

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

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Abstract

This paper presents an overview on the use of spent shale in the production of sodium carbonate, ammonium sulfate, and potassium sulfate as well as many other uses in the cement and construction industries. Apart from the main focus of producing oil and gas products, such uses will be considered as an added value in the overall assessment and evaluation of oil shale industry.

It is possible to develop suitable equipment for the production of oil from oil shale, but with different conditions to control the temperature of the residue of retorted oil shale to enable the calcium carbonate to dissociate into calcium oxide and carbon dioxide which are the main materials for the production of sodium carbonate, ammonium sulfate and potassium sulfate. A schematic flow diagram will be presented to form the basis for the construction of a pilot plant that utilizes the process of producing oil on one fold and the production of the said products on the other fold. Further uses of spent shale in the production of cement, building bricks and other construction materials will also be highlighted.

It is concluded that the focus on the production of oil from the oil shale will form a misleading indicator on the oil shale industry if the benefits from utilizing the spent shale was not taken into consideration.

Introduction

It is no wonder that the world's oil shale deposits represent a tremendous store of fossil energy. It has been estimated that the organic matter in sedimentary rocks contains 1.1×10^{16} metric tons of organic carbon, nearly 1,000 times that found in coals. Although part of that organic carbon has matured to produce oil and gas, most of it is still oil shale. Unfortunately, most of this tremendous resource is not well known. Oil shale deposits occur on every continent in sediments ranging in age from Cambrian to Tertiary. Estimates for the total oil resource in shales of all grades reached 1.75×10^{15} barrels. Just 1% of that total shale oil represents more oil than the world is expected to produce as natural petroleum (2×10^{12} bbl). Oil shale represents a tremendous supply of liquid fuels.

Although the oil potential of the world's oil shales is great, commercial production of this oil has been considered uneconomical when the oil prices were low in comparison

with the production cost of shale oil. Oil shales are lean ores, producing only limited amounts of oil which historically has been low in price. Mining and heating one ton of relatively rich oil shale yielding 25 gal/ton produces only 0.6 bbl of oil. Shale oil is produced from the organic matter in oil shale when the rock is heated in the absence of oxygen (destructive distillation). This heating process is called retorting, and the equipment that is used to do the heating is known as a retort. The rate at which the oil is produced depends upon the temperature at which the shale is retorted. Most references report retorting temperatures as being about 500°C (930°F). The huge quantities of spent shale may not be of interest to those who are after producing shale oil, especially when they steer the oil shale industry towards in situ conversion process. But it is not the case when surface retorting is utilized in the production of shale oil and gas. Attempts to utilize the oil shale retorting solid waste has been a pioneering step in this regard (Trikkel and Kuusik, 2006).

In the Middle East, the major oil shale deposits are located in Jordan (5,242 million tons of shale oil or 65 billion tons of oil shale) and a small portion is located in Israel (550 million tons of shale oil or 6.5 billion tons of oil shale). Jordanian oil shales are of high quality if compared with western US oil shale - with the exception of high sulfur content. Israeli oil shale is a relatively low in heating value and oil yield. Jordan is still rehearsing to join the oil shale countries club who are utilizing oil shale for energy in one way or another. Due to scarcity of water, the direction should be to use suitable technologies that may be convenient to Jordanian oil shale deposits. Although there is no unified national policy concerning the potential use of oil shale deposits, the door is open to both in-situ conversion as well as ex-situ retorting. This issue has been studied using the concepts of RBM-Results Based Management that outlined the a road map for the a better use of Jordanian oil shale deposits taking into consideration the scarcity of water and the environmental impact as well as the economic aspects (Resheidat et al., 2006a, 2006b). At present, the major shale oil producers are Estonia, Brazil, China, and Australia, while some other countries such as USA, Canada and Jordan have planned to start shale oil production (Bartis et al., 2005; Jamal and Sawaqed, 2006).

Scope and Objective of This Study

Oil shale could be used for production of different products like specialty carbon fibers, adsorbent carbons, carbon black, rock wool insulating material, and glass. However, oil shale usage for production of these products is still small or even in experimental stages only. However, some oil shales could be used for uranium production. In 1946-1952, a marine type of *Dictonema* shale was used for uranium production in Estonia, and in 1950-1989 alum shale was used in Sweden for the same purpose. Oil shale gas could be used as a substitute for natural gas. Spent shale is also used in cosmetics, hair dyes, tires, animal food products, and many other

uses. The prime objective of this study will be concentrating on:

- ✓ The use of oil shale, phosphogypsum and salt as raw materials for the production of soda ash, ammonium sulfate and potassium sulfate.
- ✓ The construction materials and products such as bricks, decorative blocks, soil additives, and fertilizers and special cements, etc.

Production of Soda Ash, Ammonium and Potassium Sulfates

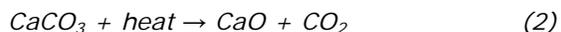
Background

In the period between 1978 and 1982, the Arab Potash Co. carried out feasibility studies for different projects. One of these projects was the production of potassium sulfate and soda ash using potassium chloride and sodium chloride. The feasibility studies showed at that time that their production was unfeasible because of high production costs. The Jordan Fertilizers company which became part of the Jordan Phosphate Mining Co. produces huge amount of unused phosphogypsum as by-product of the production of phosphoric acid. The Natural Resources Authority in Jordan was studying the use of oil shale as a source of energy to produce electricity by direct combustion of oil shale or through distillation of oil. But the study showed the unfeasibility of such project due to the low cost of oil at that time (≈ 20 \$/bbl) where the price of oil was 7-8 \$/bbl. Now we believe that the production of shale oil from oil shale will be not only feasible, but with an added value if its production can be combined with the manufacture of other products such those mentioned in the scope of this study. In North Jordan, east of the village *Saal* when cement was unknown, people were mining oil shale and burning it to produce lime (calcium oxide) used at that time in building industries.

Retorting requires heat and it is a two fold process. The prime objective is to produce oil, the production of gas is a secondary objective. Gas could be used for domestic use or a source of heat in the process of

retorting. Another significant fold must be added which is how to make use of the spent shale. The residue (spent shale) contains about 10% carbon that can be used to treat calcium carbonate and transform it by heat into calcium oxide (lime) and carbon dioxide. Lime is then used as construction material or in the cement industry as well as for other uses. All or most of the produced carbon dioxide could be further used in another stage of soda ash production. By this we honor the regulations of environmental restrictions. As a *green* industry, it is feasible as well as practical to control and use carbon dioxide whether it is the outcome of direct burning of oil shale and/or from the retorting process of shale oil.

In the following sections, after distillation of oil, we will show how we can use spent shale, phosphogypsum and sodium chloride in the production of soda ash (sodium carbonate), ammonium sulfate and potassium sulfate. Since the production of lime from oil shale is possible, particularly when we use modern equipment, the production of lime can be combined with the production of oil according to *Lurgi* process, where the spent shale after distillation of oil is burnt at 750 C° and the hot gases of combustion are used to distill the oil. By elevating the temperature to about 1000 C° (without addition of extra fuel, since the carbon content of the spent shale is sufficient) the calcium carbonate content in the oil shale residue (spent shale) changes into calcium oxide (lime) and carbon dioxide. The latter is also produced from the combustion of carbon in the oil shale residue as shown in the following two chemical reactions:



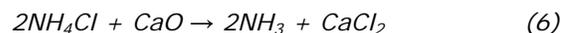
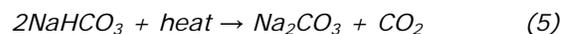
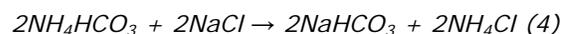
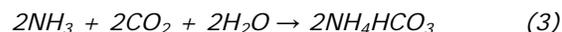
Calcium oxide and carbon dioxide can be utilized in the production of soda ash (sodium carbonate), ammonium sulfate and potassium sulfate as shown below:

Production of Soda Ash

The major process used in the manufacture of soda ash is the *Solvay* process, which can be summarized as follows:

- Limestone (calcium carbonate) is broken into pieces, then mixed with coke in a ratio of 90/10 and burnt at temperatures between 900 and 1000 C°. The products of burning are carbon dioxide and calcium oxide. Oil shale from North Jordan contains after distillation of oil a similar composition of calcium carbonate and carbon, so that it can be burnt 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 sent to sea or used as coolant in refrigeration.

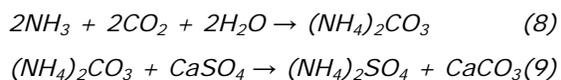
In addition to Equations 1 and 2, the additional chemical reactions are as follows:



The last reaction is the sum of all reactions. It shows materials consumed and materials produced. It should be noted that the large quantities of the soda ash product could be used in several industries such as glass and soap. Furthermore, the carbon dioxide is then used in the production of ammonium sulfate.

Production of Ammonium sulfate

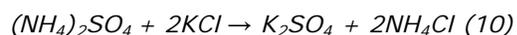
There are several processes for the production of ammonium sulfate, depending on available raw materials. One method is the *Merseburger Process* which uses carbon dioxide, ammonia and water as shown below:



It is obvious the insoluble calcium carbonate and the high soluble ammonium sulfate are produced, which can be easily 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

There are several processes for the production of potassium sulfate depending on available raw materials. It is recommended to use displacement reaction between ammonium sulfate in solution and potassium chloride (main product of the Arab Potash Company) as shown below:



While stirring, solid potassium chloride is added to the ammonium sulfate solution produced from phosphogypsum, ammonia and carbon dioxide as shown in the production of ammonium sulfate (see above), potassium sulfate is precipitated. Because of the low solubility of potassium sulfate in ammonium chloride solution, we can get around 90% of the content of potassium sulfate by crystallization from ammonium chloride solution and 98%, if the solution is saturated with ammonia.

As shown above, ammonium chloride is a byproduct, which can be recycled to produce ammonia gas, required in the ammonium sulfate production as shown below.



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.

The attached flow diagram, as shown in Figure 1, illustrates the utilization of oil shale in the production of oil, soda ash, potassium sulfate and ammonium sulfate.

Feasibility study

A feasibility study (Knutson et al., 1982) carried out for the production of sodium carbonate (soda ash) showed the following materials and inputs (Table 1) needed to produce one ton of sodium carbonate.

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.

The major materials are available at very low cost. For example NaCl (salt) is available in every 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.

To produce one ton of sodium carbonate, three tons of oil produce sufficient amount of lime and an excess amount of carbon dioxide and fuel oil. Three tons of oil shale will produce 400-420 kg of oil but only 265 kg will be required. A plant for the production of 250,000 tons of sodium carbonate from oil shale will save 34,000 tons of fuel oil.

To produce one ton of ammonium sulfate, the main materials required are shown in Table 2. Phosphogypsum is available in every amount at negligible cost in Aqaba as by-product of phosphoric acid production. Carbon dioxide and fuel oil are by-products from retorting and burning oil shale. Ammonia must be imported.

To produce one ton of potassium sulfate, the main materials required are shown in Table 3. Potassium chloride can be bought from the Arab Potash company. Ammonium sulfate is produced as shown above. Calcium oxide and fuel oil are products

Raw Materials

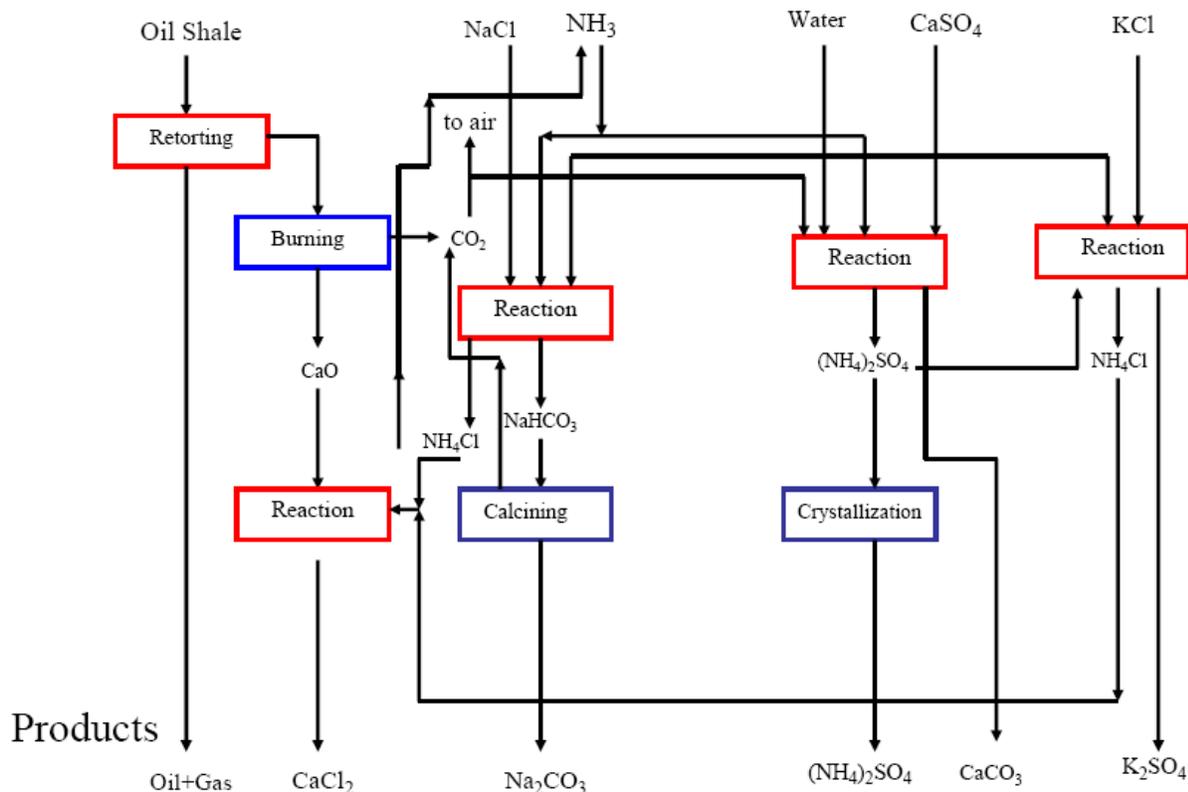


Figure 1: Utilization of oil shale in the production of oil, soda ash, potassium sulfate and ammonium sulfate (Al-Shyoukh, 1987)

from oil shale retorting and burning. Two tons of oil shale will be sufficient to produce amounts of carbon dioxide. Calcium

oxide and fuel oil required for the production of one ton of Ammonium Sulfate plus one ton of Potassium Sulfate.

Table 1: Materials and inputs for one ton of soda ash production

Item	Quantity
Sodium Chloride	1,740 kg
Limestone	1,250 kg
Coke	105 kg
Fuel Oil	265 kg
Ammonia	4 kg
Sodium Sulfide	2 kg
Water	24 m ³
Electricity	2.1 kWh
The Cost Of Steam Is Included In The Fuel Oil	40 bar : 2.7 ton 12 bar: 0.5 ton 2.5 bar : 1.8 ton

The production of 250,000 tons of ammonium sulfate and 250,000 tons of potassium sulfate requires the use of 500,000 tons of spent shale.

One can conclude that the spent oil shale plus other cheap raw materials available in Jordan can be transformed into valuable chemicals and fertilizers at low costs.

Table 2: Materials and inputs for one ton of ammonium sulfate production

Item	Quantity
Phosphogypsum	1,340 kg (30% excess)
Carbon Dioxide	340 kg
Ammonia	263 kg
Fuel Oil	150 – 200 kg (estimated)

Table 3: Materials and inputs for one ton of potassium sulfate production

<i>Item</i>	<i>Quantity</i>
Potassium Chloride	882 kg
Ammonium Sulfate	781 kg
Calcium Oxide (Lime)	350 kg
Fuel Oil	100 – 150 kg

Utilization of Spent Shale for Other Uses

Apart from the major use of spent shale and its role in major chemical industries, the utilization of the spent shale and/or its byproducts for other uses will be briefly outlined:

- Experimental tests on the spent shale indicate a very high efficiency 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.
- The spent shale may have commercial value when used, for example, as an ingredient in drywall type materials as is being pioneered in Europe. European efforts have already shown success in this area.
- 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.
- Electricity co-generation is a major byproduct. Most will be used onsite for retort energy and mining, while any surplus would be used for the production of construction materials and products.
- Some shale deposits contain aluminum oxide and perhaps other precious metals. Attempts are being carried out to investigate ways to extract such highly desirable ores.
- The potential for other byproducts exists. Many byproducts would not be

economically viable if the production was limited to just that byproduct. In conjunction with producing oil, however, the economics of production shift dramatically.

- 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 well suited as an asphalt additive. While pyridine is also used in vitamins and medicines, the asphalt additive is a high volume, proven, marketable product.
- 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 expectancy of the road surface is extended to approximately 20 years.
- Shale oil, produced by pressurized fluidized-bed hydro-retorting, was fractionated to produce shale oil asphalt additives (SOA). Three shale oil fractions boiling above 305 C° were added to standard AC-20 asphalt to improve pavement properties. The physical properties and aging characteristics of AC-20 asphalt binder (cement) containing SOA are similar to those of unmodified AC-20 asphalt binder. Asphalt pavement briquettes made with AC-20 asphalt binder containing 5 to 10 % SOA have superior resistance to freeze-thaw cracking and a greater retention of tensile strength when wet compared to pavement briquettes containing AC-20 binder alone (Rue and Roberts, 1992).

Conclusions and Recommendations

The following conclusions may be drawn from this study:

1. The focus on the production of oil from the oil shale will form a misleading indicator on the oil shale industry if the benefits from utilizing the spent shale were not taken into consideration.

2. Spent shale is an added value in the oil shale industry that employs surface retorting.
3. Three major industries are enhanced and developed: the production of soda ash, ammonium sulfate and potassium sulfate.
4. The spent shale could also be used in cement and building industry and construction products.
5. By adapting this model, carbon dioxide is no longer a problem for the environment. Most of the produced quantities could be used in the industrial processes as presented.

The following recommendations are outlined:

1. A small plant could be constructed to test, quantify and estimate the size and proportions of the products in a way to harmonize the input materials and the output products.
2. Other parameters could also be considered in connection with other energy demands such as power generation, water desalination in conjunction with other projects.
3. The feasibility study presented herein could be updated to account for current prices.

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