OIL SHALE

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Summary

Oil shale consists of solid organic polymerized matter called “kerogen” and a smaller percentage of bitumen, both embedded in an inorganic mineral matrix. Oil shale originated from planktonic organisms from ancient ages.

Oil shale deposits are abundant and occur in many countries, such as the USA, Brazil, Russia, China, Australia, etc. Oil shale deposits are either aboveground or underground (mined).

The kerogen content and its characteristics differ between oil shale deposits.

Oil shale can be retorted for producing shale oil. Depending on the shale oil composition, shale oil can be upgraded to obtain liquid fuels, such as in is done in China and USA; shale oil can also be processed to produce other chemicals, as in Estonia and Russia. Different kinds of retorts for pyrolysis of oil shale have been developed.

Oil shale can be burnt in boilers to produce steam and electric power, such as in Estonia, Israel, and Germany. The shale ash formed can be used for making cement and brick, and also for agricultural utilization.

Besides the environmental impacts, the economic problems are the main factor influencing the development of the oil shale industry. In future, when crude oil prices rise much higher, the oil shale industry may have a chance of development in the world.

1. Introduction

Oil shale is defined as a sedimentary rock, that contains solid, combustible organic matter, commonly called "kerogen", and portion of bitumen, embedded in an inorganic mineral matrix; the kerogen is insoluble in common organic solvents.

Oil shale is a kind of solid fossil fuel. As a source of energy, it can be used for producing shale oil on heating, due to the thermal decomposition of kerogen. The shale oil can be upgraded to produce liquid fuels; oil shale can also be used for producing steam and electricity on direct combustion.

Other names given to oil shale throughout the world are: algal shale, bituminous shale, black shale, cannel shale, carbonaceous shale, coaly shale, cooronite, gas shale, kerogen shale, kerosene shale, kukersite, maharahu, organic shale, tasmanite and torbanite

Oil shale has the following characteristics:

- It is usually a fine-grained, non-porous solid, frequently showing bedding, with a laminated structure. Oil shale has a color from light gray to dark brown.
- It normally contains fewer organic and more inorganic substances than various types of coal.
- The organic contents of oil shale often accounts for less than 35% of the total mass, whereas coal usually contains more than 75% organic substances in terms of dry material.
- The organic matter in oil shale is predominantly kerogen, insoluble in common organic solvents; the minor component is bitumen, soluble in organic solvents, generally not exceeding 1–2%.
- When oil shale is heated, in the absence of air or oxygen, to 400–500 ^{o}C, known as retorting of oil shale, the kerogen is pyrolyzed to produce shale oil, a gaseous product, with solid carbonaceous residue, and small quantities of decomposition water; the carbonaceous residue is obtained in a mixture with the heated inorganic minerals of the original oil shale.
- The molar ratio of hydrogen to carbon of the kerogen in the oil shale is higher than that of the organic component of coal; the retorting of oil shale normally yields a higher amount of oil than the pyrolysis of coal, based on the equivalent amount of organic material.
- Oil shale is quite different from tar sand. The organic substance of tar sand is bitumen, which can be extracted and separated from tar sand by using a hot alkaline aqueous solution, while the kerogen in oil shale cannot be extracted by the same process due to the macromolecular polymerized three-dimensional structure of kerogen.

2. Resources

Oil shale deposits occur widely throughout the world. In some countries, oil shale resources have been evaluated in detail, but in many countries resources are investigated very little, sometimes only a rough estimation has been published. In some countries, no any information about their oil shale resources exists. Further, an accurate compilation of the world's oil shale is hampered by lack of common terminologies in reporting the oil-yield value of the oil shale and in defining known resources, recoverable resources, total resources, marginal and submarginal resources, reserves, proven reserves, total reserves, etc. However, it is reported that as a solid fossil source of energy, the organic matter of the world's oil shale deposits is second in abundance, only to coal; and as a source of liquid fuel, the world's shale oil reserves calculated from known oil shale deposits are higher than world's known crude oil reserves.

The world's top ten countries with the most plentiful shale oil resources known are as follows, in billion tons:

- USA: 280
- Brazil: 112
- Russia: 48
- China: 26 (proven: 1.8)
- Australia: 25 (recoverable: 4)
- Morocco: 14
- Zaire: 14
- Canada: 12
- Jordan: 5
- Estonia: 4 (recoverable: 1)

3. Origin and Formation

3.1 Origin

It is believed that planktonic organisms such as algae are the main source materials for oil shale. Among the algae, Cyanophyceae, Chlorophyceae, Xanthophyceae are the most important ones. Besides these, unicellular protozoe and other organisms of the animal kingdom, such as worms, mollusks, etc., as well as some higher aquatic plants, are also source materials. The remnants of higher terrestrial plants brought in by winds and water currents, such as plant tissue fragments of spores, pollen, cutin, etc., may also be contributors to kerogen formation. It is interesting to mention that most geologist have recognized that petroleum and oil shale may originate from the same source materials, i.e., organic matter of lower plants and animals, and kerogen is the precursor of petroleum. It is also worthy to point out that, unlike oil shale, coal (lignite, bituminous coal, and anthracite) originates from higher plant tissue.

3.2 Formation

The formation of oil shale is as follows. In an ancient age, algae and other planktonic organisms flourished in fresh water lakes, saline lakes, or coastal strips of shallow sea. Perished organisms settled to the bottom of the water body. Some spores and pollen may also be carried into the water. These organic matters underwent a long period of biological action in an oxygen-deficient still-water bottom and turned into jelly-like algal ooze, and it changed gradually into sapropel under the action of anaerobic bacteria. In addition to organic matter, larger amount of inorganic matter, such as clay, mud, and sand, were also carried by flowing water and deposited along with the dead organisms. Sapropel underwent chemical changes under the oxygen-free condition in increased burial depths, along with inorganic matter, forming sapropelic rock; it is usually called oil shale, when the inorganic matter content is higher.

3.3 Age of Formation

The geological age of formation of oil shale deposits in the world covers from the Cambrian to Tertiary Period. Among them, the lower Silurian, Carboniferous, Permian, Triassic, and lower Tertiary are the most important ones. The formation of oil shale deposits requires a stable environment. During this period, the tectonic movement was relatively stable, so it was favorable to the formation of oil shale.

3.4 Environment of Formation

According to the aquatic environment where oil shale deposits were formed, oil shale is divided into three kinds: swamp, lacustrine, and marine formed; or simply, lacustrine and marine formed. Chinese Fushun and Maoming oil shale are of lacustrine origin; American Green River oil shale is also lacutrine; Estonian and Russian Kukercite oil shale are of marine formation.

Oil shale usually exists alone, but sometimes it is in coal- or in oil-bearing basins. For example, Fushun oil shale layer lies on the coal deposit.

3.5 Classification of Kerogen

In the broader sense, from the point of view of geochemistry, kerogen is divided into three types:

- oil shale kerogen and sapropel kerogen belong to type I, it has higher H:C mol ratio and originates from lower animals and plants;
- organic matter of humic coal (peat, lignite, bituminous coal, and anthracite) belong to type III, which has lower H:C mol ratio and originates from higher plant tissue;
- the kerogen type II is the mixed type, i.e., sapropelic and humic mixture.

4. Mining

If oil shale is to be used in a surface retorting plant, or in a power unit, it must be mined and transported to these plants. Mining costs constitute a major share of the total production costs, either for shale oil production, or for power generation. Just like coal, there are two mining methods: underground mining, and aboveground mining. Generally speaking, the oil shale with a gentle slope and thin overburden are suitable for aboveground mining, and the other cases are suitable for underground mining.

An important factor determining the technical and economic feasibility of aboveground mining is the stripping ratio, that is the overburden to be excavated in cubic meters for one ton of oil shale exploited. In general, aboveground mining has the following advantages over underground mining: shorter construction time, lower production cost, less oil shale loss, higher efficiency, safety in operation, easy production of associated minerals. Its disadvantages are: vulnerability to climate changes, occupation of too much land, large capital construction in the case of thick overburden.

4.1 Aboveground Mining

The most important aboveground methods are: open-pit and stripping mining. These methods are employed for mining oil shale in Estonia, China, Brazil, etc.

4.1.1 Open Pit Mining

In an open pit mine, the overburden is stripped off and hauled away to the waste dump in the voided part of the mine by trucks, pit railways, or belt conveyors. The exposed shale is then mechanically excavated and hauled off. The type of equipment used depends crucially on the geology and mechanical properties of the shale and overburden. Soft materials are conveniently removed by bucket-wheel excavators, whereas hard rocks require power shovels and scrapers and possible blasting.

4.1.2 Strip Mining

Strip mining employs dragline excavators that are shifted only rarely from one location to another. They discharge the excavated overburden promptly by swiveling the full bucket from the trench-like digging area to the dumping area. Therefore no overburden hauling facilities are required. Shale is excavated from a strip mine in the same way as from an open-pit mine.

4.2 Underground Mining

4.2.1 Room-and-Pillar Mining

The room-and-pillar method is suitable for conveniently accessible deposits with considerable thickness. Part of the oil shale is taken out in such a way that many underground empty rooms of regular shape are formed; the remaining shale is left in place as pillars between these rooms to support the overburden.

The pillar-and-room sizes depend upon the physical properties of overburden and oil shale. This method is widely used for ore and coal mining, and has also been employed in oil shale underground mining, such as in United States, Australia, and Estonia.

The advantage of this method is that large power shovels, loaders, and hauling equipment can be used underground. However, usually about 75% of the total oil shale can be mined, whereas about 25% must be left in place as supporting pillars.

4.2.2 Longwall Method

Longwall mining is an older method, which was used in a few oil shale underground mines. Typical face lengths are 85–90 m. To facilitate mechanical cutting along the face, holes are to be drilled, and explosives used. A lot of manual work is required to load the material, advance the conveying system, and support the roof. (For more detail about oil shale mining, see *Mining of Oil Shale*.)

5. Properties and Composition

5.1 Physical Properties

5.1.1 Color and Appearance

The colors of oil shale around the world are different from different deposits. US Green River oil shale is dark brown; Estonia oil shale is gray; Chinese Maoming oil shale has a color from gray to yellowish brown; Fushun oil shale is light brown to dark brown. The color of oil shale depends primarily on the color of the organic matter, but sometimes it is also affected by the presence of disseminated inorganic matter, such as pyrite. Black shale often contains coal materials, for example, some of Fushun oil shale contains black bituminous coal particles. For the same deposit, the oil shale with higher oil yield is usually of a darker color. Newly mined oil shale usually has a dark color, and it becomes lighter in storage.

Discrete layers are often found in oil shale, and many shales are brittle and easily cleave along the laminate boundaries. Some oil shales are very hard and compact. although a stratification pattern can be recognized.

5.1.2 Density

The specific gravity of oil shale depends mainly on the amount and specific gravity of its mineral matter. The specific gravity of kerogen oil shale, is generally of the order of 1.0, while that of the total mineral matter varies from 2.3 to 2.8, (e.g., 2.6 for quartz and feldspar) and 5.0 for pyrite. Typical specific gravities of oil shale:

- US Green River oil shale: 1.77–2.08
- Estonia Kukersite, 1.73–2.05
- Brazil Erati, 2.3
- China Fushun, 1.9–2.2
- Maoming, 2.1–2.4
- Germany Dotternhausen, 2.2

5.1.3 Hardness and Strength

The hardness and strength of oil shale generally depend on the properties of the mineral matter presented and the geological condition of its formation. Usually the oil shale formed in older geological ages has greater hardness. The oil shale hardness and strength affect the power consumption and machinery wear during mining and crushing, and are also related to the formation of small lumps and fines. Also, when shale lumps with a very low thermal strength are pyrolyzed in a common vertical retort, they cause fracture into small pieces, which results in an increase in gas flow resistance, and uneven distribution of gas and solids, thus giving operation trouble and a lower oil yield.

Fushun oil shale is harder with a greater thermal strength; Australia Rundle, Brazil Irati, US Green River are the next; Maoming oil shale is of poor thermal strength, which is prone to forming small pieces in retorting, with attendant operation trouble; Estonia Kukersite shale contains much calcium carbonate which decomposes into powder when the shale is burnt for boiler use.

5.1.4 Specific Heat

The specific heat of oil shale directly affects the heat required for retorting. Its value differs from different oil shales, even differs from different temperature ranges; for Fushun oil shale, average specific heat: 0.98 kj kg^{-1}/^{o}C (20–200 ^{o}C); 1.26 kj kg^{-1}/^{o}C (20–800 ^{o}C).

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Bibliography

Allred V. D. (1982). *Oil Shale Processing Technology,* 230 pp. Englewood, New Jersey, USA: The Science Press, Center for Professional Advancement. [Presents the oil shale retorting processes in the world.]

Cherepovsky V. F. (1988). *World's Oil Shale Deposits,* 263 pp. Moscow, Russia: Science Press. [Presents the oil shale deposits, resources and characteristics in the world.]

Gary J. H., ed. (1964 to 1992). *First Oil Shale Symposium Proceedings to Twenty fifth Oil Shale Symposium Proceedings,* Golden, Colorado, USA: Colorado School of Mines Press. [This symposium series presents representative works on the world's oil shale during its publication period.]

Hou X. L. (1986). *Shale Oil Industry in China,* 257 pp. Beijing, China: Hydrocarbon Processing Press. [This book, written in English, describes the oil shale activities in China.]

Kann J., ed. (1984 to 1999). *Oil Shale,* Vols 1–16. [This journal presents oil shale papers and is the only journal in the world specially dealing with oil shale research and development, published by the Estonian Academy Publisher.]

Qian J. L. (1998). Oil Shale. *Chemical Technology Encyclopedia.* 19 (ed. G.R. Chen), pp. 63–80. Beijing, China: Chemical Industry Press. [This article is written in Chinese.]

Piper E. M. (1996). Oil Shale. *Encyclopedia of Chemical Technology,* 4th edition. 17 (ed. Kirk-Othermer), pp. 674–701. New York: John Wiley and Sons. [This article describes the world's oil shale activities.]

Rudina M. G. (1988). *Handbook of Oil Shale Processing,* 256 pp. Leningrad, Russia: Chemistry Press. [Presents the oil shale retorting processing in the world, mainly in Russia and Estonia.]

Weiss H. J. (1991). Oil Shale. *Ullmann's Encyclopedia of Industrial Chemistry,* 5th edition Vol. A18. (ed. Barbara Elvers), pp. 101–125. Weinheim, Basel, Switzerland: VCH. [Describes world's oil shale activities.]

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