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OIL SHALE HEALTH AND ENVIRONMENTAL RESEARCH*

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INTRODUCTION

The orderly development of alternative energy resources requires an understanding of all of the associated costs. The impact on health and environment is one of the more important considerations because of the limitations that may be imposed if significant adverse effects result or cannot be mitigated. As far as possible, control requirements should be determined prior to large scale utilization in order to minimize the necessity for retrofitting and to avoid later discovery of health problems and the attendant need for compensation.

Several distinct technologies will be utilized to recover shale oil from the Green River formation (1). Each approach offers distinct and, in some cases, unique occupational health considerations requiring site and technology-specific biological/toxicological experimentation. The United States Department of Energy, through the Oil Shale Task Force established by the Assistant Secretary for Environment, is conducting occupational health and toxicological studies in conjunction with the development of the various technologies.

Industrial Hygiene Studies

Most recovery processes currently under consideration will require underground mining and processes involving surface retorting also require crushing to aid transport of the shale and to provide consistant processing results. Samples have been collected during mining operations at various locations in an effort to characterize potential occupational exposures.

Dust exposure is frequently encountered in mining operations. Two sampling methods are routinely used to determine the concentration of airborne dust and standards are expressed in terms of these sampling methods. Total airborne dust is determined by drawing the sample through a high efficiency filter, collecting all particles carried by the air flow. Dusts encountered in most mining operations are classified as mineral dust and the threshold limit value (TLV) is stated as

$$\frac{30\ \mathrm{mg/m^3}}{\%\ \mathrm{quartz} + 3}$$

for total airborne dust. The % quartz is determined from the airborne dust samples. The term respirable dust sample refers to the fraction of particles in the total sample having a high probability of penetrating to

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the gas exchange regions of the lung. Several criteria are currently used to define respirable, however, for most industrial hygiene sampling the criteria of the American Conference of Governmental Industrial Hygienists are used. This approach uses a preselector to remove a fraction of the particles according to aerodynamic diameter** and the material penetrating the preselector is classified as respirable. The penetration characteristics of the preselector are given in Table I. (2)

TABLE I

Aerodynamic Diameter (μm)	% Passing Size Selector
$\leq$ 2.0	90
2.5	75
3.5	50
5.0	25
$\geq$ 10.0	0

The threshold limit value for respirable dust (2) is stated as

$$\frac{10\ \text{mg/m}^3}{\%\ \text{quartz} + 2}.$$

Certain mineral dusts, known to be more toxic, have lower TLV values than those derived from standard formulas (i.e., asbestos, coal mine dust). (2)

Mine air samples of both total and respirable dusts were collected in two oil shale mines. Quartz content in airborne dust samples was not measured in all cases and where quartz content in airborne dust was measured all values were less than 10%. Quartz content of oil shale rock from different areas of the Piceance basin has been measured and a variety of values have been reported. (3) A value of about 15% represents a reasonable estimate of the average and would be consistent with the lower value observed for airborne mine dust which also contains dust particles from sources other than oil shale rock. The dust concentrations measured in two mines are listed in Table II. (3-4) The dust levels measured in active working areas were frequently above the TLV in the Anvil Points mine. These levels did not represent overexposure of any workers since the TLV values are time-weighted values for an 8 hour work shift. In the Anvil Points mine all workers performed several tasks and were not involved in any operation for extended periods. (5) However, these measurement do indicate that dust exposure is a potential problem and dust suppression will undoubtedly be required during mining operations.

**Diameter of a unit density sphere having the same terminal settling velocity as the particle of interest.

Particle size was measured by Andersen eight stage cascade impactors. In the Anvil Points mine the mass median aerodynamic diameter (mmad) was found to be 2.2 μm with a geometric standard deviation (σ_g) of 3.5 during mucking and loading. In the Logans Wash facility the mmad ranged from 1.5 to 3.7 μm with a σ_g of 2.6 to 4.3.

The Anvil Points mine was sampled for a variety of gases during normal operation and after blasting with conventional explosive agents (ammonium nitrate and fuel oil). These sampling results are shown in Table III. Attempts were made to collect formaldehyde samples in the mine at Logan's Wash as a possible indication of diesel exhaust, however no detectable aldehydes were found on any of the 25 samples. The mining aspects of shale oil recovery will be similar for many recovery technologies but processing procedures following mining will be technology specific and may result in significantly different occupational health exposures. Most above ground retorting methods require crushing and grading shale.

TABLE II

Dust Concentrations Measured in Mining Areas (mg/m^3)

Mine Operation	Total Dust* Range	Total Dust* Average	Respirable Dust† Range	Respirable Dust† Average
Anvil Points Drilling	6.5-31.5	14.7	3.7-14.6	9.8
Anvil Points Loading	6.6-7.0	6.8		
Anvil Points Mucking		14.1		
Anvil Points Roof Bolting		12.6		
Anvil Points General Mine	3.8-14.6	9.2	0-0.28	0.14
Logan Wash General Mine	0.32-0.82	0.50	0.05-0.48	0.23
Logan Wash Haulage Way				1.17

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*TLV assuming 15% quartz = 1.67 mg/m^3
*TLV assuming 5% quartz = 3.75 mg/m^3
†TLV assuming 15% quartz = 0.59 mg/m^3
†TLV assuming 5% quartz = 1.43 mg/m^3

We have collected samples around one crushing operation but the equipment used was not representative of a mature industry so the data is not presented.

Sampling has been conducted during operation of the Paraho above ground retort at Anvil Points. This is a gas combustion retort employing a vertical kiln, through which coarsely crushed shale moves downward and the gas and vapors flow upward. The retort may be operated in a direct or indirect heating mode to decompose the kerogen into a recoverable vapor and gas. The retort was operated in the direct mode during the sampling period. The results of dust sampling around the retort are given in Table IV. Dust concentrations around the retort were high due to the raw shale conveyor discharge, degradation of the top rotary seal and the hot shale discharge at the bottom of the retort. While these dust levels indicate a need for dust suppression, personal sampling devices on the retort operator indicated no overexposure.

Gas and vapor concentrations were measured around the retort using detector tubes and the results are shown in Table V. Carbon monoxide and hydrocarbon concentrations were significant around the upper portion of the retort. The hydrocarbon gases may include polynuclear aromatic hydrocarbons and some nitrogen compounds, which would represent an exposure to potentially carcinogenic materials. Charcoal-absorber gas badges worn by the retort operator and by workers in the retort area collected no measurable organic matter. Further studies are needed to evaluate the potential presence of polynuclear aromatic and nitrogen compounds in these areas.

TABLE III

Gas Measurements--Anvil Points Mine

	Normal Conditions	After Blasting
CO	< 20 ppm	up to 100 ppm
CO_2	trace	$\approx$ 0.12%
HCN	trace	trace
NH_3	trace	3-6 ppm
HCHO	trace	trace
SO_2	trace	trace
H_2S	trace	
NO	< detectable	20 ppm
NO_2	< detectable	20 ppm
O_2	20.8%	20.8%
Total Hydrocarbons	0 to 16 ppm	up to 120 ppm

During the operation of the retort, there was a strong odor of nitrogen bases present downwind. Nitrogen bases are nitrogen compounds which can be extracted from an oil mixture by means of strong mineral acids and consist of homologues of pyridine, pyrole, quinoline, acridine, and similar heterocyclic nitrogen compounds. Little is known of the toxicity of these materials although they are somewhat irritating to the respiratory system. No occupational health standards have been established and air samples were not collected for these materials.

A variety of above ground retorting techniques have been developed and many of the control requirements to provide acceptable working environments will be similar for all systems. However, the wide range of retorting conditions that are encountered in the different systems and that may be varied in single systems may result in unique requirements for control equipment. Some of these systems have been throughly characterized with respect to potential emissions and occupational health exposures. Several technologies remain to be characterized.

TABLE IV

Dust Concentrations in the Retort Area

		Concentration (mg/m^3)					
	No. of	Total Dust		Resp. Dust		Particle Size	
Operation	Samples	Max.	Avg.	Max.	Avg.	mmad[b]	σ_g[c]
Top Seal	7	90.8	41.5	15.6	8.7	3.9	3.6
Bottom Seal	6	54.0	17.3	4.5	1.8	7.3	2.7
Retort, Ground Level	2	12.0	0.8	4.4	2.5	7.0	2.7
Middle Distributor	4	28.6	14.6	4.2	1.5		
Bottom Distributor	1	----	59.2	----	----		
Bottom Conveyor	1	----	7.4	----	ND[a]		
Outside Landings	4	2.7	1.3	1.8	0.8		
At Thermal Oxidizer	1	----	1.1	----	0.9		
Retort Operator (Personal Sample)	1	----	1.7	----	0.4		

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[a] No detectable dust in the single sample collected

[b] Mass median aerodynamic diameter

[c] Geometric standard deviation

Modified *in situ* methods where some fraction of the shale is mined out to provide the permeability needed for retorting are also being investigated. These techniques may result in unique occupational health situations. Full scale operations will result in extensive underground mines in which retorts are in the formation phase, are burning with underground circulation of combustion gases and recovery products, are in the cooling phase or are being abandoned. To date modified *in situ* operations have been carried out with a phased approach with only limited periods where all phases of the operation were underway simultaneously. Some sampling has been conducted but more information will be required before the potential occupational health problems associated with the modified *in situ* technologies are all characterized. Large numbers of samples have been and will continue to be collected from *in situ* processing for toxicology testing.

TABLE V

Gas and Vapor Concentrations in the Retort Area

		Contaminant Concentrations in ppm									
Location	Total Hydrocarbon	CO	NO_2	NH_3	H_2S	SO_2	CS_2	HCN	HCHO	HNO_3	CO_2
Retort, Top Seal	100-400	25	N.D.[b]	N.D.	20	N.D.	----	8	2	N.D.	1000
Retort, Bottom Seal	0.7, 0.2	5	N.D.	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	----
Retort, Ground Level	100	----	----	----	----	----	----	----	----	----	----
Retort, Bottom Distributor	9.0, 3.0, 0.2	----	----	----	----	----	----	----	----	----	----
Retort, Middle Distributor	3.0, 0.2	----	----	----	----	----	----	----	----	----	----
Retort, Top Distributor	4.5, 4.0, < 25	N.D.	N.D.	N.D.	N.D.	N.D.	----	N.D.	----	N.D.	----
Retort, Off-Gas Collector	10-50	----									
Retort, Thermal Oxidizer	N.D., 0.6, < 25 ppm	200	10-15	4-6%[a]	N.D.	> 35	----	60			
Recycle Gas Blower	80-170 200-5000	20-700	N.D.	40, > 30	10-20	N.D.	5	5-15	10-15	N.D.	5000
Blower Area	----	15-25									
Retorted Shale Conveyor	----	10									
Retorted Shale Piles	N.D.	12	----	----	N.D.	N.D.	----	N.D.	----	----	----

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[a] Single sample, result highly unlikely, unknown interferences, possibly amines.

[b] None detectable.

Biological Studies

Inhalation studies. Comparative inhalation studies involving two rodent species have been completed or are in progress. Exposure materials include raw shale, two kinds of spent shale and appropriate controls (Table VI). The first study utilized Syrian hamsters because they are regarded as the species of choice for investigation of chemical carcinogenesis of the lung. The exposure period covered 16 months, or about 60% of the hamster lifespan, and the dust concentrations were considerably higher than those that might be anticipated during actual oil shale recovery operations. Most of the animals in these experiments are dead and no tumors have been observed. Many animals surviving the entire exposure period exhibited mild degrees of localized fibrosis of the lung even though the Syrian hamster is not a good model for the pnuemoconiotic diseases.

The second inhalation study, which is still in progress, utilizes Fischer-344 rats which are a more appropriate animal for the study of

TABLE VI

Inhalation Studies

STUDY I

Materials	Animals	Concentration	Duration*
Raw Shale	64 Syrian Hamsters	50 mg/m^3	16 months
Spent Shale A	64 Syrian Hamsters	50 mg/m^3	16 months
Spent Shale B	64 Syrian Hamsters	50 mg/m^3	16 months
Sham Controls	64 Syrian Hamsters	-----	16 months

STUDY II

Materials	Animals	Concentration	Duration
Raw Shale	64 Fischer 344 Rats	120 mg/m^3	Lifetime**
Spent Shale A	64 Fischer 344 Rats	120 mg/m^3	Lifetime
Quartz	64 Fischer 344 Rats	20 mg/m^3	Lifetime
Deposition Study (Raw Shale)	64 Fischer 344 Rats	120 mg/m^3	Serial Sacrifice
Sham Controls	64 Fischer 344 Rats	-----	-----

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* 4 hrs/day

** 6 hrs/day

fibrotic and obstructive lung disease. As a part of this experiment animals are sacrificed at frequent intervals for neutron activation analysis of the deposition of inhaled materials in the lung. Results of histological examinations of the sacrificed animals indicates a more general fibrotic response than that seen in hamsters and which may lead to focal emphysema with time.

Mutagenesis and Carcinogenesis Assays. Many of the materials acquired during industrial hygiene studies of specific sites have been tested by both bacterial mutagenesis (Ames Assay) procedures and mouse "skin-painting" schemes. These approaches are particularly useful for the liquid products and by-products.

Using the Salmonella histidine-reversion test, several of the product oils and some of the so-called process waters have been assayed for mutagenic activity. (6) It is apparent from the results that the product oils and the associated process waters vary considerably in their biological activity and that the variation may be process dependent. Oil from one specific MIS retort exhibited considerably less mutagenic activity than the product oil from a specific surface retort. The mutagenic activity of the oil from surface retorting, however, was greatly diminished after hydrotreating.

The mouse skin system was used to evaluate the carcinogenic potential of two crude shale oils and two natural petroleums. Four dose levels of each test oil and two dose levels of benzo-a-pyrene (BaP) were applied to C3Hf/He mice three times per week. Groups of mice, subjected to frequent shaving, application of carrier solvent or left untreated, served as controls. Each shale oil represented a different extraction process, and the natural petroleums originated from different geographic regions.

In the group treated with shale oil from an above ground process, the first tumors were observed after 20 weeks of application, and 90% of the mice had tumors by the 58th week (mean latency = 36 weeks). The shale oil from an in situ process had a latency period to first tumor of 25 weeks, and 35% of the mice had tumors after 58 weeks of treatment (mean latency = 48 weeks). Of the natural petroleums, only one, a U.S. gulf coast oil (API Reference oil #2), caused tumors with a latency period of 35 weeks and 18% tumor incidence after 58 weeks of exposure. In all cases of positive effect, only the highest dose levels (5 mg/application) have proven to be carcinogenic. The two groups exposed to BaP differed in temporal distribution of both initial tumor latency and total tumor occurrence. While 100% of the mice in each dose group experienced tumors, the mean latency in the high dose group (10 µg/treatment) was 29 weeks compared with a 40 week mean in the low dose group (2 µg/treatment) (Table 7).

Papillomas and squamous carcinomas were the only cutaneous tumors observed in any of the experiments. For the purpose of estimating latency, no distinction was made between histological types, and many of the papillomas persisted as such until the death or sacrifice of the animal. Many of the mice in each of the positive groups exhibited multiple tumors. Tumors that appeared to be papillomas at first observation were often later accompanied by apparently contiguous squamous cell carcinomas. Some of the squamous neoplasms were associated with lung metastases.

TABLE VII

Tumor Incidence

Compound	Time to First Tumor	% Tumor Incidence at 58 Weeks
Shale Oil A	20 weeks	90
Shale Oil B	25 weeks	35
US Gulf Coast Petroleum (API #2)	35 weeks	18
Kuwait Petroleum (API #1)	0	0
Benzo(a)Pyrene (10 μg)	18 weeks	100

DISCUSSION

While there have been sporadic efforts to demonstrate certain shale oil extraction technologies in recent years, none of the techniques have been thoroughly analyzed to determine the extent of potential occupational health impacts and even those technologies that have been demonstrated cannot be regarded as typical of a scaled-up, fully mature industry. Industrial hygiene studies have served to identify operations within certain technologies where mitigating methods can and should be applied to protect the industrial populations. Judging from data developed by on-site sampling it is probable that, with the possible exception of MIS techniques, oil shale mining presents no unique problems that cannot be handled with state-of-the-art control procedures. The conditions that may exist in a mine where *in situ* retorts are being simultaneously prepared, burned and abandoned have not as yet been defined.

The probability of combined exposures to spent shale dusts and fugitive emissions in the form of vapors and gases added to the potential for skin exposure to product oils and other liquid effluents raises more complex questions. It has been shown by both epidemiological evidence and experimental data gathered both in the U.S. and in foreign industries that crude shale oil and some of its products carry a higher carcinogenic potential than most of the natural petroleums (7-8). Preliminary data suggest that this particular hazard may be almost self-eliminating if hydrotreating, in preparation for refining, is universally practiced.

The determination of specific hazards should be done on a technology-specific basis since it is highly probable that the biological activity of most of the products and by-products of shale oil production is process-specific.

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