Lee

Please review and return (with comments) to Don Johnson by 9/16/81

ENVIRONMENTAL AND HEALTH RESEARCH PLAN

for the

RETORT 0 at LEASE TRACT C-a

PROGRESS REPORT

THE OIL SHALE TASK FORCE

AUGUST 1981

SOURCE CHARACTERIZATION AT RETORT 0

OBJECTIVES

The characterization studies provide data to be used in the interpretation of health and environmental effects as well as providing source characterization data to the oil shale risk analysis project. Retort 0 characterization has been used to verify analytical methodologies and identify potential emissions problems at the pilot plant stage of development. Characterization results obtained from Retort 0 also are providing information for modifying the sampling points, frequency, and size for subsequent Retort~~s~~ 1 ~~and 2 at~~ at Tract C-a.

Retort 2 will not be prepared or ignited!

A considerable effort on the source characterization has been the compilating of comprehensive environmental background data. The background data taken on mercury, arsenic, and sulfur are complimentary to the required data previously taken by Rio Blanco Oil Shale Company (RBOSC).

The sampling frequency used in the characterization studies provides information on the effluent concentration variations during the course of the burn. The priority pollutants, inorganic and organic species measured provide a better effluent characterization than that provided by priority pollutants alone. Furthermore, the inorganic and organic speciations performed allow some insight into the fate of the effluents in the environment.

RETORT 0 PROCESS DESCRIPTION

Figure 1 is a flow diagram of the MDP Retorts 0 through ~~2~~ 1. The air compressor and the steam boiler supply a mixture of air and steam to the retort. The ratio of air to steam is varied to control temperatures as the flame front progresses downward through the alternating rubblized lean and rich layers of oil shale. Condensed liquids and low BTU gas flow out of the bottom of the retort to an underground oil/water separator. The separator is designed to allow gravity separation of oil and water before they are pumped to the surface. The sour water flows to a sour water tank and then to a solar evaporation pond.

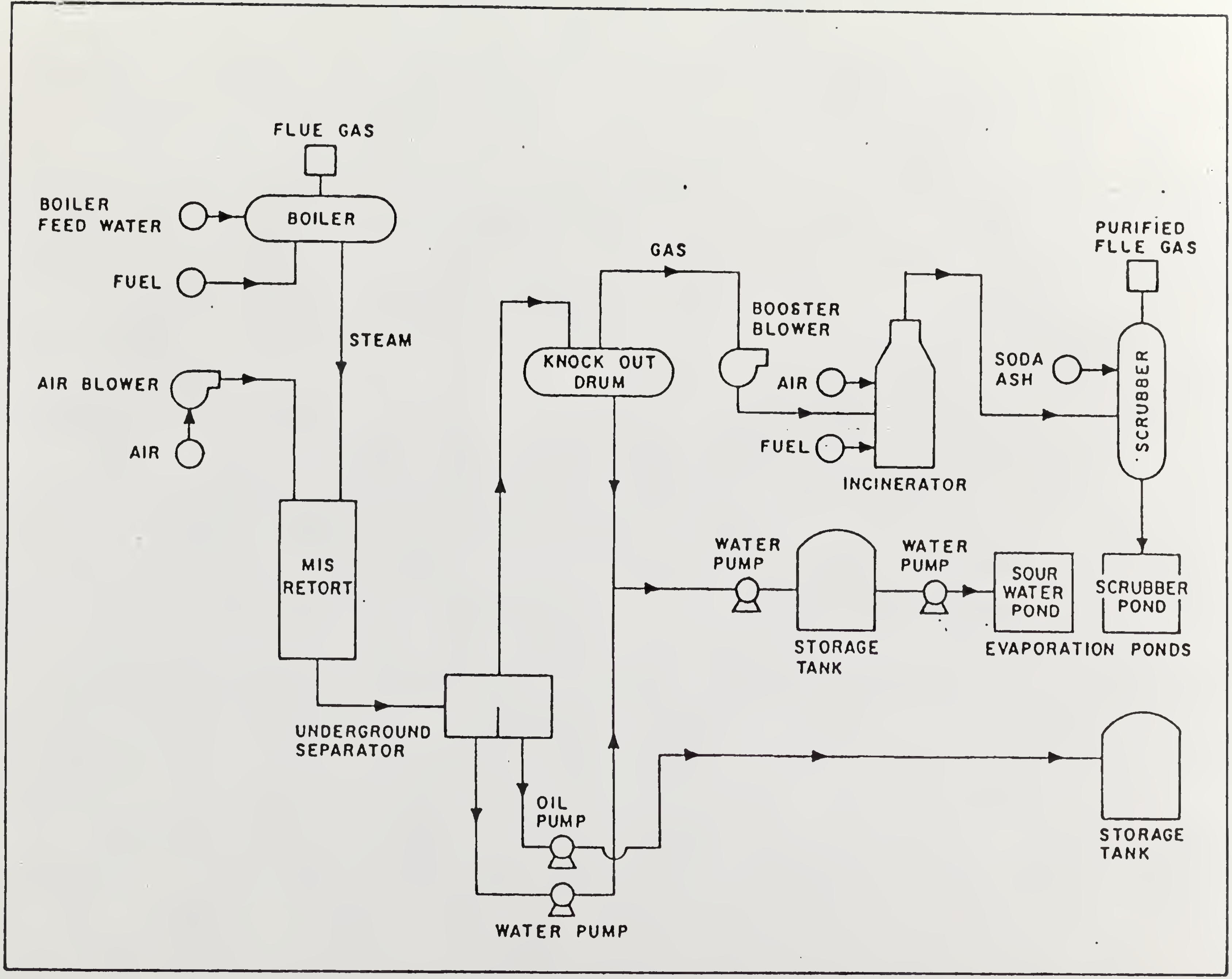

FIGURE 1

MDP RETORTS 0-2 FLOW DIAGRAM

Gas from the underground separator flows to the surface through an offgas shaft to a knockout drum before it reaches the suction of the low BTU gas booster blower. The booster blower allows the location of the zero pressure point in the retort to be varied as needed. The retort can be kept entirely under positive or negative pressure or a mixture of positive and negative pressure as dictated by retort integrity. In addition, the booster blower supplies the operating pressure for the incinerator/scrubber. The conventional gas-fired incinerator will convert all sulfur species in the low BTU gas to sulfur dioxide. The sulfur dioxide is then scrubbed from the flue gas by reaction with a solution of soda ash ($NaHCO_3$) to form sodium sulfite. The scrubber is designed to remove 90% of the sulfur dioxide from the flue gas before it is emitted to the atmosphere. The sodium sulfite solution is sent to a plastic-lined evaporation pond for disposal.

GAS ANALYSIS

Raw Retort Offgas:

The raw offgas was analyzed for sulfur species, mercury, major gaseous constituents, radon, general trace elements and polycyclic aromatic hydrocarbons. The sulfur species analyses are detailed in a separate report (PNL-9235). Sulfur compounds indentified using gas chromatography/photometry and on-line mass spectrometry included hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (CH_3SH), thiophene, methythiophene and sulfur dioxide (SO_2); one unidentified compound was observed in the spectrum. Gaseous sulfur speciation data are given in Table 1. The total of non-H_2S compounds ranged from 0.9% to 4.2% of the total sulfur.

The mercury data are shown in Figure 2. The data show relatively low levels of mercury during the first month of the burn. However, rapid increases in mercury concentrations were observed toward the end of the burn. This behavior has been noted before in laboratory scale retorts.

Radon measurements in the raw offgas are shown in Table 2. Although only four measurements were obtained they were relatively constant in the 6-7 pci/1 range. These concentrations are about ten times higher than in ambient sea

organization
of sentence
is sensitive
to oil shale
progress!

TABLE 1

PNL Data on Sulfur Gases in Rio Blanco Retort 0 (ppm or % by volume)

Sulfur Species	10/20[*]	10/22[†]	11/7[†]	11/20[†]
COS	500 ppm	130 ppm	380 ppm	85 ppm
CH_3SH	85 ppm	---	---	---
CS_2	30 ppm	15 ppm	25 ppm	15 ppm
SO_2	7 ppm	---	---	---
Peak 1 (thiophene?)	110 ppm (based on CH_3SH)	270 ppm	170 ppm	240 ppm
Peak 2 (methylthiophene?)	95 ppm (based on CH_3SH)	---	---	---
Peak 3 (unknown)	60 ppm (based on SO_2)			
Total (non-H_2S sulfur compounds)	887 ppm	≥ 415 ppm	≥ 575 ppm	≥ 340 ppm
H_2S[¶]	2.0×10^4 ppm	2.3×10^4 ppm	3.4×10^4 ppm	3.7×10^4 ppm
% of total sulfur as non-H_2S sulfur compounds	4.2%	≥ 1.8%	≥ 1.7%	≥ 0.9%

[*] based on GC/FPD data.

[†] based on GC-MS data.

[¶] based on RBOSC data.

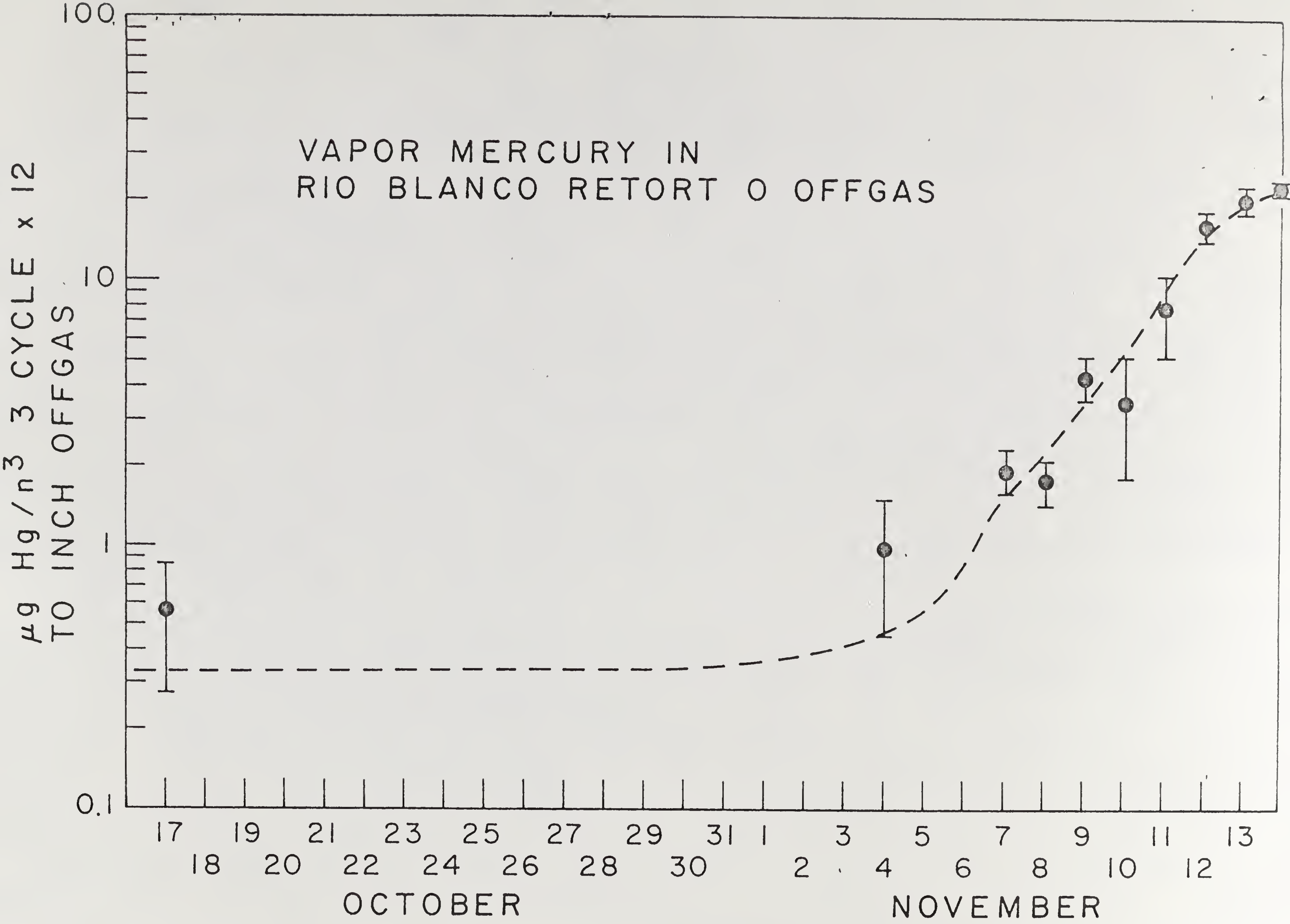
VAPOR MERCURY IN
RIO BLANCO RETORT O OFFGAS
μg Hg/n^3 3 CYCLE x 12
TO INCH OFFGAS
100
10
1
0.1
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
1
2
3
4
5
6
7
8
9
10
11
12
13
OCTOBER
NOVEMBER

FIGURE 2

TABLE 2

Radon Analysis

Date/Hrs	Hrs. Total Time	$\bar{X}$ ± 1r (Counts/hr)	Est. Radon Conc. pci/ℓ
Nov. 9 - 2000 Nov. 10 - 1400	13	6349.92 ± 548.84	7.68 ±
Nov. 7 - 1700 Nov. 9 - 0900	40	5977.10 ± 338.71	6.44 ±
Nov. 5 0700 - 1900	13	5921.77 ± 244.3	6.26
Nov. 4 1200 - 1400	3	6021.67 ± 101.32	6.59
	69	6038.85 350.19	6.65

BKG Counts 12 hours 4045 ± 58.87

level air and typical of ambient concentrations in the Rocky Mountain Region.

The major gaseous constituents are shown in Table 3. The organic and general trace element measurements have not been completed as of this date.

NO/NO_x In The Stack Gas

A Monitor Labs Model 8430 NO/NO_x analyzer was used for analysis of oxides of nitrogen in the stack gas at the crossover duct after the Venturi scrubber. The results are reported in Table 4; the major nitrogen oxide form measured was NO. NO values ranged from 62 to 176 ppm and averaged 112 ppm. The concentrations approximately tripled from the beginning to the middle of the run and decreased by 30% towards the end.

SOUR WATER SAMPLES

Sour water samples taken on different days from the underground separator room at Retort 0 were analyzed for a number of water quality parameters, cations and anions. The data are shown in Table 5. All of the sour waters analyzed were quite dilute compared to other previously measured retort product waters. This dilution is due to a large inflow of formation water which significantly increased the total amount of sour water produced. In spite of the large dilution by natural groundwater, a few parameters were definitely observed to increase systematically with time. Table 6 data show increasing values for pH, alkalinity, ammonia, organic carbon, conductivity, arsenic, potassium, molybdenum and antimony. The major anions are sulfate and carbonate/bicarbonate; the major cations are calcium, sodium, magnesium and probably ammonia. The total dissolved solids determined by the ASTM procedure is lower than the sum of ions, probably because of the volatization of $(NH_4)_2CO_3$ in the ASTM procedure. Total organic carbon (TOC) ranges from 49 to 242 ppm, which is quite low for a retort product water (again due to dilution).

3 1 2

why not list in order of relative abundance

Following sub-class fractionation by liquid chromatography on porous polymers and ion-exchange resins, individual organic compounds in the sour water (RB-0-SW-064) were identified by high resolution fused silica capillary chromatography coupled with mass spectrometry. The Leenheer and Huffman method

TABLE 3

Composition of Retort 0 Offgas

Date	H_2	CO_2	H_2	CO	H_2S	O_2	Ar	CH_4	C_2-C_5 HyCar	C_6+	S.G.	COS	SO_2	Flow (SCFM)
	Mole %										ppm			
10-19-80 @ 1107	58.24	22.65	8.76	3.35	1.56	2.35	0.71	1.50	0.84	0.00	1.02	1.56	0.01	2365
10-20-80 @ 1044	58.34	22.48	8.69	3.03	2.02	2.40	0.71	1.52	0.71	0.04	1.02	1.43	0.01	2225
10-22-80 @ 0742	57.94	22.97	9.03	2.37	2.27	1.87	0.70	1.56	0.75	0.20	1.03	1004	5.00	2570
11-4-80 @ 1027	61.21	26.04	5.05	1.56	3.01	0.89	0.74	0.19	0.31	0.00	1.07	187.2	3.74	3540
11-4-80 @ 1429	61.60	24.39	6.44	1.72	3.17	1.22	0.74	0.22	0.33	0.00	1.05	175	3.19	4564
11-5-80 @ 1128	61.22	27.17	5.48	1.51	3.33	1.25	0.72		0.24	0.00	1.08	199	3.95	3110
11-6-80 @ 1739	62.45	23.47	6.75	1.65	3.33	1.27	0.75		0.24	0.00	1.05	184	3.96	3717
11-7-80 @ 1357	60.82	25.16	6.43	1.78	3.43	1.34	0.74		0.26	0.00	1.06	238	1.90	3637
11-7-80 @ 1730	60.90	25.05	6.34	1.83	3.44	1.44	0.71		0.27	0.00	1.06	238	4.01	3505
11-8-80 @ 1249	56.03	27.33	7.82	1.38	3.99	1.72	0.67		0.29	0.00	1.07	195	3.55	1854
11-9-80 @ 0934	56.34	26.48	8.36	0.83	3.99	1.59	0.68		0.32	0.00	1.05	110	0.88	2933
11-9-80 @ 1749	55.54	26.59	8.99	0.94	3.99	1.93	0.67		0.32	0.00	1.05	93	0.89	3001
11-10-80 @ 0926	46.20	32.25	11.58	0.65	3.99	1.40	0.55		0.41	0.00	1.06	84	0.98	865
11-10-80 @ 1748	53.88	26.74	10.77	0.50	3.99	1.41	0.65		0.38	0.00	1.03	57	0.93	702
11-11-80 @ 0931	48.18	29.18	12.57	0.51	3.99	1.22	0.58		0.38	0.00	1.09	54	1.09	2266
11-12-80 @ 0958	51.94	29.82	13.57	0.46		0.13	0.62	0.75	0.47	0.20	1.02	41	1.14	435
11-12-80 @ 0726	50.28	28.73	12.59	0.50	4.07	1.11	0.61	1.25	0.55	0.39	1.03	39	0.89	1553
11-13-80 @ 1019	49.74	2950	12.27	0.59	4.09	1.24	0.60	1.20	0.52	0.39	1.04	39	0.83	1194
11-13-80 @ 1654	49.43	29.42	13.41	0.63	3.87	1.04	0.60	0.95	0.38	0.44	1.03	36	0.76	861
11-14-80 @ 1112												29		971
11-18-80 @ 1426	35.39	31.97	21.21	0.47	4.68	1.93	0.42	1.93	0.71	1.43	0.99	20	0.93	4.32

TABLE 4

DATA

NO/NO_x Concentration

Date/Time Start/End	Average Corrected Concentration	Remarks
10/21/80 - 10/21/80 1530 1800	Average 66 ppm NO	
10/21/80 - 10/22/80 1800 0830	Average 63 ppm ← NO	51 - 75 ppm
10/22/80 - 10/22/80 0830 0915	Average 75 ppm NO	
10/22/80 - 10/22/80 1915 1049	Average 62 ppm NO	Retort Compressor went down <u>0915</u>
11/4/80 - 10/22/80 1650 1330	Average 160 ppm NO	
11/5/80 - 11/5/80 1330 2000	Average 152 ppm NO	
11/5/80 - 11/6/80 2000 0800	Average 176 ppm NO	
11/6/80 - 11/6/80 0800 0930	Average 144 ppm NO	
11/6/80 - 11/6/80 0930 1700	Average 168 ppm NO	
11/6/80 - 11/7/80 1730 0900	Average 155 ppm NO	
11/7/80 - 11/7/80 0900 1615	Average 170 ppm NO	
11/16/80 - 11/16/80 1330 1930	Average 100 ppm NO	
11/16/80 - 11/19/80	Average 98 ppm NO	Strip Chart Stuck Range 88-108 ppm
11/19/80 - 11/19/80 1000 1315	Average 112 ppm NO	

TABLE 5

Chemical Characteristics of Retort O Sour Water

Parameter (mg/l unless noted)	10-18-80 (RB-O-SW-005)	10-27-80	11-5-80 (RB-O-SW-024)	11-12-80 (RB-O-SW-031)	11-14-80 (RB-O-SW-061)	11-17-80	11-19-80 (RB-O-SW-059)	11-20-80 (RB-O-SW-060)	11-21-80 (RB-O-SW-064)
pH Units	7.9	8.3	8.6	8.8	8.6	8.9	8.9	9.0	9.0
Alkalinity as $CaCO_3$	545	---	---	---	1370	---	3280	---	2480
Ammonia as NH_3-N	10	110	130	360	360	1300	1320	1060	1070
Carbon, Total	263	310	153	361	461	707	736	587	602
Carbon, Total organic	92	105	49	102	167	237	242	218	233
COD	334	---	---	---	582	---	1060	---	1100
Conductivity at 25°C (µmhos/cm)	3900	---	---	---	4900	---	10,000	---	9100
Solids, dissolved (ASTM 1888-67-A)[1]	3870	---	610	---	2420	---	4230	---	4200
Solids, dissolved (Sum of Ions)[2]	3590	3870	1130	3140	3660	6920	6690	5640 (6700)[3]	5690 (6230)[3]
Cl^-	8.5	9.5	6.9	7.9	7.1	9.3	8.8	9.0	9.8
F	4.0	4.0	4.3	2.3	2.4	5.9	6.3	6.1	5.9
SO_4^{--}	1750	1850	1080	1000	1100	2400	2020	940	1450
S_2O_3	---	---	---	---	---	---	---	205	840
Al	<0.05	<0.1	<0.05	<0.05	<0.1	<0.2	< 0.1	<0.2	< 0.2
As	<0.01	0.07	0.06	0.06	0.08	0.72	0.72	0.61	0.50
B	0.35	0.44	0.09	0.26	0.30	0.46	0.47	0.46	0.46
Br	0.07	0.06	<0.01	<0.03	<0.05	0.06	0.01	<0.05	< 0.01
Ca	132	66	10	17	22	13	14	11	11
Cd	<0.005	<0.02	<0.01	<0.005	<0.01	<0.005	< 0.02	<0.005	< 0.005
Cl	12	12	3	8	9	13	8	8	8
Co	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	< 0.005	<0.005	< 0.005
Cr	<0.005	<0.002	<0.002	<0.002	<0.002	<0.002	< 0.003	<0.002	< 0.002
Cu	<0.004	<0.004	<0.004	<0.002	<0.002	0.008	< 0.004	<0.004	0.004
Fe	1.88	0.17	0.098	0.42	1.11	0.33	0.40	0.39	0.56
K	17	26	9.2	13	16	55	55	60	55
Li	0.20	0.27	0.06	0.11	0.17	0.43	0.43	0.37	0.36

Mg	312	325	42	160	188	107	108	78	74
Mn	1.22	0.57	0.035	0.025	0.009	0.030	0.032	0.030	0.025
Mo	0.044	0.087	0.053	0.054	0.072	0.20	0.20	0.17	0.18
Na	395	440	79	269	314	424	430	440	422
Ni	0.015	0.017	<0.003	0.009	0.008	0.016	0.025	0.010	0.015
S	---	---	---	---	---	---	---	1200	960
Sb	0.005	0.008	<0.004	<0.010	0.008	0.035	0.036	0.033	0.031
Se	<0.05	<0.05	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Si	12	11	8.6	12	13	15	14	15	16
U	<0.03	<0.03	<0.02	<0.03	<0.03	<0.03	<0.03	0.06	0.04
V	<0.02	<0.03	<0.01	<0.02	<0.02	<0.02	<0.03	<0.03	<0.02
Zn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

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[1] With the possible exception of sample 10-18-80, the ASTM method yielded low results due to volatileloss of NH_3 and CO_2.

[2] Values are based on the sum of the measured dissolved species; the inorganic carbon was computed as CO_3^{--} and non SO_4^{--} sulfur is not included.

[3] Values include the non SO_4^{--} sulfur computed as $S_2O_3^{--}$.

of fractionation resulted in sub-class fractions of hydrophobic and hydrophilic acids, bases and neutrals. Compound identifications were confirmed in most cases by comparison of chromatographic and retention data and mass spectra.

In the organic characterization of the sour water (RB-O-SW-064), a large number of hydrocarbons, carboxylic acids, phenols, cresols, naphthalenes, alkyl pyridines, anilines, quinolines and elemental sulfur (S_8) were identified. Table 6 provides a partial list of the compounds found. Hexathiepane was identified by mass spectrometry in the hydrophobic neutral fraction extracted in CH_2Cl_2; this finding is being further investigated.

SHALE OIL FROM RETORT 0

Shale oil from the underground separator room was separated from emulsified sour water at 75°C and analyzed for major constituents. The data are shown in Table 7. The composition of this oil is generally similar to other shale oils, but there are a few significant differences. The sulfur content is almost three times as high as shale oils from other field retorts measured to date. The metals, nickel, which probably occurs as a porphyrin, and molybdenum, which probably is associated with the asphaltene fractions, are relatively high in these shale oils. Arsenic is on the low end of the concentration range for shale oils. These trends have been noticed for other *in situ* produced oils, but are more pronounced for the Retort 0 oil.

The analyses presented in this section were conducted to indentify those organic compounds likely to reach the atmosphere as vapors.

Gaseous samples were obtained from head space analysis of vapors derived from shale oil, since this source appears, at present, to be most likely to produce fugitive vapor emissions. These head space vapors were directly injected into a capillary column equipped Perkin-Elmer Sigma-3, Gas Chromatograph interfaced to a VG micromass MM16 mass spectrometer for analysis.

The results obtained are listed in Table 8 and are indicative of the following:

Head space analyses of shale oil samples indicate primarily volatile aliphatic compounds but a number of aromatic compounds were also present.

TABLE 6

Compounds Identified in Rio Blanco Retort-0 Sour Water - 064 by Fused Silica Capillary Chromatography Coupled with Mass Spectometry[a]

Carboxylic Acids:

hexanoic acid
ocanoic acid
nonanoic acid
decanoic acid
undecanoic acid
dodecanoic acid

Phenols:

phenol
o-cresol
m-cresol
p-cresol
2,6-dimethyl phenol

Alkanes:

nonane
decane
dodecane
heptadecane
octadecade
nonadecane
eicosane
heneicosane
docosane
tricosane
tetracosane

Nitrogen Containing Compounds:

aniline
m-toluidine
2,6-dimethyl quinoline
4-methyl pyridine
quinoline
isoquinoline
3-methyl quinoline

Polynuclear Aromatic Hydrocarbons:

naphthalene
2-methyl naphthalene

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[a] R.E. Sievers, M.K. Conditt, and R.S. Hutte, University of Colorado, Boulder, unpublished data.

TABLE 7

CHEMICAL COMPOSITION OF RIO BLANCO
DRY SHALE OIL (RETORT 0)

Major Elements (Wt%)	11-3-80 (RB-0-SO-031)	11-22-80 (RB-0-SO-109)
C	-----	83.1
H	-----	11.9
S	-----	1.9
N	-----	1.5
0 (by difference)	-----	1.6

Trace Elements (μg/g)	11-3-80 (RB-0-SO-031)	11-22-80 (RB-0-SO-109)
Fe	88	49
Ni	21	17
Mo	15.5	10.1
Na	8.0	23.9
As	7.6	7.4
Co	3.6	3.5
Se	2.62	1.94
Cl	2.0	<3
V	1.33	1.28
Zn	1.0	0.3
Al	<0.2	<0.5
Cr	<0.2	0.2
Sb	0.075	0.070
Mn	0.06	0.07
U	0.05	0.06
Br	<0.01	<0.02

TABLE 8

COMPOUNDS IDENTIFIED IN HEADSPACE ANALYSIS OF SAMPLE R-6 (SHALE OIL FROM RIO BLANCO RETORT 0)

Alkanes

2-methylpropane
2-methylpentane
Hexane
Methyl cyclopentane
trimethyl hexane
dimethyl cyclopentane
Heptane
methyl cyclohexane
up to $\sim C_{20}$ alkanes

Alkenes

Hexene
methyl pentene
methyl cyclopentene
Heptene
dimethyl cyclopentene
methyl heptene
dimethyl heptene
methyl octene
dodecene

Aromatic

benzene
thiophene
Toluene
methyl thiophene
dimethyl ethyl thiophene
trimethyl benzene
ethyl benzene
Xylene
Tetramethylbenzene
Naphthalene
Ethyl Methyl Benzene
tetra hydro dimethyl naphthalene
methyl propyl phenol
tetrahydro trimethyl naphthalene
Ethyl benzenediol
2,3 dihydro indene
Methyl Napthelene

Other

dimethyl heptadienal
butyl methoxy cyclohexen-l-one
Nonanol

The results obtained to date are only tentative, but when taken in conjunction with other shale oil head space analyses, the following observations are to be drawn:

1) shale oil head space vapors contain a multitude of organic species
2) organic species likely to be emitted to the atmosphere as gases are primarily aliphatic in nature, although substantial amounts of single and double ring aromatic compounds are present.
3) apparently, head space vapors are quite similar for shale oils produced under different operations.

what is substantial

RAW SHALE CHARACTERIZATION

Approach

Physical and chemical characterization of raw shale core material (designated core CE 709) is being performed. Elemental characterization of core material is accomplished by instrumental neutron activation analysis (NAA), x-ray fluoresence (XRF) and direct current argon plasma emission spectrometry (DCAPES). Trace element mobilities are determined by using a standardized 48-hour leaching technique with -100 mesh solid material. The procedure is detailed in the Environmental Fate and Effects, Water Quality section of this report. Elemental concentrations and leaching behavior are examined as a function of depth to determine if similar patterns exist in the chemical behavior among the solids.

After behavior patterns are identified, samples representative of the different zones are chosen for mineralogic characterization. Materials selected on the basis of trace element release are studied by optical microscopy, scanning election microscopy (SEM) and electron microprobe analysis. In addition, bulk mineralogical data by x-ray diffraction (XRD) are required so that vertical mineral variability of the region can be understood. Therefore, mineral composition as well as association of trace elements with both micro minerals and major rock fractions, can be established. This approach, although not comprehensive, make a reasonable choice on the basis of chemical factors of the materials to be characterized.

Materials

The core materials being analyzed were received directly from RBOSC and consist of a 1/8th core split of Cameron Engineers core 709. This core was drilled prior to the acquistion of lease Tract C-a by RBOSC. Currently, two types of samples are being emphasized. A survey of the elemental concentrations and leaching behavior of solid core materials is being accomplished by examining a two foot section of material every 20 feet through the length of the core. More specifically, materials from the stratigraphic horizon of Retort 0 are being studied. The latter suite of samples includes RBOSC designated zones R6, L5 and R5 at depths of 560 to 775 feet.

d single core
does not
adequately represent
C-a shale
because of the
xtent of
secondary
eposition
n this area.

Results and Discussion

1) Elemental Analysis. Results for the survey sample set are listed in Table 9. These concentrations all appear to be within reasonable levels given concentration ranges in raw shales from other development areas in Colorado. XRF results are not yet available. In addition, elemental analyses for the second sample set in the vicinity of Retort 0 will be available in the near future.

2) Leaching Behavior. The major and trace element mobilities for both sets of samples have been tabulated and are discussed in the Water Quality section of this report. Although preliminary examination of these results indicate trends that suggest zones of similar chemical behavior, final conclusions will have to await evaluation of elemental concentrations and trace element mobility data.

3) Mineralogic Characterization. Preliminary characterization by x-ray diffraction is being carried out for several samples indicated to be representative of zones of similarity on the basis of leaching studies. These results will be available soon. More extensive characterization will be performed for selected solid materials after zones of similar behavior are established.

SUMMARY

Preliminary results suggest that identifying variations in elemental

The ratio of magnesium to calcium appears to be too small.

TABLE 9

Neutron Activation Data
Tract C-a Gore CE-709 Survey
(in ppm µg/g except as indicated)

Sample^x	Avg. Depth	Ar (%)	As	Ba	Ca (%)	Ce	Co	Cr	Cs	Cu	Eu	Fe (%)	La	Mg (%)	Mn	Hg	K (%)	Sc	Se	Sm	Sr	Na (%)	Th	Ti	W	U	V	Zn
1	208.7	5.21	26	466	6.43	79	8.2	25	6.3	<340	0.61	1.69	22	1.22	399	<0.03	1.46	3.9	<0.8	3.5	<300	3.35	11.4	2617	<5	3.8	46	72
11	232.	3.46	41	539	14.6	41	8.0	41	5.6	<240	0.56	2.03	12	3.17	474	<0.03	1.34	5.9	<4.9	2.7	709	1.69	6.1	1500	<0.11	2.9	65	121
21	253	3.44	87	483	14.8	38	8.8	43	4.2	<220	0.67	2.02	13	2.89	316	<0.03	1.84	6.2	<5.1	3.6	910	1.14	5.9	1332	<3	3.6	74	<75
31	273	3.03	16	560	15.0	38	9.6	46	3.7	<230	0.54	1.84	10	4.44	386	<0.03	1.77	6.8	<6.4	2.0	886	0.85	5.5	1660	<3.2	4.2	63	<90
41	293	3.27	81	592	12.9	50	11.5	37	3.8	<250	0.59	2.18	13	2.29	287	<0.03	1.40	5.5	<5.6	2.9	1040	1.55	5.6	1668	<3.8	4.9	92	140
51	314	3.39	54	695	13.6	49	8.2	26	3.3	<230	0.60	1.79	13	3.25	312	<0.03	1.34	4.9	<5.4	3.1	874	1.22	4.4	1399	<3.8	5.8	88	51
61	339	3.56	130	415	10.6	41	9.6	36	3.1	<220	0.59	1.96	13	2.21	304	<0.03	1.41	5.5	<4.8	3.0	790	1.21	5.0	1536	<3.8	4.1	91	<75
71	359	3.06	65	560	12.5	28	9.0	23	2.3	<200	0.46	1.63	10	3.17	259	<0.03	1.08	4.4	<5.1	2.2	872	1.16	4.2	544	<0.15	5.0	87	<72
81	379	3.48	24	486	12.0	35	7.8	41	4.7	<260	0.55	1.72	12	3.99	314	<0.03	1.40	5.5	<5.3	3.0	832	1.66	5.0	1567	<3.8	4.2	78	88
91	400	3.50	51	781	11.9	49	9.3	29	3.1	<240	0.66	1.83	14	2.49	284	<0.03	1.66	5.8	<6.4	3.6	976	1.37	8.7	1758	<4.2	7.1	74	<65
101	419.7	5.32	46	342	7.8	46	10.2	43	4.1	<240	0.66	3.23	14	2.83	409	<0.03	3.99	8.9	<5.1	3.5	<250	1.49	4.5	2314	<3.9	4.1	110	<29
111	440	3.47	16	713	13.0	29	9.2	28	<1.3	<180	0.34	2.02	12	2.74	275	<0.03	2.97	5.4	<5.1	2.8	1102	0.88	6.3	1345	<0.13	5.5	82	123
121	463	3.84	7.7	560	12.2	46	9.9	35	4.8	<270	0.78	2.25	13	3.24	264	<0.03	1.49	6.1	<6.0	3.2	1010	1.90	6.4	1208	<4.0	6.1	114	78
131	485.6	4.34	44	571	7.3	43	12.5	30	6.5	<270	0.75	2.64	14	3.33	251	<0.03	1.72	6.7	<6.3	2.9	715	1.98	5.1	1329	<4.8	7.4	137	84
141	506	6.74	19	<150	4.6	71	14.0	59	6.6	<320	0.93	4.05	22	1.89	413	<0.03	2,95	9.9	<5.7	4.9	571	3.27	8.9	2534	<5.5	7.3	157	181
151	530	4.52	19	624	8.2	42	9.5	43	<1.4	<270	0.48	2.29	14	2.83	349	<0.03	1.68	6.3	<5.3	3.3	626	2.57	5.6	1706	<0.15	5.2	106	131
161	559	4.51	23	562	8.8	57	11.1	49	<1.7	<320	0.67	2.61	16	2.47	384	<0.03	1.59	7.8	<6.5	3.8	686	2.63	6.3	2079	<4.9	3.7	101	117
171	579	4.71	25	380	9.2	49	9.9	41	4.2	<260	0.66	2.71	17	3.55	350	<0.03	2.86	7.2	<5.7	3.0	528	1.78	5.0	1866	<4.4	2.8	122	83
181	605.3	6.18	8.6	304	4.7	48	10.5	45	4.2	<320	0.60	2.99	17	2.44	365	<0.03	2.06	7.8	<5.1	2.9	<280	3.25	4.2	2031	<5.3	3.0	111	<92
191	628	6.18	23	517	4.4	44	10.4	45	8.6	<270	0.65	2.57	16	2.68	252	<0.03	3.03	7.2	<5.5	3.0	<210	2.66	6.5	1971	<0.12	4.3	141	129
201	650.5	3.94	14	388	9.0	39	7.2	35	2.6	<200	0.60	1.92	12	4.38	311	<0.03	3.75	6.1	<5.5	2.7	<667	0.18	3.4	1571	<3.0	3.0	96	<67
211	674	4.77	31	447	4.6	56	14.3	39	4.9	<230	0.69	2.41	16	2.92	247	<0.03	2.57	7.7	<6.4	3.5	<230	1.27	5.4	1982	<4.2	6.7	158	<38
221	694	3.50	31	387	8.0	33	8.1	34	4.2	<230	0.71	1.91	12	3.46	344	<0.03	1.25	6.3	<5.2	2.7	<824	1.24	4.1	1576	<3.9	3.4	112	89
231	714	4.26	16	404	8.0	40	9.4	44	<1.5	<220	0.59	1.94	12	3.11	345	<0.03	1.65	6.5	<5.4	2.5	567	1.48	5.6	1619	<0.15	3.3	114	77
241	734	4.41	16	361	8.7	40	6.4	38	3.3	<240	0.52	2.38	13	3.22	350	<0.03	1.39	6.8	<6.3	3.1	704	1.33	4.1	1682	<3.7	3.1	102	107
251	754	5.36	42	515	6.1	51	13.8	44	4.9	<210	0.72	2.47	17	2.43	327	<0.03	1.79	8.1	<7.2	3.5	756	0.71	5.4	2245	<3.8	4.8	141	97
261	773.9	4.05	19	445	8.1	34	8.7	42	3.2	<240	0.50	1.55	12	3.08	318	<0.03	1.19	5.8	<4.9	2.7	599	1.34	4.4	1955	<3.9	2.7	89	110
271	796.9	3.80	69	262	4.5	43	12.1	41	6.4	<250	0.58	2.26	11	2.29	207	<0.03	1.08	6.1	<6.0	2.0	437	1.68	5.4	1547	<3.4	6.0	143	123
281	816.3	5.07	37	420	6.0	45	11.5	46	3.8	<210	0.71	2.46	15	2.53	299	<0.03	1.93	8.0	<6.7	4.0	605	0.89	6.8	1404	<2.8	6.9	150	<42
291	835.1	5.28	19	480	6.4	47	10.0	46	4.3	<180	0.68	2.83	14	3.20	328	<0.03	1.19	7.9	<5.7	2.9	648	0.67	5.6	2161	<2.9	4.0	131	125
301	857	4.17	18	409	8.3	38	7.7	38	4.3	<220	0.59	2.08	13	3.39	361	<0.03	1.45	6.3	<5.5	3.3	696	0.91	5.3	1989	<2.8	3.6	102	92

TABLE 9 (cont.)

Sample[x]	Avg. Depth	Ar (%)	As	Ba	Ca (%)	Ce	Co	Cr	Cs	Cu	Eu	Fe (%)	La	Mg (%)	Mn	Hg	K (%)	Sc	Se	Sm	Sr	Na (%)	Th	Ti	W	U	V	Zn
311	877	4.31	17	499	6.7	45	9.9	50	7.1	<230	0.68	2.05	11	3.41	321	<0.03	1.41	6.8	<6.5	2.6	579	1.07	6.0	1670	<2.9	3.6	92	76
321	897	5.15	13	322	7.3	50	7.7	35	7.6	<280	0.56	2.06	14	3.38	357	<0.03	1.67	6.8	<6.8	2.4	545	1.56	4.5	2016	<3.7	3.3	105	<79
331	921	4.63	58	356	4.8	40	12.9	46	2.0	<280	0.47	2.37	12	1.66	246	<0.03	1.38	7.2	<5.6	2.3	<220	2.55	5.1	1653	<0.9	5.4	149	112
341	941	3.77	39	361	7.7	29	9.8	34	3.1	<300	0.51	1.65	12	2.89	288	<0.03	1.39	5.8	<5.5	3.1	453	2.12	4.7	1686	<3.9	5.0	116	48
351	963	4.41	35	323	6.7	45	10.8	38	8.2	<330	0.63	2.17	11	3.00	297	<0.03	1.66	7.1	<6.2	2.1	477	2.85	4.4	1655	<4.4	4.5	126	129
361	985	5.06	18	248	3.2	67	17.8	45	8.2	<310	0.62	2.91	14	1.49	297	<0.03	1.27	7.9	<7.1	3.2	<270	2.52	6.9	1297	<4.4	7.3	159	146
371	1005	4.91	31	430	7.1	42	8.5	45	3.7	<280	0.56	2.52	11	2.58	315	<0.03	2.02	7.2	<5.4	2.2	432	2.54	5.6	1579	<0.8	4.1	103	<47
381	1026	3.18	16	418	11.7	29	5.8	26	3.5	<270	0.55	1.27	10	3.10	384	<0.03	1.30	4.0	<4.8	2.4	775	1.59	4.5	1217	<3.3	2.2	56	<0.
391	1053	3.59	31	354	9.5	39	7.4	43	<1.5	<260	0.59	1.80	9	3.25	363	<0.03	1.58	6.3	<6.0	1.9	593	1.69	5.4	1661	<3.3	2.3	93	65
401	1081	4.20	27	318	6.1	35	9.1	35	5.3	<240	0.43	1.83	13	2.98	307	<0.03	2.04	6.5	<6.1	2.7	573	1.41	4.2	1891	<3.4	4.0	108	114
411	1106	5.74	41	394	3.7	45	16.6	51	4.8	<290	0.84	3.17	14	2.10	331	<0.03	2.15	9.0	<6.1	3.1	<240	2.42	6.0	2472	<0.9	8.5	164	200
421	1126	6.34	71	350	3.0	47	13.7	40	<1.8	<370	0.65	3.35	18	1.40	326	<0.03	1.93	10.1	<6.5	4.7	<280	3.32	6.8	2352	<5.1	9.3	164	149

concentrations and trace element mobilities from solids as a function of depth and stratigraphy may be a useful approach for designating samples for extensive mineralogical characterization. These data, in conjunction with mineralogy data, can be used to understand the behavior of raw material before and during processing, and the possible implications of long-term storage of raw material not suitable for processing. The characterization efforts address both potential solid waste and water quality concerns.

SOIL MERCURY

Previous studies have shown significant mercury loss during the retorting of oil shale, and the ability of Piceance Creek Basin soils to adsorb mercury vapor during atmospheric exposure. Because of the potential for mercury loss and soil adsorption, the establishment of baseline mercury concentrations in soils surrounding the modular development is essential. The volatility of mercury and its ease of measurement in soil material will allow early detection of a soil increment due to shale oil production.

A grid of approximately six km^2 surrounding the modular development area was selected for an accurate surface soil baseline determination of mercury. A total of 189, -80 mesh surface soil samples were collected on this grid in June 1980, prior to the firing of Retort 0, and analyzed for mercury using a Jerome Model 301 gold film detector.

Within the six km^2 area, soils are developed on three different parent materials. The Uinta Formation generally occurs on ridges, the uppermost part of the Parachute Creek Member of the Green River Formation occurs along the valley sides, and alluvium is present on the valley floors. It was expected that mercury concentrations in soils developed on these parent materials would be different and the analytical data was treated accordingly.

Results and Discussion

Basic statistics were calculated for each group of soil samples derived from the three parent materials existing in the area sampled (Table 10).

TABLE 10

Summary Statistics

	Parachute Creek	Uinta	Alluvium
Number of Samples	70	80	39
Mean (ppb)	26.9	23.5	18.6
Standard Deviation	8.02	6.77	5.60
Median (ppb)	26.2	22.9	17.4
Mode (ppb)	24.1	23.6	12.4
Maximum (ppb)	48.2	42.2	31.3
Minimum (ppb)	13.6	12.6	7.3

TABLE 11

Summary of t-test

	Parachute Crk. vs. Uinta	Parachute Crk. vs. Alluvium	Uinta vs. Alluvium
Mean Hg ppg	26.9 - 23.55	26.9 - 18.6	23.55 - 18.6
Degrees of freedom	69	38	38
Calculated t-value	2.73	6.26	3.62
Critical t-value at .01	2.39	2.55	2.55

Three significant figures are retained in the data for statistical calculations, though only two can be considered significant for an individual determination. A t-test was employed to determine if a significant difference in soil mercury exists among the three populations. The t-statistic is calculated for pairs individually (Table 11).

The results of Table 10 and 11 show that at a 99% confidence level, there exists a difference in mean mercury concentrations in soils derived from the respective geologic units. A baseline concentration of 18 to 27 ppb mercury exists in surface soils around the area planned for modular development on Tract C-a. Soils developed on the Parachute Creek Member, Unita Formation and alluvium, respectively, have significantly different concentrations of mercury. The baseline data on mercury will allow an early detection of mercury accumulation by soils if there is significant loss during retorting of oil shale. ~~A replicate sampling and analysis program after firing and cooling of Retort 2 is anticipated.~~

CHARACTERIZATION OF PARTICULATE ASSOCIATED ORGANIC SPECIES EMITTED FROM OIL SHALE CONVERSION PROCESS

Analysis

Analyses were conducted to identify organic species that could be extracted from particulate matter emitted to the atmosphere from the retorting process. Consequently, emphasis was placed on compound identification rather than on quantitative measurements. Particulate samples were extracted with a Soxhlet distillation apparatus using benzene as the solvent. The extract was then subjected to capillary column gas chromatography interfaced to a V6 Micromass MM16 mass spectrometer as well as to HPLC utilizing multiple wave lengths (Reticon-photodiode array) UV-VIS absorption spectrometry for identification.

Sample Collection

The stack particulate samples were collected using an Anderson Stack Sampler; however, due to the size of the entrance of the sampling port on the crossover duct it was not possible to place the sampler inside the process effluent stream. Therefore, because samples were not collected isokinetically, no distinction was given to the size fractions obtained. Instead the samples were combined and collectively extracted for qualitative identification purposes. Stack samples were collected on the "crossover duct" located downstream from a thermal oxidizer followed by a scrubber but prior to the stack. Difficulties were encountered during sampling because a drain tap on the scrubber remained closed for most of the sampling periods. As a result, large amounts of water were carried through into the stack and condensed in the sampling system.

Results

Results are listed in table 12 and are indicative of the following: most of the organic material extracta~~v~~ble form the stack particulate samples consisted of polycylic aromatic hydrocarbons (PAHs).

Conclusions

The results obtained to date do not permit any firm conclusions. However, when taken in conjunction with results obtained for samples derived from other oil shale retorting processes, the following tentative observations can be offered:

1) Particulate emitted from an oil shale processing operation appear to be of two types. The first of these includes essentially a mineral substrate and are probably similar to retorted oil shale dusts. The second type of particle is carbonaceous in nature and is found following a thermal oxidizer of flare.

2) A wide variety of organic species are associated with emitted particles, the most abundant being polycylic aromatic species.

3) Based on limited information available it would appear that the general characteristics of particulate-associated organic materials likely to be emitted to the atmosphere are similar for different oil shale retorting operations.

TABLE 12

COMPOUNDS IDENTIFIED IN RIO BLANCO - RETORT 0 STACK SAMPLE R-3

Positive Identification	Tentative Identification
Pyrene	Benzo (e) pyrene
Fluoranthene	Benzo (i) fluoranthene
Benz (a) anthracene	Dibenz (d,e,f), (m,n,o) chrysene
Chrysene	Dibenz (a,i) pyrene
Benzo (b) fluoranthene	Dibenz (a,e) pyrene
Benzo (k) fluoranthene	1,2 Propandiene
Benzo (a) pyrene	2 Propenyl diene
Benzo (g,h,i) perylene	*N-(Phenyl methylene)benzene methanamine
Coronene	*5-Bromo pentyl benzene
Benzo (g,h,i) fluoranthene	N-Butyl benzene sulfonamide
Anthanthrene	Hexanal
1,2 Dimethyl benzene	2, 2, 3 trimethyl hexane
1, 3 Dimethyl benzene	1, 1 Dimethyl ethyl cyclohexane
1, 4 Dimethyl benzene	Hexadecanol
Ethyl benzene	Variety of amines, amides, and carboxylic acids

*Possible artifact

TABLE 13

GAS AND VAPOR SAMPLING AT RIO BLANCO OIL SHALE COMPANY

CONTAMINANT	SAMPLING METHOD	ANALYSIS METHOD	NUMBER OF SAMPLES Pre-ignition	NUMBER OF SAMPLES Post-ignition	DETECTION LIMIT	THRESHOLD LIMIT VALUE	RESULTS Pre-ignition	RESULTS Post-ignition
CO	Detector Tube	Length of Stain	16	12	5 ppm	50 ppm	<5 ppm	<5 ppm
NO_2	Detector Tube	Length of Stain	8	6	0.2 ppm	5 ppm	<0.2 ppm	<0.2 ppm
H_2S	Detector Tube	Length of Stain	14	12	0.5 ppm	10 ppm	<0.5-10 ppm	<0.5-3 ppm
SO_2	Detector Tube	Length of Stain	12	6	0.2 ppm	5 ppm	<0.2-1.5 ppm	<0.2 ppm
AsH_3	Detector Tube	Length of Stain	6	6	0.05 ppm	0.05 ppm	<0.05 ppm	<0.05 ppm
C_6H_6	Detector Tube	Length of Stain	11	10	5 ppm	10 ppm	<5 ppm	<5 ppm
HCHO	Alumina Tube	Colorimetry	11	4	0.3 ppm	2 ppm	<0.3 ppm	<0.3 ppm
Amines	Silica Gel Tube	Gas Chromatography	9	9	0.4 ppm	10 ppm*	1.3 ppm†	<0.4 ppm
C_6H_6	Organic Vapor Badge¶	Gas Chromatography	14	10	1 ppb	10 ppm	<1 ppb	<0.02 ppm
Toluene	"	"	14	10	1 ppb	100 ppm	<1 ppb	<0.02 ppm
Phenol	"	"	14	10	2 ppb	5 ppm	<2 ppb	<2 ppb
C_6H_6	Organic Vapor Badge**	Gas Chromatography	10	25	1 ppb	10 ppm	<1 ppb	<0.02 ppm
Toluene	"	"	10	25	1 ppb	100 ppm	<1 ppb	<0.02 ppm
Phenol	"	"	10	25	8 ppb	5 ppm	<8 ppb	<8 ppb
C_6H_6	Charcoal Tube	Gas Chromatography	0	16	1 ppb	10 ppm		<8 ppb
Toluene	"	"	0	16	1 ppb	100 ppm		<6 ppb
Phenol	"	"	0	16	3 ppb	5 ppm		<3 ppb
Xylene	"	"	0	16	1 ppb	100 ppm		<7 ppb
COS	Evacuated Gas Bottle	Gas Chromatography/ Mass Spectrometry	0	1	50 ppm			<50 ppm

* TLV for methyl amine
† Methyl amine detected on only one sample
¶ Personal sample
** Area sample

SUMMARY

Effluents from Rio Blanco Oil Shale Company's Retort 0 were anlyzed for a number of constituents of enviornmental interest. The behaviors of some of these constituents in Retort 0 were somewhat different than in previously measured field in situ retorts. Retort 0 effluents resembled those of laboratory retorts more than other field retorts have.

Measurements of sulfur species in the raw offgas indicated that from 1% to almost 5% of the total sulfur in gas was present as non H_2S compounds. Total sulfur in the raw untreated offgas was considerably higher than in previous in situ retorts. Mercury showed a variable behavior, with the vast majority of the mercury being emitted towards the end of the run. Radon concentrations in the offgas were found to be low. Concentrations of NO in the flared offgas averaged 112 ppm. Analysis of particulates emitted from the stack showed many of the particulates to be carbonaceous in nature. These carbonaceous particles contained a variety of polycyclic organic compounds. The spectrum of compounds was similar to that found on particulates from other retort processes.

Sour water samples from Retort 0 were found to be considerably more dilute than product waters from other retorting processes. These low concentrations of contaminants were probably due to the diluting effects of a large volume of groundwater. The major anions were sulfate and carbonate/bicarbonate and the major cations were sodium, magnesium, calcium and ammonium. Toxic trace metals were generally present in relatively low concentrations. In spite of groundwater dilution, a few sourwater parameters were observed to increase systematically with time; these included pH (7.9-9.0), alkalinity, ammonia, organic carbon, conductivity, arsenic, potassium, molybdenum and antimony.

Analysis of the product oil showed some significant differences from previously analyzed shale oils. Sulfur, nickel and molybdenum were significantly higher, whereas arsenic was lower. Other constituents, including nitrogen, were about average. Analysis of the headspace vapors showed that most of the compounds likely to volatilize are aliphatic in nature.

Analysis of a raw shale core in the same stratigraphic horizon as Retort 0 showed a number of well defined chemical and mineralogical zones in the shale. More detailed characterization of the zones is continuing. Analysis of background mercury concentrations in soils surrounding the retort area showed relatively low ambient concentrations of soil mercury. The soils also showed considerable capacity for the uptake of mercury. Thus, there is some potential for mercury contamination of the soils if significant amounts are released during retorting operations.

INTRODUCTION

A large scale oil shale industry will involve many people, and may last for hundreds of years. The potential scale of this industry requires careful investigation of possible adverse effects on human health and the environment. Determining recovery process and process controls that provide efficient recovery without adverse health and environmental effects will result from health studies conducted in concert with engineering development.

Health studies performed in conjunction with the burn of Retort 0 by the Rio Blanco Oil Shale Company (RBOSC) have included air sampling in the mine, as well as cellular screening tests on oil shale related materials.

INDUSTRIAL HYGIENE STUDIES

Air samples were collected at RBOSC during the preparation and burn of Retort 0. These samples were collected to: a) characterize potential inhalation hazards, b) provide data for design of toxicology studies using representative materials, and c) identify whether unique exposure conditions exist. All samples were collected on the "G" level of the mine, 835 ft below the ground surface. Area samples were collected at various locations on "G" level. A small number of personal samples were collected using air samplers on oil shale workers and sampling personnel. Appropriate samples were analyzed for the gases and vapors listed in Table 13. Dust samples were collected to determine total dust concentrations, particle size and respirable dust concentrations. Dust and vapor samples were also analyzed for eight specific polynuclear aromatic hydrocarbons (PAHs).

The results of gas and vapor analysis are listed in Table 13. In general, the results of the pre-burn sampling indicated low concentrations of most parameters measured -- in most cases below the lowest detectable level of the analytical method. One sample for hydrogen sulfide (H_2S) was at the numerical level of the Threshold Limit Valve or TLV (ACGIH, 1980), but the sample duration was only for several minutes whereas the TLV is for an eight hour time weighted average. Post-ignition samples also indicated low concentrations of all gases and vapors sampled. Levels of benzene and toluene were slightly higher than measured during the pre-burn sampling period, but were still well below the TLVs of these compounds. Values for H_2S were lower during post-ignition sampling. This decrease in H_2S is attributed to a decrease in water flow into the mine.

Results of dust sampling are given in Table 14. The pre-ignition samples indicated good agreement between the total dust filter samples and the cascade impactors. Free silica analysis of 20 dust samples by two laboratories indicated 2.7%±1.0% quartz. The measured dust concentrations are all well below the TLV values for dust containing 3% quartz. Sampling limitations imposed by classification of the mine as "gassy" may have caused the difference between the impactor results and the total dust filters during the second sampling period. Cascade impactor samples were collected by placing the pumps on the air intake side of the mine with sample lines extending into the return air side. The length of the lines prohibited sampling close to working areas. The difference in concentration between the total dust samples and the impactors during post-ignition sampling indicated greater separation than during pre-ignition sampling. The best measure of dust during the post ignition periods are the results from total dust sampling.

The concentrations of PAHs associated with particulates are listed in Table 15. There is no consistent correlation between airborne dust concentrations and the PAH concentration.

TOXICOLOGY

Bioluminescent Toxicity Screening

This bioassay analysis used a luminescent strain of marine bacterium, Photobacterium fisheri, whose light output decreases when exposed to toxicants (Microtox Model 2055 Acute Toxicity Analyzer). Light production in these microorganisms represents the total rate at which a complex set of energy producing reactions is operating. Inhibition of any one of many enzymes involved in these processes may cause a change in light output. Thus, this method may accommodate many different types of toxicants that have very different modes of action. The instrument is a simple photometer maintained

TABLE 14

AIRBORNE MINE-DUST SAMPLING AT RIO BLANCO OIL SHALE COMPANY

COLLECTION DEVICE	NUMBER OF SAMPLES	CONCENTRATION (mg/m^3)	TLV† µg/m^3	AVG. MASS MEDIAN AERODYNAMIC DIAMETER (µm)	GEOMETRIC STANDARD DEVIATION (δg)
Pre-ignition					
Cascade Impactor	20	1.1 ±1.00	5	2.8 ±0.9	3.5 ±1.1
Total Dust Sampler	16	1.0 ±0.80	5		
Respirable Dust Sampler*	21	0.46 ±0.33	2		
Post-ignition					
Cascade Impactor	4	0.15 ±0.08	5	0.7 ±0.4	3.5 ±1.8
Total Dust Sampler	29	1.20 ±0.90	5		
Respirable Dust Sampler*	12	0.18 ±0.06	2		

*Bureau of Mines respirable dust sampler (filter with cyclone precleaner) operated at 1.7 lpm.

† TLV-threshold limit value assuming 3% quarts

TABLE 15

AIRBORNE CONCNETRATIONS OF POLYNUCLEAR AROMATIC HYDROCARBONS AND DUST

SAMPLE	PAH CONCENTRATIONS*	DUST CONCENTRATION
C.I. -892 (Aug. 1,1980)	1.28 μg PAH/M^3	2.19 mg/M^3
C.I. -1001 (July 30, 1980)	0.698 g PAH/M^3	2.400 mg/M^3
C.I. 1001 (Oct. 29, 1980)	0.095 g PAH/M^3	0.084 mg/M^3
C.I. -935 (Oct. 29, 1980)	0.122 g PAH/M^3	0.076 mg/M^3
C.I. -930 (Nov. 3, 1980)	0.216 g PAH/M^3	0.171 mg/M^3
T.D. -277 (Oct. 29, 1980)	0.038 g PAH/M^3	0.35 mg/M^3
T.D. -35 (Oct. 31, 1980)	0.038 g PAH/M^3	2.60 mg/M^3
P.S. -30 (Nov. 3, 1980)	0.258 g PAH/M^3	0.39 mg/M^3
P.S. -19 (Nov. 3, 1980)	0.00 g PAH/M^3	0.39 mg/M^3
T.D. -278 (Nov. 4, 1980)	0.005 g PAH/M^3	1.32 mg/M^3
T.D. -35 (Nov. 4, 1980)	2.64 g PAH/M^3	1.46 mg/M^3

C.I. Cascade Impactor
T.D. Total Dust Filter
R.D. Personal Sampler
R.D. Respirable Dust Filter

* Sum of acenaphthene, anthracene, phenanthrene, benzocalpyrene, chrysene, fluoranthene, fluorene, pyrene

At 15^{o}C. The ratio of light lost to light remaining (Γ) is recorded for each of a series of concentrations for a particular toxicant. A regression line of log (Γ) versus log (toxicant concentration) is used to interpolate the concentrations that inhibited luminescence by 50%. This corresponds to $\Gamma = 1$ and is noted as EC_{50}. The EC_{50} values obtained by the Microtox method compare favorably to the LC_{50} values obtained from 24- to 96-hour fish lethality tests.

Whenever possible, triplicate analyses were performed. Values of 100% or higher have little meaning and may be interpreted as representing a non-toxic sample.Figure 3 illustrates that there is considerable variation in the toxicity of the retort waters relative to: a) time into the burn and b) location of the sampling point. The results of the toxicity screening are detailed in Table 16. The scrubber water samples are more toxic than the other samples. This is probably due to the considerably higher pH of these samples. The bacteria used in this bioassay display a toxic response above pH 7. Also, the total extractable organic carbon content of these waters is very low. Based upon this analysis, the East Holding Pond samples do not appear to be toxic. These samples represent an integrated sample set as all process waters are finally discharged into this holding pond. At this point such factors as dilution, microbial degradation and adsorption onto suspended matter may reduce the total toxicity of this "composite" water sample.

Mutagenicity Screening

Water samples, obtained at the end of the retort run from a) the underground water separator, b) the knockout drum, c) the neutralization tank and d) the holding pond were screened with the Salmonella mutagenesis bioassay (Ames Assay). The water samples were separated into organic acids, neutrals and bases by liquid-liquid extraction. The organic fractions were then concentrated and dissolved into dimethysulfoxide (DMSO). Two strains of Salmonella were used, TA 98, that responds to frame shift mutagens and TA 100, that responds to mutagens that induce point mutations. The organic bases and neutrals from the underground separator and the knockout drum were mutagenic (Table 17). However, as shown in Table 17, the concentrations of organics

THE TOXICITY OF THE PROCESS WATERS CHANGES CONSIDERABLY RELATIVE TO BOTH BURN TIME AND LOCATION

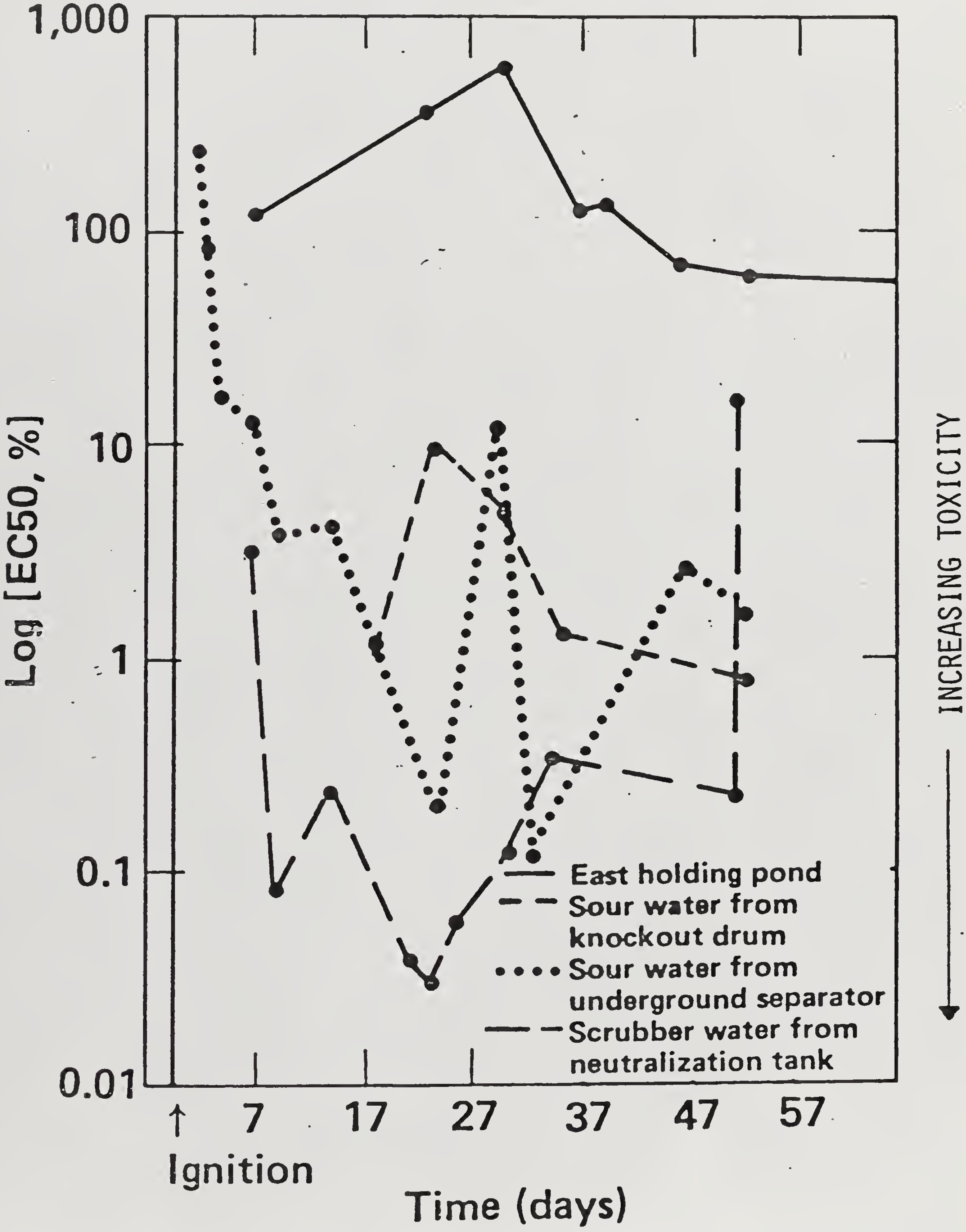

Figure 3. Toxicity of process waters as a function of time and location.

Table 16. Toxicity Data for the Rio Blanco - Burn 0 Process Waters.

Sample Code	Sample Description	Date	% Sample Concentration Yielding ECD 50%
RB001 D01	Mine dewatering water	10/12	All samples were non-toxic
D02		10/13	
D03		10/15	
D05		10/17	
D10		10/20	
D11		10/21	
D15		10/22	
D20		11/03	
D23		11/05	
D29		11/08	
D31		11/10	
D40		11/19	
D42		11/21	
D43		11/22	
D45		11/28	
D52		12/04	
RB001 K16	Sour water from the knockout drum	10/23	46.3 ± 1.93
K19		10/31	1.03 ± 0.74
K24		11/05	8.42 ± 0.23
K26		11/06	9.75 ± 0.94
K36		11/10	5.45 ± 0.19
K37		11/17	1.25 ± 0.38
K49		12/04	0.80 ± 0.060
RB001 R04	Sour water from the underground separator	10/15	235 ± 167
R06		10/16	83.3 ± 19.8
R07		10/17	17.2 ± 2.38
R09		10/20	12.7 ± 0.80
R13		10/22	3.68 ± 0.76
R18		10/27	39.6 ± 7.37
R26		11/06	0.19 ± 0.040
R32		11/10	6.51 ± 3.02
R35		11/12	12.5 ± 0.85
R38		11/14	0.12 ± 0.0071
R46		11/28	2.32 ± 0.24
R51		12/04	1.58 ± 0.17
RB001 S08	Water from the soda ash wet scrubber	10/20	3.31 ± 0.040
S14		10/22	0.080 ± 0.00
S17		10/27	0.25 ± 0.020
S21		11/03	0.040 ± 0.00
S25		11/05	0.030 ± 0.00
S28		11/07	0.050 ± 0.00
S34		11/12	0.12 ± 0.010
S36		11/16	3.49 ± 0.37
S47		12/03	0.22 ± 0.020
S48		12/04	16.0 ± 2.62

Table 16 continued. Toxocity Data for the Rio Blanco - Burn 0 Process Waters.

Sample Code	Sample Description	Date	% Sample Concentration Yielding ECD 50%
RB001 P12	East holding pond	10/20	123 ± 37.4
P22		11/05	160 ± 72.3
P33		11/12	non-toxic
P39		11/19	124 ± 6.84
P41		11/21	132 ± 27.5
P44		11/28	70.4 ± 9.16
P50		12/04	72.7 ± 14.9
P53		01/20	43.1 ± 0.26

TABLE 17

MUTAGENS IN OIL SHALE PROCESS* WATER ARE DETECTED ONLY AT CONCENTRATED SOURCE POINTS, BUT NOT WHEN DILUTED BEFORE DISPOSAL.

OURCE OF WATER	ORGANIC FRACTION	CONCENTRATION MG/ℓ	REVERTANTS/10^8 SALMONELLA TA 98 PER MG	TA 98 PER ℓ	TA 100 PER MG	TA 100 PER ℓ
nderground ater Separator	Acids	189	ND †	---	ND	---
	Bases	47	620	29,100	1,400	65,800
	Neutrals	184	170	31,300	200	36,800
nockout Drum Water Mist)	Acids	96	ND	---	ND	---
	Bases	82	160	13,100	1,000	82,000
	Neutrals	250	100	25,000	100	25,000
eutralization ank	Acids	ND				
	Bases	ND				
	Neutrals	ND				
olding Pond	Acids	0.24				
	Bases	0.9				
	Neutrals	1.53				

Underground Rio Blanco retort 0 water samples obtained at end of run.
None detectable.

in the holding pond were also very low and there was not enough material to detect mutagenicity.

It appears from these results that the mutagens found in the process waters (underground separator and knockout drum) are not passed onto the holding pond at concentrations where a mutagenic effect can be detected. This is an initial indication of effective treatment and/or dilution before disposal.

Sister Chromatid Exchange Assays

Screening tests for sister chromatid exchange (SCE) induction were done with one crude oil sample and three RBOSC water samples. (Table 18). Concentrations that did not appreciably change the cell cycle traverse rate of Chinese hamster cells (CHO) were used. The tested materials and bromodeoxyuridine (BUdR) were added to cell cultures for two cell cycles (29 h); during the final two hours the cells were blocked in metaphase with Colcemid (0.06 μg/ml). The resulting second division chromosomes were stained differentially and SCE rates were determined by counting the exchanges in 25 cells for each test. The RIO 0-A-water sample tested did not raise SCE levels above concurrent controls containing BUdR alone. The DMSO extract of RIO 0-A-oil raised SCE levels approximately two times (14.68) the control frequency (8.04) at a concentration of 0.50%. At 1% concentration in the medium, cell cycle traverse was inhibited and the cultures did not complete two S phases in the presence of BUdR to allow chromosome differentiation. The Ames test data (elsewhere in this section) showed mutagenicity with this sample. The sour water from tank 102 to the underground separator (RIO 0-C1) slightly raised SCE levels (10.44) at a concentration of 5%; however, SCE results are not considered significant unless they are at least two times the control frequency (8.64). Likewise, the sour water from the pond (RIO 0-C2) only slightly elevated SCE levels (11.20) at a concentration of 10% in the medium with a background of 8.32. Thus, all three waters tested were fairly biologically innocuous in terms of SCE induction, and the oil was not very active at levels noncytotoxic to the cells. These *in vitro* SCE assays were measurements of direct acting components and will be repeated with metabolic activation using S-9 microsomal fractions that are currently being used in the Ames testing laboratory.

Ames/Salmonella Mutagenicity Assay of Product Oil and Waters

Using the Salmonella/Mammalian microsome mutagenicity assay developed by Ames et al. (Mutat. Res. 31 (1975) 347-364), the mutagenic activity of three product waters and a crude oil resulting from RBOSC's Retort 0 burn were tested. The results for three different water samples presented in Table 19 indicate negative mutagenic activity in test strains TA 98 and TA 100 with or without rat hepatic S9 activation for sample volumes tested up to 100 µL per plate. However, a cytotoxic response (reduction in the intensity of the background lawn of bacteria) was observed for waters RIO0-C1 and RIO0-C2 (sour waters from tank 102 to underground separator and from pond #4, respectively) at doses of greater than 10 µL, in TA 98 and TA 100. No cytotoxic effect was observed for the product water (RIO0-A) over the dose range tested in either TA 98 or TA 100.

The results from testing a DMSO extract of the crude oil (RIO0-A-oil) obtained from the early part of Retort 0 burn indicated a linear dose independent increase in histidive$^+$ revertants induced in TA 98 with metabolic activation (see Table 19). From 1 to 10 µL sample tested (linear portion of dose-response curve) there were ∿4 revertants induced per µL sample, and the maximum number of histidive$^+$ revertants obtained per plate over the dose range tested (0.1 - 100 µL) was ∿2.5x our historical background for TA 98 (41±9) indicating significant mutagenic activity in this sample. No mutagenic activity was observed in TA 98 without S9 activation or in TA 100 with or without metabolic activation. There was not apparent cytotoxicity for this oil sample in either TA 98 or TA 100; however, a precipitate occurring in plates with sample loads of greater than 10 µL was observed.

Two other RBOSC Retort 0 oils (an early burn oil (30 OCT 80) and a late burn oil (26 FEB 81)) are currently being tested to compare potential mutagenic activity as a function of burn time.

TABLE 18

% (V/V) Concentration in Medium	% Mitotic Index	SCE/cell ± Standard Error of Mean	Range
RIO 0-A-oil	Collected from early part of Retort 0, as an oil-water emulsion, November 1980. Separated in laboratory by centrifugation and extracted with DMSO.		
0.00	4.2	8.04 ± 0.54	4-14
0.01	6.6	9.08 ± 0.52	4-13
0.025	7.4	8.88 ± 0.74	4-18
0.05	5.6	8.80 ± 0.71	2-17
0.10	6.6	9.24 ± 0.65	3-16
0.25	4.2	13.04 ± 0.74	5-20
0.50	2.8	14.68 ± 0.90	6-24
1.00	0.2	no differentiation	-
RIO 0-A-water	Product water emulsion from above collection and separation		
0.00	6.8	8.08 ± 0.57	2-13
0.25	6.6	8.72 ± 0.69	2-15
0.50	6.2	9.36 ± 0.61	5-17
1.25	5.0	9.28 ± 0.68	2-16
5.00	2.0	9.80 ± 0.73	3-19
10.00	4.2	9.32 ± 0.77	4-20
RIO 0-C1	Sour water from tank 102 to the underground separator, February 26, 1981		
0.00	6.4	8.64 ± 0.73	2-14
0.50	5.8	9.20 ± 0.77	3-18
2.50	5.6	10.36 ± 0.50	4-16
5.00	4.4	10.44 ± 0.76	3-20
RIO 0-C2	Sour water from pond #4, February 26, 1981		
0.00	8.2	8.32 ± 0.62	3-14
2.50	3.8	9.12 ± 0.55	4-13
5.00	5.0	10.24 ± 0.59	4-16
10.00	4.4	11.20 ± 0.59	4-17

TABLE 19

HISTIDINE REVERTANTS INDUCED IN SALMONELLA TA 98 AND TA 100 BY RIO BLANCO RETORT 0 OIL AND PRODUCT WATERS[X]

		Test Strain			
	Vol.	TA98[†] (revertants/plate)		TA100[¶] (revertants/plate)	
SAMPLE	Tested (µL)	-S9	+S9[XX]	-S9	+S9)
RIO0-A-Water[††]	0	27±4	44± 6	192±29	154±29
	1	-	42± 4	-	153± 9
	10	27±5	41±10	172±29	150±21
	30	-	41± 7	-	152±13
	50	-	45± 2	-	172±15
	100	24±1	55± 4	188±13	170±19
RIO0-C1-Water[¶¶]	0	27±4	44± 6	192±29	154±29
	1	-	39± 7	-	174±18
	10	30±4	45±10	192± 8	160±38
	30	-	50±11	-	159±17
	50	-	50± 7	-	168±12
	100	28±6	48±10	184±14	164±10
RIO0-C2-Water[XXX]	0	27±4	44± 6	192±29	154±29
	1	-	43± 6	-	157±22
	10	27±4	47±10	204±10	171±14
	30	-	30± 8	-	167±15
	50	-	45± 5	-	185±13
	100	28±6	56± 4	182±16	168±19
RIO0-A-Oil[†††]	0	20±4	37± 5	166±20	140±12
	0.1	19±3	39± 6	185±26	137± 7
	1.0	-	40± 4	161±13	146±26
	3.3	22	51± 5	133±15	147±12
	6.7	20	71± 5	182±17	162±18
	10	24±4	91±10	172±21	175±21
	33	31±6	102±12	167± 9	190±23
	100	36±7	102± 4	156± 3	177±20

[X] The data represent the results of 2-6 separate experiments in which each data point equals the average number of his^+ revertant colonies formed (three plates per dose per experiment).

[†] Historical background TA98=41±9, experimental diagnostic mutagens: 2-nitrofluorene (1.5 µg/plate)=327±10; benzo (a)pyrene (1.8 µg/plate)=395±54.

[¶] Historical background TA100=136±28, experimental diagnostic mutagens: MNNG (1 µg/plate)=285±50; benzo (a)pyrene (1.8 µg/plate)=348.38.

[XX] For metabolic activation, hepatic S-9 mix obtain from Aroclor 1254 induced Sprague/Dawley rats at 2350 µg protein/plate was used.

[††] Product water separated from oil-water emulsion from early part of retort 0 burn (collected NOV 80).

[¶¶] Sour water from tank 102 to underground separater (26 FEB 81).

[XXX] Sour water from pond #4 (sampled 26 FEB 81).

[†††] DMSO extract of crude oil from oil-water emulsion obtained from early part of retort 0 burn (collected NOV 80). 10.3% of the oil was extracted into the DMSO.

CONCLUSIONS

The industrial hygiene studies carried out to date indicate no significant health hazards in terms of known toxicology. Extrapolation to commerical scale operations can only be carried out based on current toxicology information. With these considerations it appears that normal engineering controls will be adequate for full scale operations. The most significant unknown is the question of exposure to the complex mixture of materials (particles, retort gases and liquids) normally encountered in the work environment. Comprehensive toxicology studies will be required to answer this question.

Initial toxicology studies have focused on the water samples from the Retort 0 burn. The bioluminescent tests indicate some toxicity associated with the sour waters from the underground separator and the knockout drum. This toxicity is not apparent in the waters from the holding pond. This screening test has been shown to correlate with fish lethality tests. Correlation with human health effects and other biological systems has not been established. These data should not be generalized to other systems or species.

The sample preparation procedure for the Ames assay was different at the two laboratories performing these tests. The Ames mutagenicity assay at Los Alamos National Laboratory used waters directly without concentration, and a DMSO extract of the retort oil sample. Under these conditions the screening tests indicated negative mutagenic activity for all water samples. However, a cytotoxic response was noted with sour water from the scrubber and water from the holding pond. The water samples used for Ames assay by Lawrence Livermore Laboratory were separated by liquid-liquid extraction and concentrated before extraction by DMSO. These concentrated water samples indicated positive mutagenic activity in waters from the underground separator and from the knock out drum. The water from the holding pond and neutralization tank indicated negative mutagenicity.

The sister chromatid exchange (SCE) assays conducted at Los Alamos (with the same water samples used for the Ames assay) did not show increases in SCEs significantly over control levels.

Both the mutagenic activity measured by the Ames assay (Los Alamos) and the SCEs induced by the DMSO extract of crude oil from retort zero gave positive results.

WATER QUALITY

The overall objective of this task is to predict the long-term behavior and biological impacts of inorganic and organic constituents in oil shale wastes on surface and groundwaters. The research consists of the following principal subtasks:

- The chemical/hydrologic characteristics of dewatering operations, surface and ground waters
- Characterization of raw/retorted shale and leachates
- Microbiological effects on inorganic/organic constituents
- Organic/inorganic interactions
- Chemical/hydrologic transport models

Initial efforts were focused as described below:

Geochemistry/Hydrology of Waste Disposal Operations

Objectives

The objectives of this joint laboratory and field program are to: 1) investigate the existing chemical and hydrologic controls on the composition of surface and alluvial groundwaters, 2) characterize solid wastes and liquid effluents produced by oil shale processing and mining operations and 3) define the influence of these materials on water quality with development.

Approach

Studies initiated over the past year include: 1) field sampling of surface waters and alluvial groundwaters to identify the geochemical characteristics of the various hydrologic units on and in proximity to the tract, 2) field and laboratory studies on the effects of the mine dewatering cycle in water quality and 3) laboratory investigations of the leachability of inorganic and organic components from Retort 0 raw shale.

SUMMARY OF RESULTS

Surface and alluvial groundwaters are being collected from Box Elder, Corral and Upper Yellow Creeks to define mechanisms regulating the chemical composition of these waters on a seasonal basis. Analyses of water samples included pH, Eh and electrical conductivity immediately following collection; and subsequently, major and minor cations/trace metals (acidified and non-acidified samples), major and minor anions, reduced sulfur species, reduced nitrogen species and total dissolved carbon.

The hydrology and chemistry of surface and groundwaters was found to be complex. Following the months of maximum snowmelt, surface waters at or near the southwest boundary of the Tract originate primarily as seepage from the Uinta Formation. These waters remain relatively constant in composition (conductivity ∿ 1100-1300 μgho/cm) but are occasionally intermittent in flow across most of the Tract. At the northeast corner of the Tract significant recharge of higher conductivity water (1700 μgho/cm) occurs into both Box Elder and Corral Creeks from diffuse bank seeps near their confluence. Generally, northeast of the Tract, stream flow is seasonally intermittent and concentrations of many dissolved species (Na^+, Mg^{+2}, Sr^{+2}, B, F^-, Cl^-, SO_4^{-2} and HCO_3^-) in Corral and Yellow Creeks increase in a downstream direction.

With some exceptions, the concentrations of most macroions in alluvial groundwater increase downstream in Box Elder, Corral and Yellow Creeks. Minor species which follow a similar trend include boron, fluorine, potassium, manganese and iron. Wells in Yellow Creek are significantly more reduced than upstream waters and, in some cases, contain detectable levels of sulfide and ammonia and elevated concentrations of manganese and iron. The hydrology of these surface and alluvial groundwaters is complicated and influenced by seasonal surface water hydrologic cycles, the effects of continued reinjection of mine waters and intrusion of deep groundwaters.

CHEMICAL/HYDROLOGIC CHARACTERISTICS OF DEWATERING OPERATIONS

The chemical characteristics of deep groundwaters and reinjection waters are being studied by routine collection of samples from dewatering and reinjection wells. Deep groundwaters (dewatering wells) contain comparable levels of soluble salts to surface waters; however, strontium, and more dramatically the Sr^{+2}/Ca^{+2} ratios, are elevated. Some dewatering wells are reduced with high levels of sulfide (25-35 ppm HS^-), detectable levels of thiosulfate (2-5 ppm) and are charged with dissolved CO_2. Reinjection waters are variable in composition reflecting mixtures of water from several sources. Generally, these waters are higher in pH and more oxidized than deep groundwaters but contain comparable levels of most macro and minor elements.

Dewatering wells were examined for anaerobic heterotrophic, sulfate reducing and methanogenic bacteria to account for processes responsible for the genesis of these chemically reduced groundwaters. Well waters were collected directly into closed tubes that contained a selective medium and gas phase for each bacterial group. After collection the tubes were incubated at ambient temperature for two weeks, examined visually for growth and then stored at 0^o - 4^oC for further study. All three bacterial types were found in the dewatering wells. The activity of these bacterial groups may account for at least a portion of the elevated levels of sulfide, methane and $CO_2(g)$ measured in some bedrock groundwaters.

The infrequent discharge of reduced groundwaters into oxygenated surface water produces visual and chemical changes in water and sediment upon mixing. Immediately after mine water discharge stream sediments became coated with a thick black precipitate and shortly thereafter the waters became milky and nearly opaque. The prominent chemical changes identified include CO_2 degassing with an associated pH increase, H_2S degassing and oxidation of HS^- to $S_2O_3^{-2}$. Additional chemical effects resulted primarily from dilution of higher conductivity ($\sim$1000 μmho/cm) creek water.

Laboratory studies of the controlled oxidation of deep, reduced groundwaters from dewatering well D-8 were performed to evaluate chemical processes occurring upon surface discharge of these waters. Sulfide present is oxidized initially and rapidly to colloidal S^o ($T_{\frac{1}{2}}$<30 hr) and SO_4^{-2}. Carbon dioxide degassing occurs along with the oxidation of reduced sulfur species and increases pH causing an apparent supersaturation of the water with respect to and resulting in precipitation of $CaCO_3$. The black sediment coating observed during field discharge of D-8 water into surface waters results from the precipitation of metal sulfides, principally FeS, encouraged as CO_2 degassing upon discharge increases pH and, temporarily, the activity of S^{-2}.

Leaching of Tract C-a Raw Shale

Laboratory batch and column leaching studies were performed with Tract C-a raw shale upon storage or disposal. Raw shale, removed from Retort 0 during rubblelization, was sampled with respect to pile depth and retort blast sequence during construction of the field lysimeters.

Batch extractions were used to identify the total quantity of solubles from select depths in the lysimeter pile as influenced by blast sequence and particle size. These materials were found to be relatively homogeneous throughout, releasing from 7.32 - 10.7 µg/g of soluble inorganics. Prominent species in these extractions included Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, Sr^{+2}, SO_4^{-2}, NO_3^{-}, HCO_3^{-}, and Cl^{-}. Field leaching processes were simulated in the laboratory using column studies. Percolation of distilled water through these columns produced initially saline leachates (conductivity 16.5 - 25.7 mmho/cm) with elevated levels of macroins (Na^{+}, $K^{+}Mg^{+2}$, SO_4^{-2}, NO_3^{-}, $S_2O_3^{-2}$) and some minor elements (Al, Cr, Ni, Mn, Pb and Mo) relative to natural waters of the area. This pulse of solubles diminished rapidly with leaching, with concentrations of most species equilibrating after 1.50 v/vo at levels somewhat in excess of deep tract groundwaters but comparable to some alluvial groundwaters. High levels of NO_3^{-} and some soluble trace metals in the initial leachates relative to local surface and groundwaters may reflect the effects of blasting explosives used in rubblelization.

These studies have shown that complex chemical interrelationships occur between surface, alluvial and deep groundwaters and the mine dewatering cycle. Sampling of these hydrologic units has shown that in addition to detailed chemical analyses, carefulfield measurements and sample preservation techniques coupled with analyses of desolving gases are necessary to correctly characterize complex water types from the Piceance Creek Basin. Laboratory studies performed suggest that some raw shales may release elevated levels of salts and some minor elements in the initial leachates. Additional studies are planned to evaluate the magnitude to this release relative to soils and subsoils (and at a later date, retorted shale) of the area. Hydrogeochemical field studies of surface and groundwaters on and in proximity to the Tract, as well as laboratory studies of the leachability of inorganic and organic species from oil shale waste materials (Tract C-a), will continue.

Characterization of Raw Shale Leachate for RBOSC Retort 0

Objectives

The purpose of this research is to study, quantitatively, the trace element release of C-a raw shale when leached, and to relate these data to the mineral composition and stratigraphy of the selected site.

Approach

To accomplish these objectives a raw shale core from the vicinity of the RBOSC Retorts 0, 1 and 2 has been obtained. Using this material two surveys were made; one a leaching study of samples taken along the length of the core at 20 foot intervals, and the other a leaching study of core sections in the same stratigraphic region as Retort 0 done at two foot intervals. This approach is an efficient and rapid means of identifying zones that could yield leachates with trace element concentrations of enviornmental concern. Analysis of the chemical make-up and mineral composition can then be done on selected zones as indicated by the leaching results.

The leaching experiments were done in the batch using a 1:5:10 solid to liquid to container ratio. The solid was ground to -100 mesh and leached in milli-Q water for 48 hours. In the initial phase of this investigation, the leachates were analyzed for Al, Be, B, Cd, Ca, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, K, Si, Sr, Na, Ti and V using a D.C. argon plasma emission spectrophotometer.

SUMMARY OF RESULTS

For the survey along the entire core, pH values were in the 7.95 to 8.82 range and specific conductivities varied from 350 to 3200 µmho/cm, with no strong correlation to depth. To a first approximation, trends in alkaline earth and ion concentrations are followed by Mn and Pb.

For the leachates from the samples in the Retort 0 stratigraphic region, pH values were 7.95 to 8.60 and specific conductivities varied from 600 to 3200 µmho/cm. The trends relating Ca and Mg with Pb and Mn were similar to those along the length of the core.

Overall, the leachates from Retort 0 raw shales do not appear, at first glance, to reveal any data that are unexpected or of serious environmental concern. Observed values of pH are lower than might have been predicted; however, this apparent anomaly has not been examined in any detail.

ENVIRONMENTAL CONTROL TECHNOLOGY

The objective of this task is to develop information at the bench, pilot and demonstration scales useful to the selection of water treatment processes and overall development of mitigation strategies. The research is directed toward the following principal subtasks:

- Characterization of waste waters
- Bench scale evaluation of treatment methods including spent shale adsorption, biological reaction and stream stripping.

Initial efforts were focused as described below:

The Effect of Steam Stripping Treatment on Sour Water

Objectives

1) To determine the identities of organic compounds in wastewaters from modified in-situ retorting of oil shale at the RBOSC Tract C-a Retort 0.
2) To learn which compounds are removed by laboratory simulations of countercurrent stream stripping control technology methods.
3) To determine improved, effective, interference-free analytical methodology for alkyl pyridines, alkyl quinolines, alkyl phenols and other difficult-to-analyze compound classes.

Approach

Organic compounds were separated and measured by high resolution fused silica capillary column chromatography coupled with mass spectrometry, following prior sub-class fractionation by liquid chromatography on porous polymers and ion exchange resins. The method of Leenher and Huffman was used to achieve separations of the organic compounds into following fractions: hydrophobic acids, hydrophobic bases, hydrophobic neutrals, hydrophilic acids, hydrophilic bases and hydrophilic neutrals. Compound identifications were confirmed in most cases by measuring both chromatographic retention times and mass spectra. After identifications were made by coupled gas chromatography and mass spectrometry, it was possible to develop simpler, less expensive analytical techniques based on gas chromatography with flame ionization detection and with reversed phase liquid chromatography coupled with selective wavelength ultraviolet absorption detectors.

A simple laboratory experiment was designed to mimic a few stages of a steam stripper anticipated to be part of water treatment control technology. The trace organics present in sour water from Retort 0 were compared before and after steam stripping. Selected trace element concentrations in the sour water were measured by graphite furnace atomic absorption and inductively coupled plasma emission spectrometry.

Dissolved organic carbon in the treated and untreated wastewaters was measured with a Backman Total Organic Carbon Analyzer, Model 915B.

SUMMARY OF RESULTS

In the organic characterization of the sour water (RB-O-SW-064), a large number of hydrocarbons, carboxylic acids, phenols, cresols, naphthalenes, alkyl-pyridines, anilines, quinolines and elemental sulfur (S_8) were identified by gas chromatography and mass spectrometry. The laboratory steam stripping treatment removed about 7% of the dissolved organic carbon content of the sour water. The treatment greatly reduced the concentration of hydrocarbons and carboxylic acids more volatile than dodecanoic acid. Most of the quinoline, isoquinoline, 3-methylquinoline and 2,6-dimethylquinoline were removed by steam stripping. The elemental sulfur was also substantially removed from the sour water. The compounds that remained in the sour water after steam stripping were anilines, pyridines, phenols, naphthalenes and long chain carboxylic acids.

This research has led to the development of markedly improved analytical methodology for classes of compounds that were previously very difficult to separate, identify and measure. The most significant improvements arise from advances in separation and selective detection science. Fused silica capillary gas chromatography columns are greatly superior to the older glass columns for separating phenolic compounds, alkyl aniline, alkyl pyridine, and alkyl quinoline (and isoquinoline) fractions. Peak shapes are better and irreversible adsorption losses on the walls of the fused silica columns are less than on glass. Various selective gas chromatography detectors (mass chromatograms, selective electon capture sensitization (SECS), nitrogen selective detection, etc.), and liquid chromatography detectors (selective wavelength ultraviolet absorbtion) have been studied and used successfully for detecting certain classes of organic compounds. Particularly noteworthy is the development of a rapid method for separating and measuring quinoline, isoquinoline and alkyl quinolines by reversed phase high performance liquid chromatography on C_{18}- bonded silica coupled with selective detection at 313 nm by a variable wavelength ultraviolet absorption detector.

Trace metal analyses were conducted on the sour water before and after steam stripping and on the condensed steam to determine the effectiveness of steam stripping upon the removal of arsenic, selenium, cadmium and chronium. There was little change in the concentrations of these elements following steam stripping.