

HEAVY METALS POLLUTION POTENTIAL FROM OIL SHALE LEACHATES AS
DETERMINED BY EPA PROPOSED EXTRACTION PROCEDURES

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ABSTRACT

In 1976, Congress passed the "Solid Waste Disposal Bill." Part of the bill is the Resource Conservation and Recovery Act (R.C.R.A.). Under Section 3001 of this act, the Environmental Protection Agency (EPA) is required to define the criteria and methods for the identification and listing of hazardous wastes.

The "Test Extraction Procedure" (E.P.) is their proposed method for obtaining a leachate to be analyzed to determine a waste's pollution potential. The American Society for Testing and Materials (A.S.T.M.) undertook a program to develop two alternate methods "A" and "B".

This paper addresses the use of all three methods and their evaluation of oil shale as a hazardous waste, in so far as heavy metals are concerned.

Five shale samples were used: three spent and two raw shales. None of the leachates from these samples exceeded the EPA effluent guidelines when analyzed for heavy metals. Corresponding data on other solid wastes will also be presented to place the oil shale material in proper perspective.

Section 3001 of the "Resource Conservation and Recovery Act" (R.C.R.A.) requires the Environmental Protection Agency (EPA) to define the criteria and methods for the identification and listing of all hazardous wastes generated in the United States. Their method of choice for this task is the "Extraction Procedure (E.P.)." Under R.C.R.A., all oil shale wastes must be evaluated by this method, to assess its hazard to the environment. This procedure consists of mixing sixteen parts by weight of acetic acid with one part of waste and stirring for twenty four hours and maintaining a pH of 5.0 ± 0.2 or until a maximum of four milliliters of acetic acid per gram of sample has been added. The sample is then filtered through a 0.45 micron filter and

diluted with distilled water to a volume equal to twenty times the original weight of the sample. This filtrate is then analyzed to determine its heavy metals content and it is also used for biological testing. This procedure was adopted from work done at the University of Wisconsin for EPA by Dr. Hamm.¹

After an evaluation of this method, a large contingent within the membership of the American Society for Testing and Materials (A.S.T.M.) felt that the method was not representative of "real world" conditions and also that the acetic acid would render the sample unacceptable for biological testing. The D19:12 sub-committee on solid waste undertook the development of alternative test methods to be used as standard methods for the leaching of solid wastes. The two methods they developed were designated method "A" and method "B". Method "A" consists of mixing the waste material with distilled water at a ratio of 4 to 1 on a weight to weight basis. The sample is then placed on a shaker for 48 hours before filtering it through a 0.45 micron filter. Method "B" utilizes an acetate buffer solution at a pH of 4.5, instead of distilled water; otherwise, methods "A" and "B" are the same.

The Department of Energy decided to determine how the R.C.R.A. would affect the fossil energy program. This was done using a collaborative testing program with A.S.T.M. The Department of Energy, with the help of the related industry, provided twenty-four fossil energy related wastes for this program. Five of these wastes were oil shale samples. The five shale samples selected for this study were:

(OS-1) Green River (Spent). This shale sample is from the Green River formation near Rifle, Colorado and was retorted in the LETC 150-ton retort.

- (OS-2) Antrim (Raw). This shale is from the Antrim formation in Michigan.
- (OS-3) Antrim (Spent). This shale was retorted in LETC 150-ton retort.
- (OS-4) Moroccan (Raw). This shale is from Morocco.
- (OS-5) Antrim (Spent). Same as OS-3 except for particle size.

Samples OS-1 through OS-4 were ground to pass a 2.36 mm mesh sieve. Sample No. 5 was collected as is and the particle size ranged from 0.63 centimeters to 15.24 centimeters. Table 1 shows the results of elemental analysis and X-ray diffraction analysis as well as well as oil yield for the raw shales. As would be expected, the shale samples with the higher mineral carbon content yielded higher calcium and magnesium concentrations; this appears to be the only relationship between the elemental analysis and the metals concentration in the leachates.

All five shale samples were leached in triplicate using each of the methods ("E.P.", "A" and "B"). The leachates were then analyzed for the following parameters: pH, calcium (Ca), magnesium (Mg), chromium (Cr), arsenic (As), barium (Ba), cadmium (Cd), lead (Pb), mercury (Hg), selenium (Se), and silver (Ag). These analyses were done using EPA's "Methods for Chemical Analysis for Water and Waste", March 1979.² Calcium and magnesium were determined using atomic absorption flame analysis, the other metals were determined by standard addition using the atomic absorption spectrometer equipped with a graphite furnace, except for mercury which was done by the cold vapor technique. The results of these analyses are presented in the next five tables. Calcium and magnesium were only determined for use as quality control parameters. It was felt that all the laboratories participating in the study would be able to perform these analyses with good inter-lab comparison.

The data in Tables 2 through 6 is from work that was done at the Laramie Energy Technology Center and upon examination of this data it becomes evident that none of the leach methods results in a leachate that exceeds the proposed EPA limits. The shale sample from the Green River Formation (OS-1),

was the only sample that resulted in leachates whose pH was basic for all three leach methods. Table 2 also shows that method "B" yields a leachate with concentrations of arsenic that are greater than those obtained for any of the other shale samples. Most of the leachates contained such low concentrations of metals that we were unable to effectively compare the three methods with each other, which was one of the goals for the project. As shown in Table 3, when the raw Antrim shale was leached, not only were we able to maintain the acid pH for methods "B" and "E.P." as the methods call for, but method "A", which utilizes distilled water also resulted in an acid pH. The leachate from method "B" contained significant levels of lead, but these were still ten times lower than EPA limits. The data for the retorted Antrim shale in Table 4 shows about a four-fold increase over the raw shale in the lead concentrations for the leachates from method "B". This would appear to indicate that the retorting process may increase the leachability of lead in this shale using this method. Table 6 contains the data for the spent Antrim shale OS-5, the two samples of spent Antrim shale, OS-3 the crushed shale, and OS-5 the uncrushed shale (OS-5 had a particle size of 0.63 centimeters to 15.24 centimeters). The most significant difference in the leachates from OS-5 and the crushed sample (OS-3) is for method "A"; the pH changed from 7.5 to about 4.0. The lead concentrations in the method "B" leachate had decreased to about the range of our detection limit. The A.S.T.M. method "B" yields higher concentrations for almost all the metals, but even these are far below the limits set by EPA.

The quality control program employed at the Laramie Energy Technology Center requires that every fifth sample be analyzed in duplicate and also spiked. In addition to this program, the leachates were analyzed in duplicate by inductively coupled plasma emission spectroscopy (I.C.A.P.) for comparison with the data obtained by graphite furnace analysis. The results obtained by I.C.A.P. are shown in the next five tables, No. 7 through 11, and the results compare very well on most of the samples. For the first part of the study our detection limits had arbitrarily been set at the values which are reported as less than values. For the comparison part of the study, we reanalyzed the samples for the lowest reliable values we were able to obtain using the graphite furnace. In Table 7, Cd is

reported as less than 20 µg/l, this was due to the use of a weak Cd lamp. By the time a replacement lamp was obtained, all the sample had been consumed in other tests. Because of instrument problems we were unable to obtain values for all the parameters using the I.C.A.P. One of the most obvious differences in the analysis shows up in Table 9, method "B". The atomic absorption analysis shows lead at a concentration of one-hundred and twenty-eight micrograms per liter while the plasma was unable to detect any lead. We feel the atomic absorption value is correct because it was done using standard addition techniques. This high concentration of lead had also shown up in the first part of the study, Table 4, and it had been given special attention at that time. Table 12 presents some corresponding data on other solid wastes. This data compares oil shale's pollution potential to three other solid waste materials. The fly ash, bottom ash and scrubber sludge, while not exceeding the EPA guidelines for six of the metals, do exceed the limits for selenium and arsenic. The oil shales, on the other hand, do not exceed the limits for any of the parameters and give lower results for all the heavy metals. Table 5 shows the only instance where one of the shale samples exceeds even one half the proposed limit for a metal. In this instance, using A.S.T.M. method "B", the values for cadmium are eighty micrograms per liter and the limit is one hundred micrograms per liter.

The data also shows the wide variation in metal concentrations that can be obtained by using the three different leaching methods. They also show that the methods as they are now written do not give reproducible results.

In conclusion, the data clearly shows that none of these oil shales present a hazard to the environment under the EPA guidelines for heavy metals.

TABLE 1
Elemental Analysis of the Oil Shales

	% Total Carbon	% Mineral Carbon	% Organic Carbon	% Nitrogen	% Sulfur
OS-1	6.88	2.47	4.41	-	0.45
OS-2	8.95	0.19	8.76	0.28	3.1
OS-3	3.05	0.06	2.99	-	2.92
OS-4	20.52	4.24	16.28	0.57	1.36

X-Ray Diffraction Analysis

OS-1	Quartz, Feldspar, Calcite, Dolomite, Analcime, Periclase, Oldhamite, Illite
OS-2	Quartz, Illite, Pyrite, Marcasite, Feldspar, Chlorite
OS-3	Quartz, Illite, Pyrrhotite, Feldspar, Pyrite
OS-4	Dolomite, Calcite, Quartz, Pyrite, Feldspar, Smectite, Siderite

Oil Yield for the Raw Shale Samples by Fischer Assay

	L/tonne	Gal/ton
OS-1	93.38	23.6
OS-2	40.43	9.7
OS-4	72.95	17.5

TABLE 2
Atomic Adsorption Analysis of Leachates from Retorted
Green River Formation Oil Shale Sample (Rifle, Colorado)

WASTE SAMPLE = OS-1

Analytical Procedures used: ASTM and EPA	Leachates Number	pH Units	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	1	11.09	203	0.70	<.05	<10	0.15	<50	<10	<5	<10	<.05
	2	11.13	221	0.80	<.05	<10	0.15	<50	<10	<5	<10	<.05
	3	11.06	219	0.50	<.05	<10	0.15	<50	<10	<5	<10	<.05
METHOD B	1	8.85	1332	192	<.05	70	1.00	<50	12	<5	23	<.05
	2	8.50	1300	192	<.05	105	1.30	<50	<10	<5	31	<.05
	3	8.58	1392	202	<.05	70	1.20	<50	<10	<5	32	<.05
METHOD E. P.	1	6.80	1398	260	.07	28	.43	<50	<10	<5	<10	<.05
	2	8.10	996	382	<.05	18	.43	<50	<10	<5	<10	<.05
	3	6.30	1100	278	.06	30	.50	<50	<10	<5	<10	<.05
PROPOSED EPA LIMIT		---	---	---	.50	500	10.0	100	500	20	100	.50

TABLE 3
Atomic Absorption Analysis of Leachates from
Raw Antrim Oil Shale Sample (Michigan)

WASTE SAMPLE = OS-2

Analytical Procedures used: ASTM and EPA	Leachates Number	pH Units	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	1	6.19	132	124	<.05	<10	<.10	<50	<10	<5	<10	<.05
	2	6.05	129	120	<.05	<10	<.10	<50	<10	<5	<10	<.05
	3	6.14	124	124	<.05	<10	<.10	<50	<10	<5	<10	<.05
METHOD B	1	4.58	212	165	<.05	<10	0.12	<50	40	<5	19	<.05
	2	4.56	219	166	<.05	<10	0.14	<50	32	<5	20	<.05
	3	4.60	181	150	<.05	<10	0.11	<50	40	<5	18	<.05
METHOD E. P.	1	5.14	60	34	<.05	<10	<.10	<50	<10	<5	<10	<.05
	2	4.92	51	33	<.05	<10	<.10	<50	<10	<5	<10	<.05
	3	4.72	57	33	<.05	<10	<.10	<50	<10	<5	<10	<.05
PROPOSED EPA LIMIT		---	---	---	.50	500	10.0	100	500	20	100	.50

TABLE 4
Atomic Absorption Analysis of Leachates from
Retorted Antrim Oil Shale Sample (Michigan)

WASTE SAMPLE = OS-3

Analytical Procedures used: ASTM and EPA	Leachates Number	pH Units	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	1	7.45	172	77	<.05	<10	<.10	<50	<10	<5	<10	<.05
	2	7.50	189	80	<.05	<10	<.10	<50	<10	<5	<10	<.05
	3	7.47	165	77	<.05	<10	<.10	<50	<10	<5	<10	<.05
METHOD B	1	4.60	151	224	<.05	<10	<.10	<50	128	<5	<10	<.05
	2	4.60	148	228	<.05	<10	<.10	<50	112	<5	<10	<.05
	3	4.62	158	238	<.05	<10	<.10	<50	144	<5	<10	<.05
METHOD E.P.	1	5.40	157	40	<.05	<10	<.10	<50	<10	<5	<10	<.05
	2	5.60	144	36	<.05	<10	<.10	<50	<10	<5	<10	<.05
	3	5.70	154	41	<.05	<10	<.10	<50	<10	<5	<10	<.05
PROPOSED EPA LIMIT		---	---	---	.50	500	10.0	100	500	20	100	0.50

TABLE 5
Atomic Absorption Analysis of Leachates from
Raw Moroccan Oil Shale (Morocco)

WASTE SAMPLE = OS-4

Analytical Procedures used: ASTM and EPA	Leachates Number	pH Units	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	PB µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	1	4.21	253	37	<.05	<10	<.10	<50	<10	<5	13	<.05
	2	6.70	272	37	<.05	<10	<.10	<50	<10	<5	13	<.05
	3	3.35	246	36	<.05	<10	<.10	<50	<10	<5	15	<.05
METHOD B	1	5.58	1364	69	0.13	<10	0.24	70	<10	<5	46	<.05
	2	5.80	1540	86	0.10	<10	0.24	80	<10	<5	42	<.05
	3	5.65	1432	63	0.13	<10	0.24	80	<10	<5	44	<.05
METHOD E.P.	1	6.50	648	34	<.05	<10	<.10	<50	<10	<5	<10	<.05
	2	6.20	824	37	<.05	<10	<.10	<50	<10	<5	<10	<.05
	3	7.17	835	35	<.05	<10	<.10	<50	<10	<5	<10	<.05
PROPOSED EPA LIMIT		---	---	---	0.50	500	10.0	100	500	20	100	0.50

TABLE 6
Atomic Absorption Analysis of Leachates from Large Particle Size
Retorted Antrim Oil Shale Sample (Michigan)

WASTE SAMPLE = OS-5

Analytical Procedures used: ASTM and EPA	Leachates Number	pH Units	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	1	4.06	33	58	<.05	<10	<.10	<50	<10	<5	<10	<.05
	2	4.50	41	40	<.05	<10	<.10	<50	<10	<5	<10	<.05
	3	2.50	36	25	<.05	<10	<.10	<50	<10	7	<10	<.05
METHOD B	1	4.60	71	46	<.05	<10	<.10	50	<10	<5	<10	<.05
	2	4.55	50	40	<.05	<10	<.10	50	13	<5	<10	<.05
	3	4.55	82	75	<.05	<10	<.10	50	<10	<5	<10	<.05
METHOD E. P.	1	2.81	6	6	<.05	<10	<.10	<50	<10	<5	<10	<.05
	2	3.48	7	6	<.05	<10	<.10	<50	<10	<5	<10	<.05
	3	3.46	7	5	<.05	<10	<.10	<50	<10	<5	<10	<.05
PROPOSED EPA LIMIT		---	---	---	0.50	500	10.0	100	500	20	100	0.50

TABLE 7
Comparison Data for I.C.A.P. Analysis and Atomic Absorption Analysis
of Leachates from the Green River Oil Shale Sample

WASTE SAMPLE = OS-1

Analytical Procedures used: ASTM and EPA	Type of Instrument	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	A. A.	214	0.80	.02	10	.15	<20	<10	<5	<10	.001
	I. C. A. P.	198	.86	<.01	<20	---	4.4	<20	<20	24.7	<30
METHOD B	A. A.	1341	202	.022	70	1.2	19	12	<5	30	<.001
	I. C. A. P.	---	206	<.01	71	---	29	<20	<20	37	<30
METHOD E. P.	A. A.	1165	382	.022	29	.43	<20	<10	<5	<10	.001
	I. C. A. P.	---	442	<.01	44	---	25.9	<20	<20	<20	<30

TABLE 8
Comparison Data for I.C.A.P. Analysis and Atomic Absorption Analysis
of Leachates from Raw Antrim Oil Shale

WASTE SAMPLE = OS-2

Analytical Procedures used ASTM and EPA	Type of Instrument	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	A. A.	132	124	.016	<10	<.10	<2	<10	<5	<10	<.001
	I. C. A. P.	162	143	<.01	<20	---	3	<20	<20	<20	<30
METHOD B	A. A.	215	165	.040	<12	0.13	6	40	<5	18	<.001
	I. C. A. P.	266	180	.03	41	---	14	40	<20	<20	<30
METHOD E. P.	A. A.	60	33	.020	<10	<10	<2	<10	<5	10	<.001
	I. C. A. P.	77	37	<.01	<20	---	<2	<20	<20	<20	<30

TABLE 9
Comparison Data for I.C.A.P. Analysis and Atomic Absorption Analysis
of Leachates from the Retorted Antrim Oil Shale

WASTE SAMPLE = OS-3

Analytical Procedures used: ASTM and EPA	Type of Instrument	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	A. A.	175	77	.014	<10	<.10	<2	<10	<5	<10	<.001
	I. C. A. P.	165	213	<.01	<20	---	<2	<20	<20	<20	<30
METHOD B	A. A.	152	230	.028	<10	.11	3	128	<5	<10	<.001
	I. C. A. P.	187	234	<.01	25	---	6	<20	<20	<20	<30
METHOD E. P.	A. A.	155	41	.015	<10	<.10	<2	<10	<5	<10	<.001
	I. C. A. P.	80	54	<.01	<20	---	<2	<20	<20	<20	<30

TABLE 10
Comparison Data for I.C.A.P. Analysis and Atomic Absorption Analysis
of Leachates from Raw Moroccan Oil Shale

WASTE SAMPLE = OS-4

Analytical Procedures used: ASTM and EPA	Type of Instruments	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	A.A.	257	37	.018	<10	<.10	3	<10	<5	13	<.001
	I.C.A.P.	246	41	<.01	<20	---	<2	86	<20	31	<30
METHOD B	A.A.	1392	73	0.12	<10	0.24	80	<10	<5	45	<.001
	I.C.A.P.	---	76	0.08	<20	---	80	<20	<20	65	<30
METHOD E.P.	A.A.	854	35	.024	<10	<.10	35	<10	<5	<10	<.001
	I.C.A.P.	---	36	<.01	<20	---	25	<20	<20	<20	<30

TABLE 11
Comparison Data for I.C.A.P. Analysis and Atomic Absorption Analysis
of Leachates from the Retorted Antrim Oil Shale

WASTE SAMPLE = OS-5

Analytical Procedures used: ASTM and EPA	Type of Instrument	Ca mg/l	Mg mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	A.A.	37	49	.016	<10	<.10	<10	<10	<5	<10	<.001
	I.C.A.P.	---	---	---	---	---	---	---	---	---	---
METHOD B	A.A.	71	54	.028	<10	<.05	5	<10	<5	<10	<.001
	I.C.A.P.	70	54	<.01	<20	---	6	<20	<20	<20	<30
METHOD E.P.	A.A.	6	6	.021	<10	<.05	<2	<10	<5	<10	<.001
	I.C.A.P.	6	7	<.01	<20	---	<2	<20	<20	<20	<30

TABLE 12
Atomic Absorption Analysis of Leachates from Coal Waste

Analytical Procedures used: ASTM and EPA	Sample	pH Units	Ca mg/l	Cr mg/l	As µg/l	Ba mg/l	Cd µg/l	Pb µg/l	Hg µg/l	Se µg/l	Ag mg/l
METHOD A	Fly Ash	9.09	283	.115	192	.29	13	36	<1	201	.011
	Bottom Ash	7.02	60	.010	4	.11	9	41	1	94	.012
	Scrubber Sludge	5.92	499	.017	3	.24	8	35	<1	86	.011
METHOD B	Fly Ash	4.81	796	.322	1320	.30	29	73	7	441	.015
	Bottom Ash	4.68	44	.027	4	.36	9	39	1	89	.013
	Scrubber Sludge	4.86	680	.034	4	.34	16	29	<1	115	.015
METHOD E. P.	Fly Ash	5.09	171	.033	695	.17	12	22	4	250	.011
	Bottom Ash	5.02	15	.014	6	.13	13	18	1	11	.014
	Scrubber Sludge	4.08	442	.027	22	.12	8	19	<1	53	.013
PROPOSED EPA LIMIT		---	---	0.50	500	10.0	100	500	20	100	0.50

REFERENCES

EPA Methods:

Ca	Method	215.1
Mg	Method	242.1
Cr	Method	218.2
As	Method	206.2
Ba	Method	208.2
Cd	Method	213.2
Pb	Method	239.2
Hg	Method	245.1
Ag	Method	272.2
Se	Method	270.2
pH	Method	150.1

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