On the Use of Oil Shale beyond Production of Oil and Gas

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Shale Oil + Gas

More than Oil

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Introduction
Scope and Objective
Production of Soda Ash
Production of Ammonium Sulfate
Production of Potassium Sulfate
Feasibility Study
Further Utilization of Spent Shale
Conclusions and Recommendations
Production of Soda Ash $\text{Na}_2\text{CO}_3$

- Spent shale is burned to give calcium oxide and carbon dioxide.
- Carbon dioxide is cooled, purified and reacted with ammonia, water and sodium chloride to produce sodium bicarbonate and ammonium chloride.
- Sodium bicarbonate is then separated from ammonium chloride solution, and then calcined to give soda ash and carbon dioxide, which is recycled in the production of sodium bicarbonate.
- Calcium oxide is reacted with ammonium chloride solution to give ammonia (which is recycled in the production of sodium bicarbonate), and calcium chloride, which is used as coolant in refrigeration.
Production of Soda Ash

C + O₂ → CO₂ + heat (1)

CaCO₃ + heat → CaO + CO₂ (2)

2NH₃ + 2CO₂ + 2H₂O → 2NH₄HCO₃ (3)

2NH₄HCO₃ + 2NaCl → 2NaHCO₃ + 2NH₄Cl (4)

2NaHCO₃ + heat → Na₂CO₃ + CO₂ (5)

2NH₄Cl + CaO → 2NH₃ + CaCl₂ (6)

2NaCl + CaCO₃ → Na₂CO₃ + CaCl₂ (7)
**Production of Ammonium sulfate** $\text{NH}_4\text{H}_2\text{SO}_4$

- The process uses carbon dioxide, ammonia and water:

  $$2\text{NH}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{CO}_3 \quad (8)$$

  $$(\text{NH}_4)_2\text{CO}_3 + \text{CaSO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{CaCO}_3 \quad (9)$$

- Insoluble calcium carbonate and the high soluble ammonium sulfate are separated by filtration.

  ✓ *The residue of retorted oil shale can be burnt to give the required carbon dioxide.*

  ✓ *The ammonium sulfate solution can be used to produce potassium sulfate or to produce solid ammonium sulfate by evaporation of water.*
Production of Potassium Sulfate $K_2SO_4$

- The process uses displacement reaction between Ammonium Sulfate in solution and Potassium Chloride (main product of the Arab Potash Company)

$\text{(NH}_4\text{)}_2\text{SO}_4 + 2\text{KCl} \rightarrow \text{K}_2\text{SO}_4 + 2\text{NH}_4\text{Cl}$ \hspace{1cm} (10)

- The Ammonium chloride is a byproduct, which can be recycled to produce Ammonia gas, required in the Ammonium Sulfate production

$2\text{NH}_4\text{Cl} + \text{CaO} \rightarrow 2\text{NH}_3 + \text{CaCl}_2$ \hspace{1cm} (11)
Raw Materials

Oil Shale

Retorting

Burning

CaO

Reaction

Oil + Gas

CaCl₂

NaCl

NH₃

NH₄Cl

CaSO₄

KCl

Water

Reaction

Na₂CO₃

(NH₄)₂SO₄

CaCO₃

K₂SO₄

Calcining

Crystallization

CO₂ to air

Oil + Gas

CaCl₂

Na₂CO₃

(NH₄)₂SO₄

CaCO₃

K₂SO₄

Reaction

(NH₄)₂SO₄

CaSO₄

KCl

Raw Materials

Products
## Materials for one Ton of Soda Ash

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride</td>
<td>1,740 kg</td>
</tr>
<tr>
<td>Limestone</td>
<td>1,250 kg</td>
</tr>
<tr>
<td>Coke (Spent Shale)</td>
<td>105 kg</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>265 kg</td>
</tr>
<tr>
<td>Ammonia</td>
<td>4 kg</td>
</tr>
<tr>
<td>Sodium Sulfide</td>
<td>2 kg</td>
</tr>
<tr>
<td>Water</td>
<td>24 m³</td>
</tr>
<tr>
<td>Electricity</td>
<td>2.1 kWh</td>
</tr>
<tr>
<td>Steam</td>
<td></td>
</tr>
<tr>
<td><strong>The Cost Of Steam Is Included In The Fuel Oil</strong></td>
<td></td>
</tr>
<tr>
<td>40 bar : 2.7 ton</td>
<td></td>
</tr>
<tr>
<td>12 bar: 0.5 ton</td>
<td></td>
</tr>
<tr>
<td>2.5 bar : 1.8 ton</td>
<td></td>
</tr>
</tbody>
</table>

The cost of steam is included in the fuel oil.
# Materials for one Ton of Ammonium Sulfate

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphogypsum</td>
<td>1,340 kg (30% excess)</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>340 kg</td>
</tr>
<tr>
<td>Ammonia</td>
<td>263 kg</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>150 – 200 kg (estimated)</td>
</tr>
</tbody>
</table>
# Materials for one Ton of Potassium Sulfate

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Chloride</td>
<td>882 kg</td>
</tr>
<tr>
<td>Ammonium Sulfate</td>
<td>781 kg</td>
</tr>
<tr>
<td>Calcium Oxide (Lime)</td>
<td>350 kg</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>100 – 150 kg</td>
</tr>
</tbody>
</table>
“More than Oil” Other Uses

- Spent shale is efficient in removing hydrocarbon content, leaving a byproduct material that has the characteristics of activated charcoal. This material is known to actually absorb industrial spills and pollutants.

- Spent shale may have commercial value when used, for example, as an ingredient in drywall materials.

- The remaining material is white in color and totally inert, and can be used as fillers in construction materials, cement and concrete mixes or in medical cosmetics after fine grinding.
“More than Oil” Other Uses

- Spent shale will be used on-site for retort energy while any surplus would be used for the production of construction materials.

- Some shale deposits contain aluminum oxide and perhaps other precious metals.

- Methane and propane, a valuable energy source, is a primary byproduct. The shale oil remediation process also recovers pyridine from the shale oil which is used in vitamins and medicines.

- Typically, the asphalt “cement” known as AC-20 is used to create asphalt surfaces on roads. It has a life expectancy of five years. By adding the nitrogen based compound from the shale oil, the life is extended to approximately 20 years.
Conclusions and Recommendations

As Jordan is rich with oil shale and other input industrial materials as presented, the following may be drawn:

1. The major materials are available at very low cost. For example NaCl (salt) is available in any amount at negligible cost as by-product of the potassium chloride industry. Limestone and coke are available from the retorting of oil shale. Fuel oil is available from retorting of oil shale.

2. It should be noted that the production of Soda Ash is not only feasible but also economical. Jordan is unique in the availability of the required raw materials needed for such production.

3. As shown above, the reaction between ammonium chloride and lime is common in the production of soda ash and potassium sulfate. Also the purification of carbon dioxide is common in the production of soda ash and ammonium sulfate, which will reduce capital cost and production cost.

4. It is recommended that this presentation may stimulate and invite investors to focus not only on shale oil, but on more than oil.
Can we have the 28th Oil Symposium in Jordan?

The Answer

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