Introduction

The types and amounts of water contaminants that are likely to be produced by major kinds of oil shale facilities are discussed here,

Water Pollutants Produced by Major Oil Shale Processes

Types and Origins of Pollutants

The following summarizes the major sources of each class of waterborne contaminants found in oil shale facilities.

- Suspended solids will occur primarily in water from the dust-control systems used in shale mining and crushing operations. Mine drainage water will also contain suspended solids, as will a retort condensate stream that picks up fine shale particles as it trickles down through the broken shale. In aboveground retorts, some fine shale may be entrained in the retort gas and captured in the gas condensate, but levels should be low, thus should not be a problem to treat, Cooling water will pick up dust from the atmosphere, particularly if the cooling tower is near a shale crushing or disposal site. Precipitated salts and biological matter may also be present in the cooling tower blowdown.
- Oil and grease will be present in the retort condensate water that is removed from the in situ retort together with the product oil. Some oil remains in the water after product recovery and must be removed prior to further treatment. Part of the oil forms an emulsion in the water and its removal may be difficult. 'Volatile hydrocarbons leave with the retort offgas and condense in the gas condensate water. Tests indicate that the oil in the gas condensate occurs in well-defined droplets that can be separated without difficulty.² Oils in the coker and hydrotreater condensates are expected to be similar to those in the gas condensate.
- **Dissolved gases** include all of the NH_3 and some of the CO_2 and H_2S formed in the retorting process. These gases dissolve in the retort and gas condensates. Any NH_3 and H_2S that are formed during upgrading will appear in the hydrotreater condensates.

- · Dissolved inorganic will be found in mine drainage water and retort condensates because these streams leach sodium, potassium, sulfate, bicarbonate, chloride, calcium, and magnesium ions from the shale that they contact. ³In addition, some inorganic volatilize and may be captured from the gas phase in the retort, Of the heavy metals present in raw oil shale, cadmium and mercury (probably as their respective sulfides) are expected to be present in the gas condensate in low concentrations.' An analysis of TOSCO II gas condensate water showed the presence of cyanide, sodium, calcium, magnesium, silica, and iron ions, with only trace amounts of some of the heavy metal elements.⁵
- · Dissolved organics arise largely from the organic compounds in the raw oil shale, which may be altered during pyrolysis and end up in the retort, gas, or hydrotreater condensates. The types of organics in each condensate will probably depend on the volatility and volubility of the organics and the temperature at which the wastewater is condensed. No data are available on this subject but it is known that a wide range of compounds, particularly carboxylic acids and neutral compounds, can be expected.⁶Many of the individual compounds should be biodegradable, but studies have shown that less than 50 percent of the organic matter can be removed by conventional biological oxidation. This poor performance is attributed to the effect of toxic compounds on waste-treatment bacteria. Both inorganic and organic toxic substances may be responsible. The specific types of toxic pollutants will differ with the retorting process and with raw shale composition.
- Trace elements and metals are not expected to occur in large concentrations in the major waste streams except those streams dis-

cussed under dissolved inorganics.^{10 II} Chromium was used for corrosion control in older cooling-water systems but other agents are now available and should be used to avoid the problem of chromium contamination of blowdown streams. If trace element and metal removal is required, chemical treatment, specific ion exchange, and membrane processes are available.

- **Trace organics** are toxic or hazardous organic compounds present in low concentrations. They may occur in the retort and gas condensate streams and in the wastewater stream from the upgrading section. These constituents can generally be removed together with other dissolved organics by ultrafiltration with carbon adsorption for final cleaning ("polishing").
- Toxics, including carcinogens, mutagens, priority pollutants, and other hazardous-sub-

The Amounts of Pollutants Produced

Table C-1 indicates the principal contaminated process streams and their flow rates for four commercial-scale [50,000 bbl/d)* oil shale facilities. These facilities correspond to the plants for which water requirements are estimated in chapter 9. The "aboveground direct" plant uses directly heated aboveground retorts like the Paraho direct or gas combustion. The "aboveground indirect" uses indirectly heated retorts like TOSCO II. It is similar to the design proposed by Colony Development. The "MIS" plant uses Occidental's stances, have been reported for various types of oil shale processing wastes. Any toxic substances present in the wastewater streams will be removed along with the trace organics or inorganic substances. It is not expected that thermal oxidation, which is often employed to destroy hazardous organic compounds, will be required for the wastewater streams, although it may be considered for concentrates or sludges. However, the presence of toxic substances may interfere with biological oxidation processes used for bulk organic removal. If this is a problem, the substances could be removed in any of several conventional pretreatment steps.

• Sanitary wastes in "domestic" and service waste streams can be kept separate and treated in commercially available package biological treatment units.

MIS process. It is similar to the design proposed by Occidental and Tenneco for tract C-b. The "MIS/aboveground" plant combines Occidental's MIS process-with Lurgi-Ruhrgas indirectly heated aboveground retorts. It is similar to Rio Blanco's design for tract C-a.

The flow rate estimates were derived from tables 71, 74, and 75. (See ch. 9.) Estimates have been added for the internally recycled gas washing and hydrotreater wash streams that were not considered in chapter 9. (The water availability

*Barrels per stream day.

	-	-	-	
	Aboveground direct	Aboveground redirect	MIS	MIS/aboveground
Cooling tower blowdown	1,550-1,820	1,320-2,070	1,040-1,280	910-1,130
Boiler blowdown	325	370-405	370	350
Boiler feedwater treatment wastes	165	190-210	185	180
Gas washing condensate .,	1,070-1,190	(a)	3,320-3,640	2,270-2,500
Gas condensate (net).	490-540	730-800	2,160-2,370	1,480-1,630
Retort condensate,	(a)	(a)	1,240-1,370	850-940
Coker condensate,	60	60	60	60
Hydrotreater wash condensate	875	875	875	875
Net hydrotreater condensate			40	40
Excess mine drainage	(a)	(a)	0-10,000	0 - 1 0 , 0 0 0

Table C-1 .–Flow Rates of Contaminated Streams in Oil Shale Facilities Producing 50,000 bbl/d of Shale Oil Syncrude (acre-ft/yr)

^aNeglected for processes designs or sites considered

SOURCE R F Probstein H Gold and R E Hicks, Water RequirementsPollutionEllects and Costs of Water Supply arrd Treatment for the Oil Shale Industry, prepared for OTA by Water Purification Associates October 1979 analysis presented there deals only with streams that cross the project boundaries.) These additional streams are of significance for water quality analysis because they contain all of the NH_3 , most of the CO_2 , and some of the H_2S that is removed from gas streams in the plants. Flow rate ranges are shown in some cases to account for the expected variations in shale grades and plant designs, as discussed in chapter 9. The following points should be noted with respect to the flow rate estimates.

- Cooling tower blowdown varies substantially among the plants, largely because of different modes of power generation.
- Boiler blowdowns are fairly uniform because it is assumed that boilers will generate steam for use in the upgrading units, which are identical for all four plants.
- For the same reason, all four plants have the same flow rates for coker condensate, hydro-treater wash condensate, and net hydro-treater condensate.
- Excess mine drainage is indicated for the MIS and MIS/aboveground plants because it was assumed that they would be located in the ground water areas of the Piceance basin. The other two plants were assumed to be located in drier areas (e.g., in the Uinta basin or along the edge of the Piceance basin),
- No retort condensate is shown for the AGR plants because it was assumed that condensation in the retort would be avoided by adjusting the operating temperature. A large

value is shown for the MIS retort condensate because of unavoidable condensation in the lower portions of the MIS retorts. The value for MIS/aboveground is a weighted average of Lurgi-Ruhrgas (no condensate) and MIS (large quantities of condensate).

• Large values are also shown for gas condensate and gas washing condensate in all systems except the aboveground indirect. In the aboveground direct and the two MIS operations, large quantities of moist retort gas must be treated, resulting in large volumes of condensate. Much of the moisture is a combustion product. In contrast, the above--ground indirect has no combustion within the retort and produces less gas that must be cooled and cleaned.

In table C-2, estimates are presented of the concentrations of contaminants in the condensate streams. It is important to note that extensive data on contaminant concentrations are not available for the process condensate streams and that published measurements show considerable variation. Only the estimate for the aboveground indirect gas condensate is based on extensive field measurements.¹³ The other values are consistent with material balance calculations and information from the literature but they are at best approximate. Moreover, only concentrations of major contaminants are shown. Trace contaminants, including most toxic elements, are not indicated because information on their occurrence is even more limited, Although toxic elements are not ex-

		Gas condensate		Retort condensate	Hydrotreater condensate
Contaminant	Aboveground direct	Aboveground redirect	MIS or MIS/aboveground	MIS or MIS/aboveground	All plants
N H 3	17,990C	5,150	21 ,330 ^c	720	41 ,000°
H , S	206°	810	118 ^c	_	18,000 ^c
C 0, ^b	32,400 ^c	6,150	41 ,800 [°]	9,940	None
Calcium :	Low ^d	6	Low	20	Low
Magnesium.	Low	2	Low	17	Low
Potassium	Low	04	Low	100	Low
Sodium	Low	5	Low	3,600	Low
Chloride	Low	5	Low	280	Low
Fluoride	Low	0.3	Low	39	Low
Boron,	Low	Low	Low	25	Low
Sulfate	Low	Low	Low	1,200	Low
Organic carbon	—	6,100	—	—	—
BOD °.,	10,000	10,000	2,200	2,220	10,000

	- · · ·			
Table C-2.–Contaminant	Concentrations in	Oil Shale Process	Condensate Streams	s (mg/1)°

alrace elements and organics for which data are unavailable are not shown

^DBicarbonate and carbonate concentrations reported as CO₂ equivalent

 $^{\rm C}_{In}$ internal acid wash before gas separation and wash recycle $^{\rm C}_{Based}$ on available dala or estimates

eBiochemical0xygen demand estimated al one half of thetheoretical0xygen demand

SOURCE R F Probstein H Gold and R E Hicks Wafer Requirements, Pollution Effects and Costs of Water Supply and Treatment for the Oil Shale Industry prepared for OTA by Waler Purification Associates October 1979 pected to be present to any significant extent in the gas condensates, some could be present in the MIS retort condensate. "

The hydrotreater condensate concentrations were developed for Colony's upgrading unit, but they should be typical of values for any facility (MIS or aboveground) that processes Green River shale oil. A retort condensate is shown only for the MIS and MIS/aboveground facilities, for reasons mentioned previously. Significant differences are indicated for the three gas condensate streams with respect to NH₃, H₂S, and CO₂ concentrations. The aboveground indirect stream is much lower in CO₂ and NH₃ because of the lack of combustion (which produces soluble CO₂ and NO₃ gases) in the retort. H₂S concentration is higher in the aboveground indirect stream because there is little oxygen available in the retort to oxidize the H₂S to SO₂A lack of data prevents evaluation of process-related effects on concentrations of other contaminants.

In table C-3, the likely rates of pollutant production are shown for the gas condensate streams.

Table C-3.–Production Rates for Principal Pollutants in Gas Condensate Streams (ton/d)³

			Type of facility				
Contaminant		Aboveground direct	Aboveground Indirect	MIS	MIS/ aboveground		
N H H ² C O , BOD ^c	H , S ^b	75.6 0.87 136 19.2	147 2.3 17,5 28.5	276 15 541 185	189 1.1 371 127		

^aTons per stream daytor production of 50000 bbl/dshaleoilsyncrude ^bAdditionalsulfuris recovered directly from the retortgas

^CBiochemicaloxygen demand

SOURCE R F Probstein H Gold and R E Hicks Water Requirements, Pollution Effects and Costs of Water Supply and Treatment for the Oil Shale Industry prepared for OTA by Waler Punfication Associates October 1979

The values shown were obtained by multiplying the flow rates in table C-1 by the pollutant concentrations in table C-Z. Only a single value is shown for each contaminant in table C-3 and in the other pollutant production-rate tables that follow. The rates shown were calculated for average stream flows wherever a range is shown in table C-1. This approximation is justified because the uncertainty in pollutant concentrations is larger than the relatively narrow range shown for the flow rates. These uncertainties result from a paucity of published data, and also because large differences can occur in some plants with different feed waters and process designs.

Table C-4 indicates the pollutant production rates for the retort condensate streams produced

Table C-4.–Production Rates for Principal Pollutants From MIS Retort Condensates (ton/d)^a

	Тур	e of facility
Contaminant	MIS MIS/aboveground	
N H ₃ .,	349	2.40
H , S	-	—
CO, : :	48,2	33.1
Calcium	0.10	0.07
Magnesium	008	0.06
Poťassium	0.49	0.33
Sodium	17.5	12.0
Chloride	1,36	0.93
Fluoride	0.19	013
Boron. : .	0.12	0.08
Sulfate.	5,82	3.99
Biochemical oxygen demand .,	10.07	7.32

a Tons per stream day for production of 50000 bbl/d shale oil syncrude

SOURCE R F Probstein H Gold, and R E Hicks WaterRequirementsPollutionEffects and Costs of Water Supply and Treatment for the 01/Shale Industry prepared for 01A by Water PurificationAssociates October 1979

in MIS retorting. It is assumed that retort condensates are produced only with MIS processing. These condensates leach inorganic salts from shale in the retort, as indicated by the contaminant production rates shown.

Table C-5 shows the production rates for the principal contaminants in the process waste waters generated in the upgrading portion of the Colony design. This is the only plant for which an upgrading section has been described in the literature. Since shale oils produced by different retorts are not markedly different in their nitrogen and sulfur contents, it is reasonable to apply the pollutant production estimates for the TOSCO H upgrading section to all of the facilities considered.

In table C-6, the pollutant production rates for all of the process condensate streams are combined. It can be seen that the biochemical oxygen demand (BOD) does not have a wide range between facilities. This is in large measure a result

Table C-5.–Production Rates for Principal Pollutants in Upgrading Condensates (ton/d)^a

	Waste stream			
Contaminant	Hydrotreater condensate	Coker condensate		
NH 3.,	., 133	1.15		
H ₂S [▶] .,	. 58.6	0,18		
C 0 ₂	0	1.37		
Biochemical oxygen dema	nd 1.49	2.23		

*Tons per streamday for production of 50,000 bbl/d shale on syncrude Based on a TOSCOII process design Similar values anticipated for the other process models bAdditional sulfur is recovered directly from theretor(gas

SOURCE R F Probstein, H Gold, and R E Hicks Water Requirements Pollution Effects, and Costs of Water Supply and Treatment for the Oil Shale Industry, prepared for OTA by Water Purification Associates, October 1979

Table C-6. –Sum of the Production Rates for Principal Pollutants in Retorting and Upgrading Condensates (ton/d)^a

Type of facility					
Contam	iinant	Above-ground direct	Aboveground indirect	MIS	MIS/ aboveground
NH,		210	149	414	326
Н	@	597	61 1	603	599
Со,	С	137	189	591	405
BOD⁴		229	322	329	237

^aTons per stream day for product lon of 50 000 bbldshale oilsyncrude

^bAdditionalsulfuris recovered direct y frOm the retortgas

CThisdoes not represent lota I_C0,productionC0, is also generated in combustion and lost up flie passtarks as inTOSCOII indirect **ProCess** and in steam and power production dBiochemical oxygen demand

SOURCE R F Probstein H Gold and R E Hicks Water Requirements Pollution Effects and Costs of Water Supply and Treatment for the 011 Shale Industry prepared for OTAby Waler Purification Associates October 1979

of the BOD concentrations assumed. The H_2S production, which represents about a third of the total sulfur recovered in the plant, varies little among the different facilities. This is reasonable, since the amount of sulfur removed per unit of shale oil produced should be similar for the different processes. However, this H_2S includes only that amount that dissolves in the condensate streams; it does not include the gas that goes directly to the sulfur recovery units.

The most striking estimate in table C-6 is the extremely high CO₂ production rate for the MIS facility. The rate for the aboveground indirect facility is lowest because decomposition of carbonate minerals to CO₂ is much less at the lower retorting temperatures (about 900° F or 500° C) than in the higher temperature (about $1,500^{\circ}$ F or 800° C) MIS or aboveground direct processes. The rate is highest for MIS because the shale remains at high temperatures for a long time, thus allowing nearly complete decomposition of the carbonates. The combined MIS and AGR facility shows a correspondingly lower value-a weighted average of MIS and Lurgi-Ruhrgas rates. It should be emphasized that CO₂ is also produced by combustion in the indirect AGR plant, which does not show up in the condensate streams because it is lost directly up flue gas stacks, However, even if this gas were included, the ratio of CO, produced in MIS or aboveground direct to that in indirectly heated retorting would still be large.

Differences in NH₃ production rates also result from combustion in MIS and directly heated aboveground retorts. The aboveground indirect process produces the least NH₃ because it is essentially one of pyrolysis in which the nitrogen is mostly obtained from the organic matter in the shale. In fact, almost all of the NH₃ that will be produced in the indirectly heated AGR will be manufactured in the upgrading section when nitrogen is removed from the crude shale oil by hydrotreating. Differences in BOD yields are not statistically significant, given the lack of precision in the data base.

In order to calculate pollutant concentrations in cooling tower blowdown and waste streams from boiler feedwater treatment, it is necessary to know the raw water composition to the plant. Table C-7 shows the raw water compositions assumed for this assessment. The surface water quality is that of the Colorado River near Cameo, Colo., and the mine drainage water is a composite of the expected quality of water to be drawn from the bedrock aquifers of the Piceance Basin. ¹⁵* The raw water compositions are only approximate.

Table C-8 presents the estimated composition of the cooling tower blowdown of four facilities

*The bedrock aquifer system, and other water resources in the oil shale region, are described in ch. 9.

Table	C-7Com	posite \	Nater Q	uality	Data 1	for C	olorado	River
Water	and Mine	Draina	ge Wate	er in th	e Pice	eance	Basin	(mg/l)

	Source of process water				
Contaminant	Surface water	Mine drainage water			
NH ₃	_	1.2			
'Bicarbonate	168	750			
Boron	-	3			
Calcium	72	50			
Carbonate	-	50			
Chloride	205	20			
Fluoride	-	15			
Magnesium	19	60			
Phenol	-	25 x 10 ⁻³			
Silica	7	15			
Sodium	153	300			
Sulfate	158	350			
Total dissolved solids	734	1,350			

SOURCE R F ProbsteinH Gold and R E HicksWater RequirementsPollutionEffects and CostsofWaterSupply and Treatmentfor the 011 Shale industryprepared for OTAby Water PurificationAssociates October 1979

Table C-8.–Estimated Concentrations of Principal Contaminants in Cooling Tower Blowdown (mg/l)

	Туре о	f facility	
Contaminant	AGR with surface water supply	MIS retorting with mine drainage water supply	
Calcium,	215	200	
Chloride	615	80	
Fluoride	—	60	
Magnesium	60	240	
Sodium	460	1,200	
Sulfate	840	1,400	

SOURCE R F Probstein, H. Gold and R E Hicks Water Requirements Pollution Effects and Costs of Water Supply and Treatment for the **01**/ShaleIndustry prepared for OTA by Wafer PurificationAssociatesOctober 1979 considered, based on an average of three cycles of concentration for AGR (surface water supply) and four cycles of concentration for MIS retorting (mine drainage water supply). The relatively low numbers assumed for concentration cycles are based on the assumption that all of the blowdown water is needed for solid waste disposal. Under this assumption there is no advantage to the more costly procedure of using a larger number of cycles.

Table C-9 gives the estimated composition of the waste streams from treating the raw supply

Table C-9.–Estimated Concentrations of the Principal Contaminants in an Ion Exchange Regenerant Waste Stream From Boiler Feedwater Treatment' (mg/l)

	Type of facility			
Contaminant	AGR with surface water supply	MIS retorting with mine drainage water supply		
Calcium	950	660		
Chloride :	2,400	790		
Magnesium	250	4,600		
Sodium .,	990	2,200		
Sulfate	2,080	3,460		

^aVolume 01 regenerantwastewater assumed to be approximately 75 percent ⁰¹ the volume ⁰¹ treated water

SOURCE R F Probstein H Gold and R E HicksWater Requirements Pollution Effects and Costs of Water Supply and Treatment for the Oil Shale Industry prepared for OTA by Waler Punfication Associates October 1979 water by ion exchange to obtain a high-quality water for boiler feed. The estimates assume the removal of all the calcium, magnesium, and sulfate ions from the supply water. Most of the other ions will also be removed but only the principal ones are shown for the waste streams. The waste volume is about 7.5 percent of the water treated. This corresponds to a fairly efficient ion exchange treatment system. Boiler blowdown waste composition is not shown because the quality of this water is usually equivalent to that of the raw water entering the plant. It can therefore be mixed with the raw water and used as a makeup source.

Table C-10 gives the estimated pollutant production rates in the cooling tower blowdown and boiler waste treatment streams based on the compositions of tables C-8 and C-9. Also shown are the total production rates from these two sources; the streams would usually be combined in the plant and used for solid waste disposal. There is not a great deal of difference in the total quantities of pollutants produced by the facilities considered,

In table C-1 it was assumed that oil shale mines in ground water areas might result in production of from O to 10,000 acre-ft/yr of excess mine drainage water for a 50,000-bbl/d in situ facility. At this time, it is not known whether the water will be treated for discharge to surface streams,

Table C-10.-Production Rates for Principal Pollutants in Cooling Tower Blowdown and Boiler Treatment Wastes (ton/d)

Contaminant	Aboveground direct	Aboveground indirect	MIS	MIS/aboveground
		Cooling tower b	lowdown	
Calcium.	1 35	1,36	0.86	076
Chloride	385	3.88	035	0.30
Fluoride	_	-	0.26	023
Magnesium	038	0.38	1.04	0,91
Sodium.	2.88	290	5.18	4,55
Sulfate	5.26	529	604	5.31
		Boiler treatmen	t wastes	
Calcium .	0,58	0.71	0.45	0.44
Chloride	1,47	1 79	0.54	0,53
Magnesium	015	0.19	3.16	3.08
Sodium.	061	0.74	1,51	1.47
Sulfate	1 28	1.55	2.38	2,32
—		Total		
Calcium.	193	2.06	1.32	1.20
Chloride	533	5.66	089	083
Fluoride	_	<u> </u>	0.26	0.23
Magnesium	0,53	056	4.20	3.99
Sodium :	349	3.64	6.69	6.02
Sulfate	654	6.84	8.42	7,63
Total.	17.82	1876	21.78	19,90

SOURCE R F Probstein H Gold and R E Hicks, Water Requirements Pollution Effects and Costs of Water Supply and Treatment for the Oil Shale Industry prepared for OTA by Water Purification Associates October 1979 or reinfected into the aquifer from which it was drawn. The question has economic as well as environmental implications. If it is to be discharged, then it must be treated, and wastewater streams will be produced that will require management and disposal. The level of treatment is not known at present. In DRI's analysis of the costs of environmental protection, "less strict" and "more strict" pollutant discharge criteria were assumed."" In table C-1 1 their estimates are given for the total quantities of pollutants produced by treatment for surface discharge of 10,000 acreft/yr of excess mine drainage water of the quality shown in table C-7 for the less strict and more strict regulations. These quantities could be appropriately scaled down or up for different rates of drainage-water production. The effect of the different standards on the total quantity of pollutants produced is not large. However, the costs of achieving the "more strict" criteria would be much higher.

	Regulatory scenario			
	"Less strict'		' 'More strict '	
Contaminant	% Removal	Ton/d	o/o Removal	Ton/d
N H ³	85	004	91 7	004
Bicarbonate	77	21 47	943	2630
Boron	70	008	982	011
Calcium	99	184	999	1 86
Carbonate	90	1 67	958	1 78
Chloride	94	070	996	074
Fluoride	90	050	99.0	055
Magnesium	99	221	999	223
Silcia	83	046	967	054
Sodium	94	10.49	997	11 12
Sulfate	97	1262	999	1300
Total		5208		5827

Table C-1 1Rates of Pollutant Production From Treatment
of 10,000 acre-ft/yr of Excess Mine Drainage Water
for Surface Discharge

SOURCE Adapted from T.D. Nevens et al. (DRI Wafer PurificationAssociates and Stone and WebsterEngineering)PredictedCosts of Environmental Controls for a Commercial. 011 Shale IndustryVolume1. An Engineering Analysis Department. of Energy. July 1979.

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¹⁰E. F. Bates and T. L. Thoem (editors), *Pollution* **Control** Guidance for *OilShale* Development, Revised Draft Report, Environmental Protection Agency, Cincinnati, Ohio, July 1979.

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⊸•Ibid.