a,f	a,g	4	h	i	h	i
ph (units)	8.7	8.7	9.2			7.7-8.3	9.6	8.3	9.5	9.8
TDS							4,030	1,765	10,540	1,650
TDS (after ignition)							45	35	60	25
Total Carbon				7,800	6,414					
Total Organic Carbon			9,090	5,270	3,936	3,900-4,900				
Inorganic Carbon				2,630^f	2,478^b		1,110^j	5,307^j	194^j	4,284^j
Bicarbonate (HCO_3^-)				13,400^c	12,600^c		5,642^c	26,978^c	982^c	21,794^c
HCO_3^- (as meq/l)				219^c	207^c		93^c	442^c	16^c	357^c
BOD (5 days)				13,000			9,900	13,400	9,100	5,200
BOD (15 days)				14,000						
BOD (20 days)				17,500						
COD	43,000	38,000	22,000	30,000^d	13,590		22,700	20,800	16,600	19,600
Phenol as C_6H_5OH	6,000	6,600	3,000			1500-2700	4,200	4,400	6,300	4,800
Fatty Acids as Acetic							1,250	1,670	1,390	550
Total Ammonia as N			9,500	3,618	2,785^e	3000-5000	4,385	14,540	1,720	14,380
Free Ammonia as N	9,520	7,200					3,990	14,015	1,180	13,990
Total Ammonia (meq/l)							258	855	101	840
Cyanide as CN	.23	.1	.07	5.5		<.001	2	4	3	5
Thiocyanate	23	22	31			300-800	6	16	85	75
Total Sulfur as S				ND*			150	265	160	535
Sulfide						120-140	122	108	10	301
Chloride							45	40	80	30

*ND = none detected

APPENDIX A (Continued)

NOTES

a. Two samples, analyzed by Water Purification Associates.

b. Calculated as (Total Carbon) - (Organic Carbon)

c. Calculated as equivalent to inorganic carbon.

d. Suspect value, high compared to total organic carbon.

e. Total Kjeldahl nitrogen = 2,800 mg/l.

f. Absorption spectrographic analysis gave:

Ca	17
Mg	12
Na	115

g. Absorption spectrographic analysis gave:

Ca	61
Mg	31
Na	84

Emission spectrograph gave:

	Result	Relative Scale
Calcium	high	10
Sodium	low-medium	10^{-1} - 10
Magnesium	low-medium	10^{-1} - 10
Barium, Strontium	low-trace	10^{-2} - 10
Aluminum, Boron	trace	10^{-2} - 10^{-1}
Titanium	faint trace-trace	10^{-3} - 10^{-1}
Manganese, Iron, Zinc	faint trace	10^{-3} - 10^{-2}
Silicon, Vanadium	very faint trace	10^{-4} - 10^{-3}
Chromium, Silver, Tin, and Copper	very, very faint trace	$<10^{-4}$

h. Sample from inlet tar separator (labelled t in Ref. 3).

i. Sample from inlet oil separator (labelled o in Ref. 3).

j. Given as "carbonate as CO_2" in Ref. 3; converted to C for tabulation.

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APPENDIX B

ANALYSIS OF WATER FROM KOPPERS COAL GASIFICATION
KUTAHYA, TURKEY

pH	8.9
	mg/l
Ca^{+2}	159
Mg^{+2}	68
Na^{+}	18
NH_4^{+}	122
Cl^{-}	46
$SO_4^{=}$	109
H_2S	Not detected
COD	63
Silica	43

Source:
Farnsworth, J.F., Mitsak, D.M. and Kamody, J.F., "Clean Environment with K-T Process," in Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, St. Louis, Missouri, May 1974, EPA-650/2-74-118, U.S. E.P.A. Research Triangle, Park, North Carolina.