Gaseous and Particulate Emissions from Shale Oil Operations

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World-wide and domestic demands for hydrocarbons tend to seek the most economical and convenient sources for potential exploitation. It has been said that the oil shale deposits of the world constitute many times the total of the world's reserves of liquid petroleum. The oil shale beds of some 16,000 square miles in the states of Colorado, Utah, and Wyoming constitute the world's greatest reserve of hydrocarbons.[1] It is only a question of time until these sources will be used.

President Johnson, in his state of the union message of January 4, 1965, made this pertinent remark, "... we will seek power to prevent pollution of our air and water before it happens...", a statement that emphasizes the national feeling at this time. None of the recent, comprehensive papers [2,3,4,5,6,7] on shale oil technology mentions or alludes to air pollution. In a paper delivered to the Second Symposium on Oil Shale at Golden, Colorado, on April 22, 1965, Frank J. Barry, Solicitor, U. S. Department of the Interior, mentions air pollution as one of the factors to be considered in a national policy for oil shale.[8]

The deposits in the Piceance Basin of Colorado, being the most economically attractive in the United States, will likely be the location of the first commercial oil shale plant. The major patented oil shale mining claims owned by some 25 companies, where the shale industry will likely begin, lie mostly on the southern part of the Piceance Basin and cover an area of approximately 800 square miles. The shale oil reserves in this area, containing 25 gallons of oil per ton of shale or more, contain approximately 55,000 million bbls.

The Piceance Basin lies between the Colorado and White Rivers, which are approximately 50 miles apart. Both rivers flow in a generally western direction. The elevation of the Colorado River at this point is approximately 5000 ft., and of the White River, approximately 6000 ft. Between the two rivers the land forms a plateau (see Figure 1) having an elevation of 7500 to 8500 ft.; this plateau is cut by numerous gulches running generally north and south.

The so-called "mahogany" ledge or rich oil shale strata on the southern part of the Piceance Basin varies from 50 to 100 ft. in thickness, generally has 500 to 1000 ft. of overburden, and lies from 1500 to 2000 ft. above the Colorado River valley. To minimize transportation costs, the crushing and retorting plants probably will be located near the mine portals and near the mahogany ledge, with waste dumped into the gulches.

Precipitation in the area is only 10 to 15 inches of water per year, with over half of the moisture falling as snow. Mean daily air temperatures on the plateau vary from approximately 0°F to 70°F, with an average relative humidity of about 20%. The prevailing winds in western Colorado are from the southwest and would tend to carry any pollutants from a shale industry up out of the valleys toward the Rocky Mountains; the topography of the area indicates that temperature inversions probably occur during certain times of the year. These, of course would be conducive to pollution of the air at the processing sites.

Properties of Shale and Oil

The inorganic matrix of Colorado oil shale is a laminated marlstone intimately mixed or "cemented" together with kerogen, a high-molecular-weight waxy material. When retorted at temperatures in the range of 900°F, oil and gases are given off in the vapor phase. Recent studies[9] have shown the following average individual particle-size distributions of the inorganic matrix: less than 0.3 wt %, 200-2000 microns; 8.3 wt %, 20-200 microns; 75.8 wt %, 2-20 microns; and 15.8 wt % less than 2 microns. The retorted shale, of course, does not disintegrate into this size distribution, since it still has a certain amount of mechanical strength. Depending upon the retorting process, the retorted shale ash may or may not be partially fused.

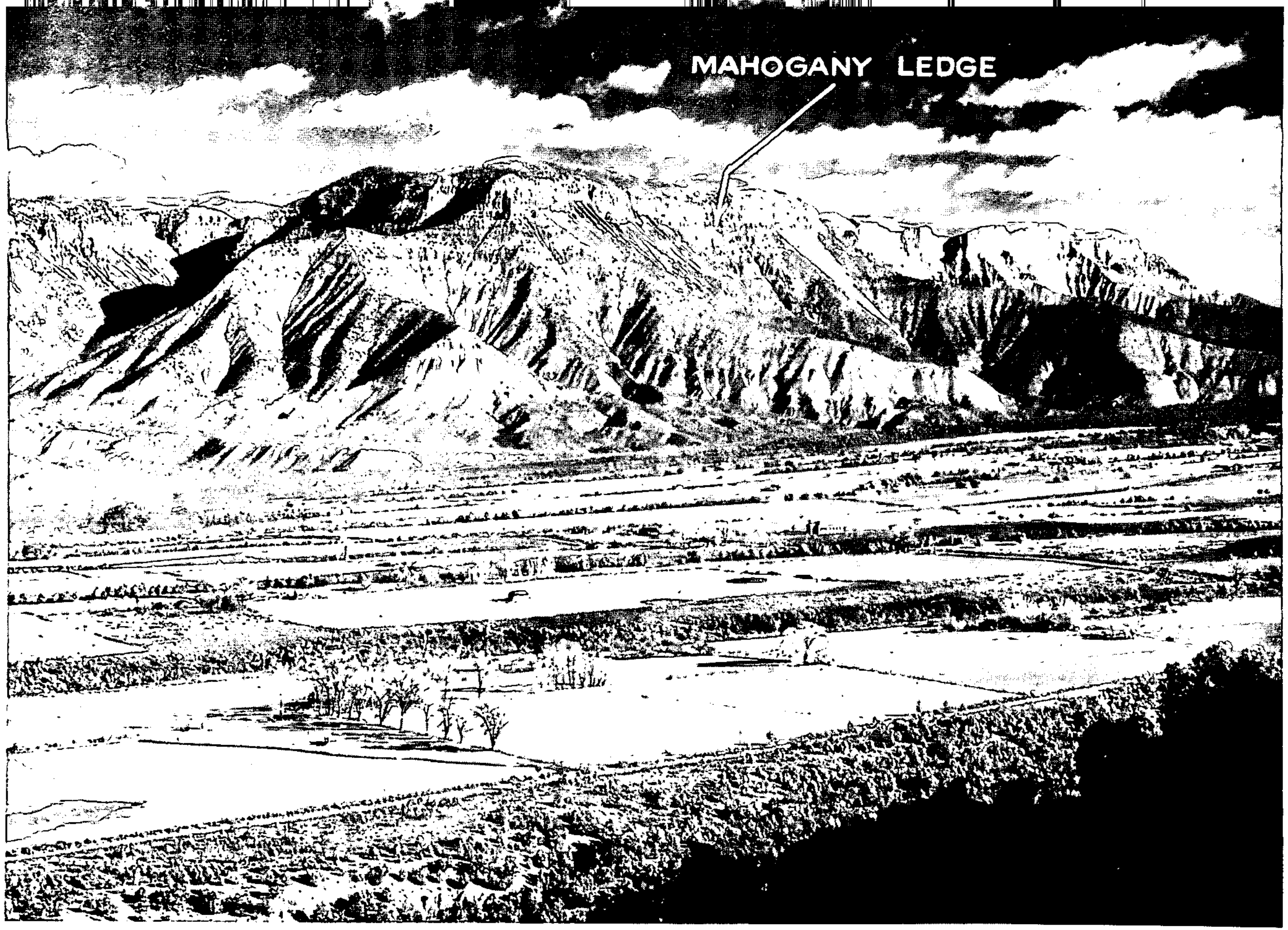

Figure 1. Photograph of the southern part of the Piceance Basin oil shale cliffs with the Colorado River Valley in the foreground.

The average ash analysis of the inorganic matrix in Colorado shale is shown in Table I. Depending upon the retorting process and the

Table I

	Wt %
SiO_2	42.1
CaO	23.8
MaO	12.5
Al_2O_3	10.0
Fe_2O_3	4.3
Na_2O	3.1
K_2O	2.3
SO_3	2.0

temperatures involved, the retorted shale ash will contain carbon up to a maximum of approximately 4%, and a part or all of the calcium and magnesium oxides may be in the form of calcite or dolamite.

Table II shows the approximate composition, on an air-free basis, of a retort gas produced from a shale yielding 30 gal/ton. The volume of gas produced will be approximately 500 ft.^{3}/ton of shale, depending upon retorting conditions.

Table II

	Volume %
Methane	17.5
Ethane	7.0
Propane	3.4
N- and Iso-butane	1.7
Pentanes	0.7
Hexanes	0.3
Ethylene	2.2
Propylene	2.6
Butenes	1.9
Pentenes	1.1
Hexenes	.9
Heptenes	.2
Carbon Dioxide	30.3
Carbon Monoxide	2.0
Nitrogen	2.0
Hydrogen	23.9
Hydrogen Sulfide	2.3

If the hydrocarbons contained in the kerogen of the shale were accompanied by amounts of impurities similar to those of liquid petroleum, there would be no occasion for extra interest or concern with respect to air pollution.

The detailed chemical structures of shale oil are largely unknown. In general, however, it is an oil of approximately 20° API gravity with a pour point of 80-90° F, containing 1.6 to 2.2 % nitrogen, 0.6 to 0.8 % sulfur, and 1.5 to 2.0 % oxygen.[10] Cady and Seelig[11] have shown that shale oil consists of 39% hydrocarbons (many of which are unsaturated) and 61% non-hydrocarbons; of these non-hydrocarbons, 60% are nitrogen compounds, 30% are oxygen compounds, and 10% are sulfur compounds.

The recovery of useful hydrocarbons from oil shale could result in air pollution from five main operations: (a) mining and crushing, (b) retorting, (c) disposal of spent shale, (d) refining, and (e) power generation.

Mining

The shale must first be mined and crushed to proper size for the retorts. One need only be reminded that for a 25,000 bbl./day operation approximately 35,000 tons of 30 gal./ton shale must be mined and crushed each day.[12] Such operations as drilling, blasting, conveying, and crushing all produce dust. With modern mining techniques and proper precautions the dust problems can be controlled.

Retorting

More than 2000 patents have been issued for various shale oil recovery methods.[13] The only industrially successful ones to date involve the destructive pyrolysis of the crushed oil shale at atmospheric pressure and at temperatures of about 900°F. The severity of air pollution from the retorting operation will naturally depend upon the type of retorting process used. Any type of retorting operation could result in emissions of complex compounds of nitrogen, sulfur, oxygen, hydrogen, and carbon and inorganic dust. It is unlikely that the low-molecular-weight retort gases (shown in Table II) would be vented or flared to the atmosphere, since economics will dictate that they be either recovered or used for process heat or power generation. Since the retorting operations will be confined to the immediate vicinity of the mines, without proper design and precautions large quantities of vapors could concentrate in the deep valleys and canyons rather than dispersing harmlessly at the higher altitudes. The area could also be subject to severe temperature inversions conducive to the accumulation of pollutants.

Although several companies are actively working on in-situ recovery of shale oil, essentially nothing has been published on the subject. The problems of in-situ recovery of shale oil are formidable, and it is most probable that a U. S. oil shale industry will begin with the more advanced above-ground retorting processes. In any case, air pollution problems in connection with in-situ recovery of shale oil would likely be akin to those associated with in-situ recovery of crude petroleum.

Disposal of Spent Shale

Since processing 35,000 tons/day of raw shale will require disposal of approximately 28,000 tons/day of spent shale ash, more than a small problem in materials handling will be involved. The canyons and dry gulches of the shale region should provide adequate space for disposal of shale ash. It is also conceivable that the waste could be returned to the mine from which it was originally removed. This procedure, of course, would preclude mining of lower levels in the future. Depending upon the particle size of the shale ash, the temperature of disposal, and the carbon content, the problems of dusting could vary widely. If shale ash containing appreciable amounts of carbon were dumped at an elevated temperature, a severe problem might arise if combustion started; the subsequent production of hot spots might release SO_2 from the small amount of pyrites in the shale. On the other hand, a well-burned shale ash will contain considerable amounts of calcium and magnesium oxide, which will recarbonate and hydrate over a period of time and stabilize the spent shale ash. In some cases, soil stabilization techniques may be required. Also, vegetation such as sagebrush and native grasses can be planted on the abandoned dump areas to minimize dusting.

Refining

The oil as recovered from most retorts "is a waxy, intermediate gravity, high nitrogen, and intermediate sulfur crude."[14] The decision whether this oil is to be transported to more populated areas and refined or is to be refined near the retorts may determine the nature of the refining techniques. Generally, these oils must first be made wax-free or cracked to lighter fractions before transmission through pipelines. The fractionation, cracking, and refining of these oils present problems different from those of processing normal petroleum crudes. At this stage the processes can be engineered to recover much of the sulfur as elemental sulfur and most of the nitrogen as ammonia. Also, sophisticated techniques can be used to produce useful chemicals containing nitrogen or sulfur. In any event, the opportunities for air pollution are always present and will offer a challenge to the chemical or petroleum engineer. The economic disposal of these products could be of great interest; their release to the atmosphere would be out of question.

Power Generation

Considerable quantities of power will naturally be required for any sizeable oil shale industry. Depending upon the economics, this power will probably be produced at or near the shale industry sites. The pollution problems will be typical of those in the power industry and will depend upon the fuel used, i.e., retort gases, refinery gases, fuel oil, or other fuel.

The vast shale oil industry is nearly upon us as the problems of finding new economical sources of liquid petroleum are becoming more acute. The next 5 or 10 years could see the emergence of shale oil industry producing a million or more barrels a day in this small area of the Rocky Mountains. Any ripples of unfavorable prices on imported crude or finished products could cause abrupt waves of decision as to the time of arrival of this industry. It is hoped that all operations involving a future shale oil and industry will take cognizance of the potential air pollution problem. To disregard air pollution at the early stages of development may require later intensive and extensive engineering at a much higher cost.

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