Possibilities for Oil Shale Development in Morocco

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INTRODUCTION

Morocco is among the world's leading countries in terms of total indigenous oil shale resources. Following the 1973 oil crisis, Morocco has been determined to develop its oil shale energy resource. In the subsequent years following the crisis, a tremendous number and variety of studies and research efforts have resulted in an enormous amount of data, covering geological, hydrogeological, mining, physical and chemical aspects of the two main deposits, Timadalat and Tarfaya. This article represents a tentative analysis of oil shale development in Morocco and offers a few means on where it might be heading.

Since 1981, data which were obtained from retorting and combustion tests, have served as a basis for eight major feasibility studies of industrial oil and electricity production projects by oil companies, oil-shale developers and power producers. The technical and economic feasibility studies of oil shale have shown that the selling price of shale oil burned, with a rate of return acceptable to investors, should range from 630 to $3.5 The commercial increase in future crude oil prices makes the potential oil shale projects more attractive. However, these temporary parameters cannot be neglected in a sole reason to move forward.

Given the present discrepancy between the price of petroleum and shale oil produced crude oil, one might be tempted to close the oil shale file. In fact, one might consider that realistically, the development of the industrial oil shale exploitation in Morocco could take place at least 30 to 30 years from now. However, a country like Morocco, which imports crude oil and coal to nearly more than 90% of its energy needs, cannot afford to discard the country's important oil shale resources from its energy agenda. An effort must be made to find a realistic strategy for oil.

Formational Mechanism of Framboidal Pyrite on Sulfur Surfaces

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INTRODUCTION

There has existed for some time, considerable controversy over the origin of framboidal pyrite. The word framboidal is derived from the French "frambouis" which means raspberry, and accurately describes the microscopic spherical pyrite aggregates which consist of minute crystals of nearly equal sizes. Several hypotheses have been put forward by previous researchers to explain the formation mechanism and raspberry-like texture. It has been suggested that framboidal pyrite is formed by replacement of fossil organisms, or fossilized bacteria, by crystallization of iron sulfide gel, due to the reaction between metahot spring water and "sulfur grains," which probably originated from sulfur bacteria. A suite of experimental studies succeeded in synthesizing spherical aggregates of minute pyrite crystals both at low (67°C) and high temperatures, which have essentially the same morphological characteristics as naturally occurring framboids. The latter studies positively demonstrated that the framboidal texture is not exclusively caused by the action of microorganisms.

Many U.S. coal and oil-shale reservoirs are sulfur-rich with pyritic sulfur dominating in most cases. Among the many types of pyrite in organic-rich sediments, framboidal pyrite are most understood. Fundamental studies on the origin and physico-chemical properties of framboidal pyrite can help support future applications of pyrite removal technologies in coal liquefaction and may contribute to a more comprehensive understanding of sulfur reaction kinetics during oil shale retorting processes.
Possibilities for Oil Shale, (continued)

shale development in Morocco. Knowledge and experience already acquired in this field, support the basic reason for or the advancement of this strategy.

Where does the investigation of the Moroccan oil shale deposits presently stand? Timahdit and Tarfaya oil shale deposits (Figure 1), which are the most important and the most studied deposits, contain 37 billion barrels of oil. Although they are obviously quite abundant locations, we should not stop there in our exploration of deposits. We must make an effort to study other deposits more thoroughly to appreciate their characteristics and particularly to judge their reserves and grade.

As a complete reserve investigation is impossible, due to financial constraints, the types of projects and production capacities to target is of primary concern. The production capacities considered in the project feasibility studies were quite large. For oil production studies have been performed, two of which were greater than 50,000 bbl/d in size. A 50,000 bbl/d production, which is considered a standard capacity for a commercial-size oil-shale project, represents more than 40% of the Moroccan national consumption today. In a study of electricity production, the 100-MW capacity, which was considered for the Timahdit power plant project, represents two-thirds of the total capacity installed in Morocco. With less than a handful of commercial-size oil-shale plants, Morocco could be completely energy self-sufficient. Such projects involve an enormous quantity of rocks, however, and necessitate a major investment. The existence of both technological and financial risks has created a road block to their development. To lessen the risk, the first projects should be of a small and easily controllable size, such as the 300 MT/d Brazilian Petrobras industrial module which was started in December. Only in this manner can an oil shale industry become a reality.

Promoting fluidized-bed reaction processes, presently in the development stage, will also require a pilot production-size or the order of 3,000 MT/d. Fluidized combustion processes, used for the production of electricity, are more developed and can be brought to commercial-size more quickly. Currently, they are used by industry to burn unconventional combustibles like refuse-derived fuel and are more acceptable to satisfying environmental constraints than conventional boilers.

The processing of oil shale generates by-products (e.g., within the case ofTimahdit and Tarfaya which have, in the case of Morocco, a real industrial and commercial importance. The retorting and combustion ash could be used for cinder production in the cement manufacturing industry. The utilization of these valuable by-product is what will make oil shale development worthwhile, and economically feasible in the future.

The encouraging result of the first studies by the Moroccan Public Laboratory for Studies and Tests on the use of Tarfaya oil shale in cement manufacturing, should motivate others to look at this option with interest, inasmuch as this use of ash cement manufacturing industry is already operational in other countries like Estonia, Germany and the United States. A cement plant, which would integrate a 20-MW oil-shale power plant for its energy needs, as well as make use of the combustion ash as an additive to the cinder, would have to be a very respectable size. A project of this type could serve as a demonstration and as an introduction to the use of oil shale for electricity production on a larger scale.

In feasibility studies of oil extraction projects, only the production of distillable liquids has been considered, but this involves scarce and costly hydrogenation methods. Alternative uses for the crude oil shale oil deserve attention because the economics for the production of a completely fuel-base product of shale oil from oil shale is simply not currently favorable. One approach is to fractionate the oil into light and heavy portions and to directly use the heavy ends as an asphalt product. With this approach, upgrading costs for the distillates are lowered, and the product would be smaller because the demand for asphalt is much lower than for transportation fuels. The point to consider here is, that with innovative approaches and the exploitation of niche markets, it is possible to initiate an oil shale industry on a modest scale in the near future.

Oil shale development in Morocco is in a promotional stage where the company in charge of the development of this raw material should be as involved as the potential users of the products of oil shale processing. Several state or private companies should then volunteer themselves and their resources for potential contributions in the many possibilities of oil shale utilization. Those companies which continue to import greater and greater quantities of crude oil, coal or sulfur, should play a pivotal role in oil-shale development. In addition, they should actively initiate and maintain oil shale research and development programs within their companies.

In summary, the first oil shale projects should be organized in a reasonably small scale and shouldn’t necessarily target an energy-based product as the final goal. The use of oil shale in cement manufacturing and building material seems to be a promising utilization at the technical as well as economic level. The future of oil shale projects is of course, bound to crude oil prices. However, the aspects of oil-shale development in Morocco were described in this article, demonstrate that the effort which has been made should be maintained so that Morocco could be, at the right time, up to the challenge of exploiting its oil shale resources.

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HYDROTHERMAL SYNTHESIS OF FRAMBOIDAL PYRITE

Hydrothermal synthesis of pyrite crystals resulted in the formation of spherical, raspberry-like aggregates of pyrite. The morphological characteristics of the pyrite microcrystals and their constituent individual crystals were investigated and a systematic comparison with natural frambooidal pyrite indicated close resemblances both in size and appearance.

The pyrite aggregates were synthesized from the system HCl + NaCl + H₂O + Fe₃O₄ + CaSO₄ + 5° in sealed silica capsules at temperatures between 150 and 350°C for periods of up to eight weeks. SEM (scanning electron microscope) investigation of the products revealed that micro-sized pyrite crystals typically coat the exterior of elemental sulfur droplets and frequently replace the entire droplet, which results in spherical pyrite aggregates. Elemental sulfur, however, was not added as reactant to the experimental system, but formed in situ of the reaction capsules from H₂S and SO₂ which were generated by the dissolution of pyrite (upon reaction with HCl) and anhydrite, respectively. Elemental sulfur recovered from the experimental product occurs in the form of droplets which formed due to the immiscibility of the sulfur liquid in the aqueous phase. After quenching of the experiments, the sulfur droplets consisted of monoclinic or orthorhombic crystals. Aggregates of variously-sized sulfur droplets typically formed clusters which are remarkably similar in their size-range compared to clusters of natural frambooidal pyrite.

The SEM study revealed the presence of small pyrite cubes embedded in the sulfur droplet surface, suggesting that pyrite crystals nucleate and grow on the sulfur surface. The SEM investigations further revealed that pyrite nucleation occurs where two or more sulfur droplets are juxtaposed. The early pyrite appears to originate within the sulfur droplet surface and a morphological variation from dendritic to polyhedral occurred with increasing run time and temperature. Although the grain size is approximately equal for pyrite crystals coating a given sulfur droplet, pyrite-crystal size typically varies among different sulfur droplets.

Experimental results suggest that there was a concentration of polysulfides at the surface of sulfur droplets, which was based on characteristic surface discolored areas. The outer shells of the sulfur droplets frequently varied in color from light to dark brown, whereas the interiors of the droplets are bright yellow. These surface colors closely resemble those that are typical for polysulfides of various chain length. Because pyrite crystals were typically observed in the neighborhood of the sulfur globule surface discolorations, it is proposed that nucleation and growth of pyrite crystals on elemental sulfur surfaces is started by the reaction between polysulfides with ferrous ions derived from dissolved pyrite crystals.

A potential mechanism for the enrichment of polysulfides in the surface layer of a sulfur droplet is the reaction of FeS with H₂S:

\[ \text{FeS} + \text{H}_2\text{S} \rightarrow \text{H}_2\text{S}_2 \text{O}_3 \]

The accumulation of polysulfides on sulfur surfaces can also be explained by the concept of equilibrium polymerization of sulfur at T > 150°C, which results in the formation of sulfur dinuclears. Polysulfides may form by reaction between sulfur dinuclears (RS₅-S-5R and H₂S₂O₃) from the experimental solution:

\[ \text{RS-S} \rightarrow \text{H}_2\text{S}_2\text{O}_3 \rightarrow \text{RS-S} \]

In order to form a pyrite nucleus within the sulfur surface, polysulfides need to react with ferrous ions from solution by:

\[ \text{H}_2\text{S}_2\text{O}_3 \rightarrow \text{FeS}_2 \rightarrow \text{FeS}_2 \rightarrow 2\text{H}_2\text{O} \]

However, since polysulfide species are only short-lived, especially at elevated temperatures, the probability of forming a pyrite nucleus increases with the number of polysulfides available at sulfur droplet surfaces. This study suggests that the relative concentration of polysulfide species in the experimental system must be highest at the junction of juxtaposed sulfur droplets (Figure 1). Indirect evidence was furnished by SEM observations which demonstrated that preenamel sites for pyrite nucleation and growth occur mainly where two or more sulfur droplets intersect (Figure 2).

This study proposes a growth model for frambooidal pyrite on sulfur droplet surfaces. The model requires that sulfur surfaces act as nucleation sites for pyrite crystals and involves three steps. Step 1 represents a sulfur droplet surface enriched in polysulfides of various chain length. Step 2 is the nucleation of pyrite crystals within the polysulfide-rich surface layer of a sulfur droplet; and step 3 suggests that numerous pyrite nuclei form simultaneously on a sulfur droplet.
Framboidal pyrite, (continued)

surface and grow at equal rates. The correspondence of the grain size of the individual pyrite crystals, while the contour of the sulfur droplet governs both shape and size of the spheroidal framoid (Figure 3). The growth model explains the spherical texture and the uniform grain size of the pyrite crystals, which are two main characteristics of a framoid. The accumulation of individual spheres into groups, which further distinguishes natural framoids, may be accomplished by the inclination of liquid sulfur droplets to form clusters due to their hydrophobic character in the aqueous phase.

Sulfur droplets in the experimental study are extensively permeated with micro-cracks. The formation of micro-cracks probably occurs upon cooling during the polymorphic transformation of monocrystalline to orthorhombic sulfur which is accompanied by a density increase from 1.94 to 2.04 g/cm³. The presence of shrinkage-cracks was observed during SEM examination at the surface layer of synthetic and natural framoids, thus resembling the surface texture of sulfur droplets in the experimental study. The cracks in the framoidal surface may be interpreted as indirect testimony for the presence of sulfur in the immediate vicinity of the crack.

The formation mechanism of front-salal pyrite introduced in this study neither requires the presence of sulfur bacteria, micro-organisms nor the presence of iron-sulfide gels which were frequently utilized in previous studies to explain framoidal pyrite formation.

Paramagnetic resonance spectra were obtained from liquid sulfur at hydrothermal temperatures. The paramagnetism, which increases at lower temperatures, provides direct confirmation for the existence of long-chain sulfur polymers. The heat of solution of a sulfur-sulfur bond was found by previous researchers to be 33.4 ± 4.8 kcal/mole. To extrapolate the framoidal growth model introduced earlier to low temperature sedimentary environments where elemental sulfur typically occurs as crystalline orthorhombic sulfur S₈, rings instead of sulfur polymers, at low-temperature mechanisms has to exist that favors the formation of sulfur droplets with polysulfides at the droplet surfaces. A mechanism to form liquid sulfur at ambient temperatures may be available in the presence of sulfur bacteria. This hypothesis was introduced by Professor Steudel at the Technical University of Berlin. Dr. Steudel suggests that sulfur globules form extracellularly by Thiothrix pneumoniae. These sulfur globules consist of S₈ and small amounts of S₂, S₃ and S₄ which impede crystalization, as in globules of supercooled liquid sulfur. Although log choć polynuclear atomic low were detected chronographically at the

New IEA Coal Research Publication Available from the Center for Applied Energy Research

Emission Standards Handbook: Air Pollutant Standards for Coal-Fired Plants
Hermine N. Bruch

This handbook includes current and proposed emission standards for particulates, SO₂, and NOₓ from coal-fired plants. Emission limits for other pollutants are included where known.

Covering 21 countries, the handbook includes legislation in the EC countries, the fourteen IEA Coal Research member countries, two East European countries (Poland and Czecho-slovakia) and other countries, both in Taiwan, which have introduced or plan to adopt, relevant emission standards. Several international agreements and standards are also discussed and explained.

The energy-related materials research group is fortunate to have Dr. Vincent Vergheen of the Coal Corporation of Victoria at the CAER as a Visiting Scientist, from July to December, 1992. Dr. Verheijen has experience in the extraction and chemical activation of brown coal using KCl. His expertise will be a valuable asset to current projects.

Dr. Moody Shinar, Assistant Director of the Geological Survey of Israel, has also joined the CAER as a visiting scientist for the next four months. He is working with the Resource Applications and Technology group on the Coolidge Waste Management project.
COMMENTARY

OIL SHALE: A SHINING LIGHT IN THE ENERGY MORASS

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The United States should be interested in generating fuels or chemical feedstocks from oil shale. Why? For all of the reasons that have existed for years:

- U.S. and world petroleum resources are fast becoming depleted.
- Need for U.S. oil shale resources could replace petroleum as a strategic material.
- Oil shale production could replace oil from foreign oil prices.
- New industry could provide dometic jobs.
- A new source of domestic energy production could improve the import/export balance.
- Revenues developed from oil shale utilization could help reduce the deficit.

The U.S. has been striving to develop synthetic fuels from oil shale for more than 70 years and has yet to build a commercial operation. It is inspiring therefore that there is a core group of people in business, government and academia who are still interested in working toward a commercial venture. Some would call these people visionaries. Whatever is driving them, we can only hope that it will continue to motivate them until they have accomplished their goal.

While other countries are investing in synthetic fuel development, U.S. government support for research and development of domestic oil shale resources has waned and may not survive the FY '93 budget cycle. This was an aggressive program that started in the Western U.S. with resource definition of large reserves, resource characterization and process development. A more recent development is the work on Eastern oil shales which has defined a vast resource and developed a process technology to address the special physical and chemical characteristics of these shales.

Since 1981, a group of scientists has been meeting annually in Lexington, Kentucky, to share with each other, and any others willing to listen, their oil shale research. This meeting was originally sponsored by the Institute for Mining and Minerals Research and later joined by the Kentucky Energy Cabinet, the U.S. Department of Energy and most recently by the Center for Applied Energy Research. In recent years, the oil shale researchers were joined by those interested in tar sands and heavy oils. The papers presented at the annual meetings are published in a proceedings each year, and for the last five years, U.S. Department of Energy funds have helped defray the printing cost of the proceedings.

I have been impressed with the dedication, the intensity and the tenacity with which the technical organizing committee addresses their responsibility to select papers for each symposium. This year, as in past years, they have met twice to select papers for the upcoming meeting in November. This year the participants will be treated to a special keynote speaker, Dr. Ian McMurtie from Sydney, Australia who is Chairman and Managing Director of Southern Pacific Petroleum N.L. He spoke to the group in 1984, and his enthusiasm and keen insight into the oil-shale business were well received, and perhaps he was part of the motivation that has helped keep this group of 80 highly focused people together all these years. In his last presentation, Dr. Ian estimated that it would take the U.S. 16 to 17 years to produce a million barrels of oil a day from the Eastern U.S. oil shale reserves; unfortunately, we did not make the proper investment required at the time to achieve this level of production.

The same economic and intellectual barriers are still present - plentiful and low priced oil on a global market and short-sighted people in the private and public sector. The Eastern Oil Shale Symposium remains a shining light in the world energy morass. You are invited to come and join us in November to be a part of the light.

STONE AND LIME FOR SO CONTROL IN THE OHIO VALLEY

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This meeting will provide technical information for stone and lime producers, utility-scrubber planners and operators, government planners and policy makers.

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1992 Eastern Oil Shale Symposium
November 17-20, 1992
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Framboidal pyrite (continued)

surfaces of bacteria-produced sulfur globules, it is conceivable that under more reducing conditions, polysulfides are stabilized at sulfur-surfaces, making the droplets hydrophilic. The hydrophilic sulfur globules, or micelles, are likely to be surrounded by a hydration sheet in which ferrous ions are present. To test this hypothesis, the author is presently preparing sedimentary framboidal pyrite to be investigated with a proton microprobe "PIXE" having a special resolution of 1-μm. PIXE measurements are expected to provide information on the Fe/S ratios of the framboidal core. If a framboidal formation mechanism involves sulfur droplets, one would expect to find some framboid centers to be highly enriched in sulfur. This research is planned in cooperation with UK Chemistry Professor David Robertson, who has a joint faculty appointment at the Center. The results of this test will be presented at the Eastern Oil Shale Conference held in Lexington, Kentucky in November.

Dr. Graham received her Ph.D. from The Pennsylvania State University and has been a researcher at the CAER since 1991.

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