Background

• During the last oil shale development period, a considerable environmental effort was funding by DOE. It consisted of faculty from CU, CSU, and CSM.

• Objective of the effort was to determine which trace elements would cause environmental issues and assess as best as possible the impact that would occur upon development.
Topics for this talk

• **Determination of baseline abundances in soil and air.**
  – Ron Klusman & students

• **Elemental balances in oil shale retorting**
  – Tom Wildman & students

• **Sulfur in raw and spent shale and in retort waters**
  – Tom Wildman & students
modified from Meglen (19--)
Eh-pH limits for living organisms (Baas-Becking 1960)

Green River oil shale depositional environment
Elements of primary interest

• Chemical elements which are potentially toxic, and form soluble anions under alkaline conditions of Parachute Creek Member deposition.
• Arsenic (As), Boron (B), Fluorine (F), Molybdenum (Mo), Selenium (Se),
• Mercury (Hg) because of its volatility if heated under chemically reducing conditions.
# Selected Constituents in Water (in mg/L)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Colorado River</th>
<th>Ground Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.3</td>
<td>7.7</td>
</tr>
<tr>
<td>As</td>
<td>0.001</td>
<td>--</td>
</tr>
<tr>
<td>B</td>
<td>0.060</td>
<td>0.320</td>
</tr>
<tr>
<td>Ba</td>
<td>0.080</td>
<td>0.008</td>
</tr>
<tr>
<td>Cu</td>
<td>0.005</td>
<td>--</td>
</tr>
<tr>
<td>F</td>
<td>0.3</td>
<td>47</td>
</tr>
<tr>
<td>Li</td>
<td>--</td>
<td>42</td>
</tr>
<tr>
<td>Mo</td>
<td>0.005</td>
<td>0.270</td>
</tr>
<tr>
<td>Se</td>
<td>0.002</td>
<td>0.040</td>
</tr>
</tbody>
</table>
Geochemical Baseline Estimates

- Media include:
  - B-horizon soils,
  - Stream sediments,
  - Vegetation – Big sage, Western wheatgrass, Indian ricegrass.
- Determine mean concentrations,
- Concentration ranges,
- Geographic scale of variability.
- Hierarchical analysis of variance,
- Geostatistical analysis and kriging.
Klusman graduate students geochemical baseline studies

- Charles Ringrose – stream sediments in Piceance B.
- Robert Candito – soils/sediments, vegetation – C-a
- Bruce Zucarro – soils/sediments, vegetation – C-b
- David Rutherford – soils/sediments, vegetation - AP
- Michelle Tuttle – soils, vegetation in Piceance B.
- James Rice – soils, vegetation in Uinta Basin
- Douglas Brown – stream sediments in Uinta Basin
- Christopher Matoske – atmospheric Hg adsorption by soils.
from Tuttle et al (1986)

Cu in Soil (ppm)
from Tuttle et al (1986)

Cu in Big sagebrush (ppm)

EXPLANATION

- <10.0
- 10.0-12.5
- 12.5-15.0
- >15.0

FF. Copper in big sagebrush (in parts per million).
Mo in Soils (ppm)

From Candito (1977)
from Malley (1984)
from Malley (1984)
<table>
<thead>
<tr>
<th>Pure Collection Samples</th>
<th>Collection Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinyon Pine</td>
<td>Vernal, Utah</td>
</tr>
<tr>
<td>Utah Juniper/Aspen</td>
<td>Flaming Gorge, Utah</td>
</tr>
<tr>
<td>Big Sage</td>
<td>Craig, Colorado</td>
</tr>
<tr>
<td>Pollen</td>
<td>Rifle, Colorado</td>
</tr>
<tr>
<td>Oil Shale</td>
<td>Parachute Creek, Colorado</td>
</tr>
</tbody>
</table>

from Malley (1984)
from Malley (1984)
Topics for this talk

• Determination of baseline abundances in soil and air.
  – Ron Klusman & students

• Elemental balances in oil shale retorting
  – Tom Wildeman & students

• Sulfur in raw and spent shale and in retort waters
  – Tom Wildeman & students
Definitions

- **Pyrolysis** – decomposition of organic matter in the absence of oxygen, (low oxygen for our purposes),
- **Fischer Assay** – laboratory method for quantitatively determining the production of bitumen(s) from kerogen-containing rock (Newer method – Rock-Eval),
- **Retort** – Large scale device for production of bitumen (shale oil) from oil shale,
- **Yield** – expressed as gallons/ton (gpt),
- **Spent shale** – left over material from retorting of oil shale.
Definitions

- **Surface Mining and Retorting** – production of shale, retorting and spent shale disposal done entirely on the surface,
- **Modified In-situ Retorting** – retorting done underground after considerable modification of the rock to enable more efficient production,
- **In-situ Retorting** – underground production without significant mining of rock; various amounts of permeability modification.
<table>
<thead>
<tr>
<th></th>
<th>Coal Burning</th>
<th>Shale Retorting</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feed Stock</strong></td>
<td>90 % organic</td>
<td>20 % organic</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>1500 °C</td>
<td>500 – 700 °C</td>
</tr>
<tr>
<td><strong>Products</strong></td>
<td>CO$_2$ &amp; H$_2$O</td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td><strong>Atmosphere</strong></td>
<td>Oxidizing</td>
<td>Reducing</td>
</tr>
<tr>
<td><strong>Solid Waste</strong></td>
<td>5-10 % fly ash</td>
<td>80 % spent shale</td>
</tr>
<tr>
<td><strong>Other Products</strong></td>
<td>Vapors &amp; particulates</td>
<td>Oil, water, &amp; vapor</td>
</tr>
<tr>
<td><strong>Losses</strong></td>
<td>Hg, Se, As</td>
<td>Hg &amp; ????</td>
</tr>
<tr>
<td><strong>Plant Size</strong></td>
<td>100 Mwatt</td>
<td>50,000 bbl / day</td>
</tr>
<tr>
<td></td>
<td>65,000 ton / day</td>
<td>70,000 ton / day</td>
</tr>
</tbody>
</table>
Retort Types

- **Direct Heating** – Adds air for combustion heating
  - Paraho Surface Retort
  - Union Retort
  - Occidental modified in-situ retort

- **Indirect Heating** – Relies on a physical method of heating absent of air
  - TOSCO process
  - Fischer Assay
  - Shell in-situ process
from Wildeman (1974)
figure from Bob Meglen (19--)
Retort Types

• Direct Heating – Adds air for combustion heating
  – Paraho Surface Retort
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• Indirect Heating – Relies on a physical method of heating absent of air
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  – Fischer Assay
  – Shell in-situ process
Shell Scenario

Water Table

Uinta Formation

Surface

Dewatered Zone

Ice Wall

Upper 50' of Parachute Creek Member (cap rock)

Drill Holes

Bitumen Production

Hydrocarbon

Vapors

Upper Parachute Creek Member

Shell Scenario
Fischer Assay Apparatus
<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Std Dev.</th>
<th>Rel Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spent shale</td>
<td>80.45</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>Liquid product</td>
<td>16.29</td>
<td>0.42</td>
<td>2.6</td>
</tr>
<tr>
<td>Oil</td>
<td>14.93</td>
<td>0.39</td>
<td>2.6</td>
</tr>
<tr>
<td>Water</td>
<td>1.35</td>
<td>0.11</td>
<td>8.0</td>
</tr>
<tr>
<td>Gas &amp; loss</td>
<td>3.26</td>
<td>0.44</td>
<td>13.4</td>
</tr>
</tbody>
</table>
Mass Balance Objectives

• Determine pathways of specific elements during retorting
  – Mobile in alkaline environments: B, F, As, Se, Mo
  – Can vaporize at 500-700 °C: Hg, Cd
• Determine possible releases from retorting.
• Determine chemical changes that may lead to environmental problems
  – Trace elements in oils & waters
  – Gaseous Emissions
  – Release from retorted shale
FISCHER ASSAY MASS BALANCE

SHALE 100 G -60 MESH

RETORT 72 MIN TOTAL 20 MIN 500°C

SPENT SHALE  OIL  SOUR WATER  GAS

ELEMENTS ANALYZED: Na, Mg, Al, Si, K, Ca, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ba, Pb, U, Th

from Wildeman (19--)
ANALYSIS PARAMETERS

ENRICHMENT RATIO \((ER)\)

\[
ER = \frac{\text{ELEMENT IN PRODUCT}}{\text{ELEMENT IN RAW SHALE}}
\]

RELATIVE IMBALANCE \((RI)\)

\[
RI = \left\{ \frac{\text{MASS IN} - \text{MASS OUT}}{\text{MASS IN}} \right\} \times 100
\]
Fischer Assay Results: Refractory Elements (Raw Shale / Spent Shale = 1.24)

<table>
<thead>
<tr>
<th></th>
<th>ER</th>
<th>RI</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1.15</td>
<td>+ 7 %</td>
</tr>
<tr>
<td>Sr</td>
<td>1.33</td>
<td>- 7 %</td>
</tr>
<tr>
<td>Mo</td>
<td>1.17</td>
<td>+ 6</td>
</tr>
<tr>
<td>U</td>
<td>1.19</td>
<td>+ 5 %</td>
</tr>
<tr>
<td></td>
<td>Not Mobile</td>
<td>Not Lost</td>
</tr>
</tbody>
</table>
## Fischer Assay Results: Volatile Elements
(Raw Shale / Spent Shale = 1.24)

<table>
<thead>
<tr>
<th>Element</th>
<th>ER</th>
<th>RI</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>1.00</td>
<td>+19%</td>
</tr>
<tr>
<td>Zn</td>
<td>1.03</td>
<td>+17%</td>
</tr>
<tr>
<td>As</td>
<td>1.20</td>
<td>-2%</td>
</tr>
<tr>
<td>Se</td>
<td>1.12</td>
<td>+6%</td>
</tr>
<tr>
<td>Hg</td>
<td>0.25</td>
<td>+80%</td>
</tr>
<tr>
<td>Pb</td>
<td>1.37</td>
<td>+5%</td>
</tr>
</tbody>
</table>
Mass Balance Conclusions

- No relation between oil yield (organic content) and inorganic content.
- Most elements – no problem
- Obvious Issues: Hg & S
- Possible Issues: F, Zn, As
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• Determination of baseline abundances in soil and air.
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Pyrite in Oil Shales

• How much of the sulfur is in pyrite?
• Can the pyrite react to form more mobile species?
• Could some of the elements normally associated with pyrite be mobilized? – As, Se, Cd, Cu, Zn, Mo, Pb
• Objectives of the Mossbauer study
Mossbauer Oil Shale 1

![Graph showing RELTRANSMISSION vs VELOCITY (mm/sec) for OIL SHALE OS-1 with peaks labeled Py and Ank.](image-url)
Iron in Raw Shale

- Comparable amounts of
  - Pyrite FeS$_2$
  - Ankerite Ca(Mg,Fe)(CO$_3$)$_2$
  - Siderite FeCO$_3$

- Majority of the sulfur is in pyrite.
Indirect Heating Retorts (500 – 600 °C)

- FeS$_2$ $\rightarrow$ FeS + S
- S $\rightarrow$ ??? (oil, water, or vapor)
- Ankerite & siderite are unchanged
Direct Heating Retorts (below 750 °C)

• Pyrite remains unchanged.
• Carbonates partially go to oxides.

Direct Heating Retorts (above 750 °C)

• All iron minerals are changed to hematite or magnetite.
Mossbauer Spent Shale SS-11

SOS 11B  \[ T = 6K \]

**Graph:**
- **Y-axis:** Relative Transmission
- **X-axis:** Velocity (mm/sec)
- **Markers:**
  - Superpar
  - Mag + Hem
  - Mag
  - Hem

The graph shows the transmission peaks and valleys for different materials at a temperature of 6K.
Conclusions on Sulfur in Oil Shale

• When oil shale was deposited, the sulfur was associated with the organic components.
• The majority of this sulfur is now in iron pyrite.
• If the sulfur was in organic compounds, diagenesis changed it to iron sulfides.
• At moderate retorting temperatures, the sulfur is retained in the iron sulfides.
• At moderate temperatures, most of the sulfur that is in spent shale is in iron sulfides.
Retorting Implications

- Sulfur release to unknown phases may occur in indirect heating retorts.
- For all retorts, keep the temperature below 600 °C so that energy is not consumed in metamorphic mineral changes, particularly the loss of CO$_2$ from carbonate minerals.
- There is possible prevention of pyrite breakdown in direct heating retorts.
Future Steps

• Leachate studies on raw and spent shales to determine what is bioavailable
• Toxicity studies on the leachates
• Study Hg, S, As, Se, and Zn using newer analytical methods.
• Intensive study on water and vapor.
Questions and Comments?
<table>
<thead>
<tr>
<th></th>
<th>RANGE</th>
<th>AVERAGE</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Shale</td>
<td>0.61 - 0.84</td>
<td>0.68</td>
<td>9.9</td>
</tr>
<tr>
<td>Ret. Shale</td>
<td>0.60 - 0.84</td>
<td>0.74</td>
<td>10.4</td>
</tr>
<tr>
<td>Oil</td>
<td>0.74 - 0.93</td>
<td>0.82</td>
<td>8.5</td>
</tr>
<tr>
<td>Water</td>
<td>2.5 - 6.1</td>
<td>3.8</td>
<td>29</td>
</tr>
<tr>
<td>Fischer Assay</td>
<td>22 - 32</td>
<td>27</td>
<td>10.3</td>
</tr>
</tbody>
</table>

Narrow range of results suggest small statistical window.
from Wildeman (19--)