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Paraho Environmental Data

Part IV. Land Reclamation & Revegetation
Part V. Biological Effects
Part VI. Occupational Health & Safety
Part VII. End Use

Bibliography

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Dr. Gerald Goldstein

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PARAHO ENVIRONMENTAL DATA

Part IV

Land Reclamation and Revegetation

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May, 1981

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4.1 INTRODUCTION

4.1.1 Paraho Environmental Data

In 1979, Paraho initiated the compilation of the environmental data generated from the Anvil Points oil shale facility. Several data groups have been organized: I. Process Characterization, II. Air Quality, III. Water Quality, IV. Land Reclamation and Revegetation, V. Biological Effects, VI Occupational Health and Safety, and VII. End Use Effects. The first three sections, I. Process Characterization, II. Air Quality, and III. Water Quality, were published by the U. S. Department of Energy in June, 1980. This report, Part IV. Land Reclamation and Revegetation, and Part V. Biological Effects, VI. Occupational Health and Safety, and VII. End Use Effects will be published in 1981.

Land Reclamation and Revegetation, Part IV, compiles characteristics of environment and ecosystems at Anvil Points, reclamation of retorted shale, revegetation of retorted shale, and ecological effects of retorted shale. Data found in another section of the Paraho Environmental Data is not reproduced here.

4.1.2 Scope of Reclamation and Revegetation Studies

Colorado State University, Battelle Pacific Northwest Laboratories and Utah State University have done extensive studies on revegetation and reclamation of disturbed lands. The CSU study was begun in 1976 and was underway during the demonstration of Paraho's technology in producing 100,000 barrels of shale oil for the U. S. Navy. The earlier USU studies were primarily performed in Utah; some Paraho retorted shale was used in those studies. Woodward-Clyde and Associates performed extensive tests on the reclamation of retorted shale.

4.1.3 Location of Anvil Points Facility

The Paraho Development Corporations's oil shale research facility is located at Anvil Points about 9 miles west of Rifle, Colorado. Anvil Points is near the southwestern edge of the Piceance Creek Basin (Figure 4.1.1). Figure 4.1.1 also shows the location of Anvil Points in relation to other oil shale developments in northwestern Colorado. A close-up of the Anvil Points area is provided in Figure 4.1.2. The Anvil Points facility, identified as the Bureau of Mines Oil Shale Experimental Station, is located on the Naval Oil Shale Reserves.

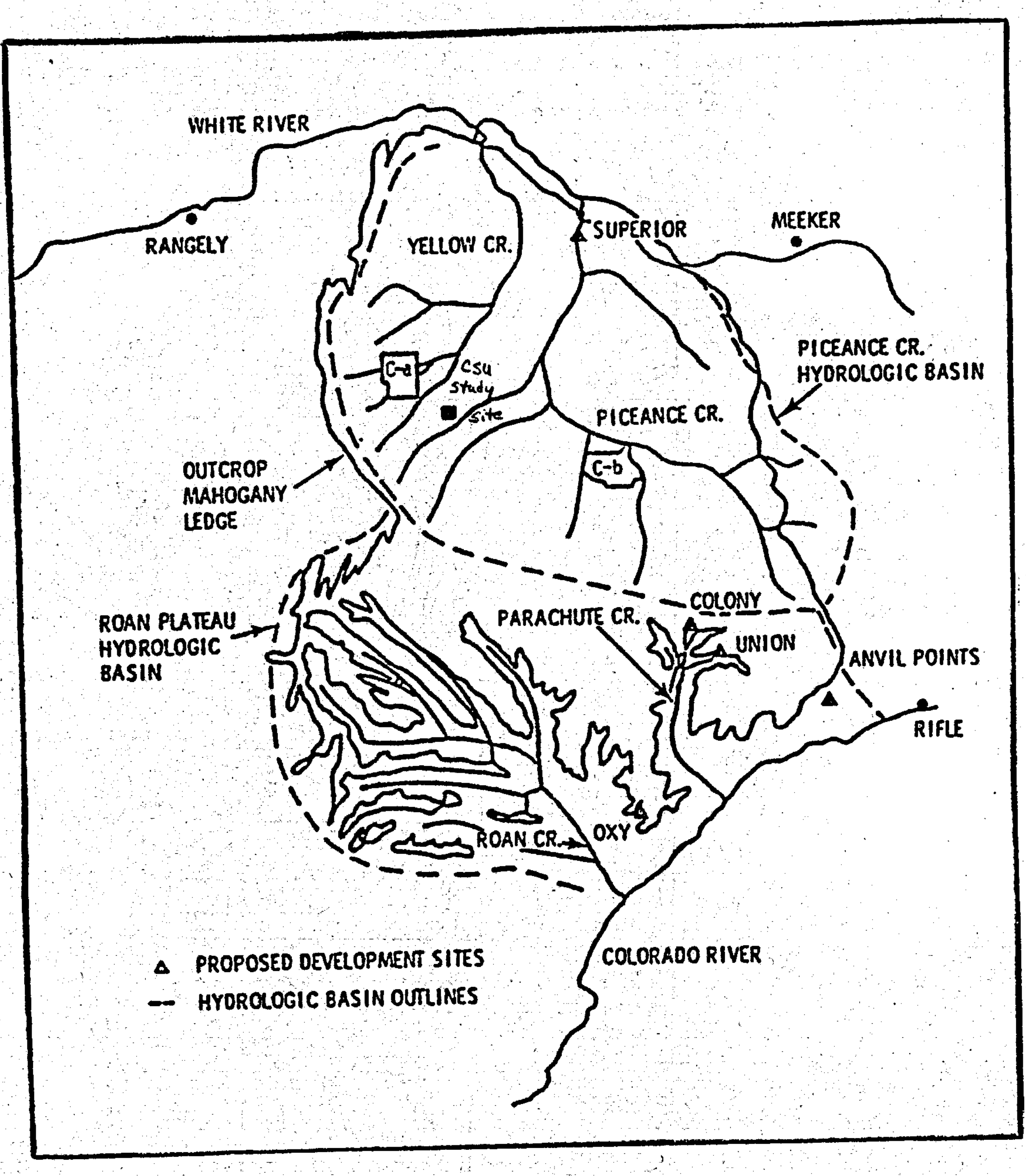


FIGURE 4.1.1

Location of Selected Oil Shale Developments in Northwestern Colorado (Wildung and Zachara, 1980)

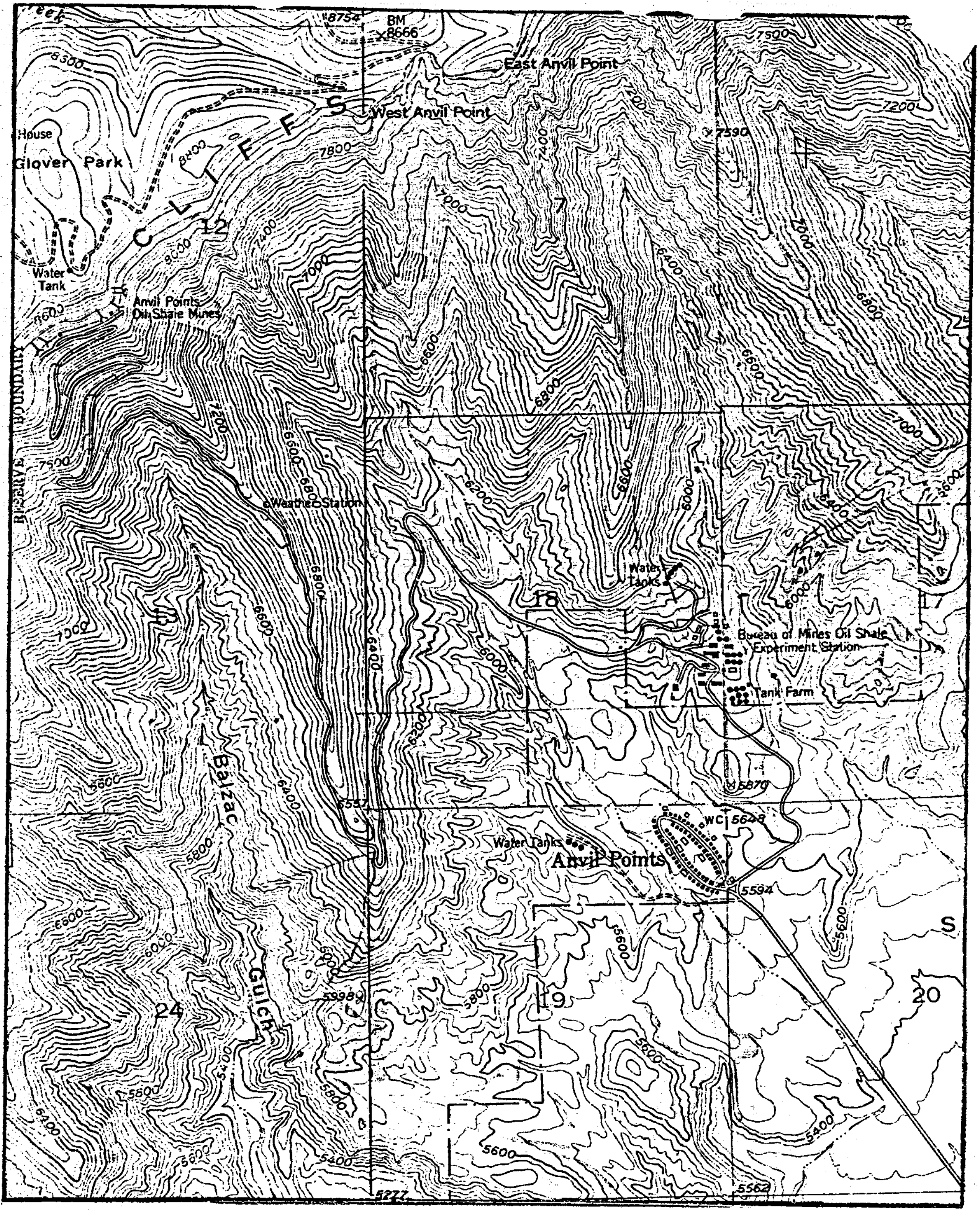


FIGURE 4.1.2

Contour Map of Anvil Points Site
Contour Interval 40 Feet
Scale 1:24000

4.2 BACKGROUND INFORMATION

4.2.1 Characteristics of Environment

Precipitation. The climate is semi-arid with average precipitation at Rifle and Grand Valley, Colorado of 27.7-30 cm per year (Malek, 1980). The snowfall of October through March accounts for nearly half of the precipitation (Table 4.2.1). Spring and fall months, June and October, have peaks of precipitation (Figure 4.2.1).

Drainage Patterns. The precipitation drainage patterns of the Anvil Points area (Eker, Waters, Skaggs, 1979) begin at the base of the Roan Cliffs and extend southward to the Colorado River (Figure 4.2.2). Measurable run-off occurs during spring snowmelt and the occasional showers of spring and summer.

Geologic Characteristics. The surface soils and stream sediments have been analyzed to determine a geochemical baseline of the Anvil Points area (Rutherford, 1979). Geological units of the Anvil Points region and Piceance Creek Basin are illustrated in Figure 4.2.3.

The elemental concentrations in soils and stream sediments vary significantly with the underlying geological units (Table 4.2.2). Geochemical baseline studies would determine natural background levels and their variability for various parameters. Geochemical baseline studies developed on stream sediments and geologic units would serve as a basis for environmental monitoring of stream and groundwater contamination from operations.

Although the statistical data is not adequate to draw definite conclusions, several geochemical trends may be suggested. The pH of soil and sediment samples decrease with increasing elevation (Table 4.2.2). Organic carbon shows the inverse relationship. Mercury concentrations do not suggest a trend. Molybdenum, boron, and fluorine appear to be higher in concentrations in samples taken from the Parachute Creek Member. Little correlation was found between selected trace element (Mo, B, F) analyses of plants and the soils they grow on. Other factors may be affecting the uptake of trace elements by plants (Rutherford, 1979).

4.2.2 Characteristics of Existing Ecosystems

The major vegetation types of the Anvil Points site, as given in the Draft Environmental Impact Statement (Harrington, 1980), are: conifer, aspen, mountain shrub, sagebrush, and pinon-juniper (Figure 4.2.4). The DEIS uses other surveys of the Piceance Basin as representative of this area. There have been no detailed studies of flora or fauna (species list, cover density, biomass, etc.) at Anvil Points.

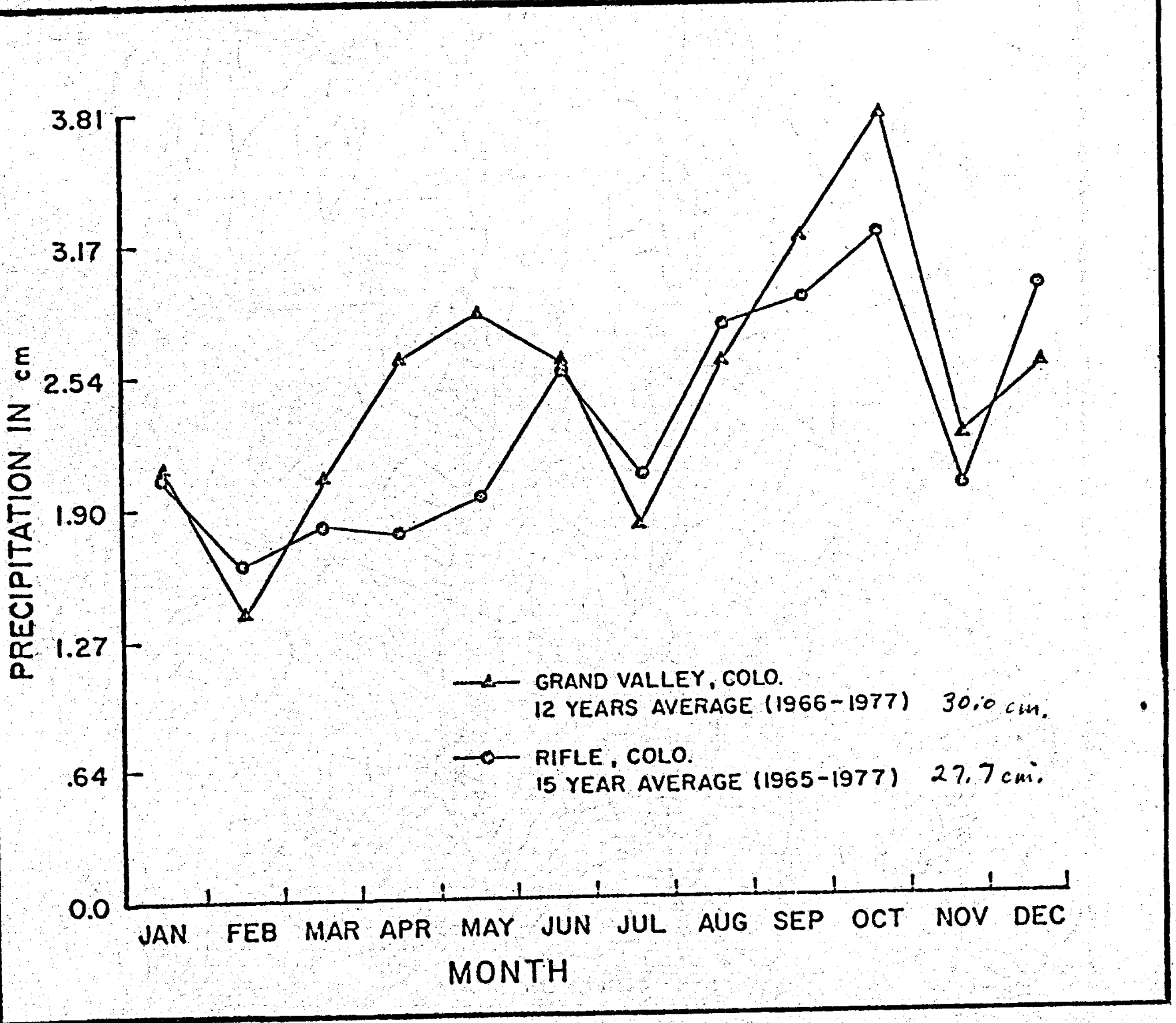


FIGURE 4.2.1

Precipitation Record for 15 Years at Rifle and
12 Years at Grand Valley, Colorado (McKell, et al., 1980)

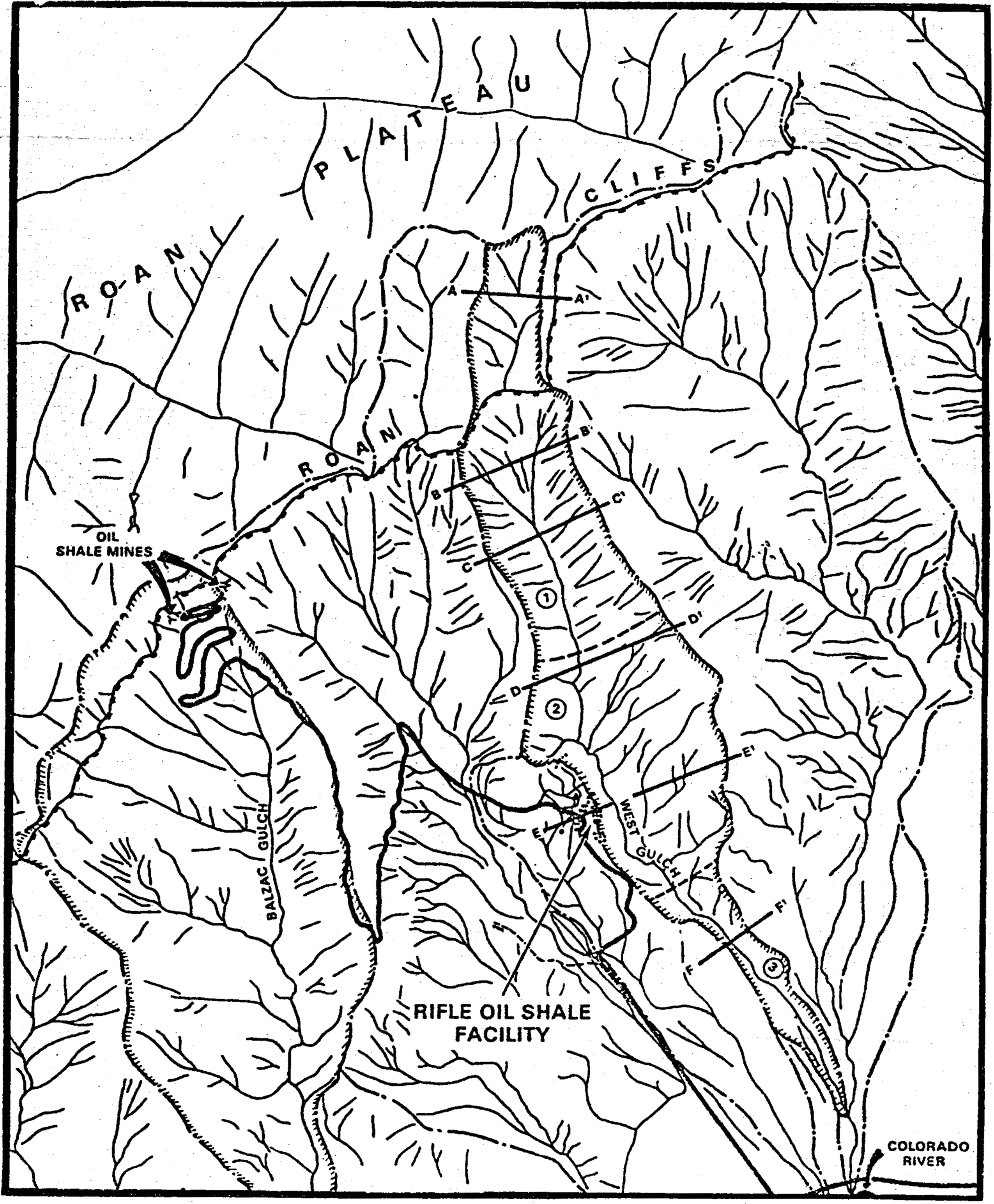


FIGURE 4.2.2

Drainage Area Map of West Gulch, Balzac Gulch, and the Roan Plateau (Ecker, Walters, Skaggs, 1979)
Scale: 1 inch ~ 0.6 miles

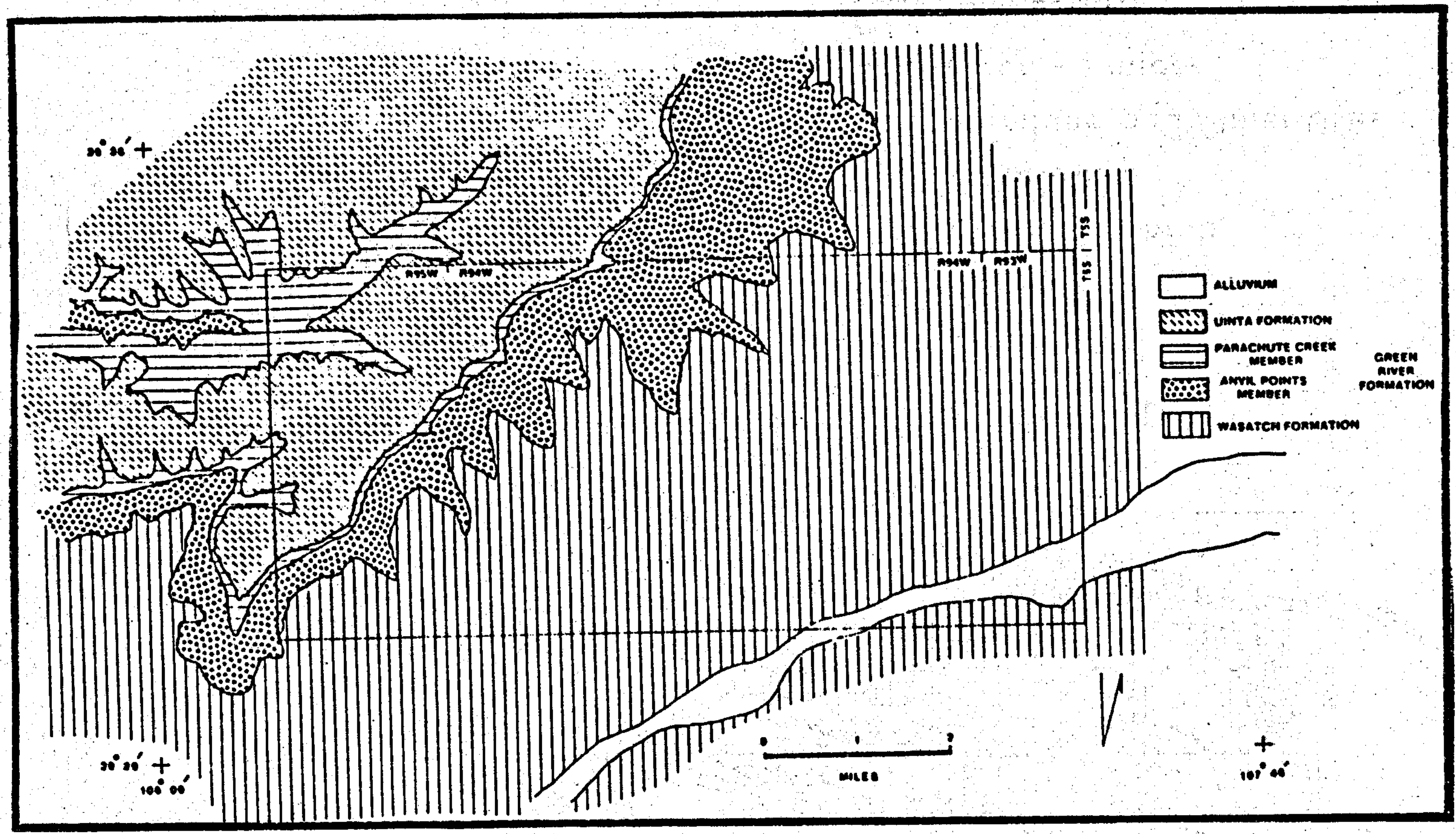


FIGURE 4.2.3

Surface Geology of the Anvil Points Region
(Rutherford, 1979)

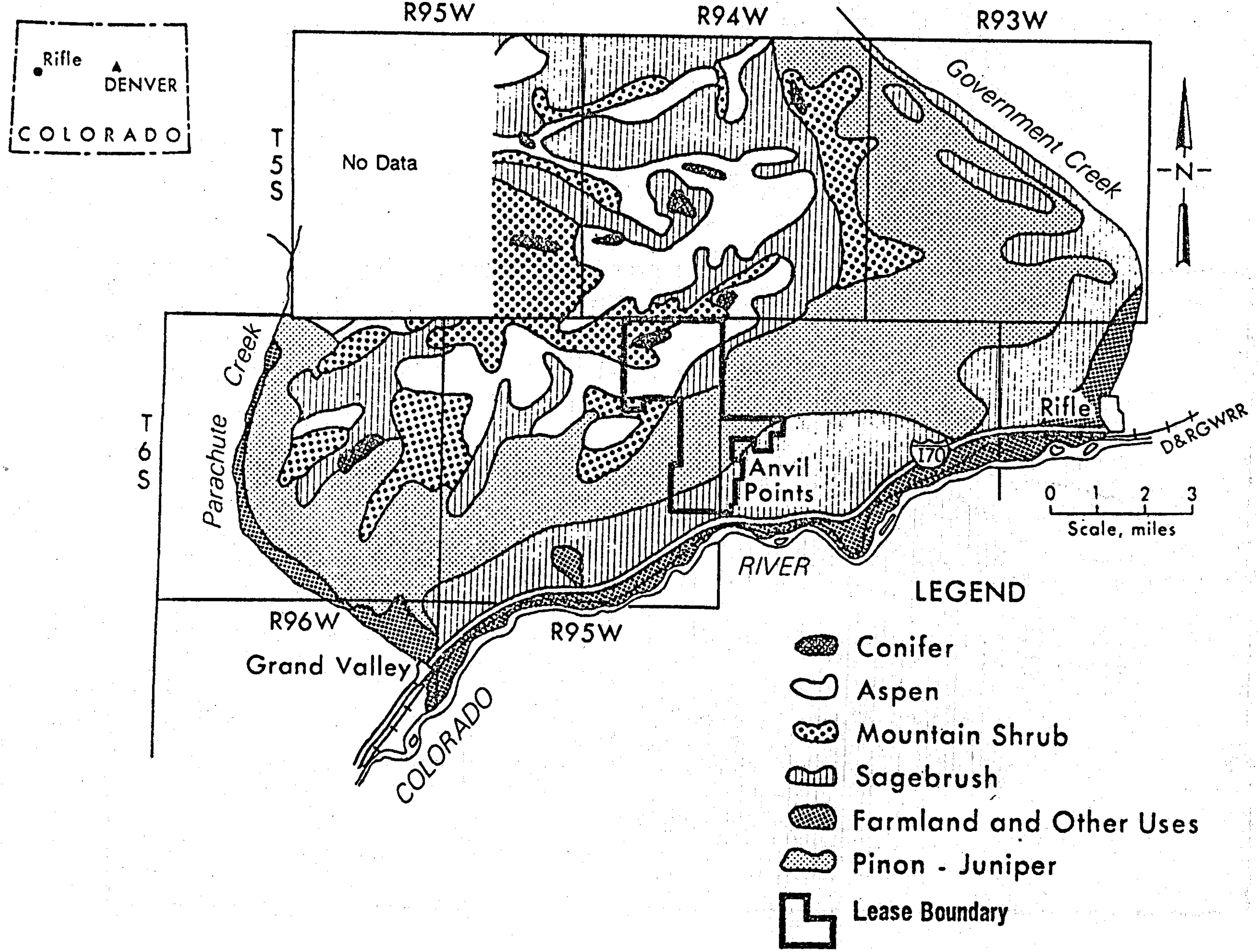


FIGURE 4.2.4

Major Vegetation Types of Anvil Points Area
(Harrington, 1980)

TABLE 4.2.1

Precipitation Distribution by Months (Malek, 1980)

Month	Rifle, Colorado Ave. 15 yrs. (cm)	Grand Valley, Colorado Ave. 12 yrs. (cm)
Jan.	2.10	2.12
Feb.	1.64	1.39
March	1.82	2.06
April	1.80	2.62
May	1.96	2.80
June	2.54	2.61
July	2.03	1.82
Aug.	2.78	2.60
Sept.	2.89	3.18
Oct.	3.20	3.78
Nov.	1.97	2.22
Dec.	2.94	2.56
Year	27.70	30.00

TABLE 4.2.2

Elemental Concentrations of Soils, Plants, Sediments

By Geologic Units

(Rutherford, 1979)

LSD/SR (least significant difference/studentized range) is the least significant difference between any two means in a population that can be considered significant at the .05 level.

The means for a population are listed from largest to smallest. All means except pH means are transformed to their logarithms.

The results of the Duncan's Multiple Range Test are shown below the group means.

		Alluvium	Wasatch	Anvil Pts	Parachute	Uinta
Soil Parameters						
pH	LSD/SR = .667	7.97^{a*}	7.78^{a}	7.75^{a}	7.69^{a}	6.87
OC	LSD/SR = .498	$-.506^{a}$	$.0212^{a}$	$.354^{ab}$	$.509^{bc}$	$.577^{c}$
Hg	LSD/SR = .399	1.53^{a}	1.37^{a}	1.48^{a}	1.41^{a}	1.37^{a}
B	LSD/SR = .204	2.13^{a}	2.16^{a}	2.20^{a}	2.26^{a}	2.25^{a}
Mo	LSD/SR = .404	$.443^{a}$	$.319^{a}$	$.293^{a}$	$.532^{a}$	$.294^{a}$
F	LSD/SR = .242	2.62^{a}	2.66^{a}	2.74^{ab}	2.92^{b}	2.70^{a}
Sagebrush (Artemsia tridentata) Parameters						
Mo	LSD/SR = .436	$.074^{a}$	$-.035^{ab}$	$-.258^{ab}$	$-.200^{ab}$	$-.372^{b}$
B	LSD/SR = .212	1.48^{a}	1.37^{a}	1.32^{a}	1.45^{a}	1.45^{a}
F	LSD/SR = .651	$.559^{a}$	1.11^{b}	1.18^{b}	$.590^{a}$	$.519^{a}$
Indian Ricegrass (Oryzopsis hymenoides) Parameters						
Mo	LSD/SR = .577		$.291^{a}$	$.342^{a}$	$.461^{a}$	$.151^{a}$
B	LSD/SR = .304		$.690^{a}$	$.675^{a}$	$.737^{a}$	$.735^{a}$
Western Wheatgrass (Agropyron smithii) Parameters						
Mo	LSD/SR = .459		$.218^{a}$		$.384^{a}$	$.0595^{a}$
B	LSD/SR = .361		$.805^{a}$		$.800^{a}$	$.780^{a}$

TABLE 4.2.2 (Cont'd)

	Alluvium	Wasatch	Anvil Pts	Parachute	Uinta
Sediment Parameters					
pH LSD/SR = .565	8.40^{a}	8.30^{a}	8.08^{ab}	7.96^{ab}	7.86^{b}
O.C. LSD/SR = 1.428	$-.823^{a}$	$-.580^{a}$	$.218^{a}$	$.493^{a}$	$.475^{a}$
Hg LSD/SR = .983	1.60	1.55	1.59	1.93	1.88
Mo LSD/SR = .762	.562	.485	.469	.641	.492
B LSD/SR = 1.62	1.59	1.68	2.15	2.30	2.29
F LSD/SR = .681	2.46	2.61	2.82	2.83	2.84

* Values not followed by the identical letters in each row are significantly different at the .05 level.

4.3 LAND RECLAMATION

Since an oil shale facility represents a large-scale solids processing plant, an oil shale plant presents several problems in land reclamation. First, top soil is removed during plant construction and operation. Second, raw shale is stockpiled during various stages of operation. And finally, retorted shale is produced at the approximate rate of 1.4 tons for each barrel of shale oil produced.

During the recent Paraho operations at Anvil Points, there were no land reclamation studies directed towards the stabilization and revegetation of topsoil. First, the facilities and all the auxiliaries (roads, pipelines, transmission lines, etc.) were installed in the late 1940's - more than 25 years before the start of the Paraho research operations. Second, the reclamation of topsoils does not pose the potential problems that retorted shale does.

No major raw shale reclamation studies were carried out during the recent Paraho research operations. All the raw shale storage areas represented "active storage". Mine rubble, crushed shale feed, and rejected fines represent non-permanent storage areas. Stabilization and revegetation studies are not practical.

Retorted shale represents the largest by-product produced from the retorting operations. The chemical properties of Paraho retorted shale are compiled in Part I, Process Characterization, of the <u>Paraho Environmental Data</u>. Two major studies involving the revegetation of retorted shale disposal areas have been carried out during the Paraho research operations at Anvil Points. These studies are discussed in Section 4.4 Revegetation of this volume, Land Reclamation and Revegetation.

During the Paraho operation, Woodward-Clyde Consultants, Inc., carried out a research project for Development Engineering, Inc., under their contract (No. J0255004) with the U. S. Bureau of Mines. The final report, "Disposal of Retorted Oil Shale from the Paraho Oil Shale Project" (Holtz, 1976) is available from the National Technical Information Service, U. S. Department of Commerce.

A second study entitled, "Seepage Through Partially Saturated Shale Waste" was conducted for the U. S. Bureau of Mines by the University of Idaho Agricultural Engineering Department (Bloomsburg and Wells, 1978).

4.3.1 Stabilization

The Woodward-Clyde project consisted of laboratory and field tests to determine the physical and chemical properties of the retorted shale for use in developing future full-scale waste disposal plans. The laboratory studies identified the physical properties of retorted shale. The field studies identified compaction and permeability characteristics of retorted shale.

Laboratory Studies. Results showed that shale retorted by the direct heat Paraho process is characterized as a silty-gravel mixture (Holtz, 1976). This is shown in the gradation data (see Figure 4.3.1). About half the sample is gravel sized (greater than #4 sieve size). Compaction causes particle breakdown with fines filling the voids between the larger particles. This increases density, promotes strength, and reduces permeability.

Research studies to determine the best method of compaction were carried out under various loads to simulate effects of various hauling, spreading, and compaction equipment which could be used in field work - light, 6200 ft-lbs/ft^3; medium, 12,375 ft-lbs/ft^3; heavy, 56,000 ft-lbs/ft^3 (see Figure 4.3.2). Results showed that moistening produces only small increases in density. Densities greater than 98 pcf can be achieved by heavy compaction, with or without water addition.

Strength, measured by unconfined compression, shows that about optimum water content is required for optimum strength (see Table 4.3.1).

TABLE 4.3.1

Effect of Added Water on Strength

Water Added, Wt%	Compressive Strength, psi
5	100
10	140
22	185
25	170

The unconfined compressive strength for the direct heat shale increases to 205 psi with curing (see Figure 4.3.3). This increase in strength with the addition of optimum water and with curing indicates that Paraho direct heat retorted shale behaves like a low-grade cement. Shale retorted by the indirect heat process did not exhibit a strength increase.

<u>Field Compaction</u>. Field compaction was carried out to confirm laboratory results and to determine proper handling techniques. The field compaction research was carried out using about 16,000 tons of retorted shale in an area measuring 180 ft. by 400 ft. (see Figure 4.3.4). The area was divided into two sections - one using dry compaction, one with optimum water added. Each section consisted of six panels which received different degrees or types of compaction. The material was placed in layers about 8-12 inches deep. The use of these panels or layers permitted heavy compaction using conventional equipment, reduced dusting even when handled dry, and allowed rapid dissipation of heat to avoid autoignition.

4.3.2 Permeability

Permeability test results, shown in Table 4.3.2, indicate that permeability can be reduced by the addition of optimum water, compactive effort, and loading. Permeabilities of less than 1 ft/yr (1×10^{-6} cm/sec) have been achieved. Leachates obtained from these permeability studies have been analyzed. The data are compiled in Part III, Water Quality.

<u>Laboratory Studies</u>. Another laboratory permeability test utilized the recirculation of the effluent (see Figure 4.3.5). These data show that recirculation of the effluent, such as may be encountered within a deep disposal area, tends to reduce permeability. This would indicate that even though percolation might occur at the surface, it would be reduced significantly as the effluent permeates within the disposal pile.

<u>Field Infiltration Ponds.</u> Two ponds were constructed to determine the permeability and infiltration of retorted shale placed by normal construction equipment and methods (see Figure 4.3.6). Pond 1, which was about 75 feet

long by 50 feet wide, was constructed using optimum techniques developed during the field compaction experiment. The retorted shale was moistened with optimum water, properly aged, placed in 8-12 inch loose layers, and compacted to an average density of 100.6 pcf by 7 passes of a heavy vibrating roller. Sloping sides were used to eliminate sidewall effects and the wall-to-bottom interfaces. Both ponds were constructed over a gravel layer and a hypalon liner installed to collect any seepage (see Figure 4.3.7). Pond 2, which was about 60 feet long by 46 feet wide, was compacted without any water addition and using only hauling-grading equipment for compaction.

After the field infiltration experiment was completed, 6 inch diameter cores were removed from Pond 1. Results from the field expermient and laboratory studies using these cores are compiled in Table 4.3.3. Moisture control was excellent - Pond 1 averaged 20 wt% water; there was no moisture in Pond 2. Densities above 100 pcf were achieved for Pond 1. The mean compressive strength from Pond 1 cores was 215 psi. Pond 2 had a permeation rate of about 2000 ft/yr while Pond 1, with a permeation rate of less than 1 ft/yr, based on drain outflow, can be considered impervious. Although Pond 2, which represented the main disposal pile, had a high permeation rate, an additional field experiment showed that deep penetration may not occur. After Pond 2 had thoroughly dried for several months, about 5000 gallons of water was sprayed on the surface to simulate a 2-inch rainfall in one-half hour. After three days, less than 2 gallons seeped through to the drain. Even though all the simulated rainfall was essentially lost to absorption and evaporation, the 2 gallons of seepage indicate a potential for leaching. Significant water flow and leaching did not occur.

The reclamation study performed by the University of Idaho Agricultural Engineering Department was designed on the laboratory and field permeability tests that the Woodward-Clyde project used. Based on the finite element analyses results, their conclusions are as follows:

(1) Surface and groundwater effects originating from waste shale piles and resulting from low intensity, low yield storms will be insignificant. Evaporation will completely reclaim most common storm yields. Most low intensity storms will

completely infiltrate with no special profile preparation. Groundwater will not accumulate as a result of common storms.

(2) High intensity, low yield storms may require a disposal zone border, or an unconsolidated, low density surface layer to contain surface water until it can be infiltrated. Evaporation will prevent groundwater accumulation with no special profile preparation.

(3) High intensity, high yield storms may require borders, or unconsolidated, low density surface layers to contain runoff. During the construction of the profile, care should be taken to produce a uniform profile so as not to restrict upward moisture movement during evaporation. Dense liners requiring a large compactive effort are not necessary in order to prevent groundwater accumulation from direct storm effects. Unlayered, naturally developing profiles are effective in severe storm yield containment.

4.3.3 Other Studies

Dusting and surface erosion were studied in laboratory wind tunnel experiments using various types of surfaces and wind velocities (See Table 4.3.4). These results indicate that dusting and surface erosion were not serious impacts and could be controlled by good engineering practices. These findings were confirmed during the field compaction and permeation studies.

Heat dissipation of retorted shale, obtained directly from the retorting operations, was observed during the construction of the field compaction and permeation sites. A long-term study of possible temperature build-up within the compacted shale was carried out in the field compaction site (see Table 4.3.5). Data show that no heat build-up was detected. When the materials were spread in 8 to 12-inch layers bypassing all extended storage piles, autoignition did not occur. There has not been a study performed on heat build-up of deeper piles.

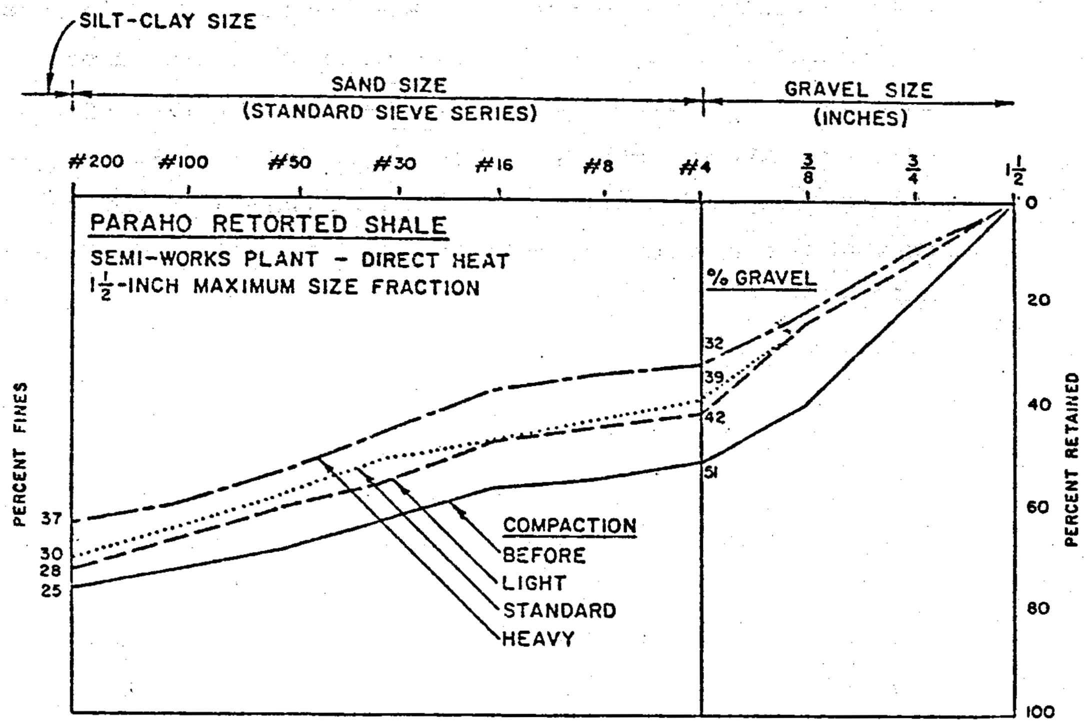


FIGURE 4.3.1

Gradation Data of Retorted Shale

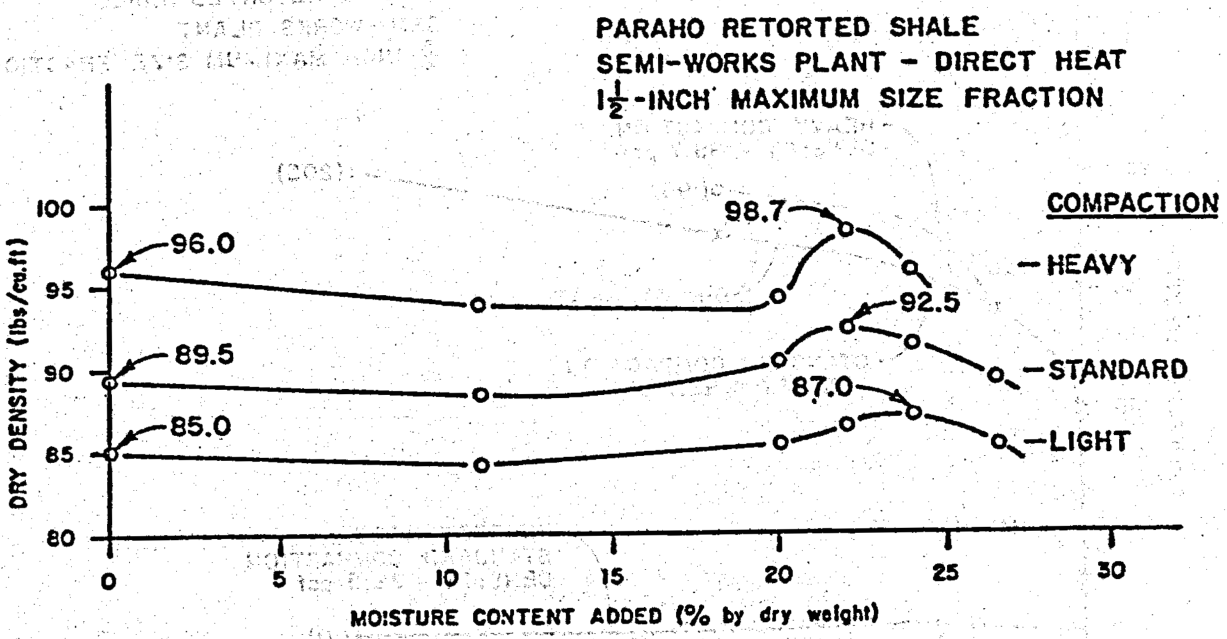


FIGURE 4.3.2

Compaction Data of Retorted Shale

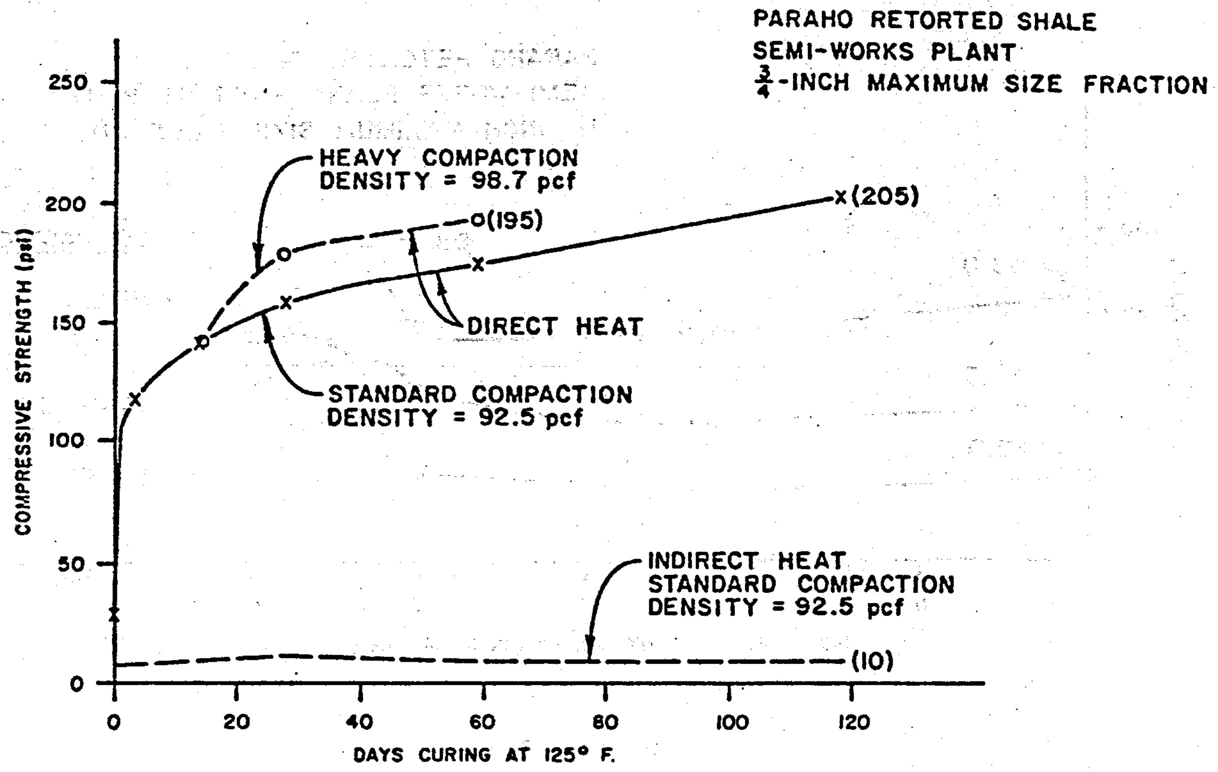


FIGURE 4.3.3

Compressive Strength Data of Retorted Shale

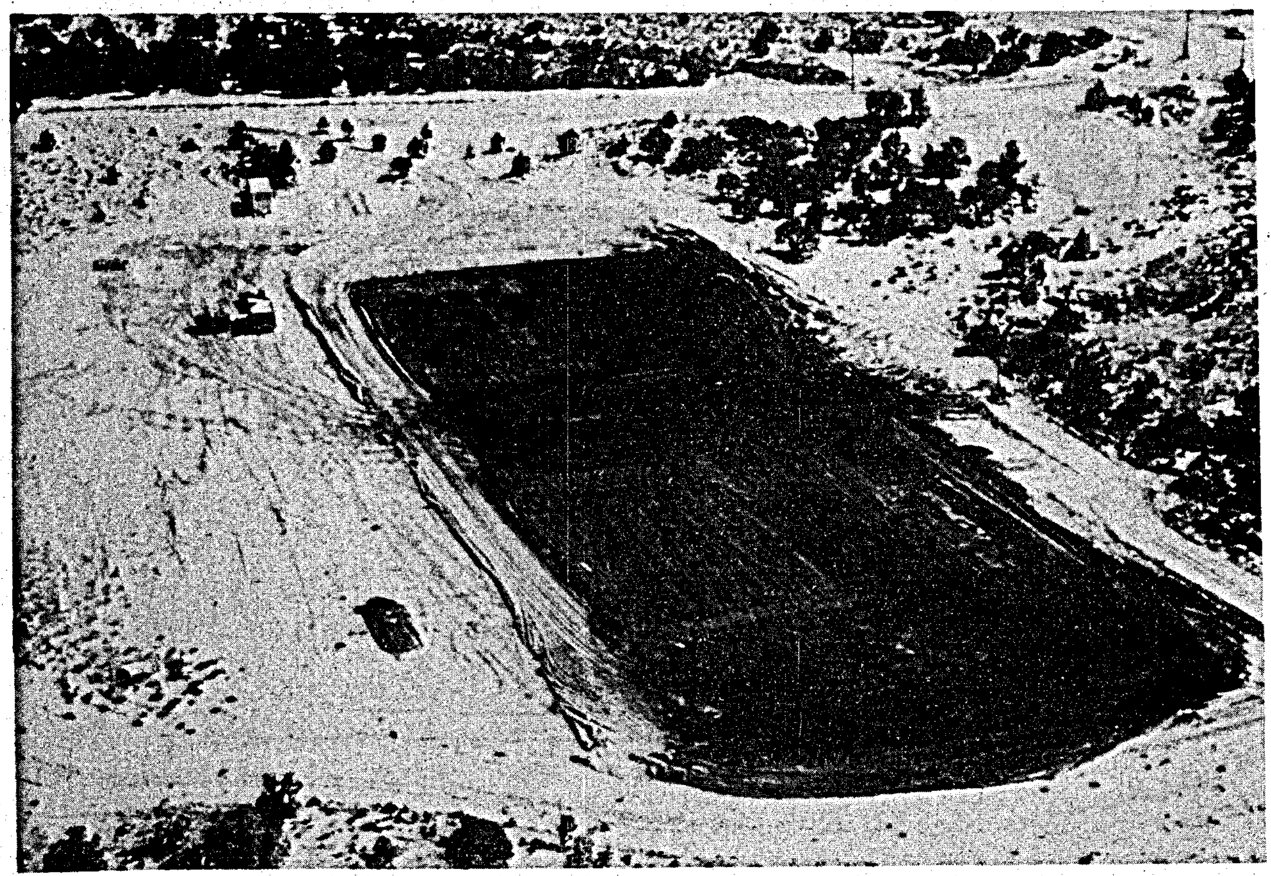


FIGURE 4.3.4

Field Compaction Site

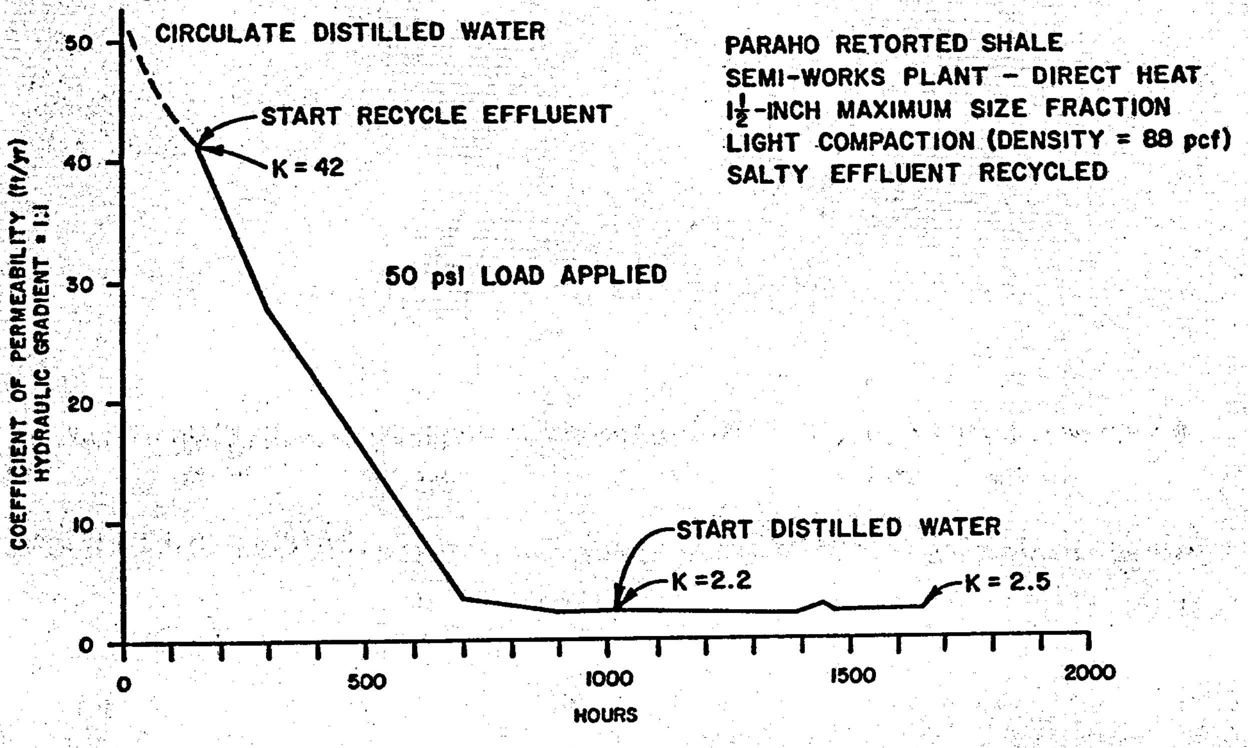
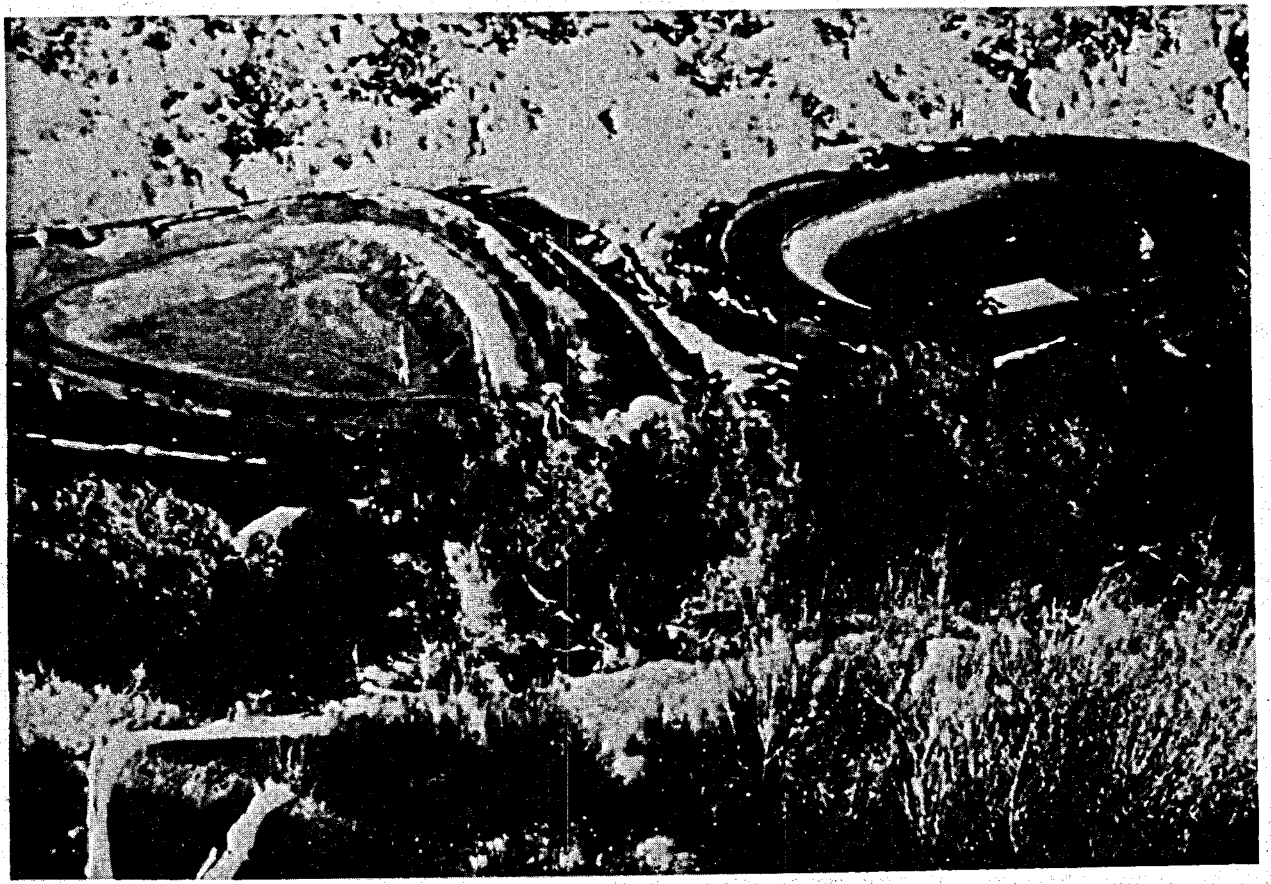


FIGURE 4.3.5

Effect of Recirculated Water

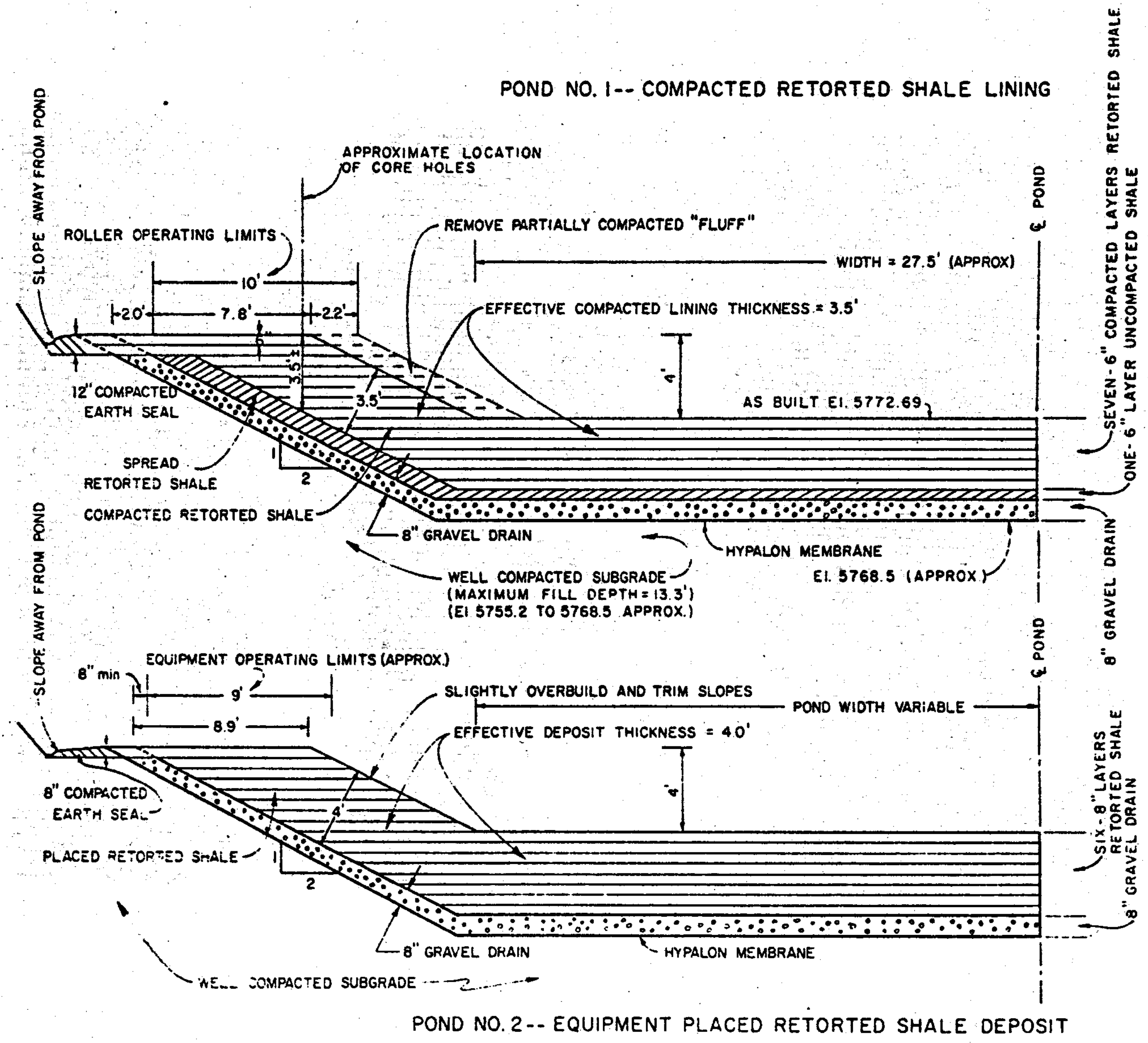


Pond 2

Pond 1

FIGURE 4.3.6

Field Infiltration Ponds



POND NO. 1-- COMPACTED RETORTED SHALE LINING

POND NO. 2-- EQUIPMENT PLACED RETORTED SHALE DEPOSIT

FIGURE 4.3.7

Cross-Section Drawing of Ponds

TABLE 4.3.2

Permeability

Compaction	Loading (psi)	Permeability (ft/yr) No Added Water	Permeability (ft/yr) Optimum Water
Standard	50	45	7
		30	1.4
	200	20	0.8
Heavy	50	40	1.1
		34	0.6
	200	26	0.1

TABLE 4.3.3

Field Infiltration Data

Parameters	Pond I Initial	Pond I Core	Pond II Initial
Moisture, Wt%	22	19	0
Density, pcf, Bottom	100	106	92
Sides	100		87
Strength, psi	-	215	-
Permeability, ft/yr	0.3	0.6	2000

TABLE 4.3.4

Dusting and Surface Erosion

Sample	Density pcf	Water Added Wt%	Surface Treatment	Wind Speed, mph 10	25	45	Dust Collected (gm)
A	90	25	None	N	S	S	0.1
B	90	25	Scarified	S	S	S	0.05
C	70	12.5	None	N	M	H	1.00
D	70	0	None	S	M	H	1.25
E	70	0	Coherex	N	N	M	0.50

Note: N = No Surface Movement
S = Slight Surface Movement
M = Moderate Surface Movement
H = Heavy Surface Movement

Note: Coherex is a comercially available dust suppressant.

TABLE 4.3.5

Auto-Ignition Tendencies

Month	Temperature, °F Top	Middle	Bottom
March	45	55	65
April	50	55	60
May	55	55	55
June	65	60	55
July	75	65	55
August	70	65	60

Note: All temperature data are means from several probes (variations of ± 10°F).

Top: about 1/2 foot below surface.
Middle: about 6 feet below surface.
Bottom: about 9 feet below surface.

4.4 REVEGETATION

4.4.1 Utah State University Revegetation Concept

Utah State University has developed a plan to revegetate Paraho processed oil shale (McKell, 1978). The plan is based on range management, watershed management, botany, and soil science concepts and practices. The limited resources of water, topsoil, and native plants are given major consideration in the revegetation plan. The objectives of the revegetation plan are to: (1) return retorted shale to a usable, productive condition compatible with existing adjacent undisturbed natural areas and supporting fauna of the same kinds and in the same numbers as those existing at the time the baseline data were obtained; (2) effectively utilize the natural resources of the area, such as locally adapted plant species, precipitation, topsoil, and topography; (3) be cost-effective by making optimum use of local resources and establishing a system that will be primarily self-sustaining after the initial development period. Once the initial plants are established, the utilization of water harvesting techniques will allow succession to take place. The creation of water harvesting techniques would allow the vegetation to perpetuate itself under natural conditions.

Although the revegetation techniques developed by Utah State University have been initially successful, the proposed methods and recommendations must remain tentative until additional amounts of processed shale are available for field plantings and plot studies.

The system proposed by Utah State University coordinates seven components:

(1) Use of native plant species: The selection criteria for natural shrubs, grasses, and forbs is based on local ecotypes of dominant species tolerant to salinity, desired rooting habits, desirable feed for wildlife and livestock, tolerant of utilization, natural beauty, easily propagated, successfully established, and compatible with other species (McKell, 1976).

(2) Transplanting of container-grown stock: Shrubs and perennial grasses would be grown from cuttings or seedlings. Plants with well developed root systems, to ensure survival, would be transplanted at appropriate seasons of the year. Seed germination and seedling establishment from direct seeding in arid regions have resulted in a high probability of failure (McKell, 1978). Container-grown and transplanted fourwing saltbush (Atriplex canescens) have had a 75% survival after four years of growth. Nine shrubs and five grasses had a 60% survival rate after four years. Irrigation and fertilization at time of transplanting have shown no significant increase in plant establishment. The most successful plants have been fourwing saltbush (Atriplex canesceus), greasewood (Sarcobatus vermiculatus), winterfat (Ceratoides lanata), black sagebrush (Artemesia nova), western wheatgrass (Agropyron smithii), and crested wheatgrass (Agropyron cristatum) (McKell, et al, 1979). Shrubs required a high concentration of rooting hormone to establish a successful cutting. The peat pellet used as a rooting medium aids in establishing the cutting after planting. Seedlings and cuttings have been more successful in larger containers. Two important shrubs, big sagebrush (Artemesia tridentata) and greasewood (Sarcobatus vermiculatus), have had poor rooting success. Other propagation procedures will need to be developed for these species.

(3) Surface shaping: The retorted shale pile should first be compacted to 98.7 pcf, stabilizing the pile and reducing its permeability. After compaction, the surface of the pile is shaped into terraces and slopes on side hills and into hillocks on the flat top (Figure 4.4.1). This shaping would provide a catchment slope for harvesting precipitation and a terrace for transplanting plants (McKell, 1978). Small basins, or small slopes and depressions as shown in Figure 4.4.1, 75 cm in diameter and 100 cm deep, shaped in the retorted shale and filled with topsoil, provide an area for better plant growth than on a flat surface. In order to facilitate movement of water without increasing sediment production, the slope of the catchment area should be smooth and reduced. A steep slope will increase the water velocity and also increase the destructive forces. Reducing the catchment area would reduce the area contributing to salt and sediment production (Wagenet and McKell, 1980).

(4) Shale surface stabilization: Substances resistant to destruction and disintegration applied to the surface of retorted shale would prevent

movement of dust particles, increase water harvest, and restrict the capillary rise of salts from the retorted shale.

A completed study by Malek (1980) with polyvinyl acetate, petroset SB, mulch, and paraffin applied to shale surface indicates that paraffin would be the best shale stabilizer. Paraffin treated shale surfaces have high runoff after simulated rainfall (Figure 4.4.2), high water harvesting efficiency (Figure 4.4.3, Table 4.4.1), low sediment delivery rate (Figure 4.4.6), low sediment production (Table 4.4.2, Figure 4.4.7), low total dissolved solids in harvested water (Table 4.4.3, Figures 4.4.8 and 4.4.9), low total dissolved solids of harvested water and corresponding electrical conductivity values (Tables 4.4.4 and 4.4.5). Based on laboratory data, Table 4.4.5 estimates values of runoff, sediment, and total dissolved solids from a one hectare processed oil shale pile. The low electrical conductivity of paraffin treated plots (0.5 kg paraffin per square meter) provides an efficient surface cover against falling rain and flowing water. The surface cover reduces direct contact of runoff with retorted shale which reduces the release of salt to water running off the surface. Paraffin treated surfaces had a negative capillary force that prevented water from moving to the surface and evaporating. Little or no salt crust was formed due to slow evaporation process and low saline concentration of harvest water.

(5) Effective but limited use of topsoil: Trenches 75 x 100 cm along the terraces and swales would be filled with topsoil. The topsoil, serving as the necessary growth medium to receive the container-grown native plants, would provide an inoculum of soil microorganisms, a partial source of native plant seeds, and a buffer against high salt concentrations that might develop from the processed shale. It is expected that harvested water from the catchment slopes will percolate through the topsoil and out into the processed shale, increasing the salinity levels around the root zone. Salt tolerant species are selected for growth in the expected high salinity of retorted shale (MdKell, 1978).

(6) Fulfillment of minimal fertility requirements: Fertilization of plants would occur as needed and as determined by existing and ongoing research. As plant roots grow into the retorted shale, some fertilization will be

necessary. Because the native plants evolved in relatively low fertility soils, their fertility requirements of nitrogen and phosphorus are not as high as crop plants or some exotic species (McKell, 1978).

(7) Supplemental irrigation for plant survival and salinity management: Supplemental irrigation may be necessary during extended drought periods in the early years of the revegetation project. One way to supply the water, if required, would be by a drip-irrigation system, periodically supplying low volumes of water through a flexible pipe system installed along each terrace. Low volume irrigation may also be needed to reduce salinity in the topsoil trench to levels tolerable to the plants (McKell, 1978). Proper management of irrigation can effectively reduce salts (sodium, magnesium, sulfate) to levels not detrimental to most salt tolerant plant species. With limited amounts of water, salts are not leached to groundwater, but are stored in the shale pile. Upward salt migration during evaporation has not been evident as a problem during evaporation. At low water contents, hydraulic conductivity values have been characteristically low for the retorted shale tested.

4.4.2 Lysimeter Study

The Environmental Protection Agency sponsored a lysimeter study (Figure 4.4.9) at Anvil Points using Paraho retorted shale. The lysimeter study performed by Harbert (1978) had two objectives: to investigate the vegetative stabilization of Paraho retorted shale covered with various depths of soil and to investigate subsurface water and salt movement through compacted and uncompacted Paraho retorted shale covered with various depths of soil cover. The subsurface water and salt movement through retorted shale will not be addressed in this volume. The initial results were included in Part III, Water Quality. The revegetation stabilization will be covered here. The seeding mixtures used by Harbert are listed in Table 4.4.6. After one year's growth, the perennial vegetation cover on the retorted shale was sparse, 2-19% (Table 4.4.7). The perennial cover of the soil control and soil-covered shale was 45-85% after one year's growth. The total cover for the retorted shale after one year was 15-50%, and the soil-covered shale and soil control varied from 49% to 100%. After three years of growth, the retorted shale total was 22-41%. The soil-covered shale and soil control was 31-72%. The total cover for the different treatments generally increased after the second year's growth (Kilkelly, Harbert, and Berg, 1981). After three years of growth, the total cover for the various treatments decreased. The total cover decrease was especially evident in the high-elevation lysimeter. The total cover for the retorted shale showed only slight variations. The natural precipitation conditions of the low-elevation lysimeter seemed to support shrub growth better than the increased precipitation of the high-elevation lysimeter. Even though the retorted shale did not grow perennial grasses very well, the species represented more closely resemble the surrounding native vegetation. The high perennial cover values of soil-covered shale and the soil controls may indicate that the perennial grasses are inhibiting species diversity.

4.4.3 Colorado State University Reclamation Studies

The Colorado State University Retorted Shale Succession Study is located in the Piceance Basin near Tract C-a (Figure 4.1.1). The Colorado State University Retorted Shale Succession Study used six artificial soil-shale profiles (Figure 4.4.10) to evaluate plant growth and succession on Paraho retorted shale (Cook and Redente, 1980 and Redente and Ruzzo, 1979). The specific objectives of the research include: (1) determining proper seeding practices of potentially usable mixtures of plant species and their relationship to cultural practices such as fertilization, irrigation, and mulching, (2) determining the rate and direction of plant succession on disturbed topsoil, subsoil, overburden, retorted shale, and retorted shale overlain by soil as influenced by natural invasion, species mixtures, and cultural practices, and (3) determining proper management procedures for long-term stabilization and reclamation of retorted shale materials (Redente and Cook, 1981). The study was designed to consist of three variables: soil-shale profile, seed mixture, and fertilizer treatment. The six artificial soil-shale profiles simulating field conditions constructed were:

1. Retorted shale to a depth of 61 cm without any soil covering.
2. 30.5 cm soil over retorted shale.
3. 61 cm soil over retorted shale.

4. 91.5 cm soil over retorted shale.
5. 61 cm soil over 30.5 cm gravel capillary barrier over retorted shale.
6. Soil control with no retorted shale in the profile.

After three years, data from the artificial soil-shale profiles indicate that soil cover is the most important factor in re-establishing a functional ecosystem. The soil-shale profiles demonstrate that plant vigor and productivity increased on soil cover depth of 30.5 to 91.5 cm (Redente and Ruzzo, 1979a and 1979b; Cook, et al., 1980; Redente and Ruzzo, 1980; Ruzzo and Redente, 1980; Redente, 1980; Mount and Redente, 1981; Redente and Cook, 1981). The soil cover of 61 and 91.5 cm produced the most total above ground biomass (Figure 4.4.11).

Topsoil of 61 cm depth over shale provides a sufficient rooting zone, a functional decomposer community, and a storage zone for moisture recharge from snow melt. Topsoiling also reduces and in come cases eliminates the need for leaching, fertilization, mulching, irrigation and long-term management. Results also indicate that the capillary barrier of gravel aids in the prevention of salinization of soil cover and aids in the water holding capacity of the soil. The adverse pH and electrical conductivity values of the retorted shale requires large inputs of resources and management for direct revegetation, while the use of topsoil reduces these inputs and accelerates the stabilization and successional process.

Three diverse seed mixtures of grasses, forbs, and shrubs were studied: an all native mixture, a combination of native and introduced species, and an introduced species mixture (Table 4.4.8). The combination mixture of native and introduced species appears to provide the most rapid stabilization of soil profiles (Redente and Ruzzo, 1979b; Ruzzo and Redente, 1980) and allows greater diversity of forbs and shrubs (Redente and Cook, 1981).

However, the native grasses and shrubs had excellent growth and the highest cover values (Figure 4.4.11). The introduced species mixture approached a closed community more rapidly than native species mixtures. Because of more rapid emergence, establishment and survival rate, along with more rapid and vigorous growth, the introduced species were able to reduce the entry of invading annuals at a significantly greater level than native species (Redente and Ruzzo, 1979a; and Mount and Redente, 1981). As shown in Figure 4.4.12, the native and introduced mixed species had a consistently higher biomass production than either the native or introduced mixture. Even though the introduced seed mixture had the lowest biomass production (Figure 4.4.13), it had the highest plant density (Redente and Ruzzo, 1979b). The density values of the species mixtures are increasing and approaching those of the native vegetation. The density of the native seed mixtures is increasing at a more rapid rate than the introduced species mixtures. While the surrounding native vegetation is dominated by sagebrush, the soil profile seeded areas are predominantly grasses with forbs and shrubs as secondary components (Redente and Ruzzo, 1980).

The addition of nitrogen and phosphorus fertilizer increased the biomass of grasses by allowing higher seedling establishment (Figure 4.4.14), decreased the biomass production of forbs (principally nitrogen-fixing legumes), and had no effect on shrub establishment and growth (Cook and Redente, 1980; Redente and Ruzzo, 1980; and Mount and Redente, 1981).

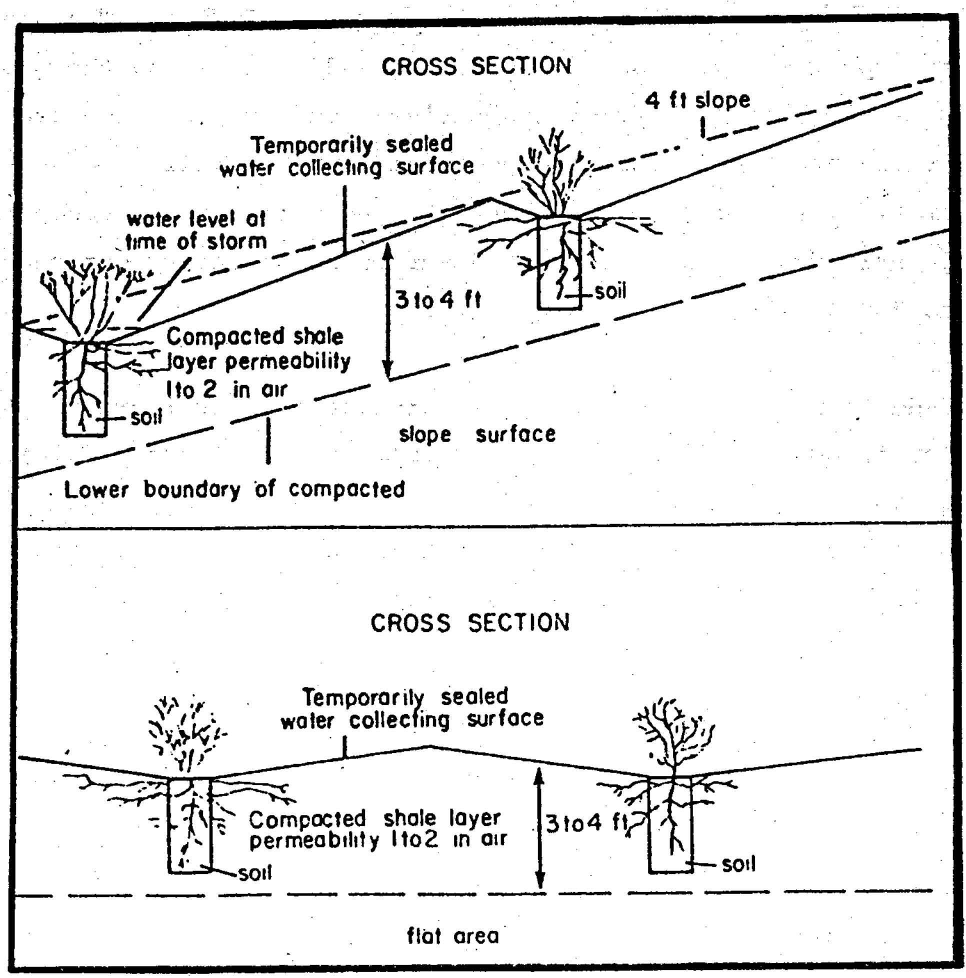


FIGURE 4.4.1

Surface Modification and Vegetation
(McKell, et al., 1979)

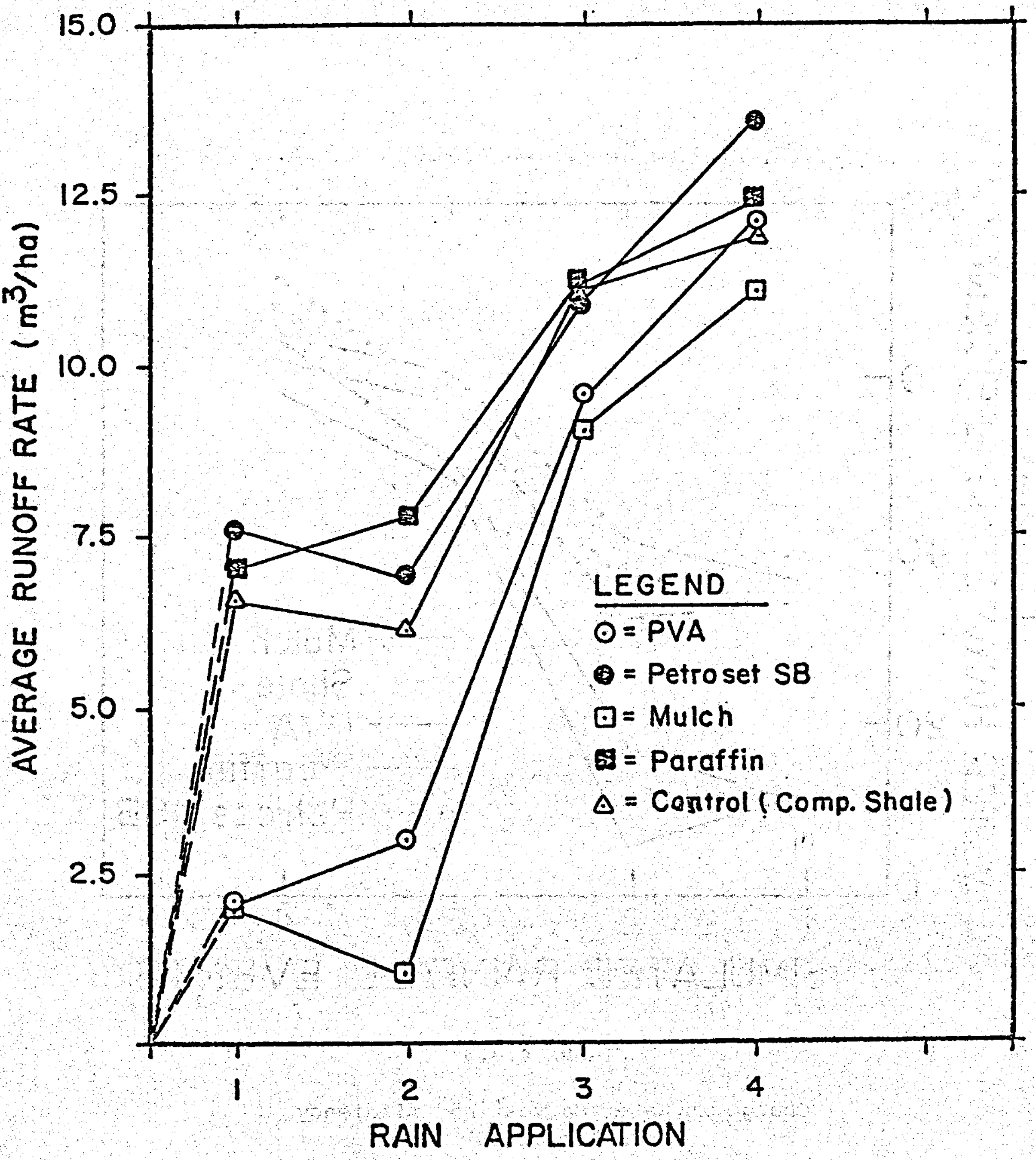


FIGURE 4.4.2

Rate of Runoff in Four Rains
(Malek, 1980)

Event	Amount of Rain	Time Interval (days)
1	2.57 cm	start
2	1.90 cm	28 days
3	3.43 cm	12 days
4	5.14 cm	3 days
	13.04 cm	

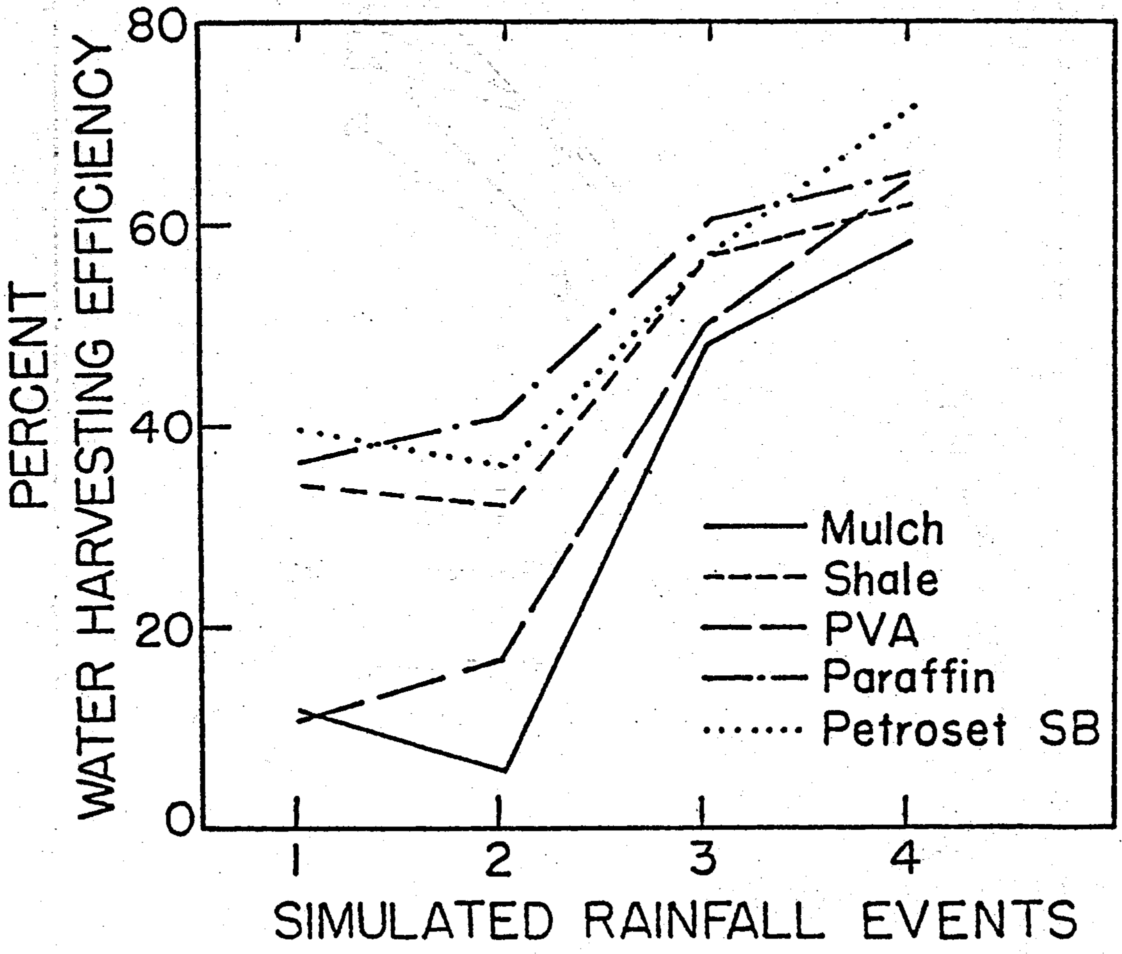


FIGURE 4.4.3

Change in Water Harvesting Efficiency
(Malek, 1980)

Event	Amount of Rain	Time Interval (days)
1	2.57 cm	start
2	1.90 cm	28 days
3	3.43 cm	12 days
4	5.14 cm	3 days
	13.04 cm	

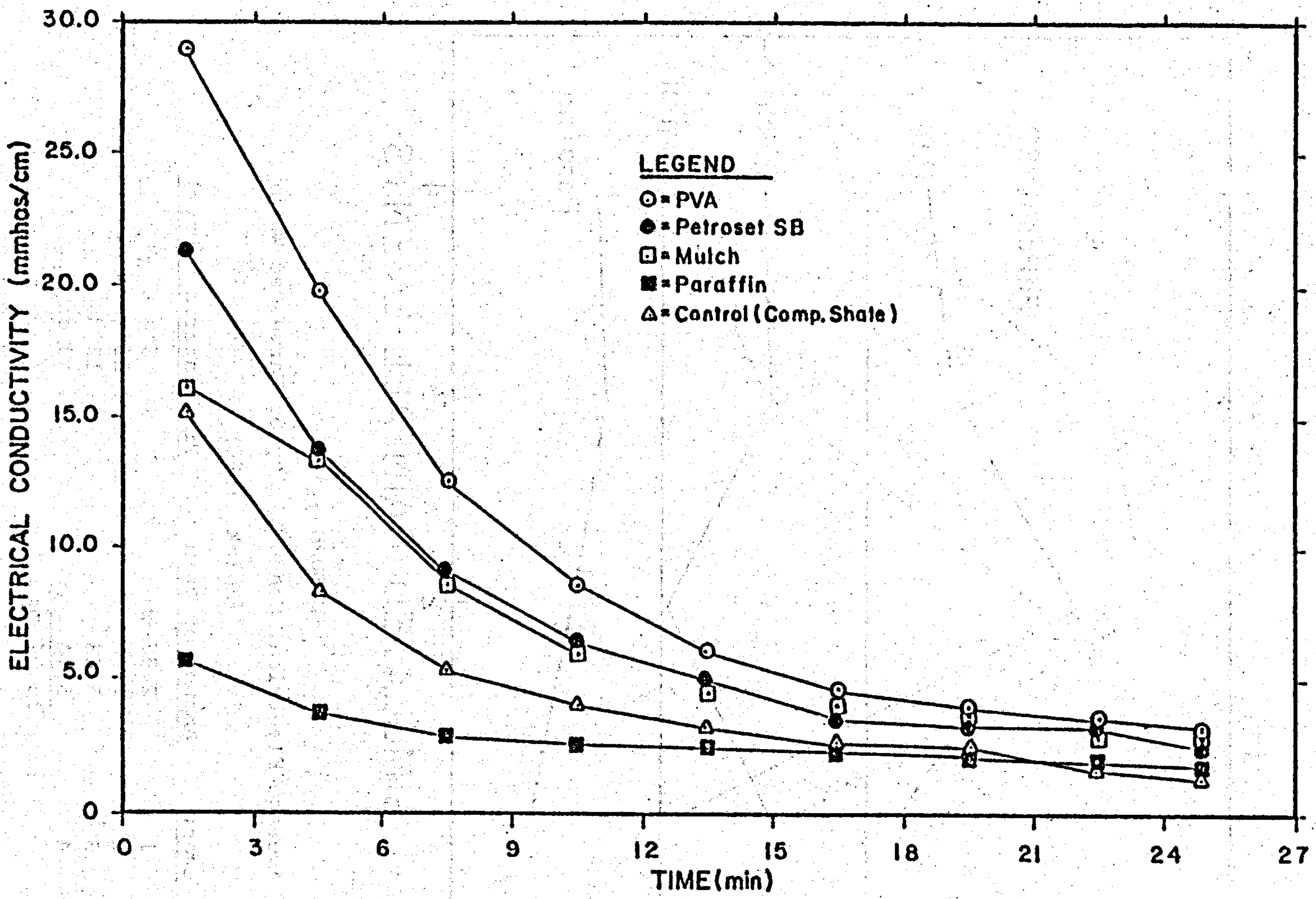


FIGURE 4.4.4

Electrical Conductivity of Runoff Water

(Malek, 1980)

(Fourth Rainfall Application)

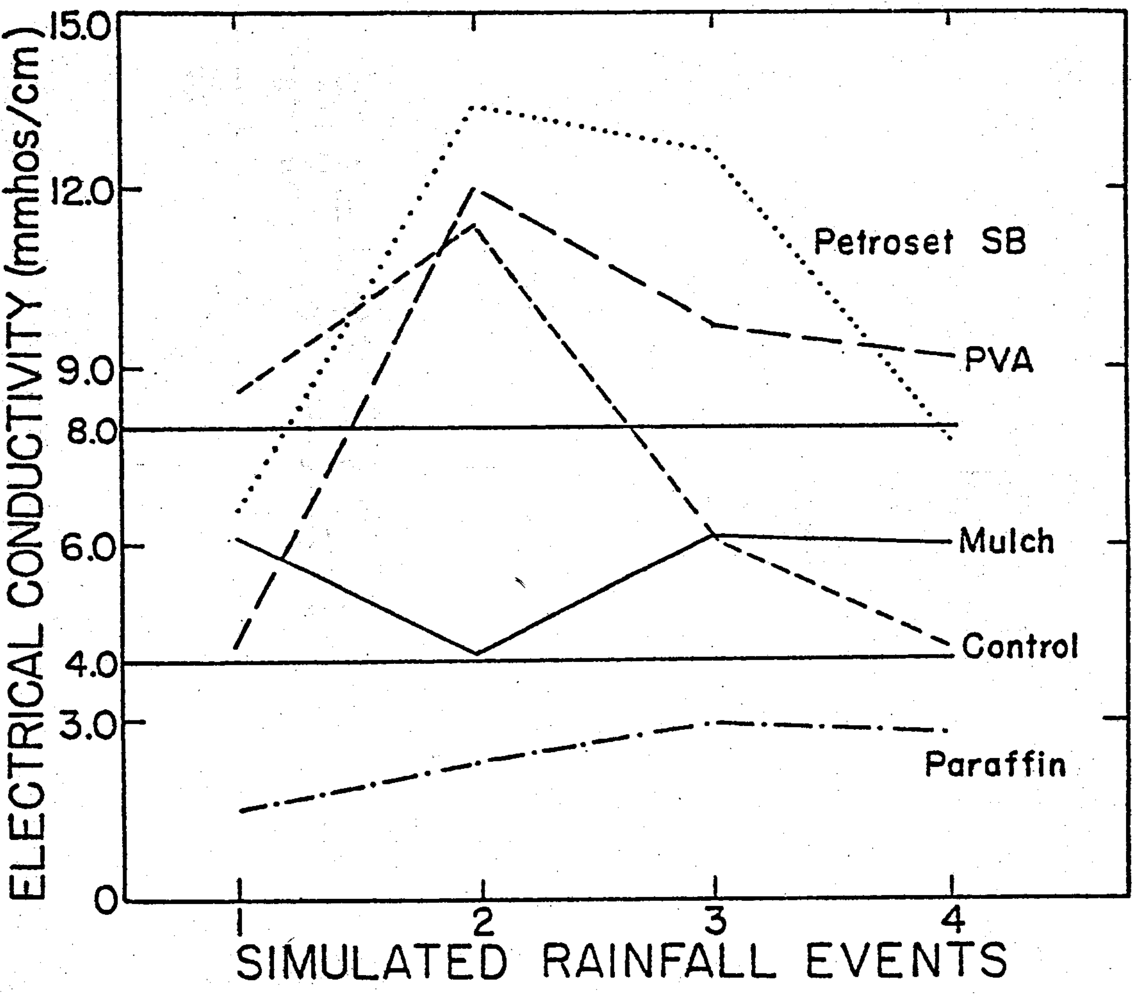


FIGURE 4.4.5

Average Electrical Conductivity of Harvested Water

(Malek, 1980)

Event	Amount of Rain	Time Interval (Days)
1	2.57 cm	Start
2	1.90	28 days
3	3.43	12 days
4	5.14	3 days
	13.04 cm	

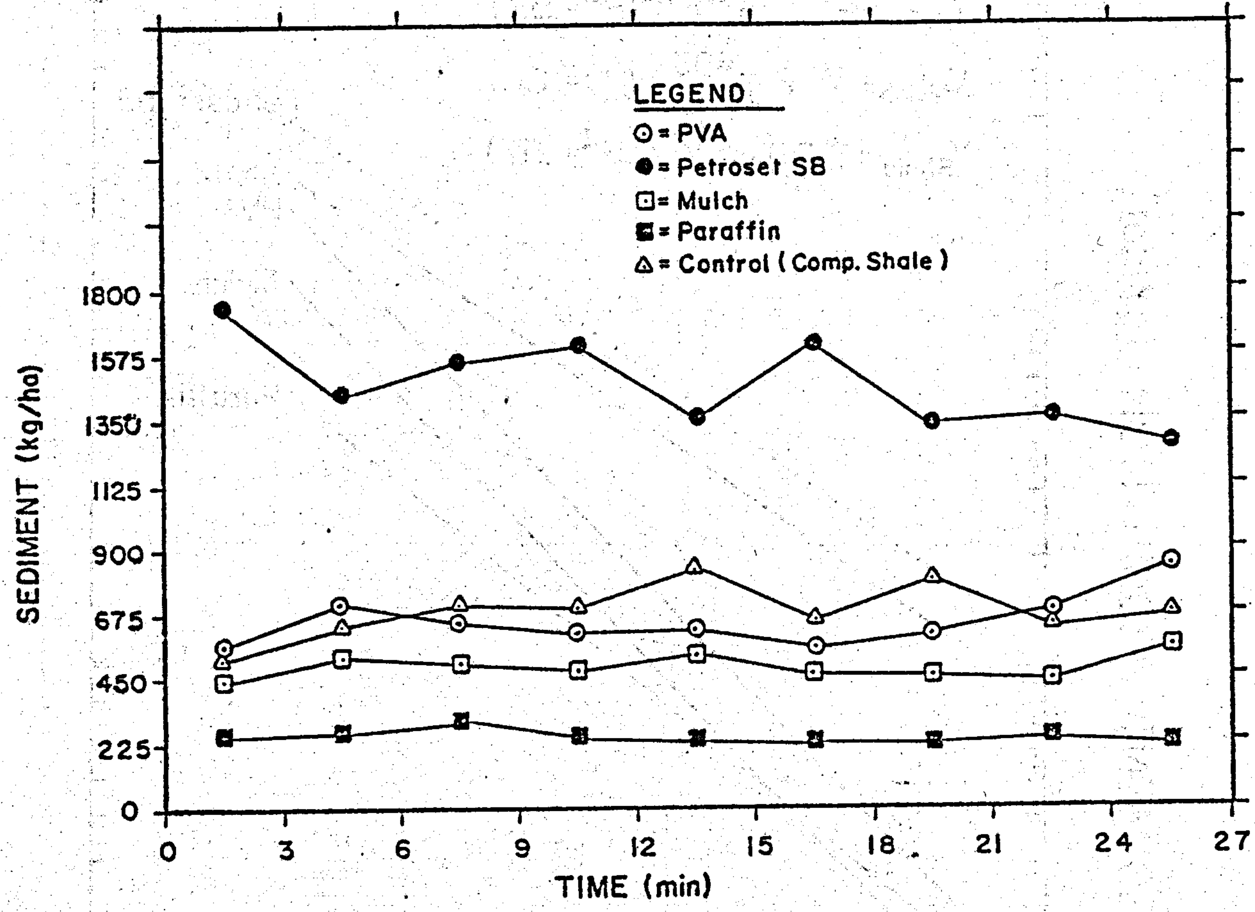


FIGURE 4.4.6

Sediment Delivery Rate
(Malek, 1980)
(Fourth Rainfall Event)

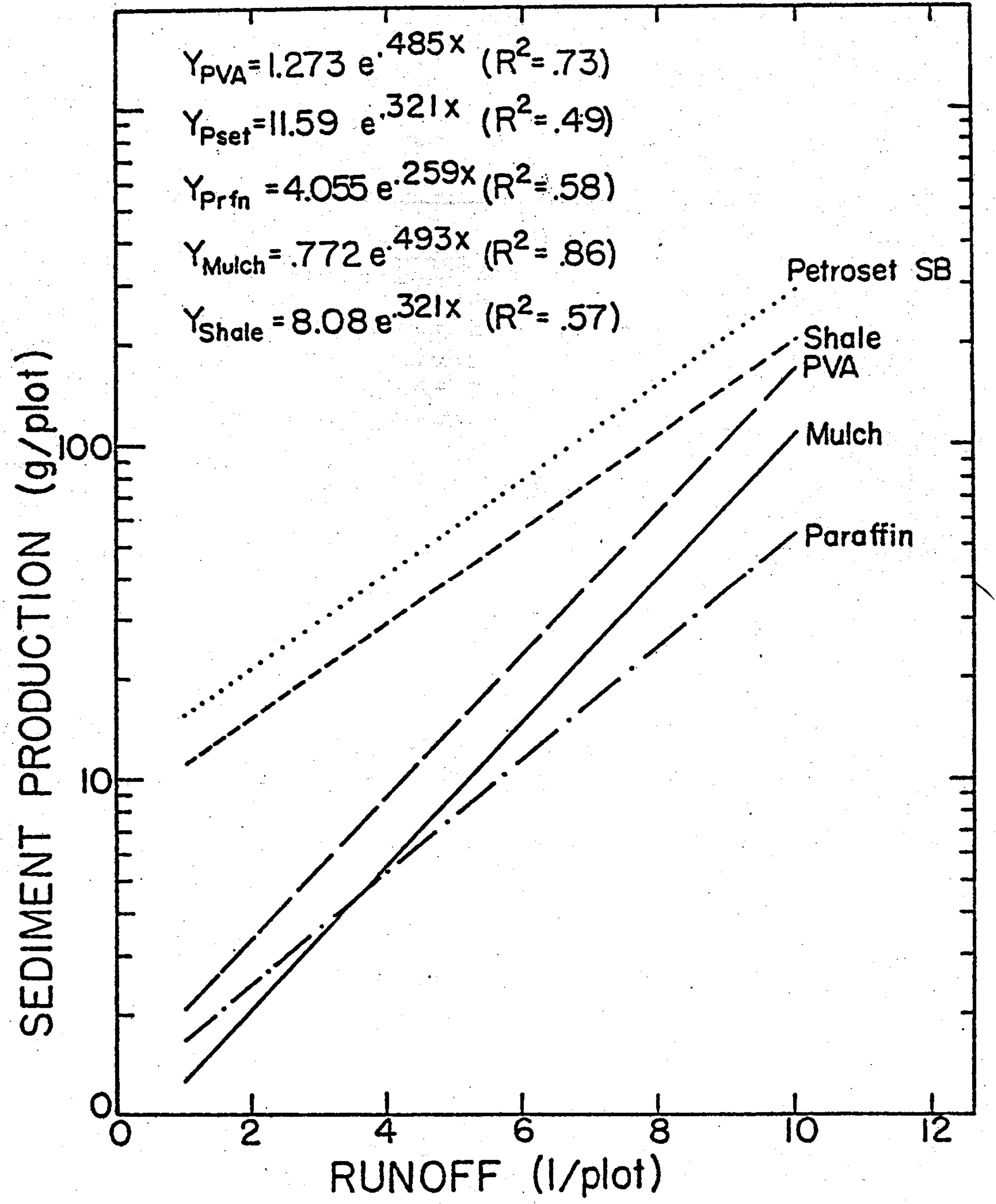


FIGURE 4.4.7

Sediment Production

(Malek, 1980)

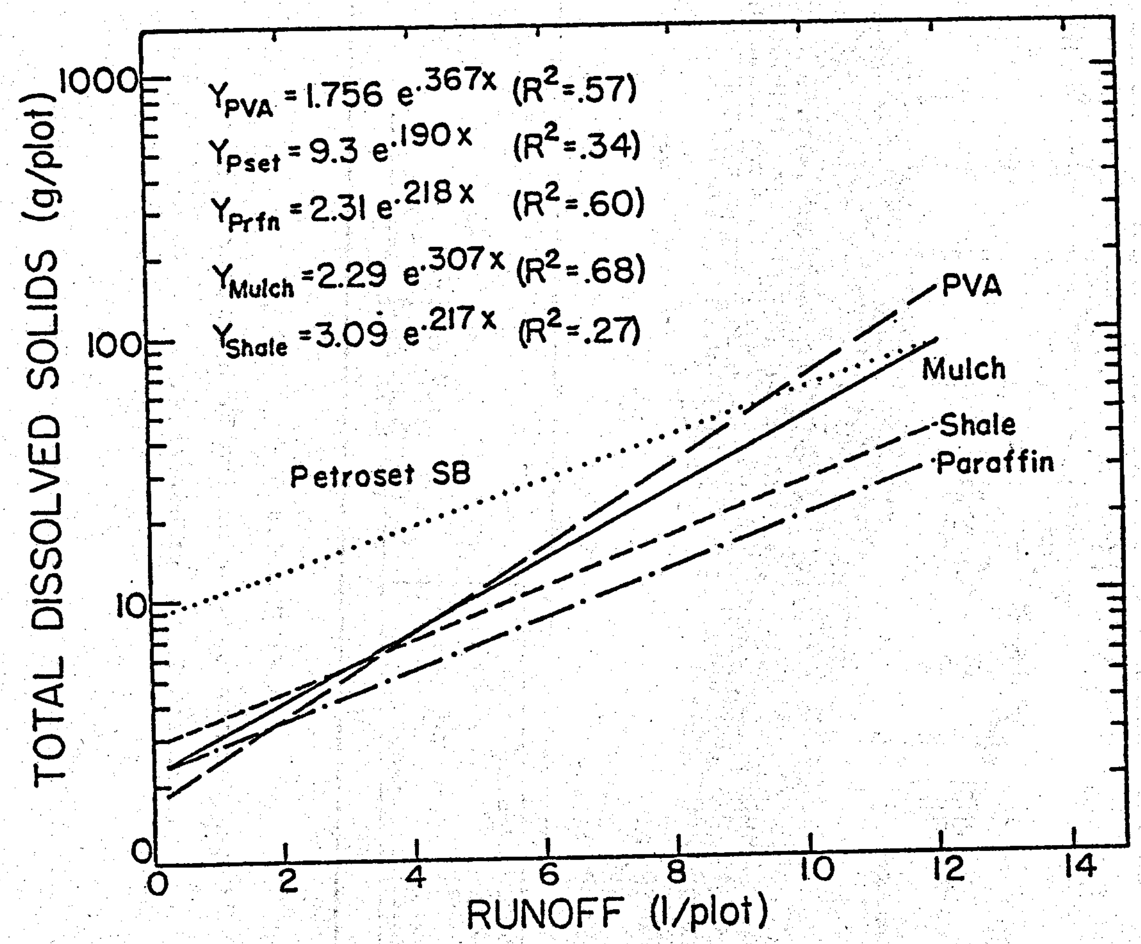


FIGURE 4.4.8

Total Dissolved Solids Concentration in Harvested Water

(Malek, 1980)

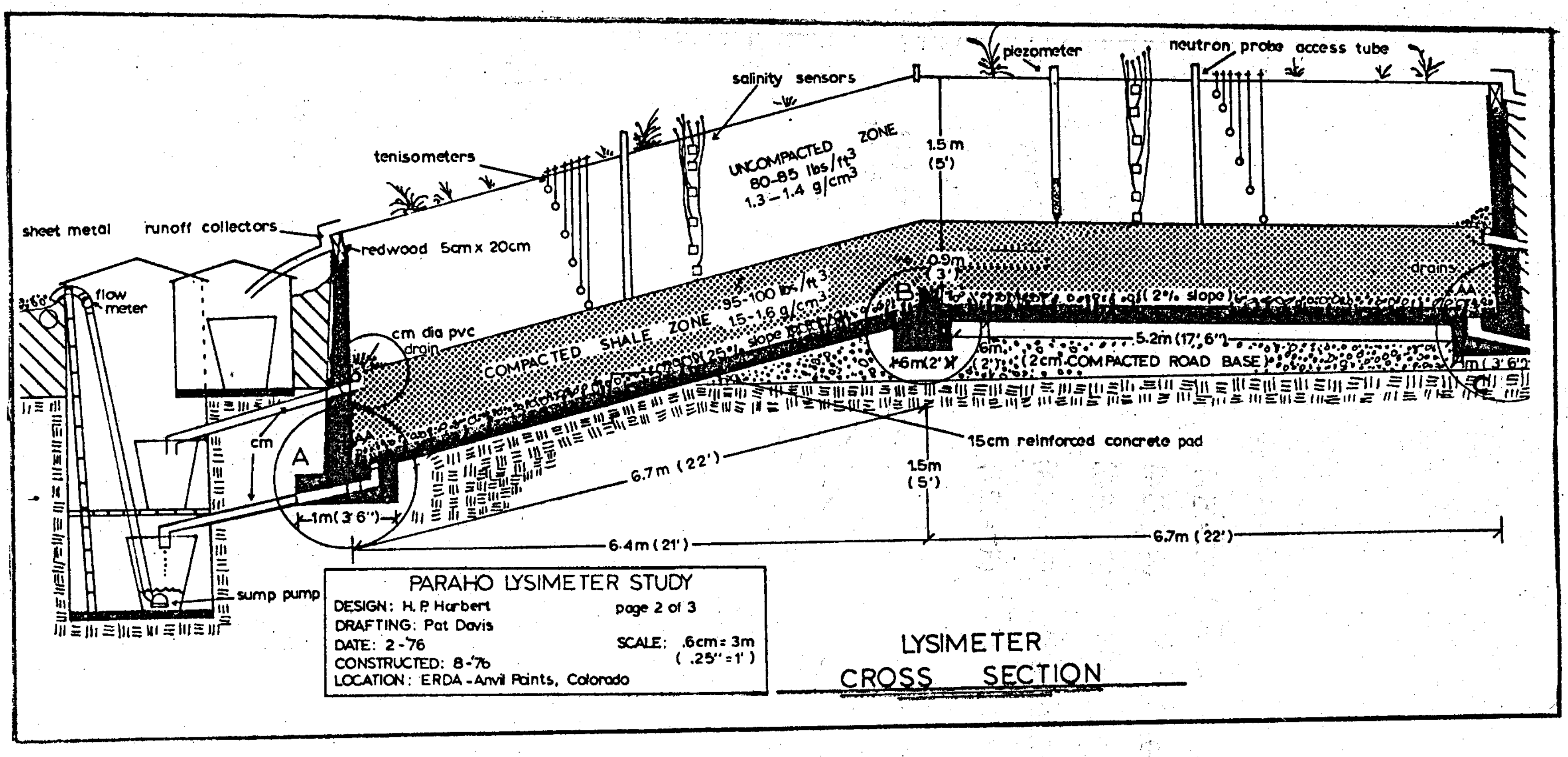


FIGURE 4.4.9

Cross Section Showing Design of Lysimeter

(Harbert, Berg, McWhorter, 1979)

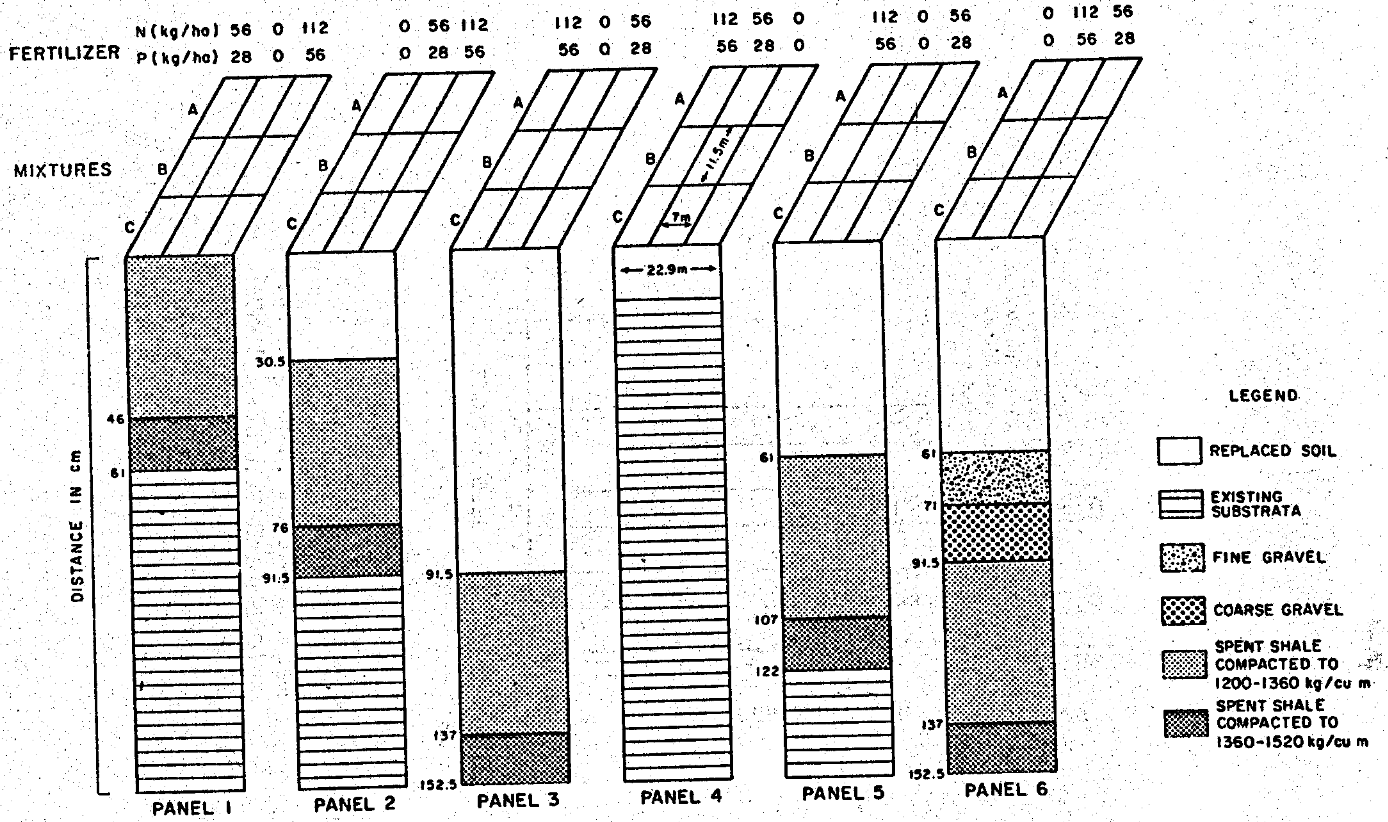


FIGURE 4.4.10

Profile Configuration for Retorted Shale Successional Plot
(Redente and Ruzzo, 1979b)

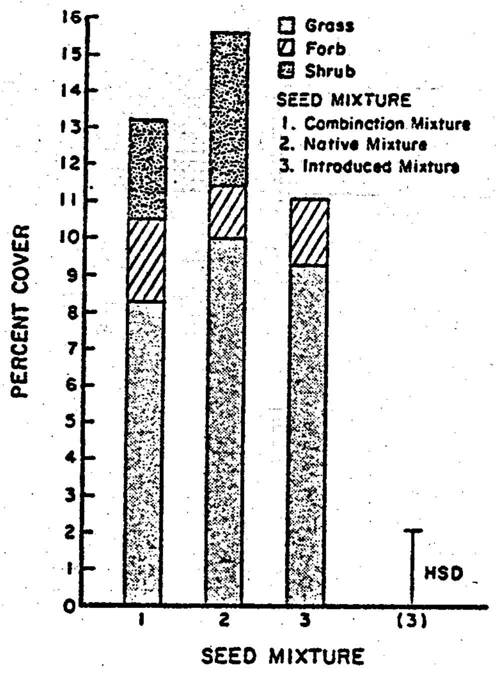


FIGURE 4.4.11

Mean Cover of Seeded Species
(Cook and Redente, 1980)

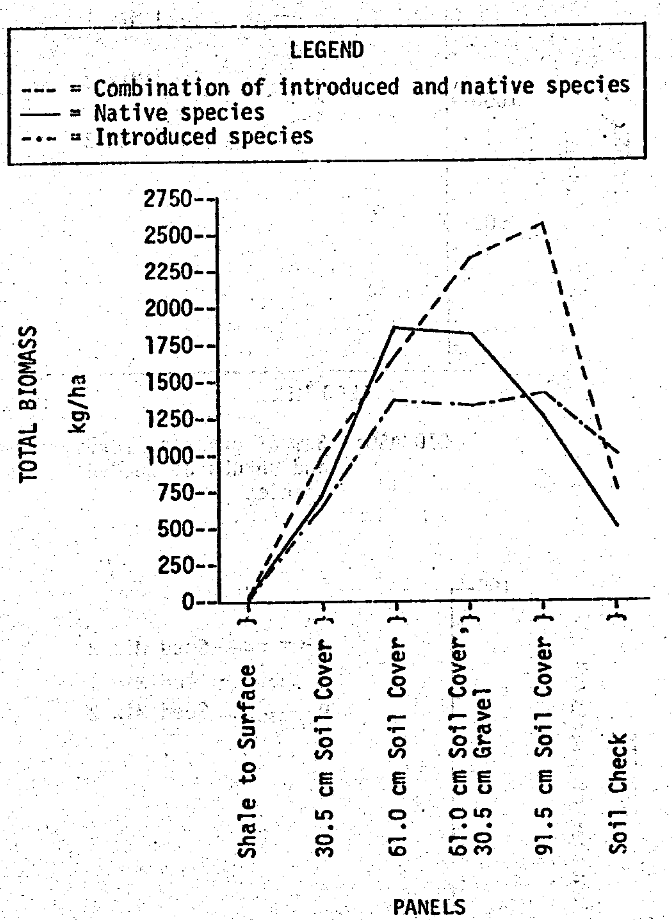
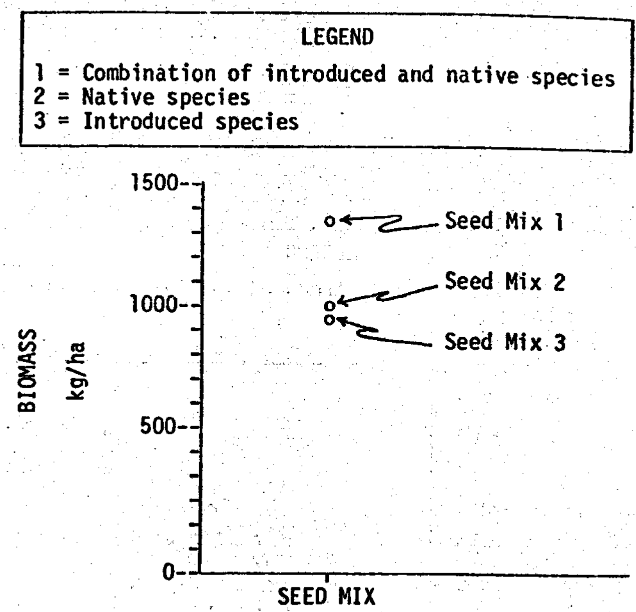
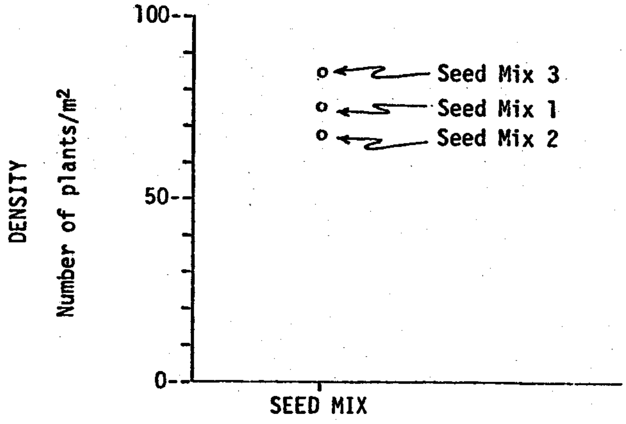


FIGURE 4.4.12

Total Biomass of Seeded Species on the Retorted Shale Topsoil Depth Study (Redente and Ruzzo, 1979b)



BIOMASS: Sum of grasses, forbs, and shrubs of seeded species



DENSITY: Sum of grasses, forbs, and shrubs of seeded species

FIGURE 4.4.13

Biomass and Density of the Species Mixtures
Data Points are Averages Over all Soil Depth Treatments
(Redente and Ruzzo, 1979b)

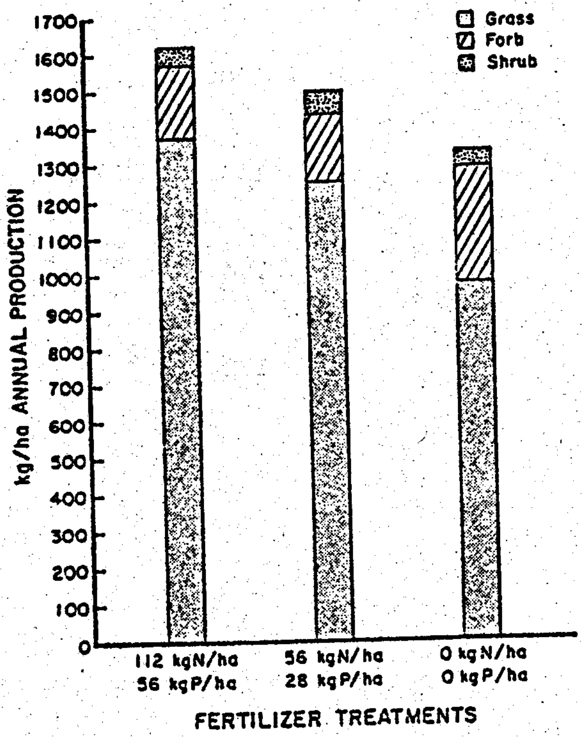


FIGURE 4.4.14

Production of Seeded Species
Fertilizer Treatments
(Cook and Redente, 1980)

TABLE 4.4.1

Quantity of Harvested Water

(Malek, 1980)

Surface Treatment	Volume of Harvested Water (ℓ/Plot)	Depth of Harvested Water Over Vegetated Area (cm)
PVA	145.4	22.9
Petroset SB	190.1	29.9
Mulch	130.8	20.6
Paraffin	184.0	28.9
Comp. Shale	172.5	27.1

TABLE 4.4.2

Sediment Production

(Malek, 1980)

Simulated Rain Events/Surface Treatment	1		2		3		4	
	g/plot	kg/ha	g/plot	kg/ha	g/plot	kg/ha	g/plot	kg/ha
PVA	15.8	61.5	123.0	476.8	636.2	2465.2	1411.2	5469.8
Petroset SB	116.0	449.6	1035.1	4011.1	2892.0	11206.7	3387.8	1312.8
Mulch	12.6	49.1	5.3	20.6	387.2	1500.4	982.4	3806.9
Parafin	45.0	174.6	88.4	342.5	426.8	1653.7	550.4	2131.9
Comp. Shale	171.2	663.5	477.1	1848.9	1312.0	5084.1	1450.0	5618.9

Event	Amount of Rain	Time Interval (days)
1	2.57 cm	start
2	1.90 cm	28 days
3	3.43 cm	12 days
4	5.14 cm	3 days
	13.04 cm	

TABLE 4.4.3

Total Dissolved Solids (TDS) in Harvested Water

(Malek, 1980)

Treatment	1st Rain		2nd Rain		3rd Rain		4th Rain	
	g/plot	kg/ha	g/plot	kg/ha	g/plot	kg/ha	g/plot	kg/ha
PVA	2.91	11.28	10.48	40.61	43.97	170.34	79.27	307.14
Petroset SB	17.00	65.91	25.65	99.39	67.52	261.6	62.2	241.03
Mulch	4.33	16.77	3.06	4.09	25.24	97.8	45.61	176.84
Paraffin	3.03	11.77	4.05	15.67	13.89	53.85	21.54	83.50
Comp. Shale	19.84	7.67	19.00	73.62	30.16	116.88	33.55	130.02

Event	Amount of Rain	Time Interval (days)
1	2.57 cm	start
2	1.90 cm	28 days
3	3.43 cm	12 days
4	5.14 cm	3 days
	13.04 cm	

TABLE 4.4.4

Average TDS of Harvested Water and Corresponding EC Values. LogEC = (LogTDS + .47413)/1.1212.

(Malek, 1980)

Treatment	1st Rain		2nd Rain		3rd Rain		4th Rain	
	wtd TDS mg/lit	EC mmhos/cm	wtd TDS mg/lit	EC mmhos/cm	wtd TDS mg/lit	EC mmhos/cm	wtd TDS mg/lit	EC mmhos/cm
PVA	4018	4.3	12622	12.0	9941	9.7	9254	9.1
Petroset SB	6424	6.6	14257	13.4	13358	12.7	6539	6.7
Mulch	5890	6.1	3831	4.2	5891	6.1	5857	6.1
Paraffin	1236	1.5	2018	2.3	2618	3.0	2492	2.8
Comp. Shale	8716	8.7	11893	11.4	5945	6.2	4041	4.4

Event	Amount of Rain	Time Interval (days)
1	2.57 cm	start
2	1.90 cm	28 days
3	3.43 cm	12 days
4	5.14 cm	3 days
	13.04 cm	

TABLE 4.4.5

Estimated Values of Runoff, Sediment and Total Dissolved Solids

(Malek, 1980)

Treatment	Harvested Water		Sediment	Salt
	ha-cm	M^3	ton/ha	kg/ha
PVA	6- 8.5	600- 850	5-7	650-700
Petroset SB	9-12	900-1200	16-20	850-900
Mulch	6- 8	600- 800	2.5-4	350-420
Paraffin	9-11	900-1100	2-3	200-220
Comp. Shale	7-9	700- 900	10-14	480-540

TABLE 4.4.6

Seeding Mixtures and Rates of Application (Harbert, 1978)

Common Name	Scientific Nomenclature	Rate Kg/ha
HIGH ELEVATION MIXTURE		
Species Seeded		
Western wheatgrass	*Agropyron smithii*	9.0
Bluebunch wheatgrass	*Agropyron spicatum*	4.5
Utah sweetvetch	*Hedysarum boreale utahensis*	4.5
Palmer penstemon	*Penstemon palmeri*	2.2
Lupin spp.	*Lupines spp.*	2.2
Arrowleaf balsamroot	*Balsamorhiza sagittata*	2.2
	TOTAL	24.6
Species Transplanted		
Serviceberry, Utah	*Amelanchier utahensis*	4/replication
Bitterbrush, antelope	*Purshia tridentata*	2/replication
LOW ELEVATION MIXTURE		
Species Seeded		
Western wheatgrass	*Agropyron smithii*	4.5
Bluebunch wheatgrass	*Agropyron spicatum*	4.5
Indian ricegrass	*Oryzopsis hymenoides*	4.5
Galleta	*Hilaria jamesii*	4.5
Winterfat	*Ceratoides lanata*	1.1
Fourwing saltbush	*Atriplex canescens*	2.2
Utah sweetvetch	*Hedysarum boreale utahensis*	4.5
Palmer penstemon	*Penstemon palmeri*	2.2
	TOTAL	28.0

TABLE 4.4.7

Vegetative Cover by Species Categories for Paraho Retorted Shale, Soil-Covered Paraho Retorted Shale, and Soil Control, 1978 through 1980 (Kilkelly, Harbert, and Berg, 1981)

		High-Elevation Lysimeter					
		2% Slope North Aspect			25% Slope South Aspect		
Treatment	Species Categories	1978	1979	1980	1978	1979	1980
		%					
Paraho Retorted Shale	Perennial grasses	19	5	3	14	6	2
	Shrubs	2	-	-	-	-	-
	Other	29	46	48	26	48	39
	Total	50	51	51	40	54	41
20 cm Soil Cover/Paraho	Perennial grasses	59	72	31	60	71	47
	Shrubs	-	-	-	-	-	-
	Other	2	11	15	8	21	9
	Total	61	83	46	68	92	56
40 cm Soil Cover/Paraho	Perennial grasses	57	63	32	49	65	46
	Shrubs	-	-	-	-	-	-
	Other	5	39	13	4	30	16
	Total	62	102	45	53	95	62
60 cm Soil Cover/Paraho	Perennial grasses	47	60	43	44	67	40
	Shrubs	-	-	-	-	-	-
	Other	7	29	24	5	31	13
	Total	54	89	67	49	98	53
80 cm Soil Cover/Paraho	Perennial grasses	40	59	29	39	73	46
	Shrubs	-	-	-	-	-	-
	Other	16	27	22	10	26	11
	Total	56	86	51	49	99	57
Soil Control	Perennial grasses	86	93	33	73	95	29
	Shrubs	-	-	-	-	-	-
	Other	14	2	-	19	2	2
	Total	100	95	33	92	97	31

TABLE 4.4.7 (Cont'd)

		Low-Elevation Lysimeter					
		2% Slope North Aspect			25% Slope South Aspect		
Treatment	Species Categories	1978	1979	1980	1978	1979	1980
		%					
Paraho Retorted Shale	Perennial grasses	8	< 1	< 1	2	< 1	-
	Shrubs	1	1	2	5	3	3
	Other	6	24	24	15	27	19
	Total	15	26	27	22	31	22
20 cm Soil Cover/Paraho	Perennial grasses	42	18	7	26	31	23
	Shrubs	2	2	1	3	-	-
	Other	23	80	61	39	38	48
	Total	67	100	69	68	69	71
40 cm Soil Cover/Paraho	Perennial grasses	45	28	12	41	20	17
	Shrubs	< 1	-	-	2	< 1	2
	Other	18	69	59	19	61	47
	Total	64	97	71	62	82	66
60 cm Soil Cover/Paraho	Perennial grasses	39	22	13	47	16	12
	Shrubs	3	3	2	< 1	< 1	-
	Other	29	62	51	12	79	43
	Total	71	87	66	60	96	55
80 cm Soil Cover/Paraho	Perennial grasses	59	48	25	45	22	13
	Shrubs	3	2	4	2	< 1	1
	Other	8	24	33	11	57	43
	Total	70	74	62	58	80	57
Soil Control	Perennial grasses	45	51	20	61	52	22
	Shrubs	4	6	3	15	18	10
	Other	33	29	30	8	14	20
	Total	82	86	53	84	84	52

TABLE 4.4.8

Seed Mixtures Used on the Retorted Shale-to-Surface Study

(Redente and Cook, 1981)

Common Name	Scientific Name	Seeding Rate PLS (kg/ha)
Mixture A--Salt-tolerant species		
1. Jose tall wheatgrass	*Agropyron elongatum*	4.48
2. Rosana western wheatgrass	*Agropyron smithii*	2.24
3. Critana thickspike wheatgrass	*Agropyron dasystachyum*	1.12
4. Oahe intermediate wheatgrass	*Agropyron intermedium*	2.24
5. Slender wheatgrass	*Agropyron trachycaulum*	2.24
6. Vinal Russian wildrye	*Elymus junceus*	1.12
7. Madrid yellow sweetclover	*Melilotus officinalis*	1.12
8. Ladak alfalfa	*Medicago sativa*	1.12
9. Strawberry clover	*Trifolium fragiferum*	1.12
10. Fourwing saltbush	*Atriplex canescens*	4.48
11. Shadscale saltbush	*Atriplex canfertifolia*	4.48
12. Mat saltbush	*Atriplex corrugata*	2.24
13. Castle Valley clover	*Atriplex cuneata*	3.36
14. Gardner saltbush	*Atriplex gardneri*	2.24
15. Winterfat	*Ceratoides lanata*	4.48
Mixture B--Native species		
1. Beardless bluebunch wheatgrass	*Agropyron inerme*	2.24
2. Sodar streambank wheatgrass	*Agropyron riparium*	1.12
3. Rosana western wheatgrass	*Agropyron smithii*	2.24
4. Paloma Indian ricegrass	*Oryzopsis hymenoides*	1.12
5. Green needlegrass	*Stipa viridula*	1.12
6. Sweetvetch	*Hedysarum boreale*	6.72
7. Lewis flax	*Linum lewisii*	1.12
8. Palmer penstemon	*Penstemon palmeri*	0.56
9. Big sagebrush	*Artemisia tridentata*	0.056
10. Fourwing saltbush	*Atriplex canescens*	4.48
11. Curlleaf mountain mahogany	*Cercocarpus ledifolius*	4.48
12. Winterfat	*Ceratoides lanata*	4.48
Mixture C--Introduced species		
1. Nordan crested wheatgrass	*Agropyron cristatum*	1.12
2. Jose tall wheatgrass	*Agropyron elongatum*	4.48
3. Oahe intermediate wheatgrass	*Agropyron intermedium*	2.24
4. Siberian wheatgrass	*Agropyron sibericum*	1.12
5. Luna pubescent wheatgrass	*Agropyron trichophorum*	2.24
6. Regar meadow brome	*Bromus erectus*	2.24
7. Vinal Russian wildrye	*Elymus junceus*	1.12
8. Lutana cicer milkvetch	*Astrogalus cicer*	2.24
9. Ladak alfalfa	*Medicago sativa*	1.12
10. Madrid yellow sweetclover	*Melilotus officinalis*	1.12
11. Small burnet	*Sanguisorba minor*	4.48
12. Siberian peashrub	*Caragana arborescens*	13.44
13. Russian olive	*Elaeagnus angustifolia*	44.80

4.5 ECOLOGICAL EFFECTS

4.5.1 Trace Element Uptake in Plants

At the Colorado State University lysimeter study site, Kilkelly and Lindsay (1979) found that alfalfa plants in 1977 had high molybdenum levels in all plots of retorted shale and soil-cover over retorted shale. In 1978, the molybdenum averaged 10.2 ppm on soil control and 23.4 ppm on retorted shale. Copper-molybdenum ratios in plant materials may indicate molybdenosis in grazing animals. Also, the ratio of copper to molybdenum is an important factor of toxicity for grazing animals. A copper-molybdenum ratio grater than 2 is regarded as safe for grazing. At the C.S.U. reclamation study site, the copper-molybdenum ratio was below 2 except on the 61 cm soil-cover with 30.5 cm gravel capillary barrier plot. On the 61 cm profile all plants except winterfat had a ratio greater than 2 (Schwab, Linday, Marx, 1980).

4.5.2 Effect of Leachates on Plant Growth

Several different laboratories have performed analyses of leachate water. The parameters relating specifically to ecological effects and revegetation are discussed in this section. The entire available results from each laboratory have been published in Part III, Water Quality, of the Paraho Environmental Data. Battelle Pacific Northwest Laboratories and Colorado State University have additional data that was published after Part III, Water Quality, was compiled. Their data presents detailed chemical characteristics of leachate water and could be included in an appendix to Water Quality.

A retorted shale pile is an adverse growth environment for most plants because of high pH, electrical conductance (EC), and sodium absorption ratio (SAR). A comparison of laboratory data for pH and electrical conductivity of retorted shale leachate water is shown in Table 4.5.1. The pH varies from about 7 to 11, while the EC varies from 3.2 to 20.6 mmhos/cm (Heistand, Atwood, Richardson, 1980). The beginning SAR value was 14.0; 3 years later the SAR value dropped to 5.0 (Redente and Cook, 1981).

Even though the retorted shale leachate has characteristics that are known to be adverse to plant growth, there have been few studies performed demonstrating the effects of leachate water on plant growth. The addition of oil shale leachates to the growth media of native Lake Powell phytoplankton may stimulate growth (Cleave, Adams, and Porcella, 1979).

4.5.3 Microorganisms

Microbial presence was first investigated (Garland, Wildung, and Harbert, 1979) and postulated as one mechanism involved with the oxidizing of reduced sulfur species to SO_4^{2-}, oxidizing NH_4 to NO_3, and oxidizing organic matter. Colonization of retorted shale by microorganisms may account for changes in leachate composition with time. As thermodynamic equilibrium is reached at the surface, a general oxidation of retorted shale is required. The presence of $S_2O_3^{2-}$ indicates that retorted shale is in the reduced phase. The oxidation of reduced sulfur species to SO_4^{2-} with $S_2O_3^{2-}$ as an intermediate compound or co-product is a likely pathway (Garland, Wildung, and Harbert, 1979; Stollenwerk, 1980; Brierley and Brierley, 1980). The change in organic carbon from 400 µg/ml in percolate water in 1977 to 25 µg/ml in 1978 may be brought about by microbiological processes (Garland, Wildung, Harbert, 1979). A combination of both chemical and microbial processes may account for decrease of pH in retorted shale (Brierley and Brierley, 1980; Wildung, et al., 1979).

Further investigations have indicated that disposed retorted shale will initially be colonized by a microbial community of restricted diversity which is composed of microorganisms capable of growth under conditions of high pH (9-11) and moderately high salt concentrations (Wildung, et al., 1978; Garland, Wildung, Harbert, 1979; Wildung, et al., 1979; Rogers, et al., 1980). It is thought that the microbial community will become increasingly diverse on weathering of the retorted shale. A succession of microbial communities will develop as chemical changes occur as the organic composition is altered by the turnover of microorganisms. These conclusions are based on a series of field and laboratory studies (Wildung, et al., 1978; Garland, Wildung, and Harbert, 1979; Wildung, et al, 1979; Rogers, et al., 1980; Wildung, et al., 1980). A single organism (species, Micrococcus) appeared to dominate the initial colonization (30% in field studies and 100% in laboratory studies) under both field and laboratory conditions as determined from enumeration of bacteria on selective media (pH 7.2) containing as carbon source: glucose, casamino acid, and yeast extract. In laboratory studies, with cultures amended with phosphate, Micrococcus species completely dominated the microbial community which developed (Tables 4.5.2 and 4.5.3). In contrast, the addition of other carbon sources in combination with phosphate, lead to the development of a mixture of organisms absent of Micrococcus species (Table 4.5.4). Micrococcus species isolated grew well at pH 9.0 and 10.0 and over a salt range of 0-5% NaCl (Wildung, et al., 1979; Rogers, et al., 1980). From analysis of a core sample obtained from the shale only portion of the field lysimeter at Anvil Points, it was determined that if diffusion of oxygen is limited and/or percolation of water is sufficient, subsurface levels of a disposal pile may become anaerobic, resulting in the development of microbial communities, in particular, anaerobic bacteria, capable of growth under such conditions (Figure 4.5.1).

Bacteria are able to utilize retort water for their sole source of carbon and nitrogen with added phosphates. However, the retort water is toxic and has growth inhibitory properties (Li and Rogers, 1979). Soil bacteria were observed to reduce the dissolved organic carbon content of 4% (v/v) retort water solutions by 25-30% in 25 days of incubation with no further detectable decrease up to 55 days (Wildung, et al., 1979). Samples analyzed at termination of this study contained no detectable levels of mono- and dicarboxylic alipatic acids previously shown to be constituents of the organic fraction of retort water (Wildung, et al., 1980). Complete degradation of the acid fraction would account for 50% of the observed decrease in dissolved organic carbon (Rogers, 1981).

The utilization of retorted shale by bacteria modifies the organic composition of the retorted shale, which may affect the mobility of trace elements (Wildung, et al., 1979). With the addition of a nutrient supplement and nitrogen, as ammonium ion, supplement to microbial growth media, the arsenic supernatant levels increase (Figure 4.5.2 and 4.5.3). The pH levels decrease with glucose additions and increase with ammonium ion additions (Figures 4.5.2

and 4.5.3). The addition of nutrients has no effect on supernatant levels of selenium (Klein, Tortoso, Meglen, 1980).

Field studies indicate that microbial activity in soil control plots is greater than in plots of retorted shale and soil cover (Sorensen, et al., 1980; Klein, et al., 1980). Although the retorted shale plot with a gravel capillary barrier appeared to have more microbial activities than control and soil-cover retorted shale plots, its effects seem to be short-term (Klein, Sorensen and Brokish, 1981). The decreased microbial activity of retorted shale may correspond to similar decreased plant community responses.

With the application of nitrogen on retorted shale plots, nitrogen fixation and phosphatase activity decrease significantly. Laboratory studies also support the inhibition of nitrogen fixation by the addition of nitrogen (Klein, et al., 1980; Sorensen, et al., 1980). However, the introduced species mixture may lead to increased dehydrogenase, phosphatase, and N-fixation activities, independent of nitrogen applications. Leguminous nitrogen fixation microorganisms are stimulated with increased concentrations of retorted shale (Hersman and Molitoris, 1979). Nitrogen fixation rates as measured by acetylene reduction in non-symbiotic microorganisms are reduced with the increase of retorted shale concentrations (Klein, Hersman, Wu, 1979; Hersman, Klein, 1978; Hersman, Molitoris, 1979; Hersman, Klein, 1979).

The invading plants of heavily disturbed areas are non-mycorrhizal plants. Additions of nitrogen and phosphate to soils do not stimulate or retard fungal growth. However, the fertilizer is useful if it stimulates plant growth. Particular mycorrhizal species are more effective in stimulating plant growth than other species are. Mycorrhizae exhibit seasonal variations in the retorted shale study plots. Greater than 50% retorted shale-soil mixtures decrease fungal growth (Reeves, Bishop, Schwab, 1980a and 1980b; Schwab and Reeves, 1980; Reeves, Moorman, Kiel, 1978). After three years of study, the mycorrhizal inoculum potential of retorted shale remains zero (Reeves, Sabaloni, and Schmidt, 1981).

The mutagenicity and toxicity studies of bacteria, plants, and other organisms are compiled in Part V, Biological Effects.

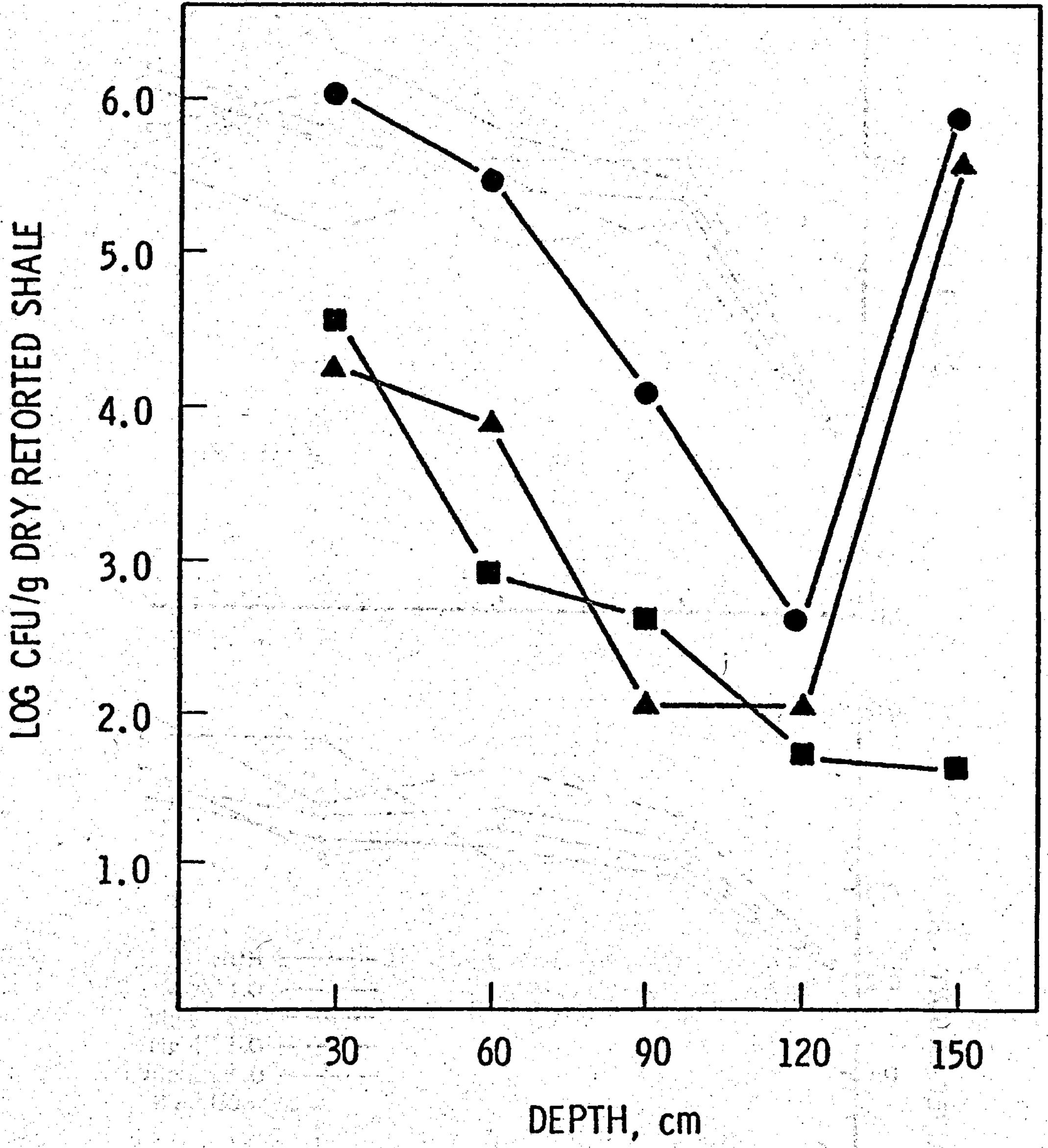


FIGURE 4.5.1

Depth Distribution of Heterotrophic Bacteria (●-●), Anaerobic Bacteria (▲-▲), and Fungi (■-■)

(Roger, et al, 1980)

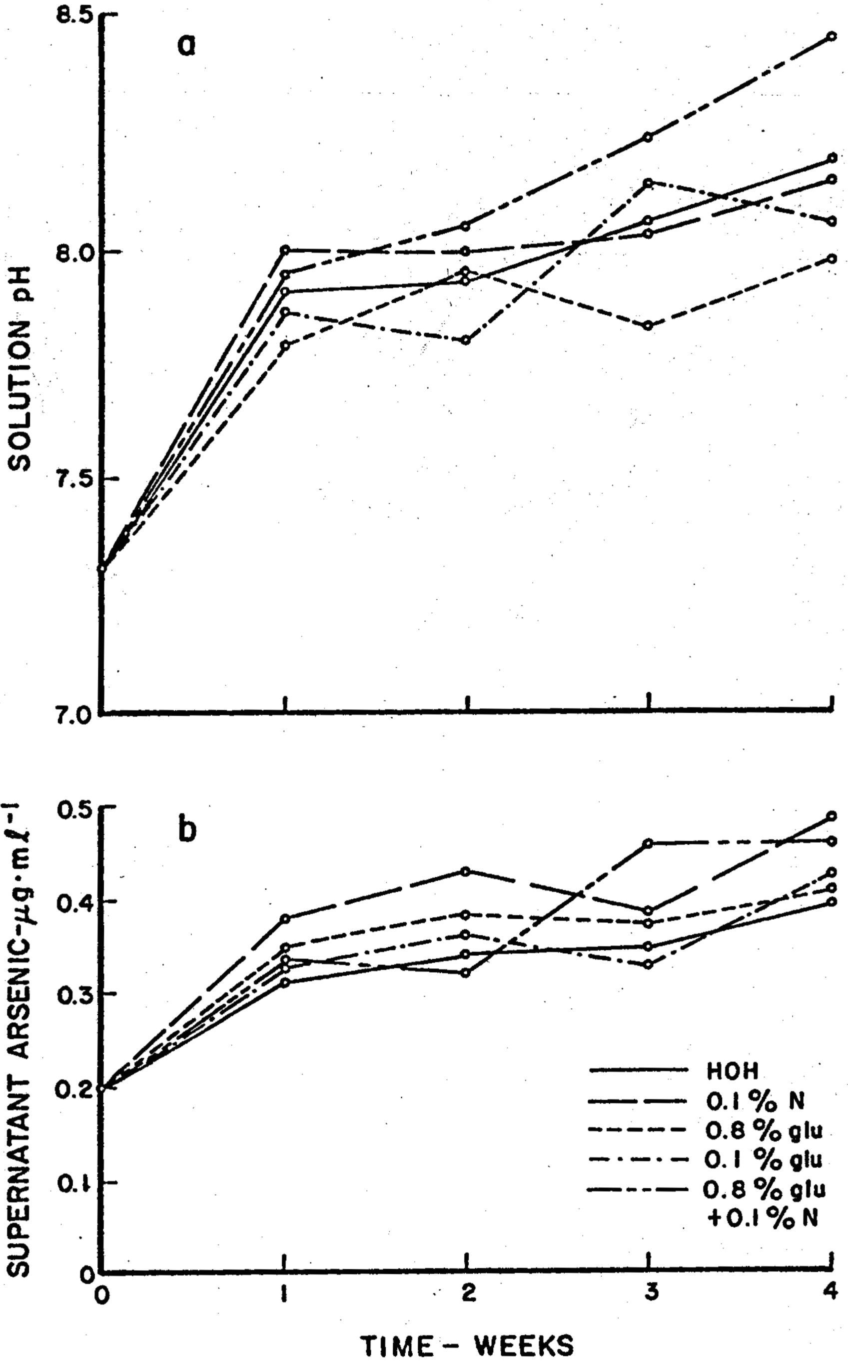


FIGURE 4.5.2

The Effects of Glucose and/or Ammonium Ion Additions on the pH (a) and Supernatant Arsenic Levels (b) in retorted Shale Slurries. For the Arsenic Values, $\sigma = \pm 0.020 ug/ml^{-1}$

(Brierley and Brierley, 1980)

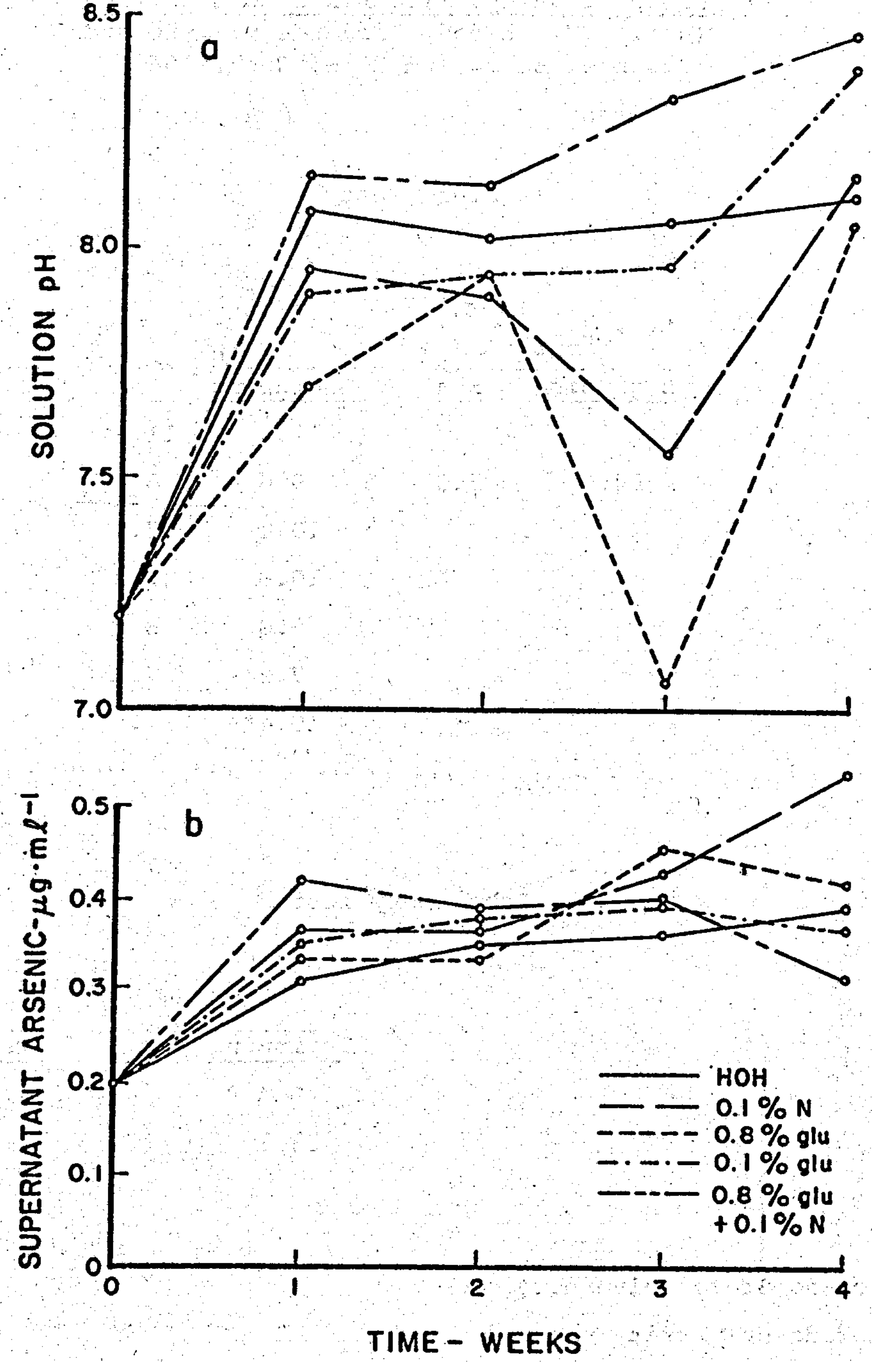


FIGURE 4.5.3

The Effects of Glucose and/or Ammonium Ion Additions on the pH (a) and Supernatant Arsenic Levels (b) in Retorted Shale-Soil Slurries. For the Arsenic Values, $\sigma = \pm 0.020$ ug/ml

(Brierley and Brierley, 1980)

TABLE 4.5.1

Comparison of pH and Electrical Conductivity (EC)

(Heistand, Atwood, Richardson, 1980 and
Redente, E. F. and C. W. Cook, 1981)

Field Tests

	SAR		pH		EC mmhos/cm	
	Beginning	End	Beginning	End	Beginning	End
CSU			11.4	11.3	3.2	4.2
CSU	14.0	5.0	9.6	8.7	7.0	4.7
CU			10.4	7.1	10.5	10.4
CU			10.8	7.2	20.6	15.7
PNL			8.0	8.2	15.4	12.2
W-C			7.2*	7.8*	-	-
			10.4**	11.4**	-	-

* Uncompacted
** Compacted

Laboratory Tests

	pH		EC	
	Beginning	End	Beginning	End
USU	9.4	-	15.7	-
W-C	11.1	8.3	-	-

CSU - Colorado State University
CU - Colorado University
PNL - Pacific Northwest Laboratory, Battelle
USU - Utah State University
W-C - Woodward-Clyde

TABLE 4.5.2

Growth of Bacteria on Retorted Shale as Sole Carbon Source in Liquid Media Containing Mineral Salts Phosphate Necessary for Growth of Micrococcus

(Wildung, et al, 1980)

Mineral Salts Composition	Time (Weeks)	Log 10 Bacterial cfu	% Micrococcus
Phosphate[a] KNO_3 $MgSO_4$	0	< 2	--
	1	6.3	99
	3	6.93	100
	7	6.92	100
Phosphate	0	< 2	--
	1	5.5	100
	3	6.84	100
	7	7.06	100
KNO_3	0	< 2	--
	1	< 2	--
	3	< 2	--
	7	4.8	67
$MgSO_4$	0	< 2	--
	1	< 2	--
	3	< 2	--
	7	4.71	0
H_2O	0	< 2	--
	1	< 2	--
	3	3.89	0
	7	5.18	0

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[a] The concentration of mineral salts was: phosphate (40 mM), KNO_3 (1 mg/mℓ) and $MgSO_4$ (0.5 mg/mℓ).

TABLE 4.5.3

Phosphate Requirements for Growth of Microorganisms on Retorted Shale as the Sole Source of Carbon

(Wildung, et al, 1980)

Concentration of Phosphate (mM)	Time (Weeks)	Log 10 Bacterial cfu	% Micrococcus
40	0	< 2	--
	1	6.55	100
	3	6.74	100
	7	6.57	100
4	0	< 2	--
	1	6.72	100
	3	6.82	100
	7	6.51	100
0.4	0	< 2	--
	1	< 2	--
	3	< 2	--
	7	4.88	0
0.04	0	< 2	--
	1	< 2	--
	3	< 2	--
	7	5.62	0
0	0	< 2	--
	1	< 2	--
	3	< 2	--
	7	5.67	0

TABLE 4.5.4

Effect of Complex Organic Materials on the Growth of Microorganisms on Retorted Shale

(Wildung, et al, 1980)

Concentration Organics	Time (Days)	Log 10 Bacterial cfu	% Micrococcus
Complete[a]	0	< 2	--
	1	8.42	0
	3	8.59	0
	7	8.52	0
1/10 dil.	0	< 2	--
	1	7.02	100
	3	7.23	80
	7	6.94	100
1/100 dil.	0	< 2	--
	1	5.95	100
	3	6.38	93
	7	6.20	100
H_2O	0	< 2	--
	1	5.15	100
	3	6.53	100
	7	6.64	100

[a] The undiluted complex organic solution contained: glucose (2 mg/mℓ), yeast extract (1 mg/mℓ) and casamino acids (5 mg/mℓ).

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PARAHO ENVIRONMENTAL DATA

Part V

Biological Effects

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PART V

BIOLOGICAL EFFECTS

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5.1 INTRODUCTION

5.1.1 Research Parameters

The crude oil, raw shale, retorted shale, and product water samples used for biological testing were produced during the 1977-1978, 100,000 barrel production of crude shale oil by Paraho at the Anvil Points research center. The refined oil products tested were hydrotreated shale oil, hydrotreated residue, JP-5 product, JP-8 product, and diesel fuel marine product. These products were refined by Sohio from the 100,000 barrels of Paraho crude shale oil. All of these samples produced by Paraho at the Anvil Points research center, except the product water, would be representative of a commercial size plant.

In a commercial plant, the gas clean-up process will produce a large volume of water. Because the Paraho operations at the Anvil Points facility were essentially small scale research operations, there was no gas clean-up equipment to produce process water. As a result, the process water escaped as vapor with the product gas combustion. In a commercial plant with gas clean-up equipment, the product (tank bottom) water would be minimal. The product water, the material examined in these biological tests, was separated from the bottom of tanks filled with crude shale oil. This water was in direct contact with crude shale oil for an unknown period of time.

Biological testing of new products is planned and carried out to determine the existence of harmful side effects. In order to obtain these results, experiments are designed and performed using experimental animals. Although experimental exposure to high doses of substances is necessary to enhance and thus ascertain side effects, the experimental doses and types of exposure are usually not relevant dosages and types of exposure to humans.

5.1.2 Outline of Research Methods

Biological testing of a substance begins with screening bioassays (Figure 5.1.1) to determine its mutagenicity. After mutagenicity is established, several experimental pathways may be followed. One pathway explores further mutagenesis and genetic studies. Another route of research investigates carcinogenicity and toxicity. A third avenue examines pathological potentials.

5.1.3 Preparation and Fractionation of Crude Shale Oil

There are three major fractionation methods of crude shale oil: distillation, liquid - liquid separation, and chromatography. The distillation method separates fractions according to their boiling points (Calkins, 1980). The distillation fractions would be similar to shale oil products that have been refined. When distillation is used in combination with other methods, it is usually performed first to separate volatile groups from non-volatile groups (Rao, et al, 1980).

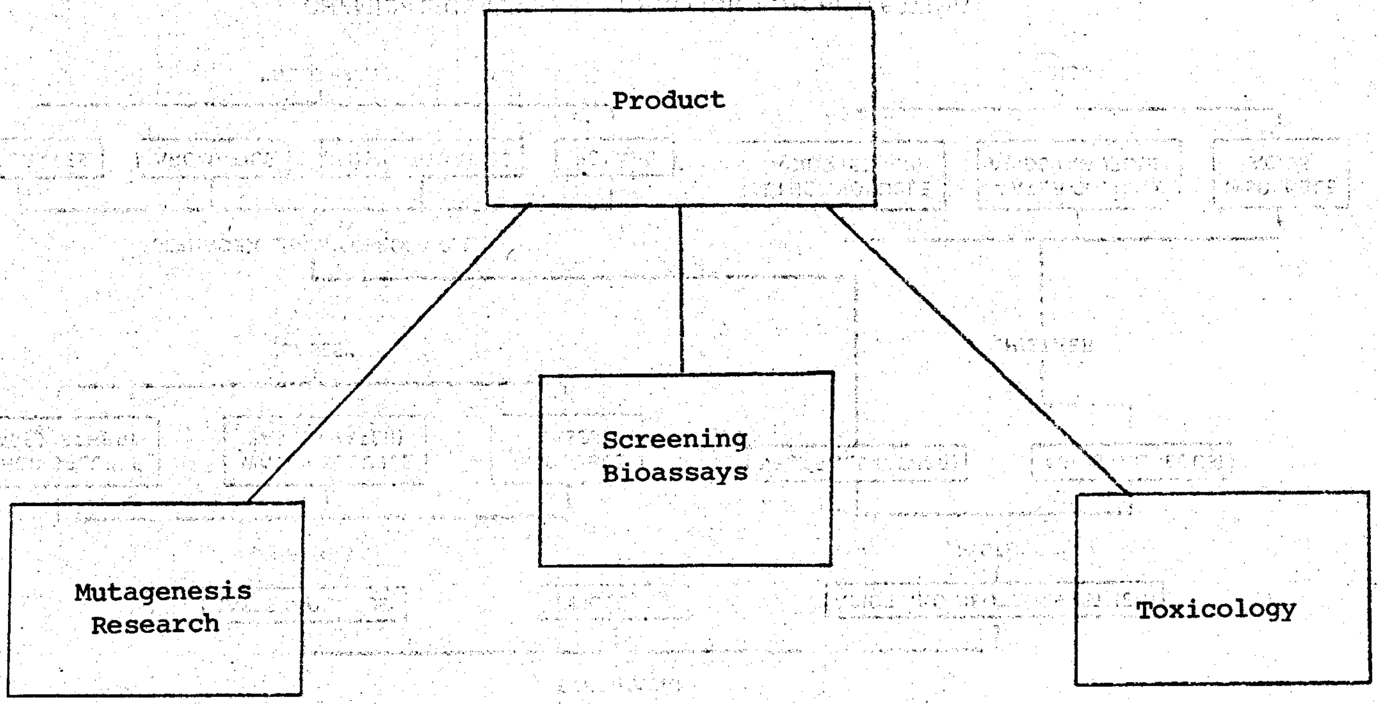
Liquid - liquid separation (Figure 5.1.2) has been used after initial separation of volatile groups from non-volatile groups by either distillation or evaporation. The liquid - liquid method uses ether/acid solvents to separate bases, acids and neutrals, and insolubles. Further liquid - liquid separation or chromatography may be performed. Secondary liquid - liquid fractionation produces ether and water soluble bases and acids, and insoluble bases and acids (Rao, et al, 1980).

Chromatography using silica gel fractionates alkanes, alkenes, cycloalkanes; aromatic hydrocarbons; extremely complex nitrogen compounds; and extremely complex phenols, acids, amides, and many multifunctional hydrocarbons (Spall, 1981).

Each fractionation method has various advantages and disadvantages, depending on the type of research to be performed. The distillation method is useful to analyze components similar to refined shale oil products. The liquid - liquid and chromatography fractionation procedures are used to determine which compounds are biologically active and to sum the total activity observed. The total activity sums may be inaccurate or confusing because of synergistic and/or inhibitory effects.

FIGURE 5.1.1

Flow Sheet of Research Methods



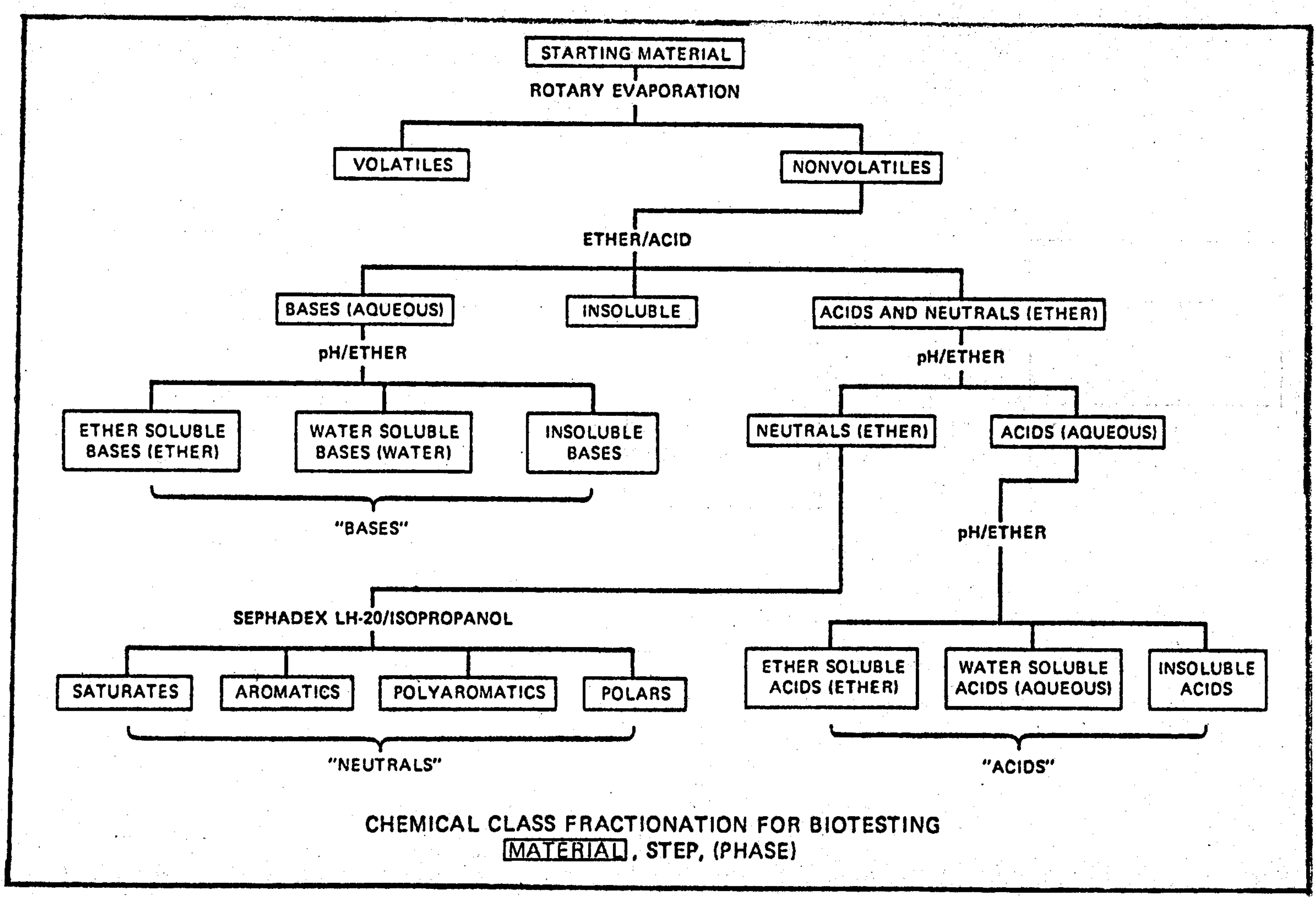


FIGURE 5.1.2

Liquid-Liquid Chemical Class Fractionation for Biotesting
Material, Step, (Phase)

Data from Guerin, et al, 1980

5.2 SCREENING BIOASSAYS

5.2.1 Ames Test

Paraho shale oil, water separated from shale oil tank bottoms, and water condensed from the Paraho process have been assayed for mutagenic activity in the Ames assay. The shale oil and tank bottom water have been chemically fractionated by one of the methods described in Section 5.1.3, Preparation and Fractionation of Test Materials. The fractions have also been assayed using the Ames test and chemically analyzed by gas chromatography and gas chromatography-mass spectrometry.

All Ames assays were carried out using standard Salmonella typhimurium strains TA 98, TA 100, TA 1535, and/or TA 1537, and S-9, a rat liver enzyme as a metabolic activator.

Mutagenicity tests have been performed on shale oil, shale oil fractions from partition chromatography-high performance liquid chromatography (HPLC) and distillation, and refined shale oil products: hydrotreated shale oil, jet fuel, and diesel fuel marine.

Oil. Crude shale oil has shown a mutagenic linear response curve (strain TA 98) based on 0-13.5 ug of crude shale oil (Figure 5.2.1). The response curve became non-linear from 13.5-270 ug crude shale oil. The TA 100 strain showed no mutagenic activity, with or without S-9 activation (Nichols and Strniste, 1981).

Hydrotreated shale oil produced no mutagenic activity with strain TA 98 or TA 100 (Nichols and Strniste, 1981; Rao et al, 1980). Mutagenesis assays with yeast (Saccharomyces cerevisiae) also indicate that hydrotreated shale oil and its ether soluble base fraction are not mutagenically active (Rao, et al, 1980). When cytotoxicity results for hydrotreated shale oil and crude shale oil are compared, the hydrotreated effects are higher than the crude shale oil effects. Possibly the cytotoxic effects of the hydrotreated shale oil are masking any mutagenic activity that may be present (Nichols and Strniste, 1981).

The mutagenicity of crude and hydrotreated shale oil and their acidic, basic, and neutral fractions has been tested. Both strains of TA 98 and TA 100 showed mutagenicity in all fractions except acidic fractions. Hydrotreatment of the shale oil decreased the mutagenicity in both strains. The neutral fraction of the hydrotreated shale oil contained most of the mutagenic activity (Timourian, et al, 1980).

Mutagenic activity was not evident in any of the refined shale oil products, as shown in Table 5.2.1 (Rao, et al, 1980).

The following crude shale oil fractions were obtained from the distillation process: light ends, naphtha, light gas oil (LGO), mid gas oil (MGO) and residue. The observed cut points are: light ends - collected in dry ice/acetone bath while naphtha distilled; naphtha - 100 mm Hg, 116°C; LGO - 5.0 mm Hg, 179°C; MGO - 3.2 mm Hg, 201°C; residue - pot reached 326°C. Of these fractions, naphtha and LGO are non-mutagenic. The residue fraction produced positive results in the Ames test. The crude shale oil and residue fraction Ames test results are shown in Table 5.2.2 (Calkins, et al, 1980).

The liquid - liquid partitioning system separates acidic and basic fractions of crude shale oil into ether soluble and insoluble acids and bases. The neutral fraction was separated using Sephadex LH-20 into aliphatics, aromatic, polyaromatic, and polar fractions by isopropanol elution. The ether soluble basic fraction was further partitioned by eluting with benzene and ethanol on an alkaline alumina column and then with isopropanol and acetone using a Sephadex LH-20 gel column (Rao, et al, 1980; Guerin, 1980; Guerin, et al, 1980).

The detailed weight distribution of volatile, insoluble matter, acidic, basic, and neutral fractions are listed in Table 5.2.3. Each of these fractions was tested for mutagenicity, using the Ames test. Mutagenic activity was present in the ether soluble basic fraction and the neutral polyaromatic fraction (Table 5.2.4, Guerin, et al, 1980). The mutagenic contributions of each fraction to the total mutagenicity were calculated, based on correction for weight contribution of the starting sample (Table 5.2.5, Guerin, et al, 1980). A summary of mutagenicity and weight distributions by chemical class is given in Table 5.2.6 (Guerin, et al, 1980).

The neutral fraction was separated into aliphatic and aromatic fractions of various ring sizes using Sephadex LH-20 gel filtration. Results from the Ames test indicate that aliphatics, mono and di aromatics, N-PAH, and residue are not mutagenic (Table 5.2.7). The PAH and polar compounds are mutagenically active (Rao, et al, 1980).

The fractions of the ether soluble base separation are given in Table 5.2.8. The acetone subfraction contained 90% of the mutagenic activity which accounted for 10% or less of the weight of the ether soluble fraction (Rao, et al, 1980). The composition of the acetone subfractions has been characterized by use of gas chromatography-mass spectrometer (Table 5.2.9). Primary aromatic amines and azaarenes have been characterized as mutagenically active. It is not known if secondary aromatic amines and mixed secondary and tertiary amines are mutagenic (Buchanan, Ho, and Clark, 1980).

As a suspected mutagen, benzo(a)pyrene (BaP) has been quantitatively determined in shale oil and refined shale oil (Tomkins, et al, 1980). The following BaP concentrations have been determined by HPLC: crude shale oil, 8 µg/g; hydrotreated, 9 µg/g; diesel fuel marine, 0.02 µg/g; and residue, 16 µg/g.

Three fractions of crude shale oil prepared from Sephadex LH-20 partition chromatography, hexane, toluene/hexane, and methanol, have been tested for mutagenicity. The non-polar hexane fraction had no mutagenic results, indicating that non-polar species do not contribute to the shale oil's mutagenicity (Toste, et al, 1980). The toluene/hexane and methanol fractions were mutagenically active throughout the moderately polar to polar HPLC regions, indicating that the mutagens are chemically heterogenous. The methane fraction was further assayed with mixed function amine oxidase (MFAO) to activate aromatic amines. The MFAO did not show any activated mutagenicity of the methanol fraction. The non-activation of methanol fraction by MFAO suggests that aromatic amines are not responsible for most of the mutagenicity of shale oil (Toste, et al, 1980). Gas chromatography and gas chromatography-mass spectrometer analyses of the methanol fraction reveal that nitrogenous species such as azaphenols, aminophenols, or nitrogenous carboxylic acids are the mutagenically active compounds (Toste, et al, 1980; and Sklarew, et al, 1981).

No mutagenic activity was detected in the polynuclear aromatic (PAH) fractions (Delroy, Sklarew, and Downey, 1981).

Water separated from shale oil storage tanks has been assayed before and after fractionation. Assays completed before fractionation have given different results. Results from S. typhimurium strains TA 98 and TA 100 indicate mutagenicity (Table 5.2.10) and cytotoxicity (Nichols and Strniste, 1981). No mutagenicity or toxicity was evident from strains TA 98, TA 100, TA 1535, and TA 1537 (Tables 5.2.11, 5.2.12; Beck and Burbank, 1980) using saturated filter discs as contact with media. Positive results were obtained with strains TA 98 and TA 100 using the plate incorporation (activated) method (Beck and Hepler, 1981).

The mutagenicity studies of high performance liquid chromatography (HPLC) fractions of water indicate that the mutagens were polar, fairly heterogenous, and hydrophobic organic compounds. Gas chromatography-mass spectrometry analyses indicate that the non-mutagenic, moderately polar HPLC region contained mainly nitrogenous compounds (alkylated pyroles and pyridines). The mutagenic polar HPLC region contained mainly oxygenated and fixed function compounds (Toste, et al, 1981).

An aqueous extract separated from shale oil contains mutagenicity comparable to the hydrophobic organic fraction of tank bottom water (Toste, et al, 1981).

Water condensed from the recycled air of the Paraho process is less mutagenic than tank bottom water (Toste, et al, 1981). The mutagens of condensate water are polar and appear to be less heterogenous.

When shale derived diesel fuel of equal or better quality was compared to petroleum derived fuel, the resulting particle bound organic emissions were not significantly different in mutagenic activity in the Ames Solmonella typhimurium plate incorporation assay (Huisingh, et al, 1980).

In Chinese hamster cells, CHO line, crude shale oil was weakly mutagenic (Table 5.2.13) at two of four gene loci testing (Timourian, et al, 1980). Hydrotreated shale oil was not mutagenic. Cytotoxic and mutagenic effects induced by crude shale oil show similar results (Okinaka and Strniste, 1981).

Light activated tank bottom water induced about 50% as many mutations (Figure 5.2.2) (6-thioguanine resistance) as the potential carcinogen, far ultra violet (FUV) light (Strniste and Chen, 1981). With the treatment of near ultra violet light (NUV) irradiation and tank bottom water dilutions on CHO cells, mutations of the hgprt system (6-thioguanine resistance) increased 20 to 40 fold (Barnhart, et al, 1978), as shown in Table 5.2.14. These results indicate a potential risk in human exposure to a combination of shale oil tank bottom water and NUV from sunlight or indoor fluorescent lighting.

The addition of the S9 activation complex to the CHO cells (Figure 5.2.3) causes a detoxification of the responses produced by tank bottom water (Okinaka and Strniste, 1981).

Mutations may occur in CHO cells at other genetic loci (in addition to the HGPRT locus) after exposure to tank bottom water (Strniste, Martinez, and Chen, 1981). The resistant mutants of ouabain, a dominant marker which affects the membrane Na^+/K^+ ATPase, increased about 60-fold over normal background mutation rates. Among the five genetic loci tested, the ouabain induced marker was the most sensitive marker tested (Chen and Strniste, 1982). Other loci tested were 8-azaadenine, 6-thioguanine, emetine, and diptheria toxin. The multipe marker CHO assay may have a broader sensitivity to detect mutagens than the commonly used cell strains (Timourian, et al, 1980).

Tank bottom water appears to be mutagenically active when tested against human embryonic skin fibroblasts (Chen, Okinaka, and Strniste, 1981). When fibroblasts were exposed to a 0.5% solution of the tank bottom water, there was approximately a 9-fold increase in 6-TG^R mutants induced (Figure 5.2.4). A 0.5% tank bottom water solution was cytotoxic to fibroblasts; only 15% of the cells survived. The cytotoxic and mutagenic effects observed in CHO cells were less severe under the same experimental conditions.

5.2.3 Somatic Cell Cytogenetics

Cytogenetic research on Chinese hamster cells (line CHO) shows increased sister chromatid exchanges (SCE) when CHO cells were exposed to 0.2% (V/V) crude shale oil tank bottom water (Campbell, et al, 1980). Tank bottom water, at a concentration of 0.2%, decreased the mitotic index by 50%. At a concentration of 0.5%, no metaphase cells were differentiated (Figure 5.2.5) indicating that the cells had not completed two cell cycles by the 29-hour collection time.

Hydrotreated shale oil produced insignificant SCE frequencies (Timourian, et al, 1980) at doses up to 40 µl in 20 ml cultures (Figure 5.2.6). Normalized samples of hydrotreated and crude shale oil showed no appreciable differences in cell cycle perturbation or SCE induction (Campbell, et al, 1980, 1981). Non-normalized samples of crude shale oil induces higher levels of SCE and increases cell cycle traverse time when compared to hydrotreated shale oil. All mutagenicity observed required activation by the S9 fraction (Timourian, et al, 1980).

A known inducer of SCE, N-methyl-N'-nitro-N-nitrosoquanidine (MNNG), an alkylating agent, and tank bottom water were added to CHO cells. Tank bottom water and MNNG are not additive or synergistic. It is thought that they may interfere with each other in some manner in SCE production (Campbell, et al, 1980).

CHO cells treated with emulsions of crude shale oil show large increases in cells undergoing endoreduplication:

Crude Shale Oil	Cells Undergoing Endoreduplication
0.02%	22%
0.3%	38%
0.5%	2% (increased cellular toxicity)

Water and medium extracts of crude shale oil indicate a maximum of 13% of the cells undergoing endoreduplication. Comparative experiments with the natural crude petroleums resulted in a maximum of 2-4% of the cells undergoing endoreduplication. It appears that some endoreduplicated cells persist in the population as normal tetraploids (Campbell, et al, 1980). The high incidence of endoreduplication found in crude shale oil treated CHO cultures may result from the arsenic in the crude shale oil.

Pregnant mice were given 1% tank bottom water *ad libitum* from day 1 to day 12 of gestation. Cells obtained from washes of embryos showed cytogenic effects in metaphase cells (Table 5.2.15). The frequency of chromatid breaks, isochromatid breaks, exchanges other than centric fusions were increased in embryo metaphase cells. There was no significant difference in centric fusion frequencies between the control and the treated embryos (Meyne and Deaven, 1980). The cytotoxicity of crude shale oil to primary oocytes is significant, but is lost after hydrotreatment (Timourian, et al, 1980). These results indicate that clastogenic compounds within the tank bottom water can cross the placenta and induce chromosomal aberrations in embryos.

5.2.4 Bone Marrow Cytogenetics

The aberration frequencies of bone marrow cells from mice that were skin painted with crude shale oil were within the levels of the control mice, 0-0.01

aberration frequency (Campbell, et al, 1980; and Meyne and Deaven, 1980). The number of chromatid breaks per cell and the number of gaps per cell were the same for both the treated and control mice groups. No other aberrations were observed.

Doses of crude shale oil, hydrotreated shale oil, and tank bottom water were injected intraperitoneally into mice. The frequencies of chromatid breaks and gaps both increased, as shown in Tables 5.2.16 and 5.2.17 (Meyne, 1982; Meyne and Deaven, 1981). The 0.5 ml/kg and 1.0 ml/kg dose induced about five times more chromatid breaks than control animals. Hydrotreated shale oil demonstrated increased aberration induction, with two-three fold increases (Meyne, 1981). The mitotic indices, as shown in Tables 5.2.16 and 5.2.17, indicate that these intraperitoneal dose levels of crude shale oil do not severely inhibit cell proliferation.

Tank bottom water induced a slight increase of aberration frequency in mice, even though the results were not dose related (Meyne and Deaven, 1981).

The SCE analysis of murine bone marrow exposed to crude shale oil, hydrotreated shale oil, and tank bottom water are shown in Tables 5.2.18 and 5.2.19 (Meyne, 1982). Crude shale oil induced 50% increase above control levels at the 2 ml/kg dose. Hydrotreated shale oil and tank bottom water demonstrated SCE frequencies within the control range at all doses tested. The number of SCEs of mice treated with either crude or hydrotreated shale oil did not increase significantly at concentrations that were one-third or less of the LD_{50} dose (Timourian, et al, 1980). At higher oil concentrations, SCEs could not be determined because cell division was significantly arrested indicating somatic toxicity.

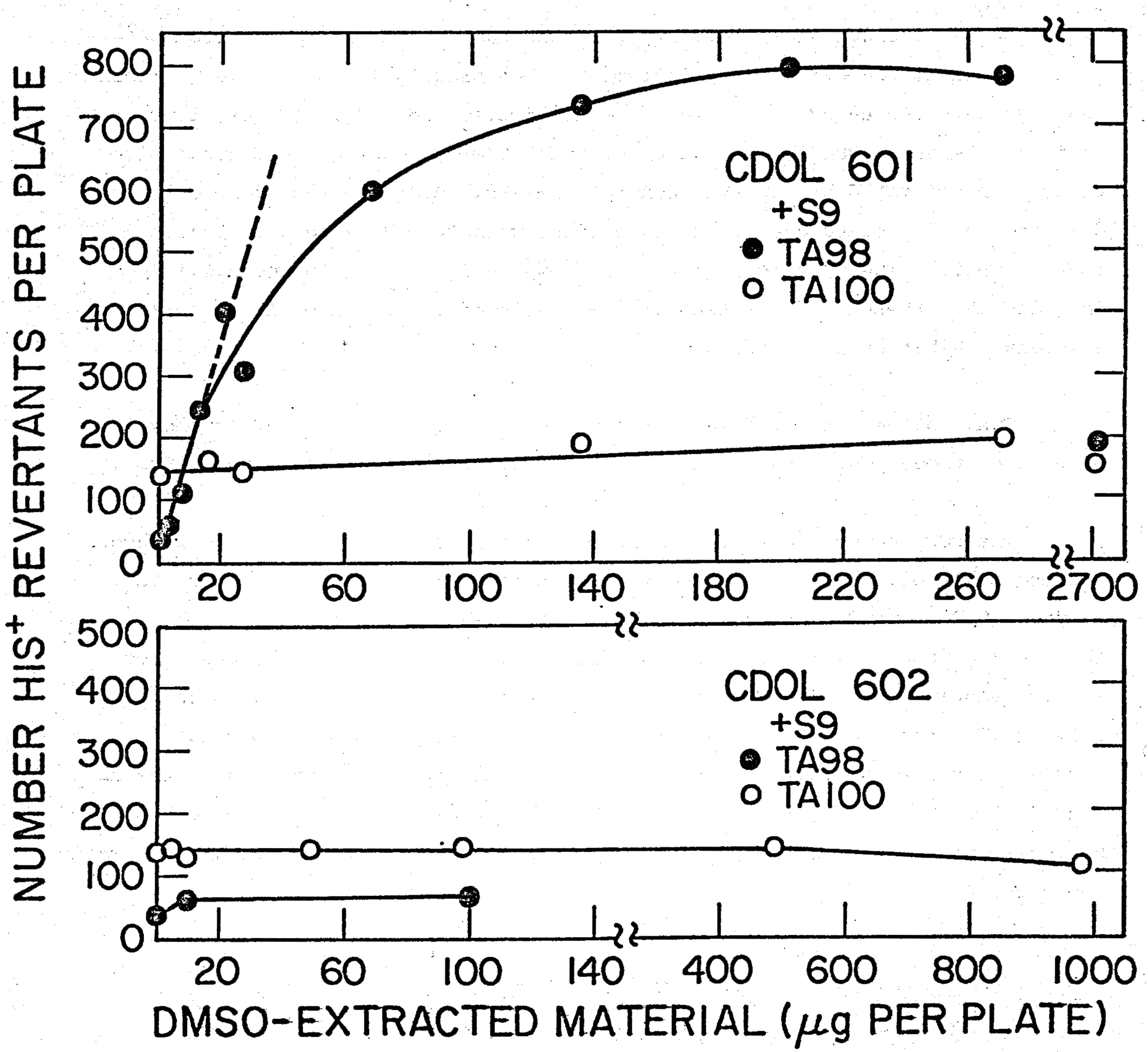


Figure 5.2.1

Mutagenicity of Paraho retort crude shale oil (CDOL 601) and hydrotreated shale oil (CDOL 602) as detected in the Ames/Salmonella test with S9 activation (Nichols and Strniste, 1981).

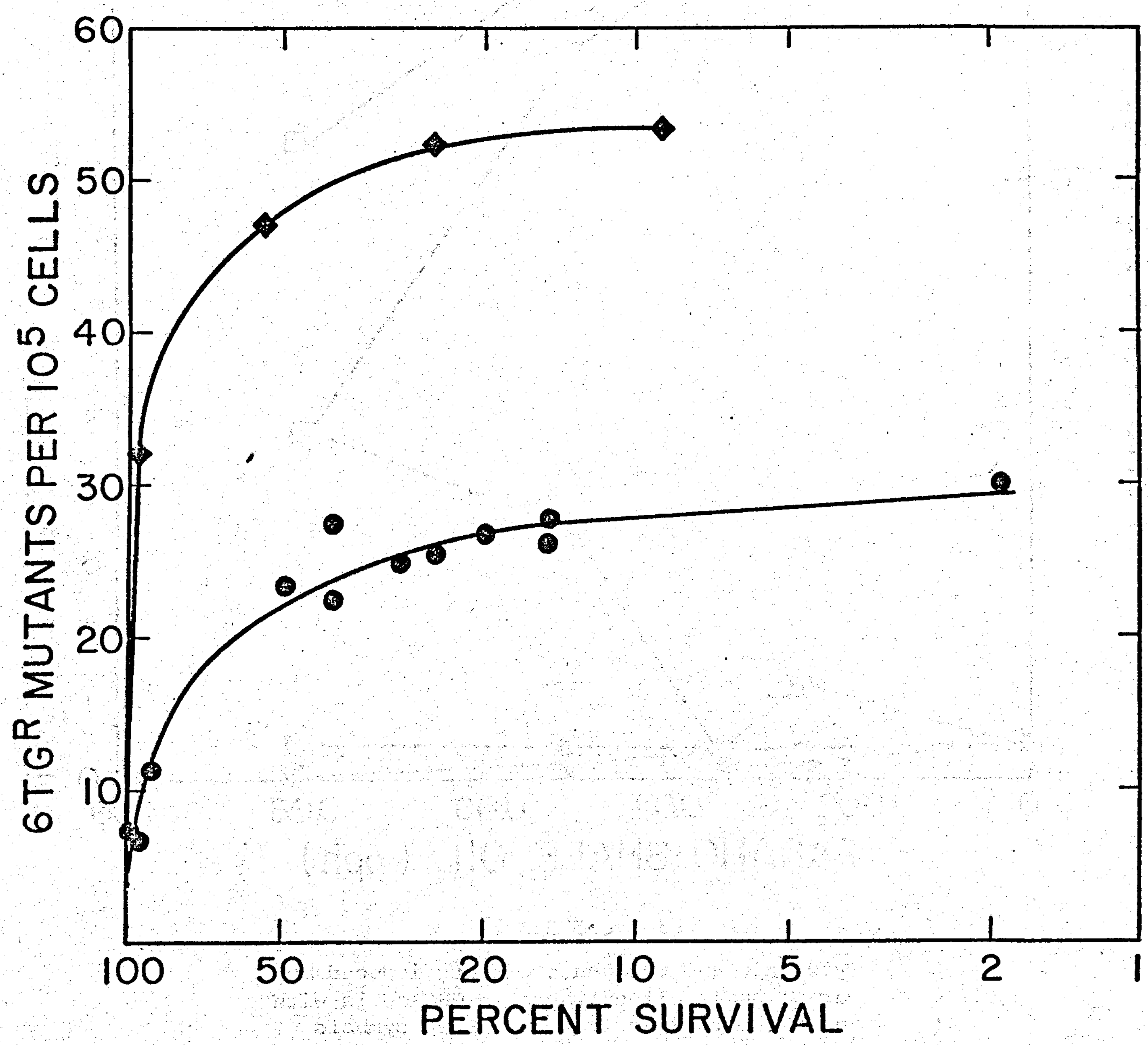


Figure 5.2.2

6-TG^R mutants induced per surviving fraction of CHO cells (line AA8-4) after exposure to shale oil tank bottom water and NUV or to FUV only. (Strniste and Chen, 1981). FUV only, —◆— ; tank bottom water, —●— .

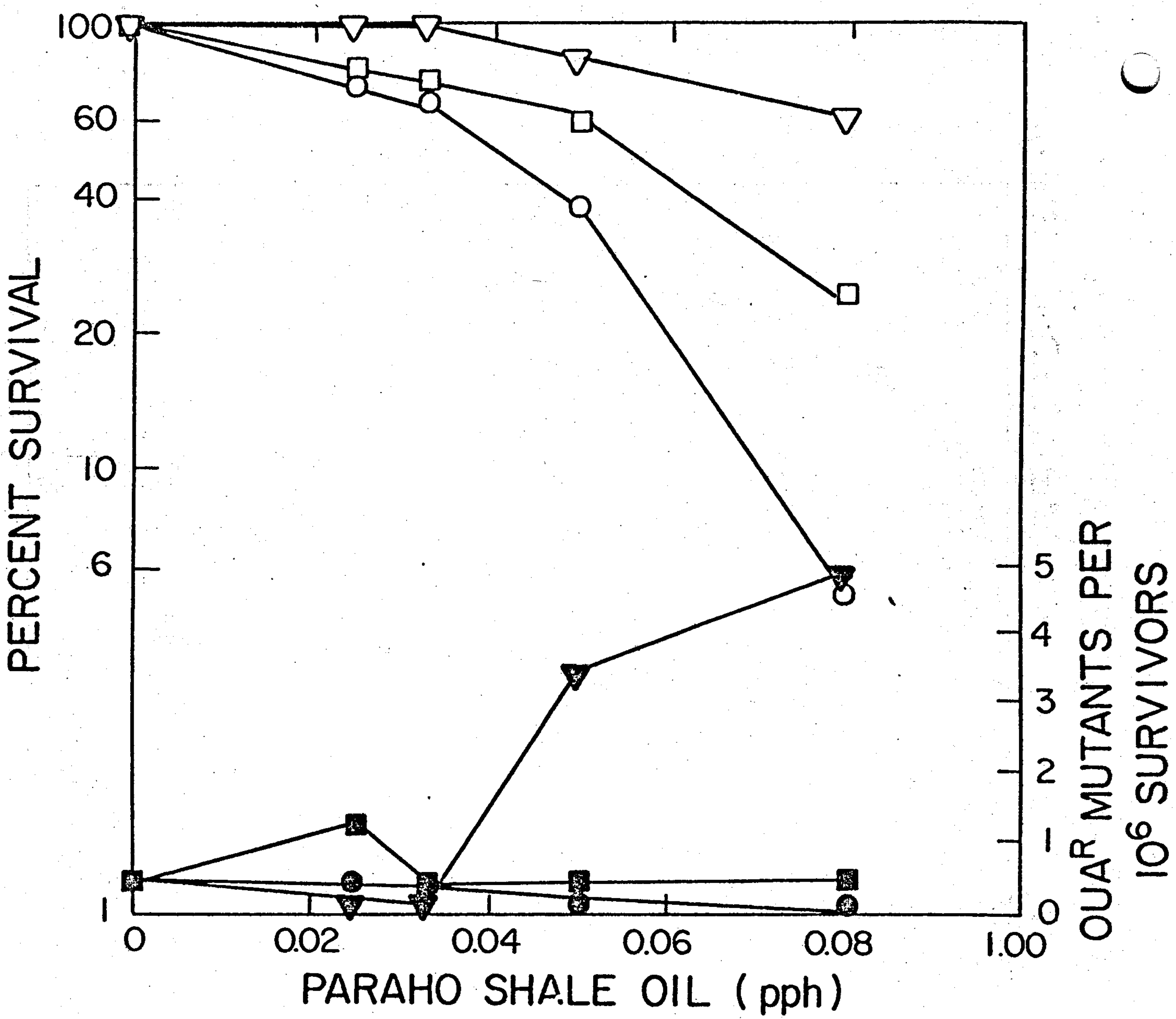


Figure 5.2.3

Cytotoxic and mutagenic effects induced by Paraho shale oil extracts in CHO cells with and without S9 activation. Open symbols represent cytotoxicity and is a measure of decrease in plating efficiency after treatment. Closed symbols represent mutation frequencies measured as colonies formed in the presence of the drug ouabain. Circles = no S9 present, squares = 0.1 mg/m l S9 mix; triangles = 0.3 mg/m l S9 mix (protein) (Okinaka and Strniste, 1981).

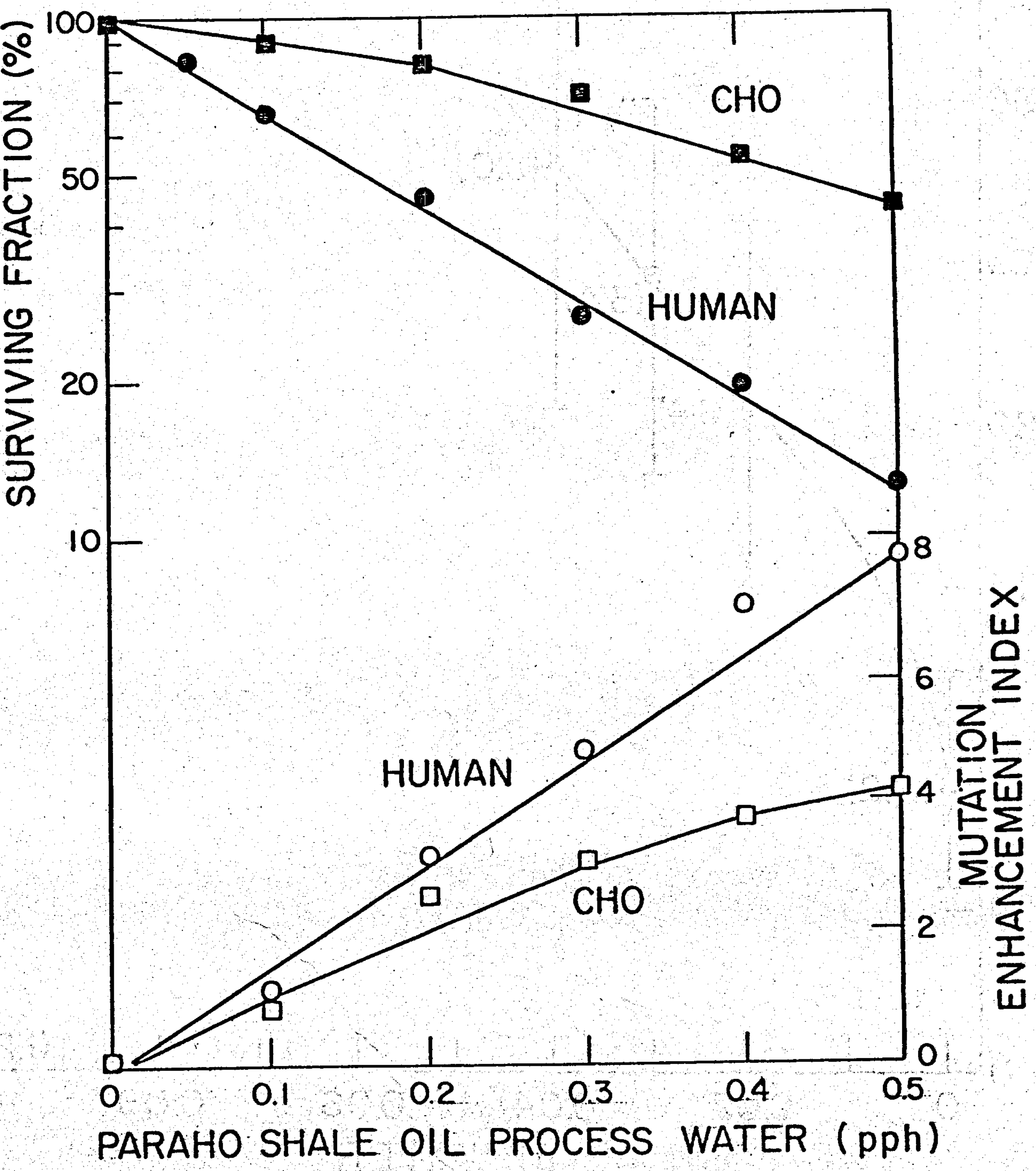


Figure 5.2.4

Toxic and direct-acting mutagenic effects of tank bottom water in CHO cells and human embyronic skin fibroblasts. 6-TG^R mutation enhancement index =

$$\frac{\text{observed mutation frequency}}{\text{background mutation frequency}}$$

Closed symbols are cytotoxic results, open symbols are mutation results (Chen, Okinaka, and Strniste, 1981).

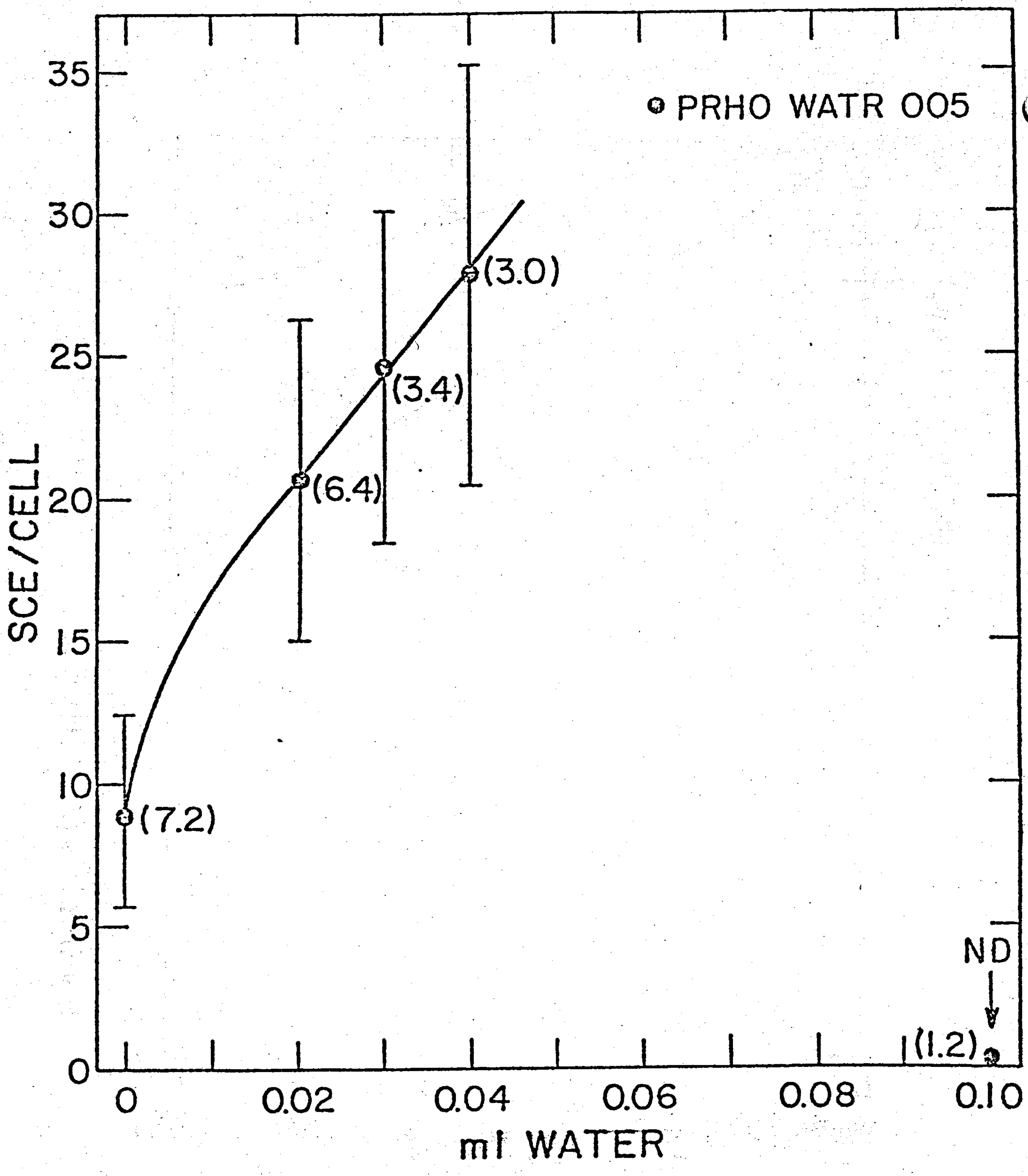


FIGURE 5.2.5

Dose Response Curve Showing Effect of Tank Bottom Water on SCE Induction in CHO Cells, (●). Number in parenthesis cites mitotic index, ND indicates no differentiation. (Campbell, et al, 1980)

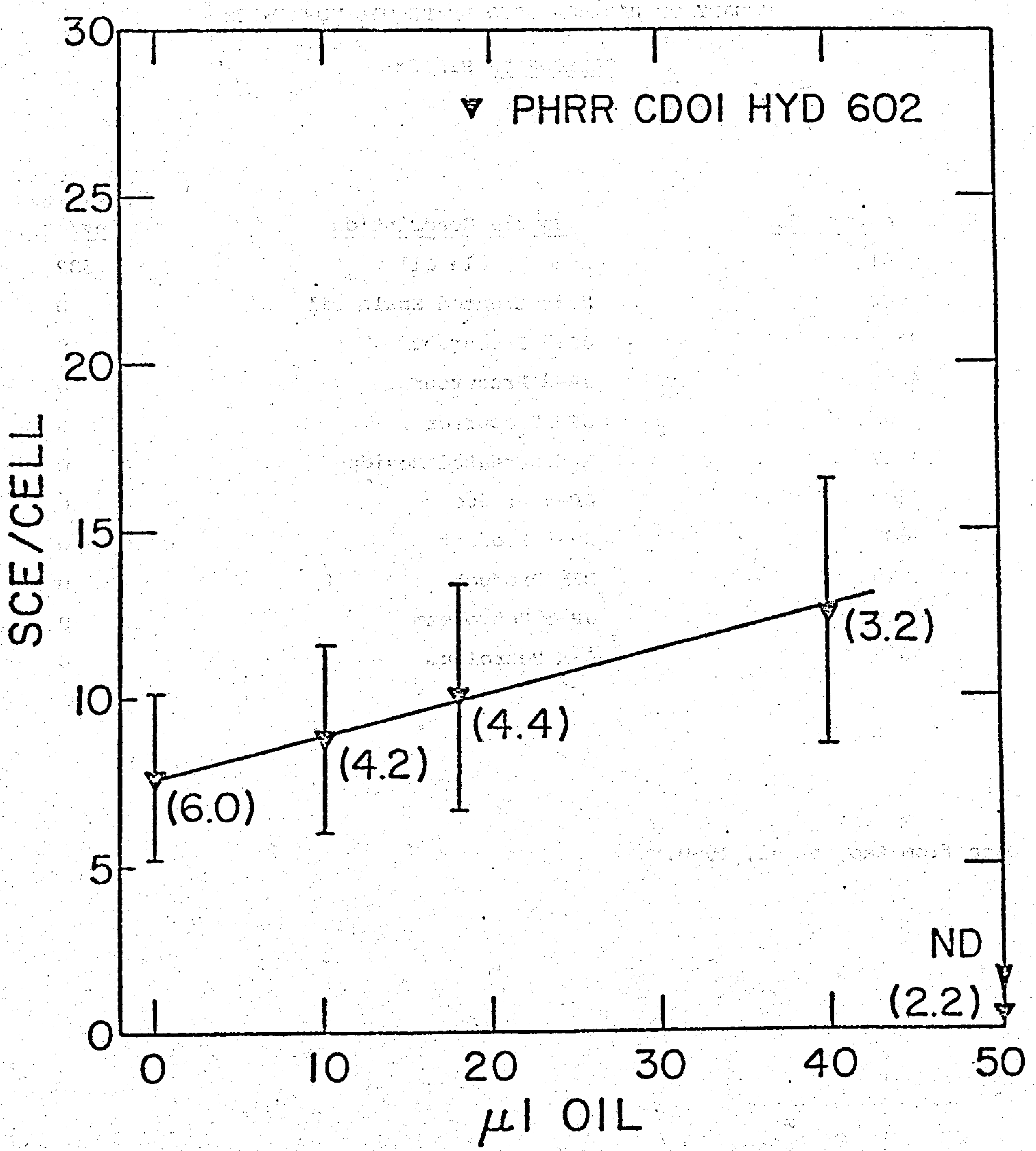


FIGURE 5.2.6

Dose Response Curve Showing Effect of Hydrotreated Extract on SCE Induction in CHO cells, (▼). Number in parenthesis cites mitotic index, ND indicates no differentiation (Campbell, et al, 1980).

TABLE 5.2.1

SUMMARY OF PARAHO-SOHIO SHALE OIL WORK WITH *SALMONELLA* SYSTEM

ORNL Repository No.	Sample Description	Mutagenic Activity (Rev/µg)
4601	Crude Shale Oil	.382
4602	Hydrotreated Shale Oil	0
4604	JP-5 Precursor	0
4605	JP-8 Precursor	0
4606	DFM Precursor	0
4607	Hydrotreated Residue	0
4608	JP-5 Product	0
4609	JP-8 Product	0
4610	DFM Product	0
4614	JP-5 Petroleum	0
4616	DFM Petroleum	0

Data from Rao, et al, 1980.

TABLE 5.2.2

MUTAGENICITY OF CRUDE SHALE OIL AND RESIDUE FROM DISTILLATION

Activity (rev/ug)

S. tymphimurium Strain	Residue	Crude
TA 98	0.3-0.5	0.6-0.7
TA 100	0.03-0.05	0.5
TA 100[a]	0.02-0.3	---
TA 1537	0.04	0.05-0.08
TA 1538	0.6-1.0	0.5-0.6

[a] No S-9 Activator.

Data from Calkins, et al, 1980.

TABLE 5.2.3

DETAILED WEIGHT DISTRIBUTION OF BIOTESTED SAMPLES IN WEIGHT PERCENT

												Neutral Fraction[c]		
	V	I	ESA	IA	ESB	IB	N-S	N-Ar	N-Ply	N-Pol	T[a]	N_e	N_s	%
Petroleum Crude Oil[b]	7.2	-	0.3	2.2	0.2	0.6	55.7	16.5	9.8	6.2	98.8	90.2	88.2	97.7
Petroleum Crude Oil	19.6	-	0.2	<0.1	0.6	-	51.0	7.4	3.9	1.1	83.9	-	63.4	90.3
Crude Shale Oil	0.3	-	0.4	0.3	3.3	0.5	55.6	27.4	7.0	2.2	96.9	95.4	92.1	96.5

[a] Using summation of neutral subfractions.

[b] US EPA/US DOE Synfuels Research Materials designation.

Data from Guerin, et al, 1980.

V - Volatiles
I - Ether Insolubles
ESA - Ether Soluble Acids
IA - Insoluble Acids
ESB - Ether Soluble Bases
IB - Insoluble Bases
NS - Neutral Saturates
N-Ply - Neutral Polyaromatics
N-Ar - Neutral Aromatics

N-Pol - Neutral Polar
T - Total
[c] N_e - Experimental (before subfractionation)
N_s - Summation (sum of subfractions)
% - Recovery (N_s/N_e)

TABLE 5.2.4

MUTAGENICITY OF CLASS FRACTIONATED SAMPLES - SPECIFIC MUTAGENICITY[a] IN REVERTANTS PER MICROGRAM OF FRACTION

	V[b]	I	ESA	IA	ESB	IS	N-S	N-Ar	N-Ply	N-Pol
Petroleum Crude Oil No.[c] 5301	0	-	0	0	0	0	0	.020	.015	0
Petroleum Crude Oil No. 5305	0	-	0	0	0	0	0	.040	.020	0
Crude Shale Oil No. 4601	0	-	0	0	8.000	.141	.020	0	1.600	0

[a] All tests using strain TA-98 with Arochlor 1254-induced S9 activation. Dash, "-", indicates "not tested" or "unable to test due to toxicity or interference".

[b] See Table 5.2.3 for names of fractions.

[c] US EPA/US DOE Synfuels Research Materials designation.

Data from Guerin, et al, 1980

TABLE 5.2.5

MUTAGENICITY OF CLASS FRACTIONATED SAMPLES -

WEIGHTED MUTAGENICITY IN REVERTANTS PER MICROGRAM OF ORIGINAL SAMPLE

	V[b]	I	ESA	IA	ESB	IB	N-S	N-Ar	N-Ply	N-Pol	T
Petroleum Crude Oil[c] 5301	0	-	0	0	0	0	0	.004	.002	0	.006
Petroleum Crude Oil 5305	0	-	0	0	0	0	0	.003	.002	0	.005
Crude Shale Oil 4601	0	-	0	0	.265	.001	.011	0	.111	0	.388

[a] All tests using strain TA-98 with Arochlor 1254-induced S9 activation. Dash, "-", indicates "not tested" or "unable to test due to toxicity or interference".

[b] See Table 5.2.3 for names of fractions.

[c] US EPA/US DOE Synfuels Research Materials designation.

Data from Guerin, 1980; Guerin, et al, 1980; Rao, et al, 1980.

TABLE 5.2.6

SUMMARY - APPROXIMATE MUTAGENICITY AND WEIGHT DISTRIBUTION BY CHEMICAL CLASS

	Mutagenic Activity					Weight Distribution				
		Percentage Contribution				Percentage of Total				
	Total Rev/µg	Acids %	Bases %	Neutrals %	Other %	Acids %	Bases %	Neutrals %	Other[b] %	Total Recovered %
Petroleum Crude Oil[a] 5301	.005	0	0	.100	0	2	1	90	7	99
Petroleum Crude Oil 5305	.005	0	0	.100	-	<1	<1	65	20	85
Crude Shale Oil 4601	.390	0	.069	.031	0	1	4	95	0	100

[a] US EPA/US DOE Synfuels Research Materials Facility designation.

[b] Volatiles and precipitates other than acidic and basic precipitates.

Data from Guerin, et al, 1980.

TABLE 5.2.7

MUTAGENIC ACTIVITIES OF NEUTRAL SUBFRACTIONS

Fraction	% Weight	Specific Activity (Rev/µg)		Weighted Activity (Rev/µg)
Aliphatic	55.61	.02		.01
Mono and Di Arom.	27.37	0		0
Polyaromatic	6.95			.11
PAH		.12		
N-PAH		0		
Polar		1.10		
Residue	2.15	0		0
			Total	.12
Total of Base Neutral Fractions				.38
Original		.50		.50

Data from Rao, et al, 1980.

TABLE 5.2.8

ISOLATION OF MUTAGENIC ACTIVITY FROM THE BASIC FRACTION (ESB)[a]

	Shale Oil-ESB (4101)		
	Relative Weight %	Specific Activity (Rev/µg)	Weighted Activity (Rev/µg)
ESB	–	–	2.500
Benzene	77	0	0
Isopropanol	12	0	0
Acetone	9	20.000	1.800
TOTAL	98		1.800

[a] ESB - ether soluble base.

Data from Rao, et al, 1980.

TABLE 5.2.9

NITROGEN CONTAINING COMPOUND TYPES IDENTIFIED IN THE ACETONE SUBFRACTIONS

	Crude Shale Oil 4601	Petroleum Crude Oil 5301
Primary Aromatic Amines		
aniline	3A%[1]	47A%
aminoindan	3	5
aminonaphthalene	t[2]	3
aminobiphenyl	t	1
aminofluorene	t	-
aminoanthracene	-	-
TOTAL	6	56
Secondary Aromatic Amines		
N-alkylnaphthalene	7	20
N-alkylindan	1	16
N-alkylfluorene	-	3
TOTAL	8	39
Azaarenes		
Pyridine	3	3
Quinoline	35	3
Azafluorene	2	t
Benzoquinoline	11	t
Azafluoranthene/Azapyrene	-	t
Azabenzofluorene	-	-
Dibenzoquinoline	-	-
Azabenzopyrene	-	-
Azaanthanthrene	-	-
TOTAL	51	6
Mixed Secondary and Tertiary Amines		
Methylpyridoindole or N-methylaminoazaacenapthylene	35	-

[1] A% = Area percent - chromatographic peak area as percent of total chromatogram area

[2] t designates trace amount detected (<< 1%).

Data from Buchanan, Ho, and Clark, 1980.

TABLE 5.2.10

HISTINE REVERTANTS INDUCED IN SALMONELLA TA98 AND TA100 BY SHALE OIL RETORT PROCESS WATER USING STANDARD AMES TEST[a,b,c]

µl sample/plate	TA98 Revertants per Plate with S9[c,d]	TA100 Revertants per Plate with S9[e,f]
	Paraho	Paraho
0.1	46 ± 6	113 ± 16
1.0	51 ± 10	133 ± 34
10.0	252 ± 64	672 ± 31
100.0	app 3200[g]	713 ± 132
300.0	app 3100	387 ± 10

µl sample/plate	TA98 Revertants per Plate without S9	TA100 Revertants per Plate without S9
0.1	31 ± 5	171 ± 19
1.0	23 ± 7	160 ± 29
10.0	25 ± 12	152 ± 7
100.0	37 ± 6	170 ± 14
300.0	59 ± 17	241 ± 37

[a] The above data represents the results of two separate experiments in which each data point is the average number of colonies formed (six plates).

[b] 1240 µg S-9 homogenate protein per plate.

[c] Diagnostic Mutagens: 2-nitrofluorene (1.5 µg/plate), (-S9) 323 ± 22: B(a)P (2.5 µg/plate), (+S9) 173 ± 67.

[d] Background revertants (controls) were 51 ± 17 (+S9), 32 ± 17 (-S9); app is the abbreviation for approximately.

[e] Diagnostic Mutagens: HNNG 2.5 µg/plate, (-S9) 920 ± 108; B(a)P2.5 µg/plate (+S9) 321 ± 110.

[f] Background revertants (controls) were: 137 ± 37 (+S9); 175 ± 22 (-S9).

[g] app = approximately.

Data from Nichols and Strniste, 1981.

TABLE 5.2.11

ACTIVATED AMES ASSAY

Tester Strain	+.Histidine	- Histidine	5.0 µl Mutagen	5.0 µl Mutagen 0.5 ml S-9 Mix	Run Number	Process Water
TA98	26 revertants	no growth	24 revertants	99 revertants	1	n.r.*
					2	n.r.
TA100	26 revertants	no growth	16 revertants	23 revertants	1	n.r.
					2	n.r.
TA1535	16 revertants	no growth	12 revertants	35 revertants	1	n.r.
					2	n.r.
TA1537	11 revertants	no growth	22 revertants	31 revertants	1	n.r.
					2	n.r.

*n.r. refers to no revertant ring around filter paper disc that would indicate mutagenesis.

Data from Beck and Burbank, 1980.

TABLE 5.2.12

INACTIVATED AMES ASSAY

Tester Strain	+ Histidine	- Histidine	0.1 ml Mutagen	Run Number	Process Water
TA98	15 revertants	no growth	30 revertants	1	n.r.*
				2	n.r.
TA100	26 revertants	no growth	TNTC (5 ul NaN_2)	1	n.r.
				2	n.r.
TA1535	25 revertants	no growth	51 revertants	1	n.r.
				2	n.r.
TA1537	2 revertants	no growth	46 revertants	1	n.r.
				2	n.r.

*n.r. refers to no revertant ring around filter paper disc that would indicate mutagenesis.

Data from Beck and Burbank, 1980.

TABLE 5.2.13

MUTAGENICITY OF CRUDE AND HYDROTREATED SHALE OIL TO FOUR LOCI IN CHO CELLS. MUTAGENICITY WAS DEPENDENT ON S9-MEDIATED METABOLIC ACTIVATION AND WAS LOST AFTER HYDROTREATMENT.

(Timourian, H., et al, 1980)

Treatment	Dose (μg/ml)	Survival	Mutant frequency/viable cell after drug exposure[a] AA (x 10^{-5})	TG (x 10^{-5})	OUA (x 10^{-6})	TFT (x 10^{-3})	FUdR (x 10^{-3})
Experiment 1							
None	0	1.00	1.6	3.4	7.0	NT	NT
Hydrotreated Oil	4000	0.45	0.4	0.3	1.0	NT	NT
+ S9	4500	0.02	0.2	0.2	0.7	NT	NT
Crude Oil	750	0.84	1.8	1.8	6.7	NT	NT
+ S9	1000	0.28	1.6	2.6	17.0[b]	NT	NT
Experiment 2							
None	0	1.00	2.9	3.4	0.6	2.6	1.4
Crude Oil	1000	0.30	5.6[b]	4.0[b]	1.57	3.8[b]	1.5
+ S9	1100	0.23	3.9[b]	2.1	1.98[c]	5.4[c]	2.1
	1400	0.03	4.2[b]	1.1	1.96[c]	6.1[c]	2.1

[a] AA, azaadenine exposure, mutation at adenine phosphoribosyl transferase locus.
TG, thioguanine exposure, mutation at hypoxanthine phosphoribosyl transferase locus.
OUA, ouabain exposure, mutation at ATPase locus.
TFT, trifluorothymidine, mutation at thymidine kinase locus.
FUdR, fluorodeoxyurindine, mutation at thymidine kinse locus.

[b] Significantly higher than spontaneous rate at 2 SEM.

[c] Higher than spontaneous but not statistically significant. NT = not tested.

TABLE 5.2.14

MUTAGENICITY OF SHALE OIL PRODUCT WATER

NEAR-UV ACTIVATION

(Barnhart et al, 1978)

SO-Product Water		NUV	Survival	6-TG^R per
(Dil)	(μl/ml)	(S)[a]	(S/S_0)	10^5 CHO Cells
1/30	33	0	1.00 (0.36)[b]	0.17
		20	0.93	2.9
		40	0.68	7.7
1/100	10	0	1.00 (0.97)	0.89
		20	0.91	9.8
		40	0.82	15.5
-	-	0	1.00	0.93
		20	0.98	0.81
		40	1.03	1.06

[a] 280 $Jm^{-2}s^{-1}$.

[b] Survival relative to control value.

TABLE 5.2.15

Cytogenetic Aberrations in Day 12 Embryos from Females Exposed To 1% Paraho Retort Water (PRW) *Ad Libitum*

(Campbell, et al, 1980)

			Number of Aberrations[b]			
Exposure	**Female**	**Total Cells Scored[a]**	**b**	**B**	**xc**	**gaps**
	I	300	9	0	0	14
	II	300	6	0	0	15
	III	300	8	0	0	18
	IV	300	6	0	0	14
	V	300	7	0	0	17
		mean/cell	0.024	0	0	0.052
			± 0.004			± 0.006
	I	300	13	3	4	26
	II	300	23	9	0	27
	III	300	17	3	3	26
	IV	300	22	1	1	31
	V	300	19	1	3	27
		mean/cell	0.063	0.011	0.007	0.091
			± 0.013	± 0.011	± 0.005	± 0.007

---

[a] A total of 50 cells scored on each of 6 embryos from each female.

[b] b-chromatid breaks; B-isochromatid breaks; xc-exchanges other than centric fusions.

Table 5.2.16 CHOMOSOMAL ABERRATION ANALYSIS OF BONE MARROW OF CD-1 MICE AFTER INTRAPERITONEAL INJECTION OF SHALE OIL

Treatment[a]	Total Cells Scored[b]	Breaks per Cell ± s.d.	Gaps per Cell ± s.d.	Mitotic Index ± s.d.
Untreated	1000	0.008 ± 0.006	0.025 ± 0.007	4.74 ± 0.45
Olive Oil	2000	0.009 ± 0.006	0.027 ± 0.007	4.79 ± 0.46
0.5 ml/kg PCSO	1000	0.023 ± 0.008	0.040 ± 0.010	4.55 ± 0.62
1.0 ml/kg PCSO	1000	0.026 ± 0.009	0.047 ± 0.009	3.91 ± 0.70
2.0 ml/kg PCSO	1000	0.045 ± 0.012	0.059 ± 0.012	4.12 ± 0.76
0.5 ml/kg PCSO-HT	1000	0.015 ± 0.007	0.028 ± 0.008	4.78 ± 0.37
1.0 ml/kg PCSO-HT	1000	0.017 ± 0.006	0.027 ± 0.007	4.82 ± 0.39
2.0 ml/kg PCSO-HT	1000	0.029 ± 0.011	0.043 ± 0.018	4.63 ± 0.69

[a] PCSO, Paraho crude shale oil; PCSO-HT, hydrotreated shale oil.

[b] A total of 100 cells per animal. Each treatment group was evenly divided between males and females.

Taken from Meyne and Deaven, 1981.

Table 5.2.17 CHROMOSOMAL ABERRATION ANALYSIS OF BONE MARROW OF FEMALE CD-1 MICE AFTER INTRAPERITONEAL INJECTION OF SHALE OIL

Treatment	Total Cells Scored[a]	Breaks per Cell ± s.d.	Gaps per Cell ± s.d.	Mitotic Index ± s.d.
Untreated	1000	0.008 ± 0.006	0.021 ± 0.019	4.26 ± 0.41
Saline	2000	0.007 ± 0.006	0.026 ± 0.013	4.00 ± 0.46
0.5 ml/kg PHRO	500	0.012 ± 0.008	0.038 ± 0.016	3.64 ± 0.34
1.0 ml/kg PHRO	1000	0.015 ± 0.012	0.029 ± 0.010	3.73 ± 0.65
2.0 ml/kg PHRO	1000	0.014 ± 0.008	0.033 ± 0.009	2.78 ± 0.37
4.0 ml/kg PHRO	500	0.020 ± 0.007	0.030 ± 0.007	2.30 ± 0.24

[a] A total of 100 cells scored per mouse.

Taken from Meyne and Deaven, 1981.

Table 5.2.18 SCE ANALYSIS OF BONE MARROW OF FEMALE CD-1 MICE AFTER INTRAPERITONEAL INJECTION OF SHALE OIL

Treatment[a]	Total Cells Scored[b]	Mean Number of SCE per Cell ± s.d.
Untreated	250	6.84 ± 0.44
Olive Oil	250	7.40 ± 0.35
0.5 ml/kg PCSO	125	8.82 ± 0.42
1.0 ml/kg PCSO	125	9.22 ± 0.59
2.0 ml/kg PCSO	125	10.68 ± 0.32
0.5 ml/kg PCSO-HT	125	6.57 ± 0.21
1.0 ml/kg PCSO-HT	125	6.10 ± 0.17
2.0 ml/kg PCSO-HT	125	6.84 ± 0.35
5 mg/kg CP	250	16.80 ± 0.97

a PCSO, Paraho crude shale oil; PCSO-HT, hydrotreated shale oil; CP, cyclophosphamide.

b A total of 25 cells were scored per mouse.

Taken from Meyne, 1982.

Table 5.2.19 SCE ANALYSIS OF BONE MARROW OF FEMALE CD-1 MICE AFTER INTRAPERITONEAL INJECTION OF PROCESS WATER

Treatment[a]	Total Cells Scored[b]	Mean Number of SCE per Cell ± s.d.
Untreated	225	6.73 ± 0.55
Saline	250	6.67 ± 0.47
1.0 ml/kg PHRO	125	6.65 ± 0.57
2.0 mg/kg PHRO	125	6.53 ± 0.39
4.0 mg/kg PHRO	125	6.74 ± 0.44
5 mg/kg CP	250	15.57 ± 0.46

[a] PHRO, Paraho process water; CP, cyclophosphamide.

[b] A total of 25 cells were scored per mouse.

Taken from Meyne, 1982.

5.3 TOXICOLOGY

5.3.1 Tumor Initiation Studies

Crude shale oil applied to mouse skin caused moderate to severe inflammatory responses at doses above 10% (Wilson and Holland, 1979). Breakdown of the epidermal layer and involvment of dermal structures were observed. At the highest dose of crude shale oil, the inflammatory response consisted of thickened epidermis, sub-dermal edema, crust formation, and ulceration with an influx of mono- and poly-nuclear cells. Frank ulceration occurred in 4 of the 6 exposed animals. Even though inflammatory responses occurred at the highest doses, no animals died and there were no significant weight changes. Histological examination of major internal organ systems revealed no alteration in micro-anatomy that could be attributed to exposure to crude shale oil. These observations enforce the need for adequate protective measures (personal hygiene and appropriate protective clothing) to be provided for higher risk industrial populations.

The repetitive application of crude shale oil to intact mouse skin has been used to determine comparative carcinogenic potential (Wilson and Holland, 1980; and Holland and Wilson, 1981). Crude shale oil induced tumors appeared in all surviving mice after 453 days, with the first tumor appearing after 78 days and two more appearing after 136 days. A statistical evaluation of crude shale oil and a crude petroleum are compared to two dose levels of benzo(a)pyrene (BaP) (Figure 5.3.1). Most of the tumors were either papillomas or squamous carcinomas; however, the histological types were not distinguished. It appears that hydrotreated shale oil produces a similar, but diminished, tumorigenic response. Investigations of epidermal responses to conditions of crude shale oil exposure have been initiated: dose frequency versus total dose, comparative solubility of the oils in various vehicles, and DNA synthesis by epidermal cells following chronic and acute exposure (Wilson, Valdez, and Holland, 1981).

After 20 weeks of treatment, frequency of exposure induced higher percentages of epidermal degeneration than single total doses. Mice exhibiting severe cytotoxicity did not produce tumors; tumor bearing mice had exhibited severe cytotoxicity (Wilson, Valdez, and Holland, 1981).

The comparative solubility of the oils in various solvents indicates that: 30/70 cyclohexane/acetone elicits tumors beginning at about 20 weeks and shows cytotoxic effects in 10% or less of the animals after 30 weeks. A chronic contact dermatitis was demonstrated by mice in the control group treated with cyclohexane. After 20 weeks no overt cytotoxicity has been observed in any group. Five percent of the mice in the cyclohexane group have exhibited confirmed tumors (Wilson, Valdez, and Holland, 1981).

Visual observations during chronic exposure indicated a cell proliferation followed by eventual degeneration after high dose/high frequency treatment. Flow cytometry (FCM) analysis of DNA content of cell suspensions obtained from mice treated daily for 14 days with 40 mg of crude shale oil or a natural petroleum indicate that DNA synthesis increases and is sustained, followed by degeneration (Wilson, Valdez, and Holland, 1981).

Chronic dermal exposure to crude shale oil, hydrotreated shale oil, and hydrotreated residue induces skin tumors (Holland, J. M., et al, 1981) in mice. Distillates of crude shale oil seem to have a low skin tumor induction (Table 5.3.1).

Dermal applications of crude shale oil, hydrotreated shale oil, and hydrotreated residue (2g/Kg) to male and female rats demonstrated no visible toxic responses (Smith, Hascheck, and Witschi, 1980). No visible skin lesions or manifestations of central nervous system perturbations were observed. No deaths occurred during the 2 weeks following application of the substances. All rats showed a progressive gain in body weight (Table 5.3.2). These results are similar to the observations obtained from petroleum-derived JP-5, JP-8, and diesel fuel marine products: no animals died, no skin lesions developed, and weight gains over a 2-week period were normal.

Mouse skin tumor initiation-promotion tests were conducted on Paraho crude shale oil and four distillates (Calkins, et al, 1980; McAlack, et al, 1980). These results are shown in Table 5.3.3. The Salmonella mutation test data correlated well with the results from the initiation/promotion test (Table 5.3.4). The mutation and initiation-promotion test exhibited mutagenic and tumor initiation activities in the crude and high boiling fractions of petroleum and shale oil. Both screening test results exhibited the greatest activities in the high boiling fractions. The naphtha fractions were considered to be inactive. The crude shale oil and its fractions exhibited biological activities quite similar to those observed with the petroleum sample and its fractions selected as controls.

Daily application of crude shale oil to hairless mice followed by near ultra-violet (NUV) light induced skin abnormalities (Gomer and Smith, in press). At lower concentrations of crude shale oil, minor skin reactions were observed. At higher concentrations, a characteristic dry desquamation with the formation of scabs was observed. Without exposure to NUV, the skin was characterized by erytherma and flaking of the epidermis.

Tank bottom water (dosage of 5 ml/kg) applied to rabbit skin abrasions showed no abnormal observations or signs of toxicity during the observation period. No systemic toxicity or treatment-related systemic lesions were observed during postmortem examinations. Thus, crude shale oil may be placed in EPA Category III, dermal LD_{50} greater than 5 g/kg (Beck and AlbinaDia, 1980).

5.3.2 Systemic Toxicity

<u>Acute Systemic Toxicity</u>. Tank bottom water produced acute deaths in mice at 11.3 g/kg (Table 5.3.5) when given orally (Smith, Hascheck and Witschi, 1980; Beck, Morita, and Hepler, 1979). Another laboratory observed oral LD_{50} of crude shale oil at 8-10 g/kg (Disbennett, 1980). Intraperitoneal injection produced deaths at 2 g/kg and 5 g/kg body weight (Smith, Hascheck, and Witschi, 1980; Timourian, et al, 1980). Hydrotreated shale oil produced LD_{50} of 17 g/kg and >16 g/kg (Timourian, et al, 1980: Smith, Hascheck and Witschi). The LD_{50} for refined shale oil products was 6-16 g/kg (Table 5.3.6).

Hydrotreated and refined shale oil products appear to be slightly less toxic in whole mammals.

Raw and retorted shale produced acute deaths in rats >10 g/kg (Disbennett, 1980).

Impregnated mice drinking 7.0% tank bottom water showed no significant toxicity; there is no fetal toxicity (Gregg and Hutson, 1980).

<u>Chronic Toxicology</u>. Neither shale oil nor its derivatives indicate any primary skin irritation in rabbits (Smith, Hascheck, Witschi, 1980). No visible redness or edema was observed. Applications of JP-5 and diesel fuel marine derivatives of shale oil produced only slight dermal irritation in rabbits (Cowan and Jenkins, 1980). Crude and hydrotreated shale oil produced visible redness in rabbit eye. The irritation was slight, transient, and insignificant (Smith, Hascheck, Witschi, 1980). Other research of JP-5 and diesel fuel marine products show only slight irritation of eye in only one rabbit from the diesel fuel marine product (Cowan and Jenkins, 1980). None of the products were judged to be sensitizers based on test criteria. Tank bottom water is minimally irritating to rabbit skin (Beck, Morita, and Hepler, 1979).

During delayed-type allergic contact with crude shale oil, hydrotreated shale oil, jet and diesel fuels in guinea pigs, only slight redness and focal scab formation were noted in some animals. After a challenge injection, crude and hydrotreated shale oils produced a greater degree of redness and edema, and a slight necrosis was noted (Smith, Haschek, Witschi, 1980). No reaction was observed from diesel fuel sensitization. Other research shows no sensitization in guinea pigs to shale oil or raw and retorted shale (Disbennett, 1980). Tank bottom water is non-sensitizing to guinea pigs (Beck, Mills and Hepler, 1980).

Histopathology. Serositis and thymic cortical depletion were the only histopathologic reactions observed following intraperitoneal injections of crude and hydrotreated shale oil. Superficial pyogranulomatous serositis of the peritoneal cavity resulted from local reaction to the substances (Smith, Haschek, and Witschi, 1980).

Teratogenesis. Female rats were exposed to airborne oils and dusts during gestation. No teratogenic activity was observed (Disbennett, 1980). Offspring from female mice exposed to 1.0% shale oil tank bottom water, *ad libitum*, exhibited malformations (Gregg and Hutson, 1981). Offspring with palatal abnormalities failed to form posterior portion of palate. Single cleft, double and multiple cleft abnormalities were observed. Other malformations observed were increase of sternebrae abnormalities and increase of enlarged or rudimentary 14th ribs.

Reproductive Study. Male and female rats were given 10% and 15% tank bottom water for an entire reproductive cycle of mating, whelping, and weaning. There was no decrease in reproductive behavior for the test animals. It is thought that the observed decreased conception rate, fetal viability, pup survivability after parturition, and decreased weight gain of pups are due to water deprivation and nutritional deficiencies (Beck, et al, 1980) rather than to the induction of reproductive abnormalities by a toxic effect of the tank bottom water.

5.3.3 Inhalation-Intratracheal Studies

Inhalation studies of Syrian hamsters and Fischer-344 rats have been completed or are in progress (Holland and Tillery, 1980). Many of the hamsters 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 pneumoconiotic diseases. Most of the shale particles inhaled accumulated in macrophages (Holland, Spall, Garcia, 1979). Retorted shale dusts appear to cause more inflammatory reaction with varying degrees of fibrosis; epithelial hyperplasia with extention of bronchiolar cells into proximal alveoli and thickening of intra-alveolar septa are present in all observed cases. The shale dusts appear as agglomerations rather than as individual particles and a peribronchiolar pattern is common to all materials (Holland, et al, 1979).

Hamsters in each group were allowed to complete their lifespans and histological examination of all relevant tissues has been completed. Two hamsters in the group exposed to raw shale and one animal from the group exposed to retorted shale exhibited a proliferation of reticulo-endothelial cells within the lung. A generalized hyperplasia of this tissue is not uncommon in rodents as a response to toxins and may even be associated with tissue necrosis and cell death. In one of the raw shale exposed animals, the cellular characteristics were more typical of neoplasia than an inflammatory response. The significance of these changes is problematical at best. Indications of fibrotic tissue response, ranging from slight interalveolar thickening to extensive fibrotic scarring, were observed in most animals completing the exposure period and both focal and generalized pneumonitis were common (Holland, et al, 1980).

Syrian hamsters, exposed to inhalation of raw shale, were used for serial sacrifice to study early lung response and hematological values (Holland, Smith, Thomas, 1979). No significant differences of total white blood cell counts, differential counts, red blood cell counts, packed cell volumes, and hemoglobin values were noted between the experimental animals and control animals during and after exposure. Early histopathology observations on the inhalation animals have shown a minimal response to the raw shale materials. A slight increase in macrophage activity was the only change noted. Under the conditions of exposure used, most of the material was found near the termination of respiratory bronchioles, with only a slight deposition in the deep lung. Animals exposed to shale materials intratracheally exhibited a more intense macrophage response in foci located near the bronchiolar terminations.

Fischer rats have been sacrificed at frequent intervals for neutron activation analysis of the deposition of inhaled materials in the lung. Preliminary results of the histological examinations of the sacrificed animals indicate a more general fibrotic response than that seen in hamsters. Most of the inhaled shale dust particles are accumulated in macrophages (Holland, et al, 1980).

Cytological and biochemical indicators for measuring damage to respiratory tract cells of experiment animals exposed by inhalation or intratracheal instillation to shale dusts are being developed (Steinkamp, et al, 1979; Steinkamp and Wilson, 1979). Flow cytometric methods are used to analyze and detect changes in lung epithelium as a function of exposure to shale dusts. The purpose of the automated flow-analysis assay is to determine atypical changes in exposed lung macrophages and epithelial cells.

Hamsters have been exposed to raw and retorted shale particles, silica dust, and ozone. The lungs were lavaged four times with saline to obtain exfoliated macrophages, leukocytes, and epithelial cells, which were fixed in 35% ethanol prior to staining for DNA content with mithramycin. Cell samples were analyzed using flow cytometric methods, where cellular fluorescence (DNA content) was measured on a cell-by-cell basis as frequency distribution histograms. Cell counts (cells/ml) also were made on lavage samples using a hemocytometer. Cytology was performed to determine the number of different cell types present (Steinkamp and Welson, 1979).

Hamsters were exposed to raw and retorted oil shale particles via intratracheal instillation (Steinkamp, Wilson, and Svitra, 1979). DNA content distributions for the period 4 to 49 days postexposure appear normal

(Figure 5.3.2) except for a region of dead cells (or debris) to the left of the 2c DNA cells, Peak 1 (Figure 5.3.3). The peak of binncleates and cell doublet, Peak 2, is present in all distributions. After 60 days of exposure to raw shale, Peak 1 splits into two regions, demonstrating a bimodal distribution. This indicates a change in DNA content, differences in stainability between cell types, or other factors. Total cell counts, leukocyte cells, and epithelial cells showed a definite increase compared to controls. Macrophage cells showed a small increase.

DNA content distributions of hamsters exposed to retorted shale particles appear similar to those determined for hamsters exposed to raw shale particles (Figure 5.3.3). There is a region of dead cells and/or debris to the left side of Peak 1. Peak 1 illustrates a general broadening; and after 28 days of exposure, Peak 1 splits into two distinct peaks similar to respiratory tract cells exposed to raw shale for 60 days.

At 35 and 42 days postinstillation, a definite shoulder appeared on the right side of Peak 1, and the number of cells within region 3 increased. The region of cells to the right side of Peak 1 appears to be similar to the results from hamsters exposed to ozone. Initially, cell counts were slightly elevated compared to controls but then decreased with further exposure. Total numbers of macrophages and leukocytes were also initially elevated whereas epithelial cells remained nearly constant throughout the exposure period.

The DNA content frequency distribution histograms of hamster respiratory tract cells exposed to silica particles appear similar to hamsters exposed to raw and retorted oil shale (Figure 5.3.3). At 28 days postexposure, Peak 1 splits into two distinct peaks. At 35 and 42 days, a region though to be dead cells has appeared to the left of Peak 1. The percentage of binncleated cells (4c DNA content cells), Peak 2, appears to be increasing also.

By 49 days and continuing through 90 days postexposure to silica, Peak 1 of the DNA content distributions were divided into two regions (Steinkamp and Wilson, 1979). The DNA content distributions of cells exposed to retorted shale similarly were bimodal but appeared to be reverting to normal as the time after exposure increased. At 60 to 90 days postexposure to raw shale, bimodal distributions began to appear (Figure 5.3.3 I and 5.3.3 J).

Cell counts performed on hamsters exposed to silica were elevated by an order of magnitude compared to controls. Macrophages and leukocytes greatly increased and remained high throughout the 90-day exposure period, indicating an inflammatory response. Epithelial cells also increased in number during the 30-day exposure period, but then decreased to nearly zero at 40 to 60 days exposure (Steinkamp, Wilson, Svitra, 1979).

The DNA distribution of hamster cells exposed to acute levels of ozone shows a bimodal distribution of cells in Peak 1 (Figure 5.3.4). The percentage of cells has increased in Peaks 1 and 2. Figure 5.3.4H shows a DNA content distribution for hamster cells 48 hours after ozone exposure, which "resembles" a typical DNA distribution for randomly growing CHO cells in which Peak 1 represents G_1 - phase cells (2 c DNA content, such as macrophages and leukocytes) and Peak 2 represents G_2 - and M-phase cells (4 C DNA content, such as epithelial cells). Cells located between Peaks 1 and 2 would then be S-phase cells (Steinkamp and Wilson, 1979).

Intratracheal instillation of raw shale particles on Syrian hamsters exhibited increased phagocytosis, and then decreased. The raw shale particles were of varying sizes, and the macrophages could only ingest the smaller particles. The larger particles or groups of particles of raw shale seemed to be surrounded by macrophages but could not be ingested due to their large size. The combination of raw shale and silica increased phagocytosis similar to the observations of raw shale. This may suggest that silica does not have a synergistic effect when combined with raw shale (Wilson, Hansen, and Holland, 1978).

Microscopic examinations of cytocentrifuge sample preparations of exposed hamster respiratory tract cells reveal that macrophages cluster around large raw and retorted shale particles to form rosettes (Steinkamp, et al, 1977). Macrophages appear to be "chemically attracted" to the shale particles. Large silica particles attracted only a few macrophages (Table 5.3.6). Increased multinucleation of "giant cells" was also observed in lung cell samples from hamsters exposed to raw shale and silica at 7 to 14 days postexposure (Steinkamp, Wilson, Svitra, 1979). Even though "giant cells" were not observed at other times or in cell samples exposed to retorted shale, they are expected to be present.

5.3.4 Cytotoxicity

Cytotoxicity of crude shale oil on mouse hepatoma cells (line Hepa-1) was eight times greater than exposure to hydrotreated shale oil (Timourian, et al, 1980). Crude shale oil treatment of CHO cells was twice as toxic as hydrotreated shale oil exposure. Crude shale oil exposure to female mice at LD_{50} for whole mouse was toxic to oocytes (Table 5.3.7), while hydrotreated shale oil was not cytotoxic to oocytes (Timourian, et al, 1980). Crude shale oil DMSO extract exhibits cytotoxic properties (Okinaka and Strniste, 1981). The addition of S9 activator (Figure 5.2.1) reduces cytotoxicity (Timourian, et al, 1980) of crude shale oil extracts (Okinaka and Strniste, 1981; and Timourian, 1980).

Hydrotreated shale oil appears to produce less cytotoxic effects than crude shale oil.

Blastogenesis. Treatments of retorted shale extracts on CHO cells show a 10 to 20 inhibition of blastogenesis. The same treatment on mouse lymphocytes failed to show any inhibition (Wilder and Cram, 1978). The inhibition of blastogenesis may be an indication of immunological competence.

5.3.5 Miscellaneous Toxicity Tests

Aquatic Toxicity. Acute toxicity tests were performed on two freshwater algae. The test organisms were *Selenastrum capricornutum*, a unicellular green alga, and *Microcystis aeruginosa*, a non-nitrogen-fixing, blue-green alga. Photosynthetic inhibition is the criterion of toxicity.

Crude and hydrotreated shale oil water soluble fractions (WSF) were more toxic than petroleum WSF (Table 5.3.8, Figure 5.3.5), with significant inhibition at WSF concentrations of 1 to 10% (Giddings and Washington, 1981). Hydrotreatment reduced the toxicity to both species (Table 5.3.8). The WSFs of refined shale oil products (JP-5 and DFM) were similar in toxicity to those of the petroleum products (Table 5.3.8). The shale oil residue, a No. 6 fuel oil, was more toxic than any of its petroleum equivalents; *S. capricornutum* was inhibited by 1% WSF.

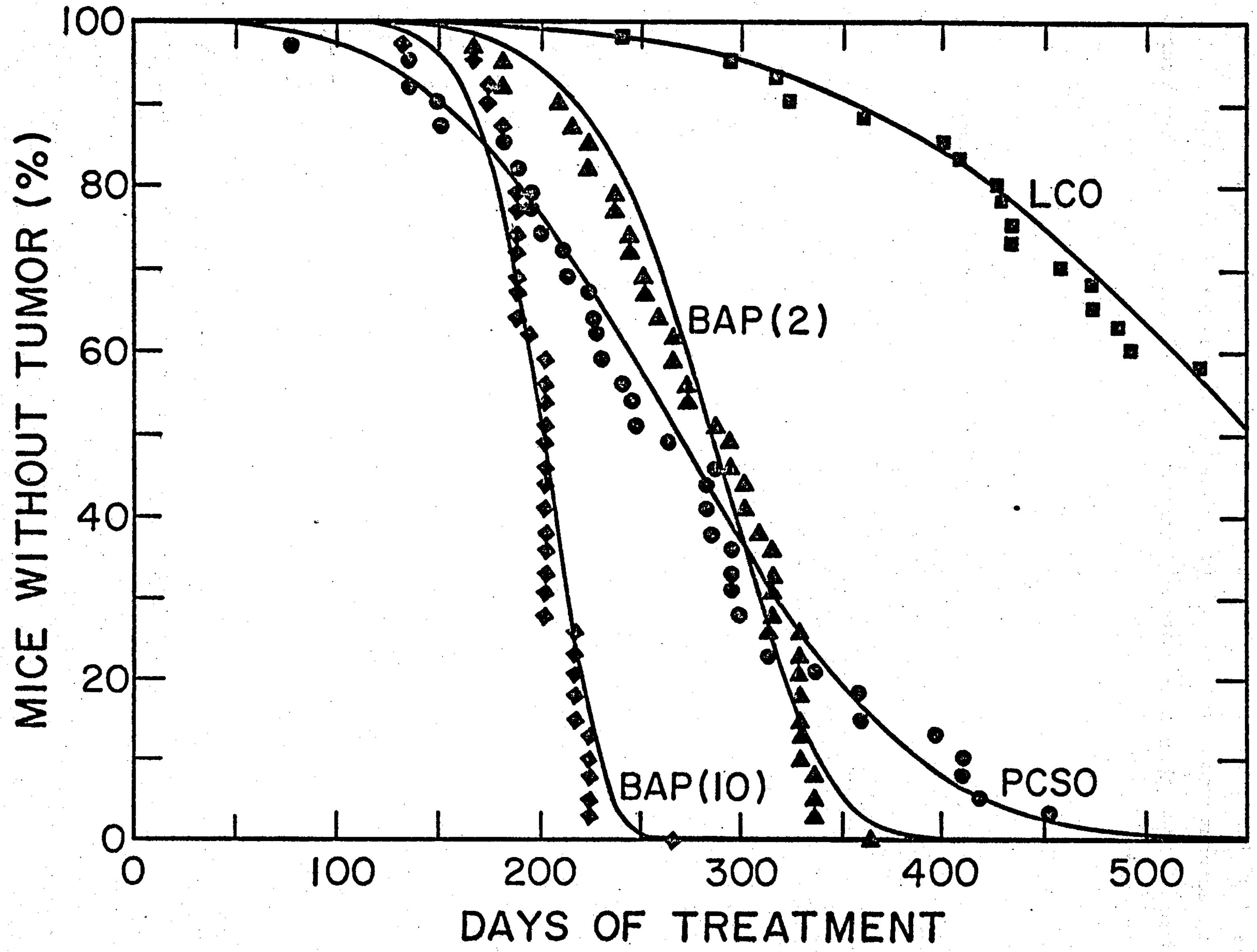
The reduction in toxicity by hydrotreating is thought to be due to the removal of nitrogen and oxygen from the oil during hydrotreating. The nitrogen- and oxygen-containing compounds, especially primary amines and phenols, are among the most toxic aromatic compounds to freshwater algae. These compounds are also much more soluble in water than their hydrocarbon analogs, so their abundance in WSFs is greater, proportionally, than their abundance in oil (Giddings, 1981).

Shale oil extracts were cytotoxic when exposed to Tetrahymena pyriformis, a large mobile ciliate. One hundred per cent cell mortality of T. pyriformis within 24 hours is achieved with exposure to 90% crude shale oil extract (Cowser, 1980). Hydrotreated shale oil exhibited slightly reduced mortality when compared to controls (Table 5.3.9). A 72-hour reproduction impairment was conducted. Crude shale oil responded three times more toxic than hydrotreated shale oil (Table 5.3.10).

Two tank bottom waters were assayed to determine acute aquatic toxicity levels. Ninety-six-hour flow-through acute bioassays indicate that LC_{50} values of rainbow trout, fathead minnows and Daphnia pulicaria exposed to tank bottom water 75-76 are 0.52%, 0.64% and 3.00%, respectively (Table 5.3.11). The 96-hr LC_{50} values for the same species exposed to tank bottom water 77-78 are 0.068%, 0.071% and 0.147%, respectively. An embryo-larval test was performed with tank bottom water 77-78 (Tables 5.3.11,5.3.12). An estimated safe concentration (ESC) can be predicted for this water at 0.001%. By using the same application factor (0.01) as tank bottom water 75-76, the ESC for tank bottom water 77-78 was calculated at 0.005% (Table 5.3.12).

Tank bottom water 77-78 was fractionated into hydrophilic and hydropholic basic, acidic and neutral components. Twenty-four-hour static acute bioassays exposing fathead minnow fry and Daphnia pulicaria to each of these fractions were then performed. The highest toxicities were found in the hydrophilic fractions. A portion of this toxicity can be attributed to ammonia which is found in the hydrophilic fractions. When ammonia was removed from the hydrophilic fractions, toxicity was significantly reduced.

Phytotoxicity. Two phytotoxicity tests were performed: short-term root (radicle) elongation test with radish and sorghum and longer-term seedling growth studies with wheat and soybean. A tenfold dilution extract of retorted shale reduced root growth of the monocotyledon species (sorghum and wheat) in both types of tests (Epler, et al, 1980). Raw shale caused a growth reduction of 14% in sorghum roots (Table 5.3.13). Both raw and retorted shale were phytotoxic at less than a tenfold dilution and may display a toxic interference of acetic acid.



Tumor Initiation in Mice Treated With
Crude Shale Oil, Crude Petroleum, and Benzo(a)pyrene

Figure 5.3.1

Taken from Holland and Wilson, 1981.

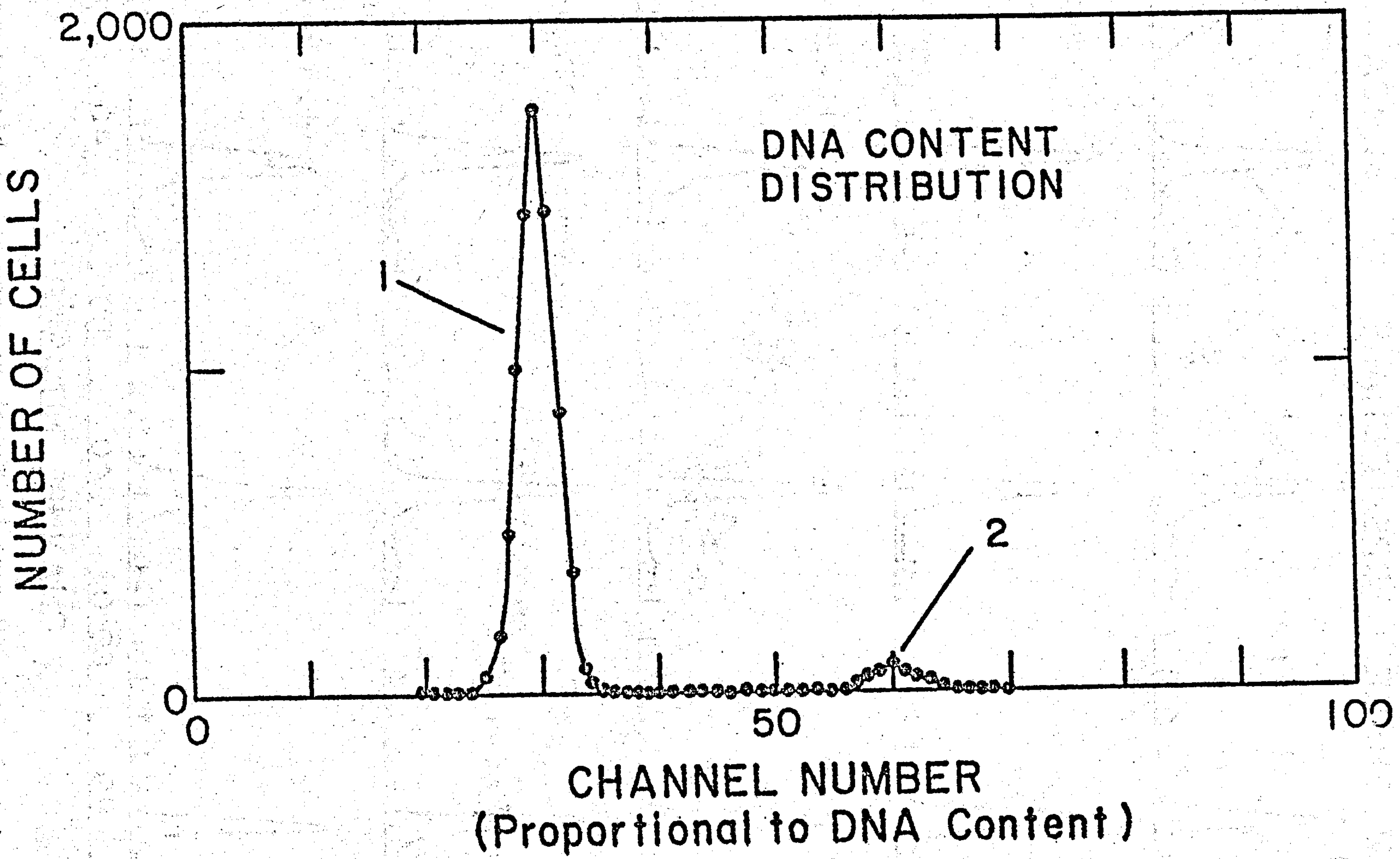


Figure 5.3.2 Frequency distribution histograms (DNA content per cell) of normal hamster respiratory tract cells fixed in 35% ethanol, stained with mithramycin, and analyzed for fluorescence.

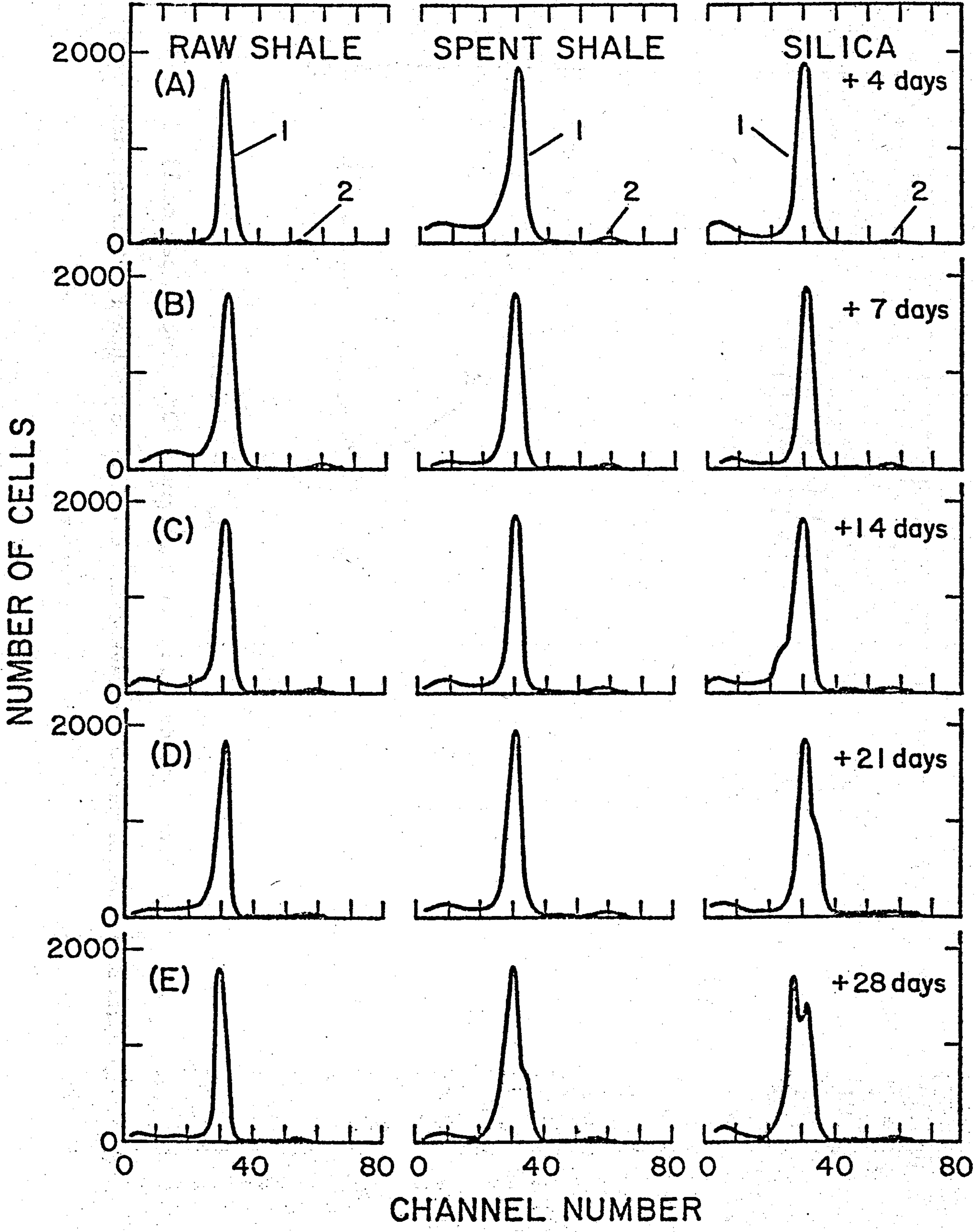
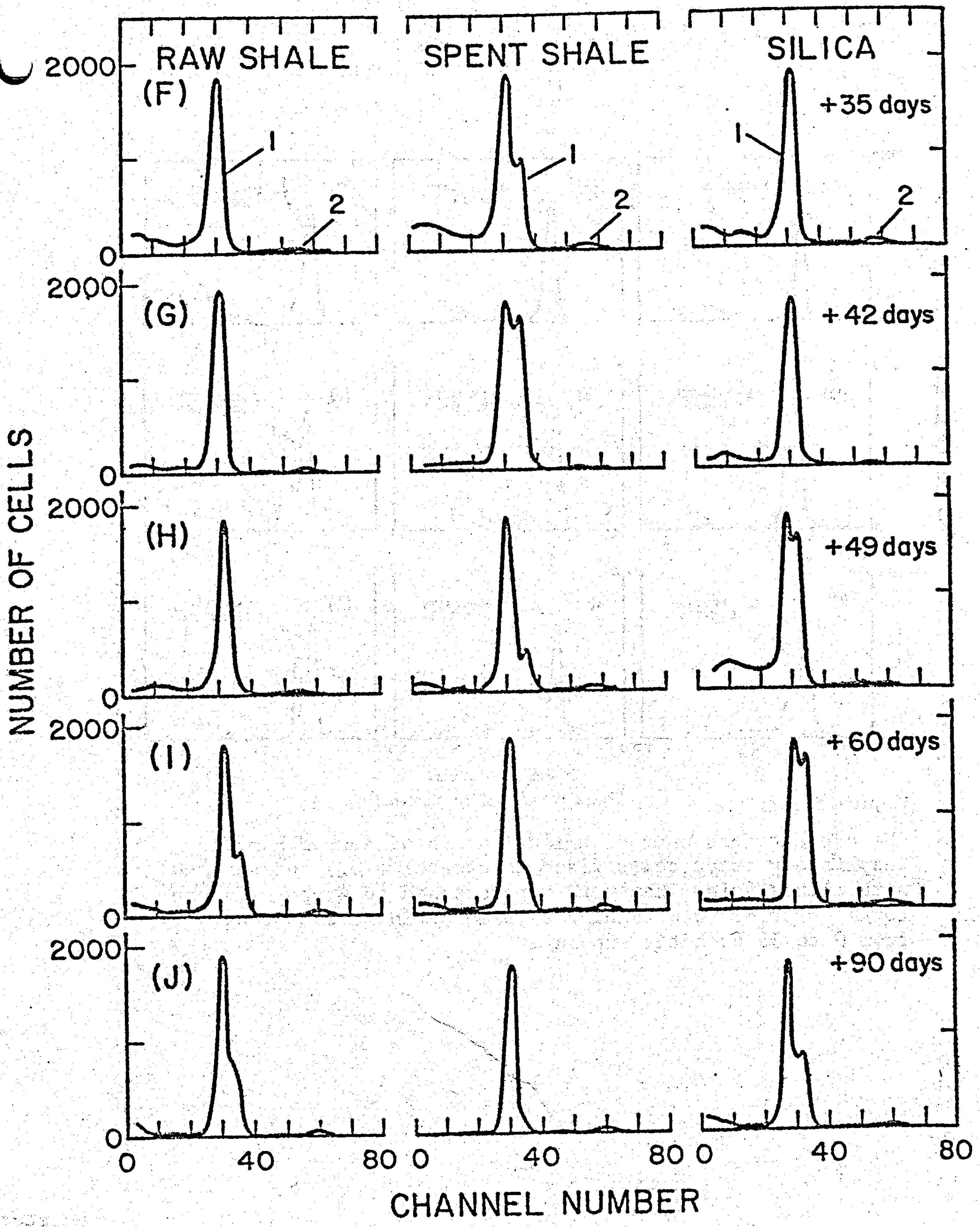


Figure 5.3.3 Typical DNA content frequency distribution histograms of hamster respiratory tract cells exposed to raw and spent oil shale and silica particulates via intratracheal injection


RAW SHALE
SPENT SHALE
SILICA
NUMBER OF CELLS
CHANNEL NUMBER
2000
0
40
80
(F)
(G)
(H)
(I)
(J)
+35 days
+42 days
+49 days
+60 days
+90 days
1
2

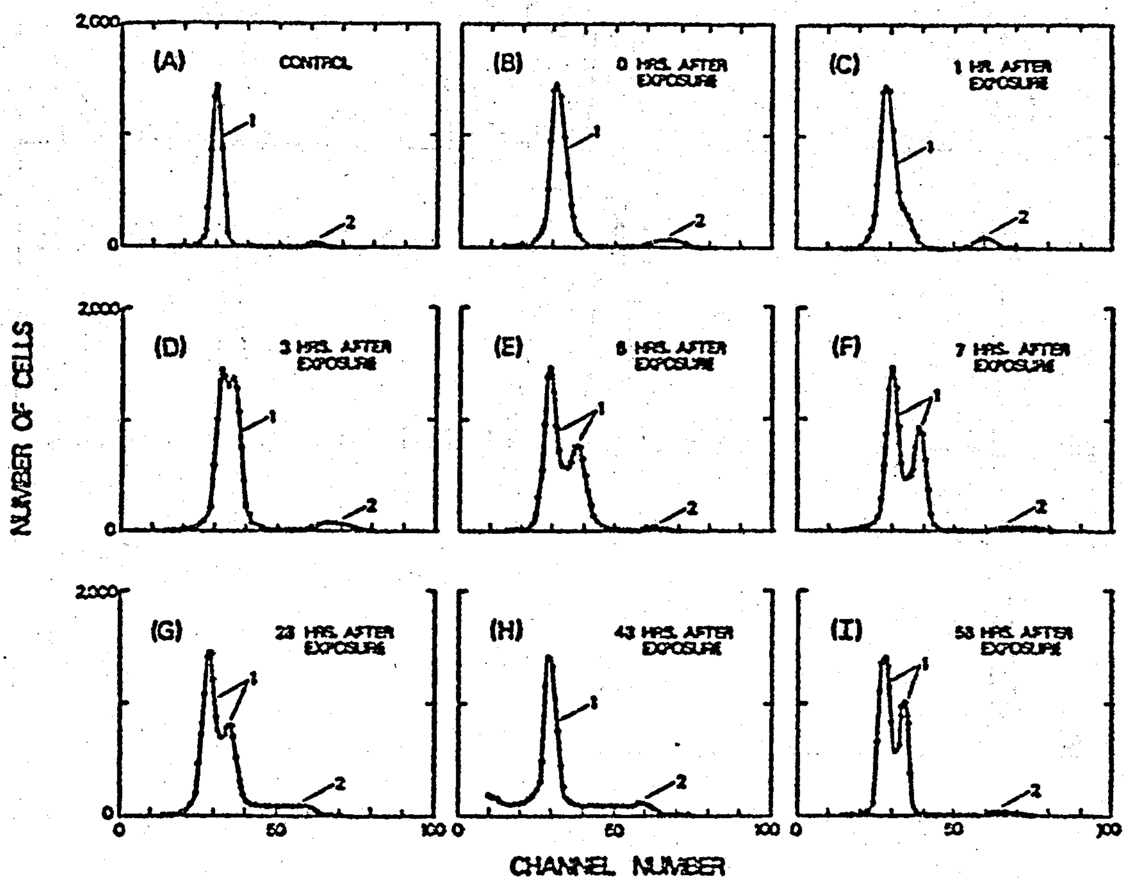


Figure 5.3.4 (Proportional to DNA Content)

DNA content frequency distribution histograms of hamster respiratory tract cells fixed in ethanol (70%) and stained with mithramycin. Hamsters were exposed to 4 ppm of ozone for 4 hr prior to obtaining samples at increments ranging from 0 to 56 hr after exposure.

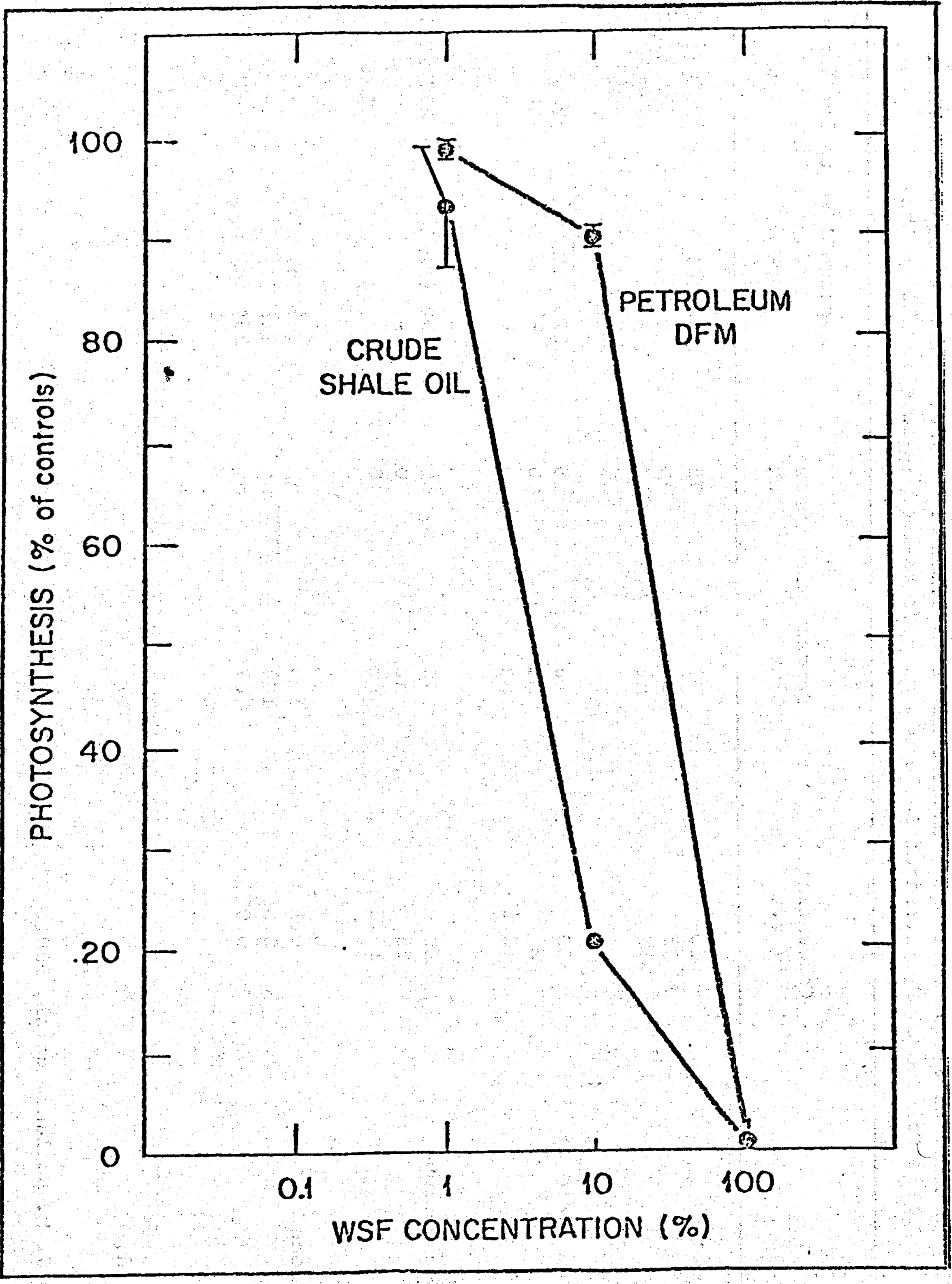


FIGURE 5.3.5

Relative photosynthesis (% of controls) of Selenastrum capricornutum exposed to water-soluble fractions (WSFs) of petroleum DFM and crude shale oil. Error bars indicate ± 1 S.D. (Giddings, 1980)

Table 5.3.1 Skin Tumor Frequency in Mice Exposed Either 3 Times or 2 Times Weekly to Graded Doses of Shale Oil Crude, Hydrotreated Shale Oil or Hydrotreated Residue for 10 months.

Material	Concentration (w/v%)	Percent with Tumor 3/wk	Percent with Tumor 2/wk	Average Time to 1st Tumor (days + S.E.) 3/wk	Average Time to 1st Tumor (days + S.E.) 2/wk
Shale Oil Crude	50	93	75	206 (6)	261 (11)
	25	nt[a]	35	-	271 (18)
	12.5	nt	10	-	278 (52)
Hydrotreated Shale Oil	50	46	5	228 (12)	280
	25	nt	0	-	-
	12.5	nt	0	-	-
Hydrotreated Residue	50	70	20	192 (11)	270 (26)
	25	nt	0	-	-
	12.5	nt	0	-	-
Benzo(a)pyrene	0.1	100	nt	169 (6)	-
	0.05	100	nt	215 (4)	-
	0.025	67	nt	254 (4)	-

[a] Not tested.

Taken from J. M. Holland, et al, 1981.

Table 5.3.2 Weight Gain in Male and Female Rats Following Dermal Application of 2 gm/kg of Shale Oil, Hydrotreated Shale Oil, or Hydrotreated Residue [a].

	Mean Body Weight (g) ± SE			
	Male		Female	
Substance	Day 0	Day 14	Day 0	Day 14
Crude Shale Oil	358 ± 8	415 ± 7	209 ± 5	241 ± 2
Hydrotreated Shale Oil	352 ± 9	422 ± 9	209 ± 3	238 ± 4
Hydrotreated Residue	370 ± 4	435 ± 7	225 ± 5	256 ± 6

[a] Six animals per group except for substance 4602 females, for which there were five rats.

Taken from Smith, Haschek, and Witschi, 1980.

TABLE 5.3.3

MOUSE SKIN PAINTING INITIATION-PROMOTION STUDY

(Calkins, et al, 1980)

Sample	# Mice With Tumors Lasting >30 Days	Average # Tumors/ Tumor Bearing Mouse	Number of Days to 1st Mouse With Tumor
Controls			
Toluene/Acetone	0	0	0
Toluene/PMD	4	1.5	111
None/PMA	3	1.0	92
Benzo(a)pyrene	26	7.4	48
Petroleum			
Naphtha	2	1.0	111
LGO*	3	1.7	71
MGO	3	1.0	83
Residue	5	1.6	62
Crude*	5	1.4	71
Paraho Shale Oil			
Naphtha	0	0	-
LGO	0	0	-
MGO*	2	1.5	113
Residue*	7	3.1	62
Crude	9	1.9	59

* 29 Surviving mice in group.

TABLE 5.3.4

COMPARISON OF SALMONELLA AND INITIATION-PROMOTION TEST RESULTS

PARAHO SHALE OIL

	Salmonella Mutation Assay (with Activation)					Initiation-Promotion Assay		
Fraction	TA 1535	TA 1537	TA 1538	TA 98	TA 100	Number Mice With Tumors Lasting >30 Days	Total Tumors Lasting >30 Days	Number of Days to First Mouse With Tumor
Naphtha	-	-	-	-	-	0	0	-
Light Gas Oil	-	-	-	-	-	0	0	-
Mid-Gas Oil	-	0.05*[a] (8.1)+	0.20 (6.5)	0.20 (6.7)	0.40[b] (1.8)	2	3	113
Residue	-	0.4 (16.1)	0.80 (31.3)	0.40 (40.6)	0.40[c] (4.4)	7	22	62
Crude	-	0.07 (12.0)	0.55 (41.9)	0.70 (29.7)	0.50 (2.8)	9	17	59
Benzo(a)pyrene						26	193	48

- Not mutagenic (only refers to Salmonella data).

* Revertants per µg (average).

\+ The maximum number of revertants observed expressed as a multiple of the average solvent control reversion frequency.

a Without activation 0.01 (2.3).

b Without activation 0.06 (1.3).

c Without activation 0.03 (1.4).

Taken from Calkins, et al, 1981.

TABLE 5.3.5

Acute Lethality Test in Mice: Shale Oil and Its Derivatives

(Smith, Haschek and Witschi, 1980)

	LD_{50} (g/kg)			
	Oral		Intraperitoneal	
Substance	Male	Female	Male	Female
Crude Shale Oil	11.3	11.3	6.1 (4.5-8.2)[b]	4.3 (2.0-6.1)
Hydrotreated Shale Oil	> 16.0	> 16.0	> 16.0	> 16.0
Hydrotreated Residue	> 16.0	> 16.0	> 16.0	> 16.0
Jet Fuel JP-5	ND[b]	> 16.0	ND	8.0 (5.4-12.8)
Jet Fuel JP-8	ND	> 16.0	ND	6.4 (5.0-8.0)
Diesel Fuel Marine Product	ND	> 16.0	ND	> 16.0

a 95% confidence limits.

b ND = not done.

TABLE 5.3.6

NUMBER OF MACROPHAGE ROSETTES AS A FUNCTION OF TIME AFTER EXPOSURE TO RAW SHALE, SPENT SHALE, AND SILICA

Time after Exposure (days)	Number of Rosettes (raw shale)	(spent shale)	(silica)
4	5	35	-
7	20	25	3
14	9	51	-
21	8	7	-
28	29	5	-
35	17	30	8
42	26	--	1
49	3	7	-
60	9	--	-
90	1	--	-
Total	127	160	12

TABLE 5.3.7

The Cytoxicity of Crude and Hydrotreated Shale Oil to Primary Oocytes in Young Female Mice

(Timourian, et al, 1980)

Oil	Oocytes counted	No. Ovaries from Individual Mice Counted	% Survival
Corn (control)	173 ± 27.5	5	100 ± 15.8
Crude Shale	106 ± 2.9[a]	4	59 ± 1.6
Hydrotreated Shale	153 ± 16.9	4	88 ± 9.7

Each tested at LD_{50} for whole mouse.

[a] Significantly different from control at $p < 0.05$.

TABLE 5.3.8

RESPONSE OF SELENASTRUM CAPRICORNUTUM AND MICROCYSTIS AERUGINOSA TO WATER SOLUBLE FRACTIONS OF SHALE OIL AND PETROLEUM PRODUCTS[a]

(Giddings and Washington, 1981)

		S. capricornutum				*M. aeruginosa*			
Sample	WSF Concentration	0.1%	1%	10%	100%	0.1%	1%	10%	100%
Shale Oil									
Crude		-	94	21*	1*	-	70*	10*	1*
Hydrotreated		-	113	82*	2*	-	84	67*	1*
Hydrotreated residue		108	82*	24*	13*	94	101	84*	26*
JP-5		103	110	101	99	-	-	-	-
DFM		-	93	106	84*	-	-	-	-
Petroleum									
DFM		-	99	90	1*	-	-	-	-
No. 2 Diesel Fuel		95	97	91	39*	97	100	98	50*
JP-5		99	108	109	90	-	-	-	-
No. 6 Fuel Oil		96	112	106	90*	87	92	88	41*
No. 6 Fuel Oil		87	101	98	124	100	110	103	83*
No. 6 Fuel Oil		111	98	97	93	114	105	103	75*

[a] The values shown are photosynthesis expressed as a percentage of controls.

Asterisks (*) indicate significant photosythetic inhibition (P = 0.05). Dashes indicate tests not performed.

TABLE 5.3.9

Lethality of Water-Soluble Extracts of Selected Paraho Shale Oil Materials[a]

(Cowser, 1980)

Sample	pH	LC100
Crude Shale	6.9	9%
HDT-Shale Oil	6.9	100%
HDT-Shale Oil Residue	7.1	100%
Shale Oil Derived Diesel Fuel Marine	7.6	100%
Conv. Petro. Derived Diesel Fuel Marine	7.6	100%

[a] Special Notice. These samples are intended for generic and scoping research only at this time and are not intended to define or compare specific processes in the absence of process operating conditions and detailed sampling and storage histories.

TABLE 5.3.10

Reproduction Impairment of Medium-Soluble Extracts of Selected Paraho Shale Oil Materials

(Cowser, 1980)

Sample	Regression Equation	Correlation Coefficient	IGC50[a] (%)
Crude Shale Oil	$Y = 0.024X + 0.483$	-0.938	13.9 (5.8 - 33.2)
HDT-Shale Oil	$Y = 0.003X + 0.298$	-0.983	45.4 (13.1 - 152.5)
HDT-Shale Oil Residue	--	--	100% No Effect
Shale Oil Derived Diesel Fuel Marine	--	--	100% No Effect
Conv. Petro. Derived Diesel Fuel Marine	--	--	100% No Effect

[a] 95% confidence limits in parenthesis.

TABLE 5.3.11

SUMMARY OF BIOASSAY RESULTS FOR RAINBOW TROUT (RBT), FATHEAD MINNOWS (FHM), AND *DAPHNIA PULICARIA* (DP) EXPOSED TO PARAHO RETORT WATERS.[a]

(Bergman, 1980)

				Embryo-larval lowest concentrations causing effects			
Retort water	Species	24-hour static acute LC_{50}	96-hour flow-through acute LC_{50}	hatchability	survival	weight	length
Tbw[c] 75-76	RBT	---[b]	0.52		---		
	FHM	0.9	0.64		---		
	DP	2.85	3.00		---		
Tbw 77-78	RBT	---	0.068		---		
	FHM	< 0.05	0.071	0.0063	0.0063	0.0016	0.0016
	DP	0.079	0.147		---		

[a] All values expressed as volume percent.

[b] --- = test not performed.

[c] Tbw = tank bottom water

TABLE 5.3.12

SUMMARY OF RECOMMENDATIONS ON MAXIMUM ACCEPTABLE TOXICANT CONCENTRATIONS (MATC) AND ESTIMATED SAFE CONCENTRATIONS (ESC) FOR PARAHO RETORT WATERS.

(Bergman, 1980)

	Acute toxicity bioassays		Embryo-larval bioassay				Recommendations	
Retort water	Most sensitive species	LC_{50}	most sensitive species	measure(s)	threshold effects concentration	MATC	application factor	estimated safe concentration
Tbw[b] 75-76	RBT	0.52%	—	—	—	—	0.01[a]	0.005%
Tbw 77-78	RBT,FHM	0.07%	FHM	length,wt.	0.0016%	0.001%	0.01	0.001%

[a] Based on application factor for tank bottom water 77-78.

[b] Tbw = tank bottom water.

TABLE 5.3.13

SUMMARY OF RESULTS FROM THE ROOT ELONGATION BIOASSAY AND THE SEEDLING GROWTH STUDIES*

(Epler, et al, 1980)

Extract	Seed Type	Concentration (%)	Toxic Effects		Acetic Acid (meg/l)
			Root	Shoot	
Acetic Acid	radish	2	yes	---	
		1	yes	---	
		0.5	no	---	
	sorghum	2	yes	---	
		1	yes	---	
		0.5	no	---	
	wheat	2	yes	yes	
		1	yes	yes	
		0.5	yes	yes	
		0.1	no	yes	
	soybean	2	yes	yes	
		1	yes	yes	
		0.5	yes	yes	
		0.1	yes	no	
Raw Shale**	radish	4	no	---	2.74
	sorghum	4	yes	---	2.74
		2	no	---	1.37
	wheat	10	no	no	6.85
	soybean	10	no	no	6.85
Retorted Shale**	radish	2	no	---	2.0
	sorghum	2	yes	---	2.0
		1	yes	---	1.0
		0.5	no	---	0.5
	wheat	10	yes	no	10
	soybean	10	no	no	10

*Significant difference was calculated with standard t-test comparing results of treated plants with results of control.

**Possible acetic acid interference at a 10% concentration in long-term studies.

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PARAHO ENVIRONMENTAL DATA

Part VI Occupational Health and Safety

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PART VI

OCCUPATIONAL HEALTH AND SAFETY

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6.1 INTRODUCTION

6.1.1 Relationship with Environmental Information

This report, Part VI, Occupational Health and Safety, represents one section in the seven-part data compilation, Paraho Environmental Data. Detailed discussions of these data are not provided in the data compilation. Those discussions are provided in the original literature. The parts of this compilation are:

Part I	Process Characterization
Part II	Air Quality
Part III	Water Quality
Part IV	Ecosystem Effects and Land Reclamation
Part V	Biological Effects
Part VI	Occupational Health and Safety
Part VII	End Use Effects

Particular information is restricted to individual sections; for the most part, data are only compiled once. For example, details of the Paraho process, the air quality and water quality are found in Parts I-III (Heistand, Atwood and Richardson, 1980).

This report, Part VI, Occupational Health and Safety, contains information concerning the industrial hygiene and medical studies made at Anvil Points during Paraho research operations. Background data and associated information are compiled in other parts of the Paraho Environmental Data. Following the guidelines established for the earlier parts (Heistand, Atwood, Richardson, 1980), the information contained in this report is based, for the most part, on operations and materials produced during the 1977-1978 operations.

6.1.2 Scope of Occupational Health and Safety Studies

The scope of the occupational health and safety studies of the recent Paraho operations at Anvil Points was quite limited. No sampling was performed to evaluate compliance or worker exposure. These limitations resulted, for the most part, from limitations of the Paraho operations. Those operations represented early stages of short-term field research; in many cases the optimum occupational health and safety measures were not utilized. The sustained operations, directed towards the production of 100,000 barrels of shale oil, lasted less than two years. The total work force consisted of less than 100 workers; of these, nearly one-third represented a minimally exposed group consisting primarily of office workers, guards, administrative personnel, etc. Nevertheless, some occupational health studies were carried out.

Much of the data utilized in the occupational health and safety evaluations were obtained from other studies. For example, data that appear in Part II, Air Quality, of the Paraho Environmental Data (Heistand, Atwood, Richardson, 1980) have been used extensively in the occupational health and safety studies. There was little personal monitoring performed. Instead, the studies relied on the area samples and emission samples for information rather than actual worker exposure. The data compiled in this occupational health and safety report should be considered as a preliminary indication rather than the final assessment of an above-ground oil shale retorting facility. The potential effects of sustained, long-term exposure have not been evaluated.

This compilation does not contain the information obtained in the NIOSH study (Costello, 1978) concerning the health of oil shale workers. Although a few of the workers from Paraho's work force were asked to take part in that study, the NIOSH study centered on the health of workers associated with earlier oil shale projects. The NIOSH study examined long-term health effects associated with those operations. It does not contain any information dealing with the occupational health and safety aspects of the recent Paraho operations.

6.2 INDUSTRIAL HYGIENE

6.2.1 Introduction

During the Paraho research operations at Anvil Points, there were three studies concerning industrial hygiene (Holland, 1976) (Volkwein and Flink, 1977) (Rudnick, Garcia, Voelz, and Schulte, 1980). Both earlier studies were made before the 1977-1978 operations and contain information collected before the crusher was updated and ventilation systems were installed in the plant. The latter study was carried out during the 1977-1978 operations, but relied heavily on air quality and emission data obtained earlier during that two-year operating period. All studies indicated that, for the most part, personal exposures were not in excess of industrial hygiene standards. Area samples, however, indicated that the potential for significant worker exposure to dusts, gases, and noise do exist. It is not possible to predict on the basis of these data what exposures will exist in an adequately designed and controlled commercial operation.

The data compiled in this industrial hygiene section are divided into three subsections: 6.2.2, Dust; 6.2.3, Gases and Vapors; 6.2.4, Noise. Whenever possible, the data compiled in these subsections are compared with data compiled in Part II, Air Quality.

6.2.2 Dust

Because an oil shale facility is essentially a large-scale materials handling plant - from mining to crushing to screening and storage to retorting to shale disposal - dust presents the most serious industrial hygiene problem. Total and respirable dust have been measured in the mine area (see Table 6.2.1), in the crushing area (see Table 6.2.2), in the retort are (see Table 6.2.3) and in the shale disposal area (see Table 6.2.4). Samples were not taken concurrently and values obtained at a specific location would show wide variations with time. Total and respirable dust values are both time and site specific and therefore cannot be compared directly. Many of these data represent samples obtained near fugitive emission sources (such as the bin area,

Table 6.2.2; and top seal, Table 6.2.3) in locations where none of the work force spend time during normal operations. For the most part, both the maximum and average concentrations listed in Tables 6.2.1-6.2.4 represent higher values than those obtained by other researchers and listed in Part II, Air Quality. The values observed for industrial hygiene sampling are higher than area samples because the industrial hygiene samples were often obtained in close proximity to the sources of contamination.

Particle size information was obtained on dusts collected at various operations at the Anvil Points facility. These data, obtained by cascade impactors, are presented in Table 6.2.5. Mass median aerodynamic diameters (MMAD), ranging from 2.2 um to 7.3 um, would indicate that a large portion of these dusts would be classified as respirable. Particle size data, compiled in Part II, Air Quality, and obtained from several investigators, show more scatter, ranging from less than 1 um to greater than 20 um.

The dusts produced during oil shale operations pose several problems in the area of industrial hygiene. First, the levels are high enough to cause simply a nuisance and general discomfort to the worker. Secondly, the dusts contain alkaline carbonate minerals and free silica which can cause serious health problems. Finally, the dusts contain organics. Benzene extractable portions of dust ranged from 0.2 to 2.6 wt% (see Table 6.2.6). Although this benzene extractable material can contain condensed polynuclear compounds, biological availability from the solid material is quite limited. Inhalation tests of raw and retorted shale have not indicated induction of cancers of the lung in test animals. Handling the shale does not appear to represent a significant skin risk. Data compiled in Part I, Process Characterization, show that mean concentration of benzo(a)pyrene, a commonly measured polynuclear carcinogen, is only 0.002 ppm in Paraho direct mode retorted shale.

These data, although not indicating any serious industrial hygiene problems associated with the small-scale Paraho research operation do indicate the need for future studies to adequately assess the requirements for future control measures and worker protection when scaling up to commercial-sized operations.

6.2.3 Gases and Vapors

Fugitive emissions measured at sources do exceed standard levels. However, various measurements by several investigators have not followed a standard industrial hygiene plan, so it is not possible to relate these values to worker exposure. Commercial scale operations will require well-designed equipment and operation and a well-planned industrial hygiene program to avoid potential health and safety problems.

Concentrations of gases and vapors were measured in the mine area (Garcia and Schulte, 1979)(see Table 6.2.7). These data, compiled in Part II, Air Quality, similarly, were not obtained in a pattern that would be representative of worker exposure. They are not based on 8-hour workday time weighted averages. These data show: carbon monoxide, less than 20 ppm; total hydrocarbons, 0-16 ppm; nitrogen oxides, below detection limits; ammonia, cyanide formaldehyde, sulfur dioxide, and hydrogen sulfide only traces. Oxygen levels were normal (20.8%). Immediately after blasting, the concentrations of most gases increased: carbon monoxide rose to 100 ppm; nitrogen oxides increased to 20 ppm; total hydrocarbons to 120 ppm. These data do not show any serious occupational exposure. These were confirmed by nitrogen oxide dosimeters worn for 2-1/2 hours by miners during drilling operations; concentrations were 1.0 ppm or less.

Gas and vapor concentrations have been measured at various locations in the retort area (Rudnick, Garcia, Voelz, and Schulte, 1980). These data are presented in Table 6.2.8. Most of these data represent fugitive emissions associated with the equipment used with the earlier Anvil Points research operations and are not indicative of planned commercial operations. Many were obtained in locations where none of the work force spent time during normal operations. Some of the concentrations (ammonia in thermal oxidizer effluent, Table 6.2.8) exceed the concentrations normally found in recycle gas.

During the earlier industrial hygiene survey (Holland, 1976), various gas and particulate concentrations were measured in specific work areas. These data are presented in Table 6.2.9. Also presented in Table 6.2.9 are the analytical procedure, the 8-hour TWA and the TLV. The high levels (exceeding the TLV) of dust and lead found in one welding location has been corrected by improved ventilation. None of the other gaseous concentrations exceed the TLV standards.

6.2.4 Noise

Noise levels, though representing a significant portion of any industrial hygiene program, were not measured during the Anvil Points research operations. High noise levels in the mine were mitigated by personnel working for the most part in closed cabs. Ear muffs were provided to miners and workers at the crushing operations. Both operations present high noise levels. In a commercial operation, workers exposure to noise could be controlled by equipment design, the use of baffles, and protective equipment for the workers. A quantitative assessment of noise levels will be needed for a well-designed industrial hygiene program.

TABLE 6.2.1

Dust Concentrations - Mine Area

	Concentration (mg/m^3)							
	Total Dust				Resp. Dust			
Operation	No.	Max.	Avg.	Other	No.	Max.	Avg.	Other
Drilling	7	31.9	14.7		3	14.6	9.8	2.1
Loading	2	7.0	6.8	5.0 3.7		----	----	3.0,1.0
Mucking	1	----	14.1			----	----	0.6
Rock Bolting	1	----	12.6			----	----	0.6
General Mine Area	2	14.6	9.2		2	0.3	0.1	
Mine Entrance (before blast)	1	----	1.9		1	----	3.1	
Mine Entrance (after blast)	1	----	9.7		1	----	3.4	0.8
Travel on Mine Road	1	----	12.6			----	----	
Drilling (Personal Sampler) 4 Hrs. Exp.	2	11.2	8.7		2	3.2	2.6	

Note: Max., avg. from (Rudnick, et al, 1980); other from (Holland, 1976); and (Volkwein and Flink, 1977).

Mass median aerodynamic diameter (MMAD) 2.2 um.

Geometric standard deviation (g) 3.5.

TABLE 6.2.2

Dust Concentrations - Crushing Area

	Concentration (mg/m^3)					
	Total Dust			Resp. Dust		
Operation	No.	Max.	Avg.	No.	Max.	Avg.
At Primary Crusher	2	33.6	18.0	2	6.5	4.2
At Secondary Crusher	1	----	4.7	2	20.0	10.4
At Tertiary Crusher	2	47.2	28.1	2	11.0	8.3
Crusher - Retort Area	1	----	0.8		----	----
Crusher - End Conveyor	1	----	45.2	1	----	5.2
Bin Area - During Screening	1	----	1180.0		----	----

Note: data from (Rudnick et al, 1980).

Particle size of dust:

	MMAD	σg	Total Dust Conc.
Primary Crusher	3-9 µm	3-4	11 mg/m^3
Secondary Crusher	6-8	2-4	22
Tertiary Crusher	3	---	36

TABLE 6.2.3

Dust Concentrations - Retort Area

Operation	No. of Samples	Concentration (mg/m^3) Total Dust Max.	Total Dust Avg.	Resp. Dust Max.	Resp. Dust Avg.
Top Seal	7	90.8	41.5	15.6	8.7
Bottom Seal	6	54.0	17.3	4.5	1.8
Retort, Ground Level	2	12.0	8.0	4.4	2.5
Middle Distributor	4	28.6	14.6	4.2	1.5
Bottom Distributor	1	----	59.2	----	----
Bottom Conveyor	1	----	7.4	----	ND*
Outside Landings	4	2.7	1.3	1.8	0.8
At Thermal Oxidizer	1	----	1.1	----	0.9
Retort Operator (Pers.)	1	----	1.7	----	0.4
Pilot Plant Retort, 1st Level (Pers.)	1	----	10.5	----	1.2
Pilot Plant Middle Distrib. (Pers.)	1	----	11.7	----	1.1

* No detectable dust in the single sample collected.

Note: Data from (Rudnick et al, 1980).

TABLE 6.2.4

Dust Concentrations - Shale Disposal Area

		Concentration (mg/m^3)			
	No. of	Total Dust		Resp. Dust	
Operation	Samples	Max.	Avg.	Max.	Avg.
At Retorted Shale Pile	6	18.6	7.3	7.2	3.2
Over Retorted Shale Conveyor	3	640*	10.0	16.7	14.1

* Sample was taken at ground level of retorted shale pile near the location where the retorted shale falls from the conveyor to the piles. This area has a heavy, localized concentration of dust. This sample is not included in the "average".

Note: Data from (Rudnick et al, 1980).

TABLE 6.2.5

Particle Size Data

Location	σg	MMAD, μm
Mine	3.5	2.2
Primary Crusher	4.0	3.2
Inside Bins	4.4	4.2
Retort, Top Seal	3.6	3.9
Retort, Bottom Seal	2.7	7.3
Retorted Shale Area	2.2	6.2

MMAD - mass median aerodynamic diameter
σg - geometric standard deviation

Note: Data from (Rudnick et al, 1980).

TABLE 6.2.6

Benzene Extractable Data

Sample Source	Per Cent Extractable by Benzene
Air Sample, Outside Retort Top Seal	2.6
Air Sample, at Auger Conveyor, Retorted Shale Pile	0.4
Bulk Sample, Retort Baghouse Fines	0.3
Settled Dust, Near Bottom Retort Seal	0.8
Settled Dust, Product Shale Conveyor, Top of Retort	1.6
Raw Product Shale Sample	1.4
Retorted Shale Sample	0.2

Note: Data from (Rudnick et al, 1980).

TABLE 6.2.7

Gases and Vapors - Mine Area

Constituent	Normal Operations	After Blast
Carbon Monoxide, ppm	< 20	100
Total Hydrocarbons, ppm	0-16	120
Nitrogen Oxides, ppm	ND < 1	20
Ammonia, ppm	Trace	-
Cyanide, ppm	Trace	-
Formaldehyde, ppm	Trace	-
Sulfur Dioxide, ppm	Trace	-
Hydrogen Sulfide	Trace	-
Oxygen, vol%	20.8	20.8

Note: Data from (Garcia and Schulte, 1979) and (Holland, 1976).

TABLE 6.2.8

Gas and Vapor Concentrations - Retort Area

		Contaminant Concentrations (ppm)									
Location	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.	----	----	----

a Single sample, result highly unlikely, unknown interferences, maybe amines.

b None detectable.

Note: Data from (Rudnick et al, 1980).

TABLE 6.2.9

Gases, Vapors and Particulates - General

Area	Constituent	Procedure	Conc.	8-hr TWA	TLV
Mine	NO_2	Solid Absorber	0.3 ppm	0.3 ppm	C5 ppm
	NO	Solid Absorber	1.6 ppm	1.6 ppm	25 ppm
	Formaldehyde	Solid Absorber	< 2 ppm	< 2 ppm	C2 ppm
		Solid Absorber	< 2 ppm	< 2 ppm	C2 ppm
	NO_2	Det. Tube	0.4 ppm	-	C5 ppm
	SO_2	Det. Tube	0.4 ppm	-	5 ppm
	CO	Det. Tube	< 5 ppm	-	50 ppm
	NO_2 + NO	Det. Tube	5 ppm	-	-
	H_2SO_4	-	0.27 mg/m^3	0.27 mg/m^3	1 mg/m^3
Control Room	Alkanes (<C8)	Charcoal Tube	0.26 ppm	0.26 ppm	~ 500 ppm
	Aromatics(<C12)	Carcoal Tube	0.30 ppm	0.30 ppm	~ 100 ppm
Weld Shop	Fe_2O_3	PVC Filter	10 mg/m^3	6.7 mg/m^3	10 mg/m^3
	Cd	PVC Filter	<0.004 mg/m^3	<0.003 mg/m^3	C0.1 mg/m^3
	Mn	PVC Filter	0.6 mg/m^3	0.4 mg/m^3	C5 mg/m^3
	CrO_3	PVC Filter	<0.02 mg/m^3	<0.01 mg/m^3	0.1 mg/m^3
	Zn	PVC Filter	0.04 mg/m^3	0.03 mg/m^3	5 mg/m^3
	Pb	PVC Filter	0.8 mg/m^3	0.5 mg/m^3	0.15 mg/m^3
	Ni	PVC Filter	0.02 mg/m^3	0.01 mg/m^3	1 mg/m^3
Laboratory Sampling	CO	Det. Tube	< 1 ppm	-	50 ppm
	CO_2	Det. Tube	0.04%	-	0.5%
	NH_3	Det. Tube	2 ppm	-	25 ppm

Note: Data from (Holland, 1976)

6.3 SAFETY

There were no detailed safety studies made during the Paraho research operations at Anvil Points. Routine inspections were made at the Anvil Points facility by Colorado Bureau of Mines and/or MSHA personnel. As part of the occupational history, during the medical examinations (Rudnick et al, 1980), employees were asked about any lost-time injuries they incurred during the previous 12 months. Among the 87 employees evaluated, there were 7 lost-time accidents resulting from accidental physical trauma. Although the operations and equipment are not representative of future commercial operations, these findings indicate the importance of occupational traumatic injury as a safety factor in the oil shale industry.

6.4 MEDICAL

Although the Paraho operations did not constitute a large work force that would provide a statistically reliable sample, a comprehensive medical evaluation of Paraho employees was made during August, 1978 (Rudnick et al, 1979, 1980). These evaluations concisted of:

- Medical History
- Occupational History
- Accident History
- Physical Examination
- Laboratory and X-ray
- Special Studies
- Epidemiologic Record

Of the 92 employees, 95% volunteered to participate in the study. In order to analyze the results, the work force was divided into three groups: Group I, highest exposed (mining, crushing, retorting, maintenance); Group II, less exposed (remaining plant employees); Group III, minimally exposed (administrative and office employees).

A summary of the results are compiled in Table 6.4.1. Most skin problems were associated with the group having lowest exposure (Group III) which probably reflects the 11-12 year older mean age of this group. No skin cancer was detected. Pulmonary problems existed in all three groups and does not appear to be related to shale or shale oil exposure. Overall, the employees were found to be in good health with no apparent incidence of chronic or acute disease attributable to exposure to oil shale operations. These findings do not confirm the earlier oil shale occupational health study which implicate skin and pulmonary disorders as areas of primary concern. Nor do the findings of the recent evaluation (Rudnick et al, 1979, 1980) take into account diseases of long latent periods.

6.4.1 Pulmonary Function

Pulmonary problems that were encountered appeared to be largely related to cigarette smoking rather than exposure to shale or shale oil. Chest x-rays indicated some members in each group with pulmonary problems associated with smoking or lengthy mining careers (uranium, molybdenum, coal). Sputum cytology and pulmonary function tests also showed positive correlation with smoking but not with oil shale exposure.

6.4.2 Body Chemistry

Routine laboratory tests were run on both urine and blood samples. A total of 25 tests were performed on the blood samples. Results from these tests did not provide any significant correlation with exposure to shale or shale oil.

6.4.3 Skin Disorders

Frequency of skin disorders was greater in Group III than for the other Paraho employees. The five disorders (see Table 6.4.1) found among the employees in Groups I and II are not attributable to oil shale exposure. All skin disorders were benign. It is worth noting that many of the Paraho employees lived in the region (5,000 ft. and higher elevation) for many years where they are subjected to higher levels of natural radiation caused by reduced shielding effect of the atmosphere.

6.4.4 Special Tests

The LASL medical personnel who conducted the medical examinations used the opportunity to evaluate some special medical tests. These special tests, aryl hydrocarbon hydroxylase (AHH) and the Ames assay may have some usefulness to detect effects of hydrocarbons.

The AHH test was measured in cultured lymphocytes from blood samples of 83 employees. The AHH inducibility, expressed as a ratio between AHH activity induced cells/AHH activity noninduced cells, is presented in Tables 6.4.2 and 6.4.3 and compared with shale exposure (Groups I - III) and amount of cigarette smoking. The results are striking - there is no correlation with shale exposure; there is a pronounced correlation with smoking.

A total of 288 Ames tests of urine samples were run on 24 workers using morning and evening samples over a 24-hour period. Each urine specimen was incubated in the Salmonella typhimurium strain TA98, TA100, TA1535, and TA1537 containing medium, with and without S_9, metabolic activation with controls. Results were negative from 21 individuals. Three individuals, all users of tobacco, yielded positive or unexpected results. It is not known why these three individuals yielded positive results. Based upon these limited data, Paraho employees do not appear to be excreting unexpected amounts of mutagenic material in their urine.

TABLE 6.4.1

Summary of Medical Results

	Group I	Group II	Group III
Number	15	45	27
Mean Age (years)	38	37	49
Skin Problems (all types)	1	4	6
Skin Cancer (at time of examination)	0	0	0
Skin Cancer (past)	0	0	2
Pulmonary Problems (all types)	3	4	3
Opacities noted on chest X-ray	1	5	4

Note: Data from (Rudnick, et al, 1980).

TABLE 6.4.2

AHH Inducibility vs Shale Exposure

Group	N	AHH Inducibility Mean ± S.D.
I	14	10.7 ± 1.3
II	43	12.6 ± 1.0
III	26	14.7 + 1.8
Total	83	AV = 12.9 ± 0.8

Note: Data from (Rudnick et al, 1980).

TABLE 6.4.3

AHH Inducibility vs Cigarette Smoking

Group	N	AHH Inducibility Mean ± S.E.
None	49	11.4 ± 0.9
< 1 pack/day	15	13.5 ± 1.8
1 to < 2 packs/day	11	14.9 ± 2.4
≥ 2 packs/day	7	18.9 ± 3.8
Total	82	Av = 12.9 ± 0.8

Note: Data from (Rudnick et al, 1980).

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PARAHO ENVIRONMENTAL DATA

Part VII

End Use

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7.1 INTRODUCTION

7.1.1 Background

The Paraho operations, carried out at Anvil Points Oil Shale Research Facility near Rifle, Colorado from 1974 through 1978, produced nearly 110,000 barrels of crude shale oil. This oil produced during the research operations of retorting technology was investigated for several end uses. These included direct combustion as boiler fuel, use as a petrochemical feedstock, and as a refining feedstock. More than 100,000 barrels of crude shale oil was shipped to refineries for processing into various military fuels and for use as a normal refinery feedstock. These military fuels, produced from Paraho shale oil, have been subjected to detailed characterization testing, performance testing, and biological testing.

This section of the Paraho Environmental Data, Part VII, End Use, discusses the end uses of crude shale oil and the possible health effects associated with the end use. The following sections of this report deal with a discussion of the following end uses that have been studied. In Chapter 7.2, the end uses of crude shale oil in direct combustion as boiler feedstock, as a petrochemical feedstock, and in refining to produce distillate fuels are discussed. In Chapter 7.3, material properties, industrial hygiene, and health effects of refinery feedstocks, intermediate products, and final products has been reported in detail and compiled in a small number of symposia proceedings (see 7.4) or other data reports. An annotated appendix has been included (see 7.4) to detail the contents of those proceedings and reports.

7.1.2 Paraho Environmental Data

This report on end use represents the seventh and final part of the compiled Paraho Environmental Data. The other parts of this compilation are:

Part I	Process Characterization
Part II	Air Quality
Part III	Water Quality

Part IV Land Reclamation and Revegetation
Part V Biological Effects
Part VI Occupational Health and Safety

Part I, Process Characterization, discusses the chemical characterization of the process streams found in the Paraho retorting process used at Anvil Points. These characterizations were made to assess probable impacts these streams could impart on environmental and health aspects by virtue of normal process operations, fugitive emissions, and accidental spills. Much effort has been spent on the quality assurance of these process data by the calculation of material balances for many species. A discussion of the Paraho retorting technology used at Anvil Points is also included in this section.

Part II, Air Quality, discusses the particulate and gaseous emissions that were found in the various steps in the operations carried out at Anvil Points. These steps included: mining, hauling and crushing, retorting, and shale disposal.

Part III, Water Quality, discusses the effects of the Paraho Anvil Points operations on water quality. The chemical characterization of water produced by the process, groundwater and surface water are discussed in this part.

Parts I, II, and III were published as a single volume in May, 1980 (Heistand, Atwood, Richardson, 1980).

Part IV, Land Reclamation and Revegetation, compiles the data obtained in those areas during the Paraho operations at Anvil Points. For the most part, this section deals with the effects of retorted shale disposal on microbial and plant growth. There were no studies conducted during the Anvil Points operation concerning vertebrates or land disturbance other than retorted shale disposal.

Part V, Biological Effects, compiles the toxicity test data obtained on the products and by-products produced from the Paraho retorting operations carried out at Anvil Points. Also included in Part V are the results of biological testing of the end products - particularly those obtained from refining operations,

Part VI, Occupational Health and Safety, compiles the available industrial hygiene data obtained during the Paraho operation. For the most part, fugitive emissions and the levels of various gaseous and particulate contaminants are compiled and discussed in Part II, Air Quality. Any industrial hygiene studies dealing with end use - the production and use of products obtained from Paraho retorting operations - will be discussed in this volume, Part VII, End Use.

7.2 END USES

7.2.1 Direct Combustion

The use of crude shale oil as fuel in direct combustion to produce steam and electrical power is an attractive alternative for end uses. Although this alternative would be considered anytime the economics would warrent it, it may be most useful during the early development of a commercial oil shale industry. Since many existing refineries would require extensive retro-fitting in order to be able to process crude shale oil, the end use of shale oil in direct combustion would present an alternative use for shale oil produced from the pioneer plants and would free the oil now used in combustion for other uses.

The main drawback to the direct combustion of crude shale oil is the same as that facing direct refining - the high nitrogen content. In the case of direct combustion, the 2 wt% total nitrogen would lead to unacceptable emissions of nitrogen oxides in the stack effluents.

Combustion studies were carried out by Southern California Edison at their Highgrove Generating Station (CA) using Paraho crude shale oil (Jones and Mansour, 1978, see 7.4.2). Using blends containing 25 wt% crude shale oil and specially designed burners, it was possible to meet the stringent NO_x emission standards of southern California with no additional controls.

7.2.2 Petrochemical Feedstocks

Although extensive characterization studies of crude shale oil have not been made, preliminary studies indicate that it can be used as a feedstock to produce petrochemicals. This end use, like direct combustion, would free conventional crude oil and natural gas, currently used as petrochemical feedstocks, for other end uses. The higher concentrations of hetero-atoms, such as nitrogen, which can cause problems with direct combustion and direct refining, could be the source of unique petrochemical products. Many additional, detailed studies are needed to more fully exploit this end use of crude shale oil.

The available information concerning the end uses of Paraho crude shale oil as a chemical feedstock is based upon research carried out at the du Pont research laboratories at Wilmington, DE, and reported at the AIChE seminar "Feedstock Alternative I - New Technologies for the Production of Chemical Feedstocks from Unconventional Resources" (Glidden and King, 1980, see 7.4.4). This study focused upon the preparation of important unsaturates - ethylene, propylene, and benzene - from crude and hydrotreated shale oil.

7.2.3 Refinery Feedstocks

The use of crude shale oil as a refinery feedstock, replacing the main use of the dwindling world supply of conventional crude oil, represents the most attractive end use. This use, the production of liquid fuels, represents the main driving force behind the development of shale oil production. Nearly all of the crude shale oil produced at Anvil Points using the Paraho retorting technology was used in studies as refinery feedstocks. In addition to several smaller (10-100 barrel) refinery studies, there were two major refinery runs - one at the refinery at Fruita, Colorado (10,000 barrel) and one at the refinery at Toledo, Ohio (100,000 barrel). The refining studies will be presented separately under the headings: 10,000 Barrel Refinery Run, 100,000 Barrel Refinery Run, and Miscellaneous Refining Studies.

Crude shale oil has several characteristics which can cause problems in refining operations. Some of these characteristics are:

1. High nitrogen and sulfur contents
2. Low hydrogen/carbon ratios
3. Low yields of low boiling materials
4. Moderate arsenic and iron contents
5. Suspended ash and water (BS&W).

However, by the proper selection of refining operations and the use of proper pre-refining procedures, all these problems can be eliminated.

10,000 Barrel Refinery Run. Crude shale oil, produced during the early Paraho operations under the privately-funded Paraho Oil Shale Demonstration, was provided to the U. S. Navy for refining at the small Gary-Western refinery located at Fruita, Colorado. Crude shale oil was shipped by truck from Anvil Points to the Fruita refinery - a distance of about 80 miles. Details of the refinery run are described in the final, 148-page report "Production and Refining of 10,000 Bbl. Paraho Crude Shale Oil into Military Fuels" (DEI, 1977, see 7.4.3).

A total of about 9,600 barrels of Paraho crude shale oil were received at the Gary-Western refinery and stored in heated tanks. The untreated shale oil was fed into a guard bed to remove organic iron and arsenic as well as traces of ash and solids and then into a coker/distillation unit to produce naphtha (see Figure 7.2.1). Not shown in this simplified line diagram are the various recycle loops. The products produced in this run are listed in Table 7.2.1. The naphtha was passed through a hydrotreater and a catalytic reformer to produce motor gasoline; hydrotreating, alone, was used to produce JP-4. The kerosene fraction was hydrotreated to produce JP-5 and Jet-A. Shale diesel was acid treated to produce an improved quality diesel oil. No upgrading was required to produce fuel oil. These upgrading operations were carried out sequentially in this refinery run.

The results from this early refinery run can be summarized as follows:

1. Yields of eight products met the requirements of the contract.
2. Due to the lack of adequate hydrotreating, high severity coking was required to maximize yields of usable fuels.
3. All fuels met initial specifications.
4. Again due to the lack of hydrotreating, many of the fuels did not meet thermal stability requirements.
5. No unusual problems were noted during the refinery run. A probe in the light gas oil tray indicated that corrosion rates were slightly higher than normal. There was no measurable loss in catalyst activity during the run.

In order to process crude shale oil more efficiently, the following recommendations were made:

1. Install new facilities (steam stripper, salt drier, clay treater) to improve quality and yields of jet fuels.
2. Install hydrogen plant and hydrotreater to improve product stability.
3. Improve pollution control devices (sulfur plant, MEA plant) and offsites (rail car loading facilities, tankage, boilers).

100,000 Barrel Refinery Run. Based upon the success of the earlier 10,000 barrel refinery run, the Office of Naval Research and the Department of Energy, through a series of contracts, requested Paraho to produce, store, ship and refine 100,000 barrels of crude shale oil. The production took place at Anvil Points during 1977-1978. It was this production run that provided the basis of the environmental data compiled in the first three parts of this Paraho Environmental Data report.

The crude oil was stored in tankage at Anvil Points including eight 10,000 barrel tanks erected during 1976-1977 for this purpose. Nearly 90,000 barrels of shale oil was shipped in jumbo tank cars to the Standard Oil Company of Ohio (SOHIO) refinery located at Toledo, Ohio.

The results of this refinery run were reported in the formal final report and in technical presentations included in the proceedings from several symposia (see 7.4.3).

Based upon the information obtained during the earlier 10,000 barrel refinery run and the research pilot run performed at SOHIO's Warrensville (Ohio) laboratory, a catalytic hydrocracking process was used in the 100,000 barrel refinery run. A simplified block flow diagram is shown in Figure 7.2.2. A more detailed process fow diagram is shown in Figure 7.2.3. The success of this larger operation was due primarily to hydrotreating which lowered the heteroatoms (S,N,O) to about 5% of the concentration found in the crude shale oil. Heavy metals (As,Ni,Fe,V) were also reduced to less than 1% of the level found in the crude shale oil. More details concerning the composition will be presented in Section 7.3.1, Characteristics. The military fuels produced at the Toledo refinery are listed in Table 7.2.2. All products met the military specifications normally required for fuels.

Conclusions drawn from the refinery run include:

1. Proven technology exists to refine crude shale oil into military quality transportation fuels.
2. The finished products produced from shale oil are compatible with and similar to products produced from conventional crude oil.
3. Supplemental research tests show that high severity hydrotreating could eliminate the need for acid treating, thus improving yields and reducing waste sludge. More severe hydrotreating also improves jet fuel stability.

Miscellaneous Refining Studies. Because of the large number of refining processes available to process crude shale oil into distillate fuels and because of the many energy companies interested in producing these fuels from shale oil, there have been many small-scale refining studies. Results from many of these have not been published in the technical literature nor presented at technical symposia. Reports of three miscellaneous refining studies will be presented in this section. These are the pilot runs performed before the previously discussed 10,000 barrel and 100,000 barrel refinery runs. The pilot runs established operating conditions for the 10,000 and 100,000 barrel refinery runs and researched various hydrotreating schemes.

Pilot refining studies were carried out at SOHIO's research laboratories at Warrensville, Ohio, prior to the 10,000 barrel and 100,000 barrel large-scale refinery runs. These pilot research studies examined the properties of the crude shale oil, selected a refining scheme, established operating conditions and estimated the quantities and properties of the products produced. The properties of the crude shale oil will be presented in detail in Section 7.3.1, Characterization. The refining schemes have been discussed (see Figs. 7.2.1-3). For the most part, the operating conditions, yields, and product quality estimated in the pilot runs were met in the refinery runs. A comparison of product composition is presented in Table 7.2.3. A limited comparison of product quality along with the military specifications is presented in Table 7.2.4. These data show that the pilot study did predict the properties of refinery products and that the refinery products did meet military specifications. Acid treating is an effective means of reducing nitrogen in jet fuel (JP-5) and diesel fuel marine (DFM); nearly 100% of the nitrogen was removed from the raw JP-5, 99% of the nitrogen was removed from raw DFM. A more complete listing of these properties can be found in the original papers (Robinson 1979, Cawein 1980, and Winward and Burdett, 1979, see 7.4.3 and 7.4.5).

Research studies involving the use of Chevron hydrotreating on Paraho shale oil indicates that hydrocracking can remove essentially all the sulfur, nitrogen, oxygen and heavy metals (Sullivan and Strangeland, 1978, see 7.4.3). The effect of sulfur and nitrogen removal using a Chevron proprietary catalyst at hydrogen pressure at 1850 psi at various liquid hourly space velocities (LHSV) are illustrated in Table 7.2.5. Three cases were studied in the Sullivan and Strangeland study (see Figs 7.2.4-6).

> Case 1, shown in Figure 7.2.4, is a refinery in which the whole shale oil is hydrotreated and then distilled. The naphtha is reformed, the middle distillate is further hydrotreated, and a vacuum gas oil fraction is hydrocracked. This refinery scheme offers the most flexibility and is the preferred scheme, if jet fuel is an important product.
>
> Case 2, shown in Figure 7.2.5, also uses whole oil hydrotreating as the first catalytic step. This is followed by fluid catalytic cracking as the major conversion process. Again, the naphtha from the first-stage hydrotreater is catalytically reformed; and the middle distillate is further hydrotreated. This processing route is probably the choice for high volumes of high octane motor gasoline as a major product.
>
> Case 3, shown in Figure 7.2.6, involves delayed coking followed by hydrotreating. This refinery is the least costly but the least energy efficient in the production of transportation fuels. It is particularly attractive if the production of diesel fuel is to be maximized.

These studies, representing preliminary feasibility studies, show that hydrotreated shale oil is an ideal refining feedstock. The hydrocracked shale oil contains no residuum, no nitrogen or sulfur, and no heavy metals. It is essentially a middle distillate. Additional information concerning process conditions, product quality, comparisons with other conversion processes can be found in the original paper (Sullivan and Strangeland 1978, see 7.4.3).

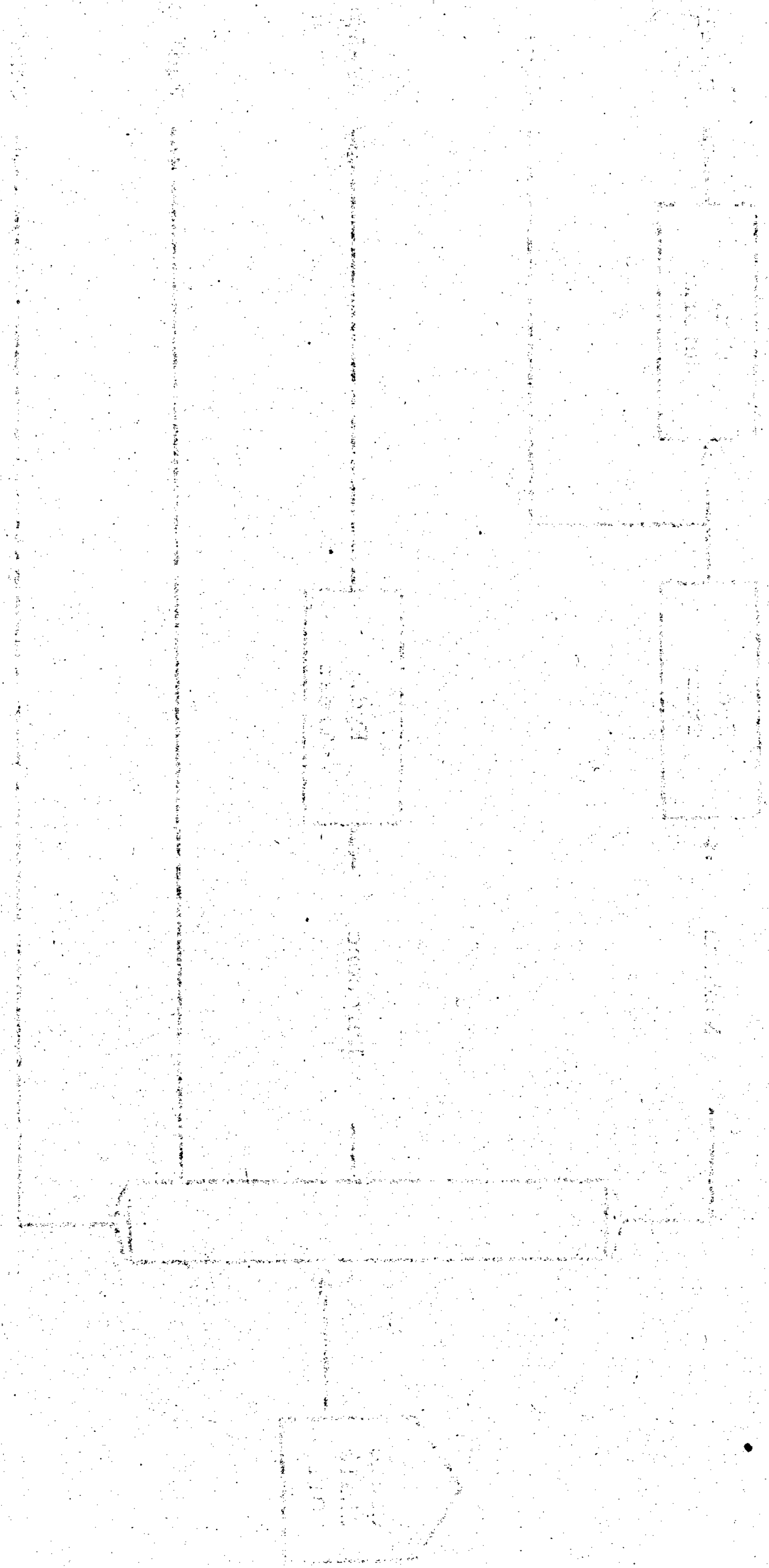


FIGURE 7.2.1

BLOCK FLOW DIAGRAM

10,000 BARREL REFINERY RUN

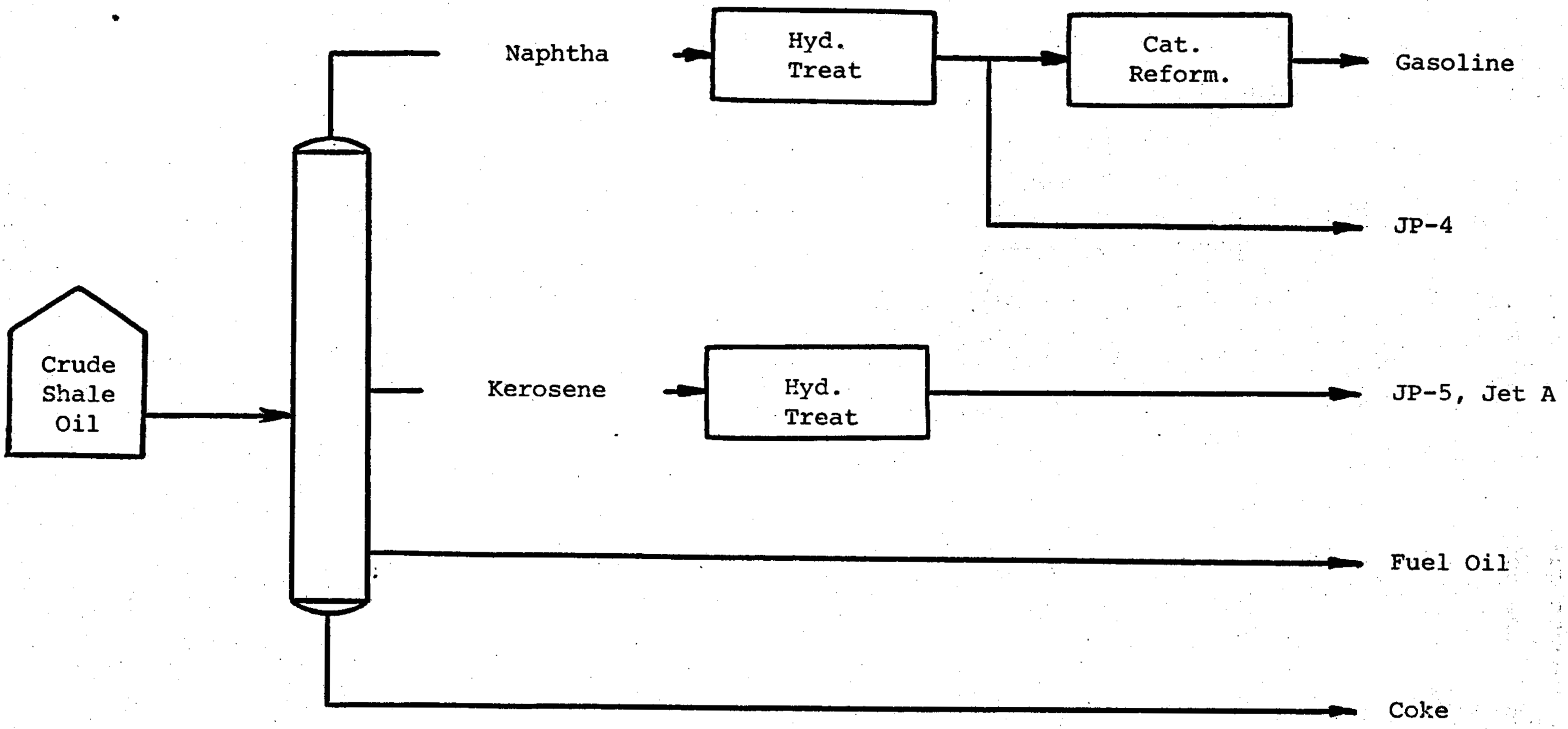


FIGURE 7.2.2

BLOCK FLOW DIAGRAM - TOLEDO REFINERY

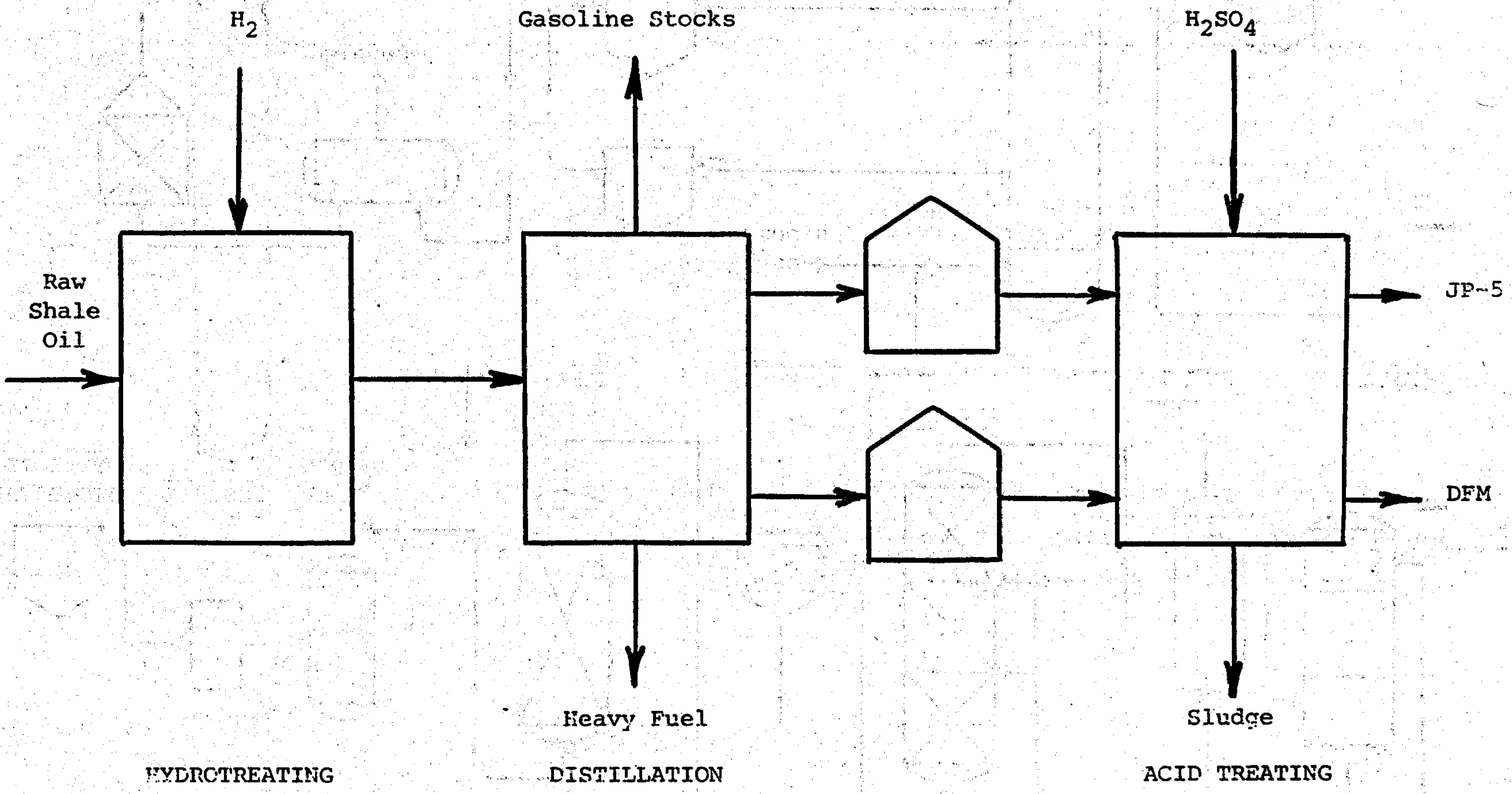


FIGURE 7.2.3
100,000 BARREL RUN
PROCESS FLOW

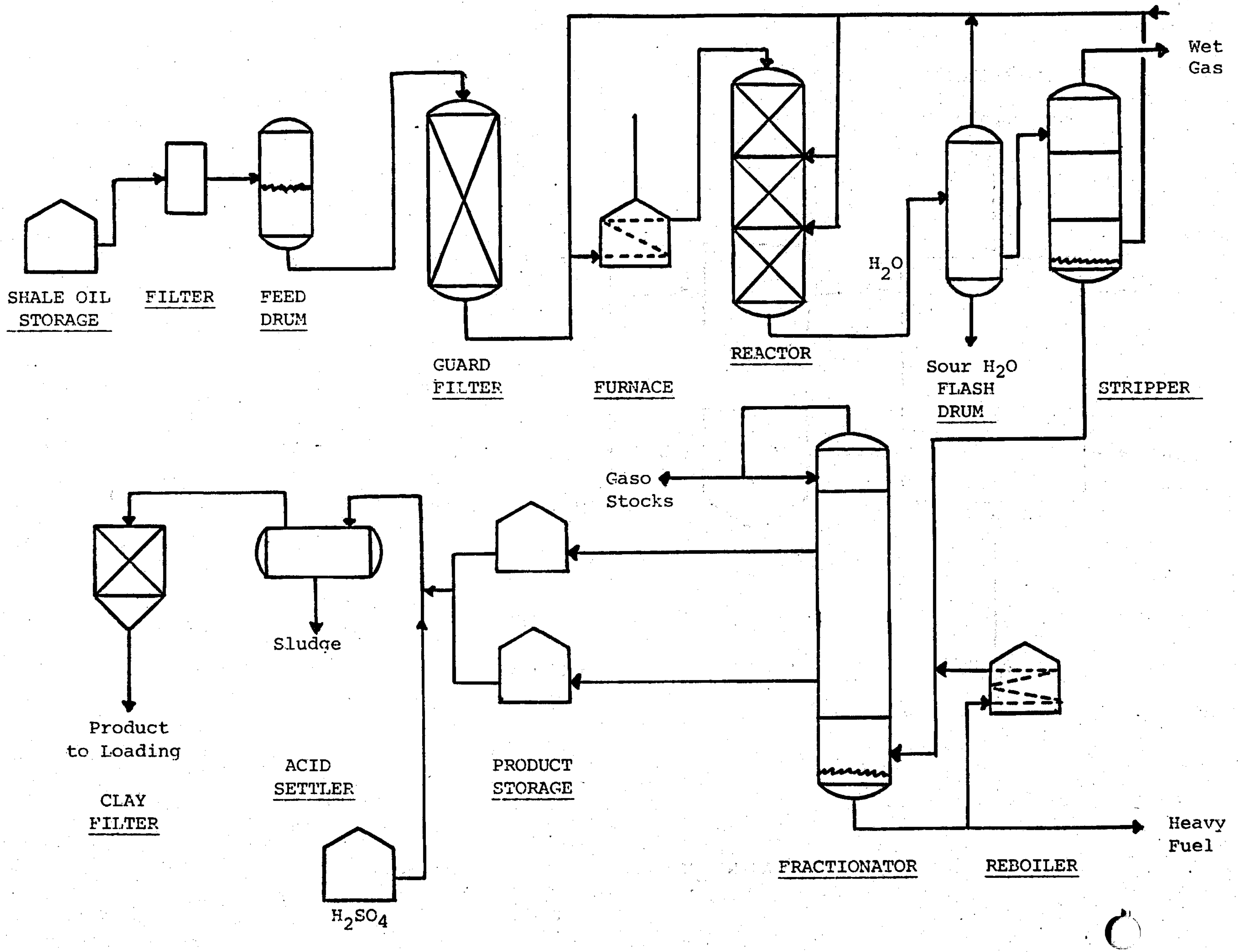
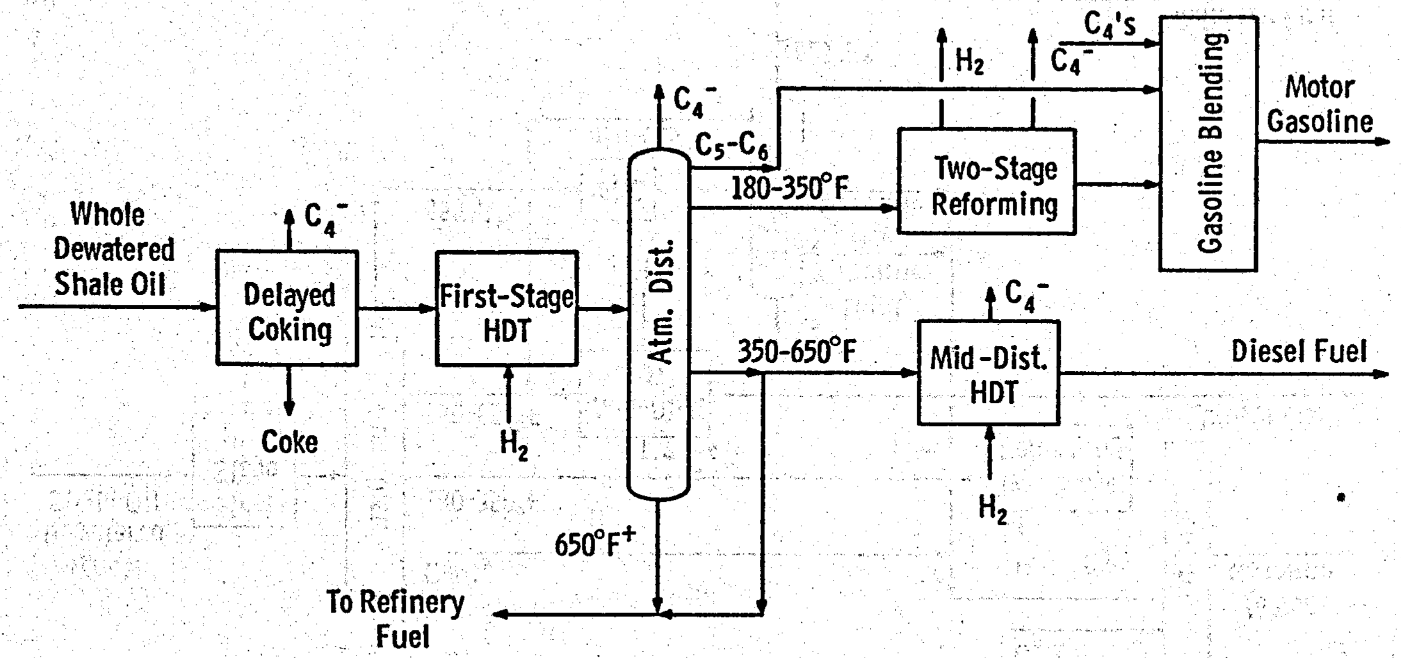


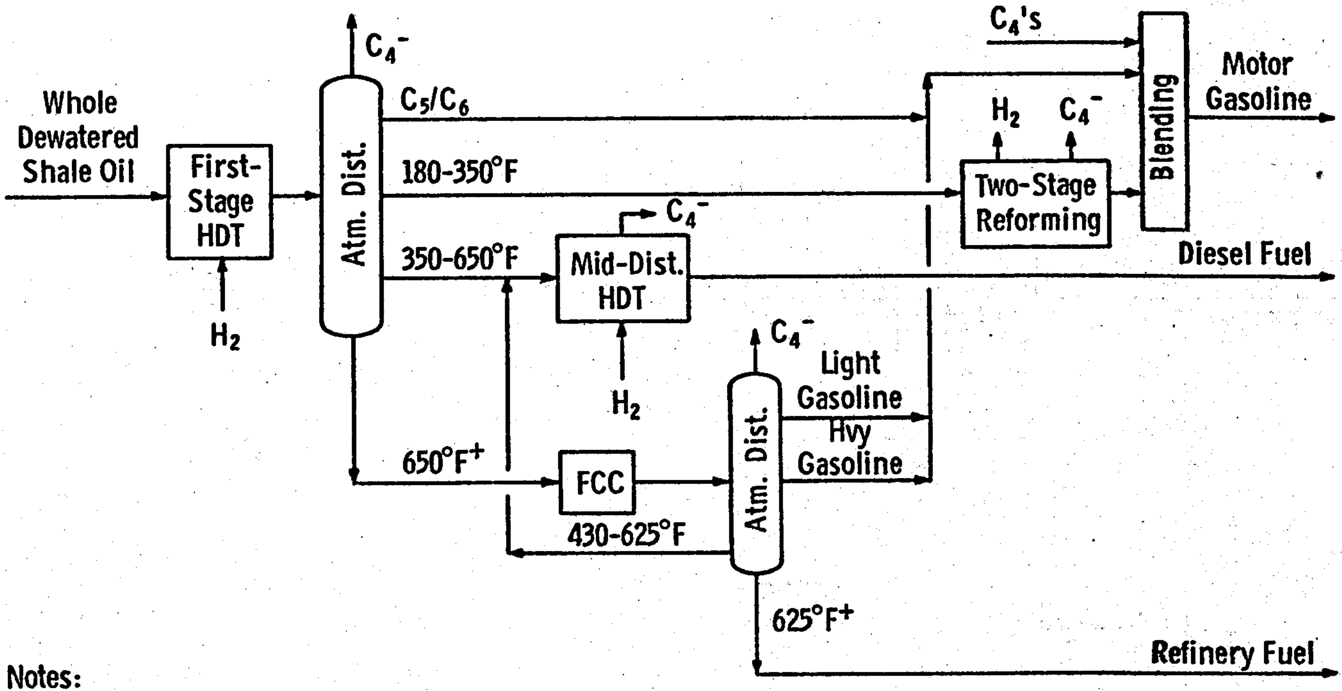
FIGURE 7.2.4

CASE 1 - HYDROTREATING-HYDROCRACKING



Notes:

1. C_4^- is butanes and lighter. Used for hydrogen plant feed, gasoline blending, refinery fuel, and liquified petroleum gas (LPG).
2. Foul gas and water treated to recover NH_3 and sulfur.
3. HDT = Hydrotreating.



Notes:

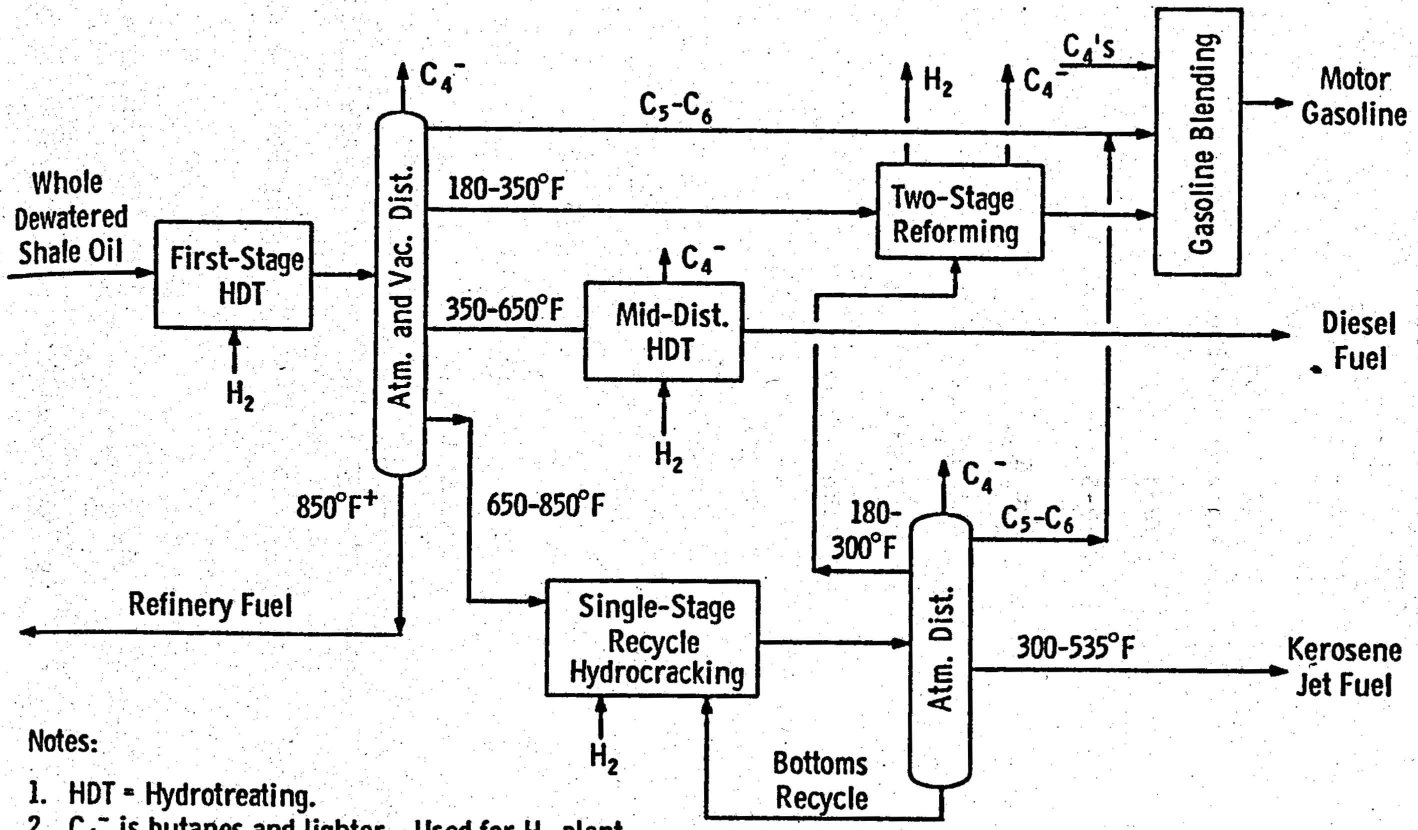
1. C_4^- is butanes and lighter. Used for H_2 plant feed, gasoline blending, and refinery fuel.
2. Foul gas and water treated to recover NH_3 and sulfur.
3. HDT = Hydrotreating; FCC = Fluid Catalytic Cracking.

FIGURE 7.2.5

CASE 2 - HYDROTREATING-FCC

FIGURE 7.2.6

CASE 3 - COKING-HYDROCRACKING



Notes:

1. HDT = Hydrotreating.
2. C_4^- is butanes and lighter. Used for H_2 plant feed, gasoline blending, and refinery fuel.
3. Foul gas and water treated to recover NH_3 and sulfur.
4. Some naphtha from first-stage HDT also used for H_2 plant feed.

TABLE 7.2.1

PRODUCTS PRODUCED

10,000 Barrel Refinery Run

Motor Gasoline

JP-4

JP-5

Jet A

Diesel Oil

Fuel Oil

Coke

TABLE 7.2.2

PRODUCTS PRODUCED

100,000 Barrel Refinery Run

Gasoline Stock

Jet Fuel (JP-5)

Jet Fuel (JP-8)

Diesel Fuel Marine

Heavy Fuel

TABLE 7.2.3

COMPARISON OF OVERALL PRODUCT COMPOSITION

100,000 Barrel Run

	Pilot Plant	Toledo
C_4 - 163°C (Gasoline)	10.3%	11%
163 - 249°C (JP-5)	24.0%	26%
249 - 343°C (DFM)	32.5%	31%
343°C ⊕ Btms	33.2%	32%
	100.0%	100%
Net H_2 Cons ($L/M^3 \times 10^3$)	267.2 - 285.0	240.5 - 258.3

TABLE 7.2.4

COMPARISON OF PRODUCT PROPERTIES

100,000 Barrel Refinery Run

Product	Test	Pilot	Refinery	Mil. Spec.
JP-5, Raw	Gravity, °API	41.8	42.7	36-48
	Flash, °F	69	70	60 min
	Freeze, °F	-84	-89	-83 max
	Nitrogen, Wt%	0.32	0.29	-
	Distillation, °C			
	10%	193	195	205 max
	End Point	247	249	290 max
JP-5, Acid Treat	Acid No., mgKOH/gm	nil	~ 0.006	0.015 max
	Nitrogen, ppm	8	0.6	-
	JFTOT, 260°C			
	Visual	< 2	1	3 max
	TDR	10	0	17 max
	ΔP, mm Hg	1	0.5	25 max
Diesel Fuel Marine, Raw (DFM)	Gravity, °API	33.4	36.8	-
	Flash, °F	143	72	60 min
	Pour Point, °F	-9	-18	-7 max
	Nitrogen, Wt%	0.40	0.32	-
	Distillation, °C			
	90%	312	294	357 max
	End Point	331	306	385 max
	% Residual	1	1	3 max
	Octane No.	50.1	52.5	45 min
DFM, Acid Treated	Nitrogen, ppm	90	4	-
Heavy Fuel	Gravity, °API	30.3	29.6	-
	Pour Point, °F	105	80	-
	Nitrogen, Wt%	0.33	0.44	-
	Distillation, °C			
	End Point	522	540	

TABLE 7.2.5

EFFECT OF HYDROTREATING ON SULFUR AND NITROGEN CONCENTRATIONS

	Feed	Hydrotreated Product				
LHSV	-	0.6	0.6	0.6	0.3	0.2
Temp, °F	-	742	744	767	766	767
Sulfur, ppm	6600	145	33	45	-	42 (?)
Nitrogen, ppm	21800	2800	1325	505	30	1.3

Source: Sullivan and Strangeland, 1978.

7.3 ENVIRONMENTAL/HEALTH INFORMATION

7.3.1 Characterization

The refinery feedstock, refinery intermediates, and final products were characterized as part of an extended study by American Petroleum Institute (Burdett, 1978; see 7.4.5). The earlier studies by American Petroleum Institute characterized raw shale, retorted shale, and crude shale oil (Winward and Burdett; see 7.4.5). The materials examined for their chemical and physical properties include the following:

1.	Crude Shale Oil	Sample No. 4601
2.	Hydrotreated Shale Oil	Sample No. 4602
3.	Weathered Gas Feedstock	Sample No. 4603
4.	JP-5 Precursor	Sample No. 4604
5.	JP-8 Precursor	Sample No. 4605
6.	DFM Precursor	Sample No. 4606
7.	Hydrotreated Residue (#6 Fuel Oil)	Sample No. 4607
8.	JP-5 Product	Sample No. 4608
9.	JP-8 Product	Sample No. 4609
10.	DFM Product	Sample No. 4610
11.	Sulfuric Acid Sludge (from DFM treatment)	Sample No. 4612

Data obtained from these detailed characterization studies were designed to provide comparisons with conventional crude oil refined products and to assess potential health problems. Some of the physical properties studied include:

- Refractive Index
- Molecular Weight
- Viscosity
- Solvent Fractionization
- Simulated Distillation
- True Boiling Point Distillation

Some of the physical properties are listed in Table 7.3.1. Organic elemental analyses are listed in Table 7.3.2. Trace elements are listed in

Table 7.3.3. Simulated distillation curves are shown for many of the materials in Figure 7.3.1.

In Addition to the foregoing extensive characterization, polynuclear aromatic compounds (PNAs) and nitrogen heterocyclics and amino-aromatics (N - PNAs) have been measured in many of the shale oil liquids (Robbins 1980, and Robbins and Blum 1980, see 7.4.5). This work, also under the direction of the American Petroleum Institute, met these objectives:

1. To develop a separation scheme for the shale oils which would yield an aromatics rich fraction that could be analyzed for PNAs by the GC/UV procedure.
2. To adapt the GC/UV procedure for specific N-PNAs (carbazole, acridine and their benzo analogs).
3. To apply the GC/UV procedure for specific N-PNAs to a N-rich fraction isolated in the separation scheme.
4. To qualitatively characterize other N-heterocyclics in the isolated fractions.

The separation scheme developed for these materials is shown in Figure 7.3.2. The GC/UV procedure, used to detect the PNAs and N-PNAs, produced valid results. Validity was assured by examining residues with low voltage, high resolution mass spectrometry (LV/HR/MS). Results obtained for PNAs in shale oil liquids are shown in Table 7.3.4. Concentrations of nitrogen analogs are listed in Table 7.3.5 (N-PNAs) and Table 7.3.6 (alkyl N-PNAs).

Additional characterizations of shale oil liquids have been performed at Oak Ridge National Laboratory (Griest, et al, 1981). Boiling point properties are listed in Table 7.3.7. The chemical class fractionation data for shale oil liquids is found in Table 7.3.8. Benzo(a)pyrene has been measured in some crude, process and refined shale oil liquids (Table 7.3.9). Concentrations of n-Paraffins are found in Table 7.3.10.

These studies have shown that the chemical composition and physical properties of refined shale oil products compare favorably with conventional refined petroleum products. The close comparison of the two types of refined products indicates that the related health hazards would not differ significantly.

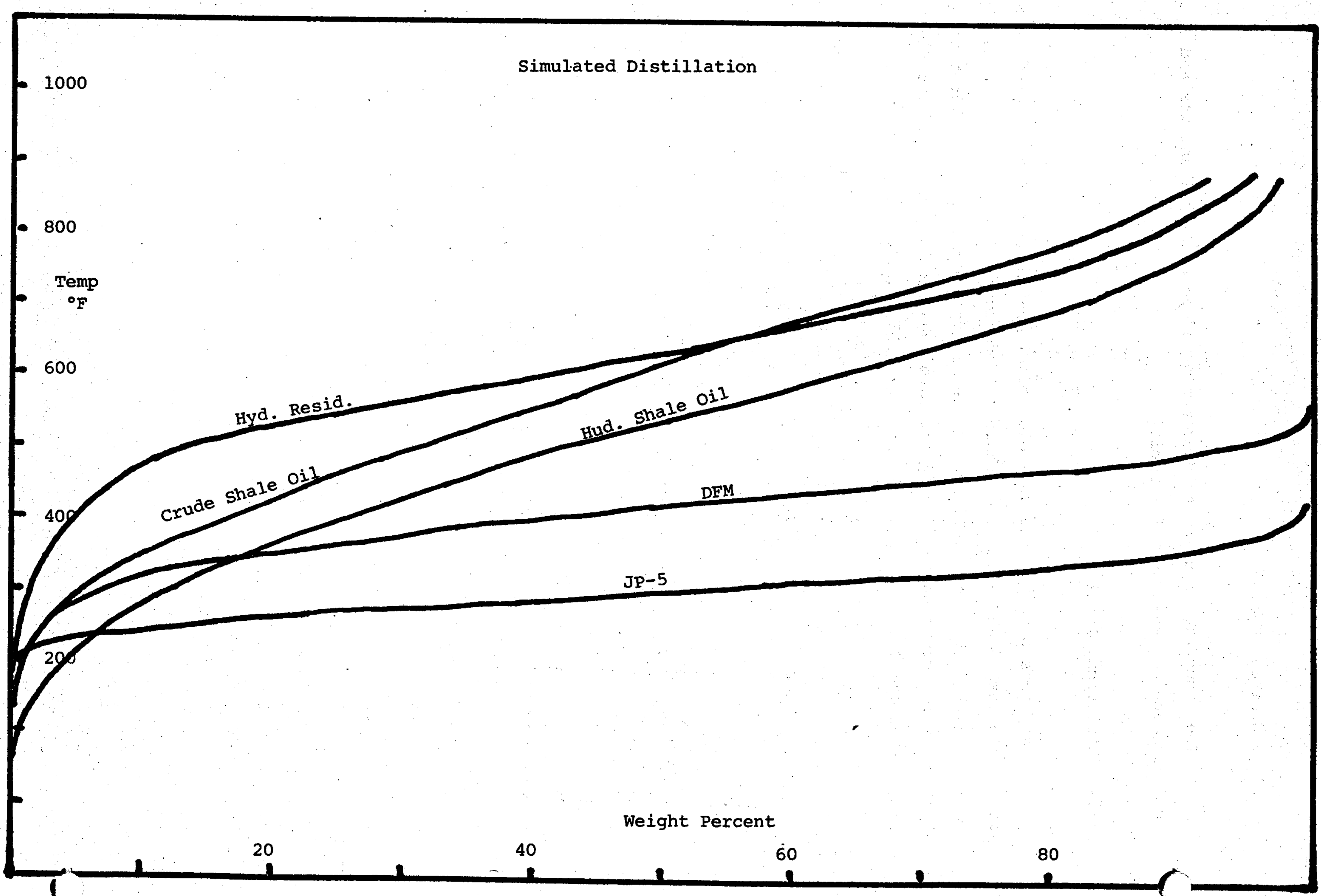
7.3.2 Industrial Hygiene

The industrial hygiene studies performed on shale oil and its end products were not available for review.

7.3.3 Biological Testing

There has been considerable biological testing performed on crude shale oil, hydrotreated shale oil, and shale oil products. This information is found in Part V, Biological Effects. The biological tests and publication references for crude shale oil, hydrotreated shale oil, jet fuels, and diesel fuel marine are listed in Tables 7.3.11, 7.3.12, 7.3.13, and 7.3.14.

FIGURE 7.3.1



Distillation Curves - Oil Shale Liquids

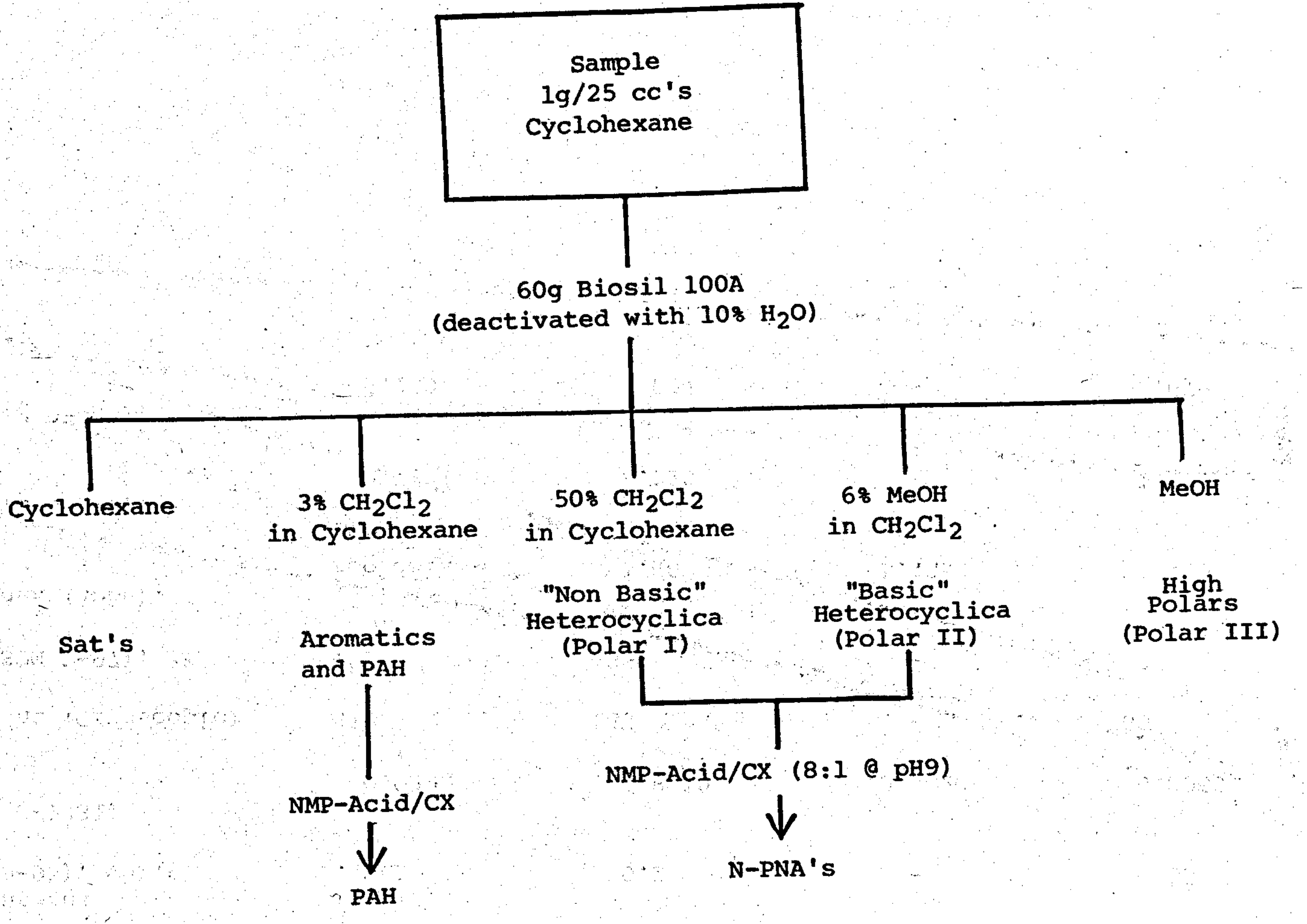


Figure 7.3.2. Separation Scheme for Shale Liquids

TABLE 7.3.1

Physical Properties of Shale Oil Liquids

	Crude Shale Oil 4601	Hydrotreated Shale Oil 4602	Weathered Gas Feedstock 4603	JP-5 Precursor 4604	JP-8 Precursor 4605
Bottom Sediment and Water (ASTM D-96), vol.%	0.1	0.2	-	< 0.05	< 0.05
Density (ASTM D-1481) @60°F, gm/ml	0.9290	0.8610	0.7620	0.8063	0.8101
Molecular Weight (Cryoscopic)	310	245	-	160	160
Pour Point (ASTM D-97), °F	+85	+85	-	< -60	-60
Refractive Index (Abbe) @67°C	too dark	1.46	1.4052	1.4293	1.4313
Viscosity (ASTM D-445), cSt @40°C	40.79	6.329	-	1.271	1.336
Viscosity (ASTM D-445), cSt @100°C	5.359	2.004	-	0.679	0.694

TABLE 7.3.1 (Cont'd)

	DFM Precursor 4606	Hydrotreated Residue 4607	JP-5 Product 4608	JP-8 Product 4609	DFM Product 4610
Bottom Sediment and Water (ASTM D-96), vol.%	< 0.05	0.5	0.05	< 0.05	< 0.05
Density (ASTM D-1481) @60°F, gm/ml	0.8409	0.8880	0.8068	0.8036	0.8342
Molecular Weight (Cryoscopic)	204	300	167	156	201
Pour Point (ASTM D-97), °F	-5	+95	-60	-60	-5
Refractive Index (Abbe) @67°C	1.4448	1.4749	1.4299	1.4283	1.4471
Viscosity (ASTM D-445), cSt @40°C	2.678	9.068 @140°F too waxy	1.352	1.299	2.599
Viscosity (ASTM D-445), cSt @100°C	1.113	3.727	0.706	0.687	1.101

TABLE 7.3.2

Organic Elemental Analysis of Shale Oil Liquid

	Crude Shale Oil 4601	Hydrotreated Shale Oil 4602	Weathered Gas Stock 4603	JP-5 Precursor 4604	JP-8 Precursor 4605	DFM Precursor 4606
Carbon, Wt.%	84.9	86.6	85.7	85.8	85.3	86.5
Hydrogen, Wt.%	11.5	13.1	14.3	13.6	13.6	13.2
Nitrogen, ppm	2.20 wt.% (M-H)	3300 (M-H)	890 (MC)	3000 (M-H)	3600 (M-H)	3600 (M-H)
Oxygen, ppm	1.05 wt.%	260	80	200	270	310
Sulfur, ppm	0.70 wt.% (XRF)	3 (HA)	3 (HA)	.4 (HA)	1 (HA)	.6 (HA)

TABLE 7.3.2 (Cont'd)

	Hydrotreated Residue 4607	JP-5 Product 4608	JP-8 Product 4609	DFM Product 4610	Acid Sludge 4612
Carbon, Wt.%	87.1	86.2	86.2	86.6	-
Hydrogen, Wt.%	12.9	13.8	13.8	13.4	-
Nitrogen, ppm	4600 (M-H)	0.5 (MC)	22 (MC)	15 (MC)	1.85 wt.% (M-H)
Oxygen, ppm	330	1100	90	80	-
Sulfur, ppm	5 (HA)	15 (HA)	.6 (HA)	7 (HA)	16.2 wt.% (IF)

HA = Houston Atlas
IF = Induction Furnace
MC = Microcoulometric
M-H = Mettler-Heraeus
XRF = X-Ray Fluorescence

TABLE 7.3.3

Trace Element Analysis of Shale Oil Liquids

	Crude Shale Oil 4601	Hydrotreated Shale Oil 4602	Weathered Gas Feedstock 4603	JP-5 Precursor 4604
Aluminum, ppm	1.5 (FE)	0.040 (FE)	0.031 (NAA)	0.081 (NAA)
Antimony, ppm (XRF)	ND(<3)	ND(<3)	ND(<3)	ND(<3)
Arsenic, ppm (XRF)	29	<0.5	ND(<0.5)	<0.5
Beryllium, ppm (AA)	ND(<0.005)	<0.005	<0.01	<0.01
Cadmium, ppm (AA)	0.010	ND(<0.005)	<0.03	<0.02
Calcium, ppm	3.8 (FE)	0.052 (FE)	ND(≤0.6)(NAA)	ND(≤0.6)(NAA)
Chlorine, ppm (XRF)	ND(<2)	ND(<2)	ND(<2)	ND(<2)
Chromium, ppm	0.036 (FE)	0.010 (FE)	ND(≤0.1)(NAA)	ND(≤0.16)(NAA)
Cobalt, ppm (FE)	1.0	ND(<0.03)	<0.07	<0.01
Copper, ppm (AA)	0.035	0.030	<0.03	<0.02
Iron, ppm (FE)	57	0.24	<0.01	0.5
Lead, ppm	0.06 (FE)	ND(<0.05)(FE)	<0.07 (AA	<0.06 (AA)
Magnesium, ppm	2.1 (AA)	0.002 (AA)	ND(≤5.3)(NAA)	ND(≤5.3)(NAA)
Manganese, ppm	0.092 (FE)	<0.005 (FE)	<0.03 (AA)	<0.02 (AA)
Mercury, ppm (XRF)	ND(<2)	ND(<2)	ND(<2)	ND(<2)
Molybdenum, ppm	0.07 (FE)	ND(<0.02)(FE)	ND(≤0.032)(NAA)	ND(≤0.042)(NAA)
Nickel, ppm	3.2 (FE)	<0.05 (FE)	ND(≤1.7)(NAA)	ND(≤1.6)(NAA)
Selenium, ppm (XRF)	ND(<0.5)	ND(<0.6)	ND(<0.5)	ND(<0.5)
Silicon, ppm	7.4 (AA)	<0.3 (AA)	ND(≤7.0)	ND(≤18)(NAA)
Silver, ppm	ND(≤0.01)(FE)	<0.01 (FE)	<0.03 (AA)	<0.02 (AA)
Sodium, ppm (FE)	1.1	0.15	0.08	0.05
Strontium, ppm	0.034 (FE)	0.003 (FE)	ND(≤0.8)(NAA)	ND(≤0.97)(NAA)
Thallium, ppm (XRF)	ND(<6)	ND(<6)	ND(<6)	ND(<6)
Tin, ppm	<0.5 (AA)	<0.5 (AA)	ND(≤1.5)(NAA)	ND(≤1.5)(NAA)
Titanium, ppm (XRF)	<0.4	ND(<0.4)	ND(<0.4)	ND(<0.4)
Vanadium, ppm	0.28 (FE)	<0.03 (FE)	ND(≤0.0008)(NAA)	ND(≤0.0008)(NAA)
Zinc, ppm (AA)	1.7	0.064	<0.03	<0.02

TABLE 7.3.3 (Cont'd)

	JP-8 Precursor 4605	DFM Precursor 4606	Hydrotreated Residue 4607	JP-5 Product 4608
Aluminum, ppm	0.045 (NAA)	0.041 (NAA)	0.055 (FE)	0.048 (NAA)
Antimony, ppm (XRF)	ND(<3)	ND(<3)	ND(<3)	ND(<3)
Arsenic, ppm (XRF)	<0.5	<0.5	ND(<0.5)	0.5
Beryllium, ppm (AA)	<0.01	<0.01	<0.005	<0.01
Cadmium, ppm (AA)	<0.02	<0.02	<0.005	<0.02
Calcium, ppm	ND(≤0.6) (NAA)	ND(≤0.6) (NAA)	0.26 (FE)	ND(≤0.6) (NAA)
Chlorine, ppm (XRF)	4	ND(<2)	ND(<2)	ND(<2)
Chromium, ppm	ND(≤0.11) (NAA)	ND(≤0.074) (NAA)	0.010 (FE)	ND(≤0.094) (NAA)
Cobalt, ppm (FE)	<0.04	<0.02	<0.03	<0.04
Copper, ppm (AA)	<0.02	<0.02	0.023	<0.02
Iron, ppm (FE)	1.5	<0.01	0.41	<0.01
Lead, ppm	<0.06 (AA)	<0.06 (AA)	<0.05 (FE)	<0.06 (AA)
Magnesium, ppm	ND(≤5.3) (NAA)	ND(≤5.3) (NAA)	0.052 (AA)	ND(≤5.3) (NAA)
Manganese, ppm	<0.02 (AA)	<0.02 (AA)	0.004 (FE)	<0.02 (AA)
Mercury, ppm (XRF)	ND(<2)	ND(<2)	ND(<2)	ND(<2)
Molybdenum, ppm	ND(≤0.028) (NAA)	ND(≤0.024) (NAA)	<0.02 (FE)	ND(≤0.031) (NAA)
Nickel, ppm	ND(≤2.7) (NAA)	ND(≤2.5) (NAA)	<0.05 (FE)	ND(≤3.9) (NAA)
Selenium, ppm (XRF)	ND(<0.5)	ND(<0.5)	ND(<0.5)	ND(<0.5)
Silicon, ppm	ND(≤10) (NAA)	ND(≤9.3) (NAA)	0.35 (AA)	ND(≤10) (NAA)
Silver, ppm	<0.02 (AA)	<0.02 (AA)	<0.01 (FE)	<0.02 (AA)
Sodium, ppm (FE)	0.01	0.11	0.11	0.14
Strontium, ppm	ND(≤0.74) (NAA)	ND(≤0.56) (NAA)	0.004 (FE)	ND(≤0.94) (NAA)
Thallium, ppm (XRF)	ND(<6)	ND(<6)	ND(<6)	ND(<6)
Tin, ppm	ND(≤1.8) (NAA)	ND(≤1.4) (NAA)	<0.5 (AA)	ND(≤0.93) (NAA)
Titanium, ppm (XRF)	ND(<0.4)	ND(<0.4)	ND(<0.4)	ND(<0.4)
Vanadium, ppm	ND(≤0.0008) (NAA)	ND(≤0.0008) (NAA)	<0.03 (FE)	ND(≤0.0008) (NAA)
Zinc, ppm (AA)	<0.02	<0.02	0.28	<0.02

TABLE 7.3.3 (Cont'd)

	JP-8 Product 4609	DFM Product 4610	Acid Sludge 4612
Aluminum, ppm	0.056 (NAA)	0.047 (NAA)	2.2 mg/l (FE)
Antimony, ppm (XRF)	ND(<3)	ND(<3)	-
Arsenic, ppm (XRF)	ND(<0.5)	ND(<0.5)	-
Beryllium, ppm (AA)	<0.01	<0.01	ND(<0.5 mg/l)
Cadmium, ppm (AA)	<0.02	<0.02	0.7 mg/l
Calcium, ppm	ND(≤0.6) (NAA)	ND(≤0.6) (NAA)	1.6 mg/l (FE)
Chlorine, ppm (XRF)	ND(<2)	ND(<2)	-
Chromium, ppm	ND(≤0.068) (NAA)	ND(≤0.047) (NAA)	0.3 mg/l (FE)
Cobalt, ppm (FE)	<0.06	<0.06	ND(<0.2 mg/l)
Copper, ppm (AA)	<0.02	<0.02	3.0 mg/l
Iron, ppm (FE)	<0.01	<0.01	54 mg/l
Lead, ppm	<0.06 (AA)	<0.06 (AA)	3.5 mg/l (FE)
Magnesium, ppm	ND(≤5.3) (NAA)	ND(≤5.3) (NAA)	0.65 mg/l (AA)
Manganese, ppm	<0.02 (AA)	<0.02 (AA)	0.54 mg/l (FE)
Mercury, ppm (XRF)	ND(<2)	ND(<2)	-
Molybdenum, ppm	ND(≤0.024) (NAA)	ND(≤0.019) (NAA)	ND(<0.02 mg/l) (FE)
Nickel, ppm	ND(≤1.6) (NAA)	ND(≤2.4) (NAA)	<0.1 mg/l (FE)
Selenium, ppm (XRF)	ND(<0.5)	ND(<0.5)	-
Silicon, ppm	ND(≤13) (NAA)	ND(≤10) (NAA)	<2 mg/l (AA)
Silver, ppm	<0.02 (AA)	<0.02 (AA)	<0.5 mg/l (FE)
Sodium, ppm (FE)	0.06	0.16	4.3 mg/l
Strontium, ppm	ND(≤0.58) (NAA)	ND(≤0.75) (NAA)	<0.03 mg/l (FE)
Thallium, ppm (XRF)	ND(<6)	ND(<6)	-
Tin, ppm	ND(≤0.87) (NAA)	ND(≤0.57) (NAA)	<10 mg/l (AA)
Titanium, ppm (XRF)	ND(<0.4)	ND(<0.4)	-
Vanadium, ppm	ND(≤0.0008) (NAA)	ND(≤0.0008) (NAA)	0.72 mg/l (FE)
Zinc, ppm (AA)	<0.02	<0.02	2.3 mg/l

AA = Atomic Absorption
FE = Flame Emission
NAA = Neutron Activation Analysis
XRF = X-Ray Fluorescence

TABLE 7.3.4

PNA Measured by GC/UV in Paraho Shale Liquids

	4601.3 Crude Shale Oil	4602.3[a] Hydrotreated Shale Oil	4607.3 Hydrotreated Residue	4606.3 DFM Precursor	4610 DFM Product
	ug/g	ug/g	ug/g	ug/g	ug/g
Fluorene	<29	28	14	208	124
Phenanthrene	77	133	124	193	281
Anthracene	11	<10	<10	<10	<10
Fluoranthene	4.7	23	109	<0.5	<1
Pyrene	2.6	146	287	<0.5	<1
Benz(a)anthracene	9	12	10	<0.5	<1
Chyrsene	<4.6	16	16	<0.5	<1
Triphenylene	<6.5	2.0	1.7	<0.5	<1
Me-B(a)A	<4.6	23	58	<0.5	<1
DMe/Et-B(a)A	<4.6	5.0	48	<0.5	<1
Benzo(g,h,i)fluoranthene	<10	125	276	<0.5	<1
Benzo(b)fluoranthene	<10	3.8	<12	<0.5	<1
Benzo(j)fluoranthene	<10	<5.1	<11	<0.5	<1
Benzo(k)fluoranthene	<1.5	1.0	1.6	<0.5	<1
Perylene	<1.1	2.5	3.7	<0.5	<1
Benzo(e)pyrene	<5.5	40	54	<0.5	<1
Benzo(a)pyrene	2.0	10	14	<0.5	<1
Methyl B(e)P	<1.7	44	39	<0.5	<1
Methyl B(a)P	<5.7	12	11	<0.5	<1
1,2,3 Indeno(c,d)pyrene	<0.9	0.5	<1.1	<0.5	<1
Dibenz(a,h)anthracene	<3.2	1.1	<3.9	<0.5	<1
Benzo(g,h,i)perylene	5.0	77	83	<0.5	<1
Coronene	<1.7	8.8	11	<0.5	<1

[a] Analyzed by Method A, all others analyzed by Method B.

TABLE 7.3.5

N-PNAs Measured by GC/UV

	4602.3 Hydro. Shale Oil (µg/g)	4607.3 Hydro. Residue (µg/g)	4606.3 DFM Precursor (µg/g)	4610.3 DFM Product (µg/g)
3 Ring				
Carbazole	2.0	4.9	31.7	4.9
Benzo(h)quinoline	--	--	--	--
4-Ring				
Azapyrene	--	13	--	--
Benzocarbazole	3.0	22	--	--
Benzacridine	--	--	--	--
5-Ring				
Dibenz(a,h)acridine	--	--	--	--

TABLE 7.3.6

Alkyl N-PNAs Estimated in Shale Liquids From GC/UV Data

	(µg/g)				
	4601.3 Crude Shale Oil	4602.3 Hydro. Shale Oil	4607.3 Hydro. Resid.	4606.3 DFM Precursor	4610.3 DFM Product
3 Ring					
C_n Carbazoles	--	6	18	10	5
C_n Benzoquinoline	--		43		
4 Ring					
C_n Azapyrenes	--	11	128		
C_n Benzocarbazoles	--				
C_n Benzacridines	--				

TABLE 7.3.7

Measurements of Benzo(a)pyrene in Some Crude, Process, and Refined Samples

No.	Description	Conc., ug/g
4601	Crude Shale Oil	11
4602	HDT Shale Oil	11
4607	HDT Residue	16
4608	JP-5 Product	N.D.[a]
4614	Petroleum JP-5	~ 0.04
4606	DFM Precursor	0.03
4614	DFM Product	0.04

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[a] ND = not detected.

TABLE 7.3.8

Physical Properties of the Crude,

Process, and Refined Product Samples

Repository Sample No.	Description	Boiling Points (°C) by Simulated Distillation		
		Initial	Average	Final
4601	Crude Shale Oil	20	358	514
4602	Hydrotreated Shale Oil	158	369	514
4603	Weathered Gasoline Feedstock	17	92	168
4604	JP-5 Precursor	124	201	271
4605	JP-8 Precursor	125	207	272
4606	DFM Precursor	152	278	330
4607	Hydrotreated Residue	255	401	513
4608	JP-5 Product	117	211	274
4609	JP-8 Product	113	206	273
4610	DFM Product	135	277	333
4612	Acid Sludge from DFM Treatment	-	-	-
4614	Petroleum JP-5	60	225	287
4615	Petroleum JP-8	25	205	291
4616	Petroleum DFM	96	268	363

Table 7.3.9

Chemical Class Fraction Data for Crude, Process, and Refined Product Samples

Chemical Class Fraction	Percentage Composition[a]											
	No. 4601	No. 4602	No. 4603	No. 4604	No. 4605	No. 4606	No. 4607	No. 4608	No. 4609	No. 4610	No. 4614	No. 4616
Volatile	0.3	1.2	36.1	1.9	2.1	0.7	0.6	3.8	5.5	0.6	2.3	1.0
Base (Ether Soluble)	3.7	1.3	0.16	2.25	4.1	2.2	0.8	0.1	0.2	0.02	0.3	0.02
Base (Insoluble)	1.0	0.4	0	0.6	0	0.7	0.7	-	0.2	-	-	-
Acid (Ether Soluble)	0.4	0.2	0.07	0.6	0.3	0.1	0.3	0.5	-	0.07	0.9	0.1
Acid (Insoluble)	1.1	0.3	0	0.5	0	0.5	0.6	-	0	-	-	-
Total Neutrals	93.3	92.2	27.1	89.1	86.1	105	99.4	90.8	90.3	97.9	93.9	97.5
Aliphatic	58.9	51.5	2.2	40.4	50.0	84.8	53.2	37.8	36.4	82.4	59.3	65.0
Mono/Diaromatic	26.4	21.0	0.05	5.2	5.7	12.3	34.2	4.5	5.2	7.2	4.1	17.9
Polyaromatic	2.8	4.1	0.6	0.09	0.2	0.6	10.0	0.1	0.1	0.1	0.1	1.3
Residue	2.1	4.6	-	2.4	1.3	1.8	5.1	1.1	1.8	2.1	2.0	1.3
Total Recovery[b]	97.7	95.3	63.4	48.1	63.7	102	102	47.5	49.4	92.5	68.2	86.7
Number of Replicates	2	4	1	2	2	2	2	2	1	1	2	1

[a] Percentage of original sample.

[b] Based on neutral fractions.

TABLE 2.3.10

Measurements of Total n-Paraffins in Some Crude, Process, and Refined Samples

No.	Description	Conc., mg/g	Major Species
4601	Crude Shale Oil	27	C_{10}-C_{33}
4602	HDT Shale Oil	102	C_{10}-C_{34}
4607	HDT Residue	65	C_{18}-C_{34}
4608	JP-5 Product	197	C_{10}-C_{13}
4610	DFM Product	155	C_{10}-C_{18}
4606	DFM Precursor	158	C_{10}-C_{18}

TABLE 7.3.11

Crude Shale Oil (Feedstock)

Biological Test	Reference
Screening Bioassays	
Ames Test	Buchanan, Ho, and Clark, 1980 Calkins, et al, 1980 Guerin, 1980 Guerin, et al, 1980 Nichols and Strniste, 1981 Pelroy, Sklarew, and Downey, 1981 Rao, et al, 1980 Toste, et al, 1980
Somatic Cell Mutagenesis	Barnhart, et al, 1978 Streniste and Chen, 1981 Timourian, et al, 1980
Cytogenetics	Campbell, et al, 1980 Meyne, 1981 Meyne and Deaven, 1980
Toxicology	
Carcinogenesis	Beck and Albinana, 1980 Gomer and Smith, 1981 Holland, J.M., et al, 1981 Holland, L.M. and Wilson, 1981 Holland, L.M., Wilson and Foreman, 1981 Lewis, 1981 McAlack, et al, 1980 Wilson and Holland, 1979 Wilson and Holland, 1979 Wilson, Valdez, and Holland, 1981
Systemic Toxicity	Beck, Morita, and Hepler, 1979a Beck, Morita, and Hepler, 1979b Beck, Morita, and Hepler, 1979c Disbennett, 1980 Smith, Hascheck, and Witschi, 1980 Timourian, et al, 1980
Cytotoxicity	Cowser, 1980 Okinaka and Strniste, 1981 Timourian, et al, 1980
Aquatic Toxicity	Giddings, 1980a Giddings, 1980b Giddings and Washington, 1980

TABLE 7.3.12

Hydrotreated Shale Oil (Intermediate)

Biological Test	Reference
Screening Bioassays	
Ames Test	Nichols and Strniste, 1981 Rao, et al, 1980
Cytogenetics	Campbell, et al, 1980
Toxicology	
Carcinogenesis	Holland, J. M., 1981 Holland, L. M., Wilson, and Foreman, 1981 Lewis, 1981
Systemic Toxicity	Smith, Hascheck, and Witschi, 1980 Timourian, et al, 1980
Cytotoxicity	Cowser, 1980 Timourian, et al, 1980
Teratogenesis	Disbennett, 1980
Aquatic Toxicity	Giddings, 1980 Giddings and Washington, 1981

TABLE 7.3.13

Jet Fuels (JP-4, JP-5, JP-8)

Biological Test	Reference
Toxicology	
Systemic Toxicity	Cowan and Jenkins, 1980 Holland, J.M., et al, 1981 Smith, Hascheck, and Witschi, 1980
Aquatic Toxicity	Giddings, 1980 Giddings and Washington, 1981

TABLE 7.3.14

Diesel Fuel Marine (DFM)

Biological Test	Reference
Toxicology	
Carcinogenesis	Lewis, 1981
Systemic Toxicity	Cowan and Jenkins, 1980 Holland, J.M., et al, 1981 Smith, Hascheck, and Witschi, 1980
Aquatic Toxicity	Giddings, 1980a Giddings, 1980b Giddings and Washington, 1981

7.4 ANNOTATED BIBLIOGRAPHY

The annotated bibliography of Part VII, End Use Effects, describes the type of information to be found in each publication of the bibliography. Many of these reports contain extensive data and are quite voluminous. For this reason, the available information is summarized.

7.4.1 General

Coffin, L.D., Proceedings of a Conference, "A Matrix Approach to Biological Investigation of Syn Fuels," cosponsored by the U.S. Environmental Protection Agency and Oak Ridge National Laboratory. April 26, 1979. Research Triangle Park, N.C. 1979.

This report contains the seven presentations from the conference held April 26, 1979 in Research Triangle Park, N.C. Topics presented include: the matrix research program, distribution of Paraho shale oil liquids, recent Paraho operations, the refining of Paraho shale oil, the overall research work plan of the biology division at Oak Ridge National Laboratory, shale oil bioassays at Battelle Pacific Northwest Laboratories, and the application of bioassays to determine genetic toxicity of Paraho shale oil products. It has 81 pages, 21 tables, and 14 figures.

Griest, W.H., Mr. R. Guerin, and D. L. Coffin, eds. Proceedings of Symposium on "Health Effects Investigation of Oil Shale Development." June 22-24, 1980. Gatlinburg, Tenn. Ann Arbor Science Publishers, Inc./The Butterworth Group. 1981.

The report contains 17 presentations of the symposium held June 23-24, 1980 in Gatlinburg, Tenn. Topics presented include: an overview of the research matrix program, Paraho operations, results of the Sohio refining run, distribution of shale oil liquids, PAH analysis of shale oil liquids, data collection and computer processing systems in occupational health programs, dermal toxicity of shale oil liquids, carcinogenic bioassay of shale oil liquids, toxicity studies of shale oil liquids (Navy study, acute toxicity, mammalian genetic toxicity, and algae toxicity studies), microbial testing of shale oil materials, and environmental and health problems associated with oil shale technology. The book has 269 pages, 83 tables and 66 figures.

Heistand, R.N., R. A. Atwood, K. L. Richardson, "Paraho Environmental Data; Part I, Process Characterization; Part II, Air Quality; Part III, Water Quality," U.S. Dept. of Energy, May, 1980.

This report represents a compilation of the available environmental data obtained during the Paraho 1977-1978 operations at Anvil Points in the areas of process characterization, air quality, and water quality.

Process Characterization, Part I, is divided into solids, liquids, gases, and quality assurance. The solids data is organized into tables of organic data, major elements, and minor elements. The liquids information is organized into product oil and process water. The gases data is presented as product gas, thermal oxidizer, and miscellaneous stacks. Elemental mass balances are given in the quality assurance section.

Air Quality, Part II, gives extensive data of total suspended solids (TSP) from various sections of the oil shale retorting facility. Respirable dust quantities, elemental analysis, toxic elements, and mineral analysis have been performed on TSP. Effluents from retort, thermal oxidizer, and product gas were analyzed for composition, elemental analysis, toxic elemental analysis, and toxic metals.

Water Quality, Part III, lists bulk properties, major inorganics, trace elements, organic analyses, and miscellaneous parameters for product water, water from the evaporation pond, ground and surface water. Data generated from leachate studies is included in Part III, Water Quality.

All three parts of this compilation contain 348 pages, 159 tables, and 45 figures.

7.4.2 Combustion

Jones, D.G. and M. N. Mansour, "Low NO_x Combustion of Paraho Shale Oil in a 45-MW Boiler." J. Eng. Power, 1978, presented Am. Soc. of Mech. Eng. Atlanta, GA. Nov. 27-Dec. 2, 1977.

Combustion tests of crude Paraho shale oil (0.7 percent sulfur and 2 percent nitrogen) were conducted in a 45 MW boiler equipped with six frontface mounted burners each rated at 85 million Btu/hr. Shale oil was blended in various proportions with low sulfur oil and natural gas so that the sulfur content of the fuel did not exceed 0.5 percent. It was found that significant levels of NO_x reduction were obtained using dual fuel combustion. This result was confirmed during further testing of the two blending methods at various combustion stoichiometries using both conventional and steam-atomized low NO_x burners. The maximum reductions in NO_x emissions occurred during fuel-rich combustion of shale oil in the bottom row of burners followed by combustion of a low-nitrogen fuel in the top row of burners. (5 pages, 2 tables, 4 figures.)

7.4.3 Refining

Cawein, D. L. "Refining of Shale Oil by Sohio," in Proceedings of a Conference Cosponsored by the U.S. EPA and ORNL. Research Triangle Park, N. C. April 26, 1979.

Cawein, D. L. "Results of the Sohio Refining Run." in Proceedings of the Symposium on Health Effects Investigation of Oil Shale Development. Gatlinburg, Tenn. June 23-24, 1980.

The first presentation of the Sohio refining run describes Sohio's Toledo refinery, parameters of shale oil that required special considerations in refining shale oil, and the steps involved in the Sohio refining process. No refinery run results or conclusions were presented. The paper is 8 pages, with 1 table and 2 figures.

The second presentation of the Sohio refining run discusses the special requirements of shale oil and the conclusions of the pilot test run. The refinery run is described and its results and conclusions are given. A block flow and a process flow diagram are given. Results of the pilot test run and the refinery run are listed in tables. Product yield characteristics of the pilot plant and refinery runs, and JP-5 and DFM quality data is presented. The paper contains 11 pages, 5 tables, and 3 figures.

Frumkin, H.A. "Refining and Upgrading of Synfuels from Coal and Oil Shales by Advanced Catalytic Processes." 4th Interim Report to U.S. DOE, Updated Costs for Processing of Paraho Shale Oil. FE-2315-50 Dist. Category, UC-90d. June, 1980.

* This report updates the cost estimates of processing Paraho shale oil that were presented in the first interim report (FE-2315-25, Sullivan, et al, April, 1978). The two tables of the report contain the updated bases for cost estimates and comparisons, and the revised overall cost summary. The report is 5 pages long, including 2 tables.

Frumkin, H.A., E. J. Owens, and R. B. Sutherland. "Cost Comparisons - Alternative Refining Routes for Paraho Shale Oil." Presented at AIChE 86th National Meeting, Houston, Texas. April 1-5, 1979.

A Colorado shale oil produced in a surface retort at the Paraho test facility was refined in pilot plant facilities at Chevron Research Company. Advanced commercial petroleum processing technology was employed to produce transportation fuels (primarily gasoline, kerosene jet fuel, and diesel). Three likely refining routes were identified and demonstrated sufficiently to permit preparation of screening-type process designs and cost estimates. These routes are: (1) hydrotreating followed by hydrocracking, (2) hydrotreating followed by catalytic cracking, and (3) coking followed by hydrotreating. In addition, a fourth alternative was evaluated where raw shale oil was hydrotreated to produce a synthetic crude suitable for processing in an existing refinery.

The presentation estimates refining costs for each of the three process routes based on producing (1) 50,000 BPCD of transportation fuels from a "grass roots" refinery in a remote Rocky Mountain location, and (2) 100,000

BPCD of transportation fuels from a "grass roots" refinery located near a Rocky Mountain or Mid-Continent urban center. The costs for hydroprocessing to produce a synthetic crude also are estimated both for a "grass roots" site near the shale oil retorting facilities and for location at a typical existing Mid-Continent refinery. All refineries are designed with facilities to meet present environmental requirements and anticipated near-term environmental and energy conservation regulations. This presentation is taken from Sullivan, et al, 1978. The presentation is 54 pages in length, with 26 tables and 7 figures.

Paraho Development Corporation. "Production and Refining of 10,000 barrels, Paraho Crude Shale Oil into Military Fuels." May, 1975.

The report discusses the production and refining of 10,000 barrels of Paraho crude shale oil. The major areas summarized are the Paraho process, preprocessing studies, and refining. Appendix A contains a schematic diagram, flow diagram, and material balance for the Paraho process and refining process; and physical properties of crude shale oil and estimated yields of the products.

Appendix B gives distillation data of crude shale oil, physical and chemical properties of distillates, and nitrogen, sulfur, and oxygen balances for crude shale oil.

The experimental parameters for crude shale oil distillation, coking, coker gas oils distillation, hydrogenation, and blending and trimming of hydrotreated fractions are presented. The discussion involves crude shale oil pilot coking and distillation, pilot plant hydrotreating of shale oil fractions, blending and testing of hydrotreated fractions for finished products, and projected yield for full-scale refining at Gary Western. Results and conclusions are also given. The schematic flow diagrams and schematic diagrams of distillation, coking, preprocessing pilot study, weight yields through coking and hydrogenation, jet fuel freeze, flash testing, diesel pour and flash testing are included. Weight balance, inspections of feed and liquid product, and composition of off-gas and recycle gas for each run are found in the tables.

The post refining analysis report is under Appendix D. The refinery preparation, shale oil processing, laboratory analyses, and recommended future modifications are discussed.

Appendix E summarizes the shale oil byproduct disposition.

Appendix F lists the product supervision.

This report with appendices A-F contains 162 pages, 73 tables, and 31 figures.

Paraho Development Corporation. "The Commercial-Scale Refining of Paraho Crude Shale Oil into Military Fuels: Phase II and Phase III." June, 1980

The Phase II report from Sohio's refinery at Toledo, Ohio presents an overall material and volume balance, a description of processing scheme, and a summary of daily progress reports (daily data) of the commercial-scale refining of crude shale oil. It contains 17 pages, 3 tables, and 2 figures. The figures are schematic diagrams of the hydrocracker unit and acid-clay treater unit.

The Phase III report on commercial-scale refining of crude shale oil by the Sohio refinery at Toledo, Ohio presents the results of Phase II and Phase III. The discussion centers around the processing scheme, logistics of production, shipment and handling of products, the refinery preparation, and shale oil processing. Preparations for the refinery include shale oil receiving and storage, hydrocracker, acid-clay treater, and product storage and shipment. The hydrocracker processing results include overall material volume balance comparison of actual vs. pilot plant yields, catalyst performance actual vs. pilot plant, and the hydrocracker mechanical performance. The acid-clay treater results discussed are the overall material balance and production of JP-5 and DFM, comparison of actual vs. pilot plant yields for JP-5 and DFM, and acid usage, sludge formation and clay life for JP-5 and DFM, and acid-clay treater mechanical performance for JP-5 and DFM. The fuels distribution is also given. Appendices A-G list fuel properties and analysis of battery limits, summarize daily verbal reports, discuss reactor guard-bed fouling, and list assays of crude shale oil and hydrotreated shale oil. The Phase III report is 168 pages in length, with 73 tables and 29 figures.

Pforzheimer Jr., H. and E. T. Robinson. "Processing of Oil Shale - from Rock in the Ground to Finished Petroleum Products." Presented at National Petroleum Refiners Association, March 8, 1979.

The presentation addresses production operations in Part I and results from the pilot plant refining program and preliminary results from the commercial-scale refining run in Part II. In Part II, the pilot plant program objectives and properties of Paraho shale oil are discussed. The commercial-scale refining run describes the logistics of the run, compares pilot plant and refinery performance, and lists conclusions. The presentation contains 24 pages, 6 tables, and 2 figures.

Robinson, E.T. "Refining of Paraho Shale Oil into Military Specification Fuels," in 12th Oil Shale Symposium Proceedings, Colorado School of Mines, Golden, Co. April 18-20, 1979.

This paper presents the results of refining Paraho crude shale oil into military specification fuels. This program was a joint effort by the DOE and Department of Defense, sponsored by the Navy. The paper includes the final results of the Phase I pilot plant program and the preliminary results from the actual refinery run at Sohio's Toledo Refinery (Phase II) and wrap-up analysis (Phase III). It was demonstrated that military specification transportation fuels such as JP-5 and diesel fuel marine can be produced from shale oil utilizing conventional refining technology. The processing scheme (whole shale oil hydrotreating followed by distillation and acid/clay treating) and the physical characteristics of the fuels are reviewed and discussed. The paper contains 18 pages, 11 tables, and 2 figures.

Sullivan, R.F. and B. E. Strangeland. "Catalytic Hydroprocessing of Shale Oil to Produce Distillate Fuels." Presented at Symposium on Refining of Synthetic Crudes, Petroleum Division, 174th N.A.C.S. Meeting, Chicago, Ill. Aug. 28-Sept. 2, 1977.

This paper presents results from a feasibility study to demonstrate the conversion of whole shale oil to a synthetic crude resembling a typical petroleum distillate. The synthetic crude thus produced can then be processed, in conventional petroleum-refining facilities, to transportation fuels such as high octane gasoline, diesel, and jet fuel. Background information, pretreatment of raw shale oil, whole oil hydrofining, FCC processing, and shale oil refinery are discussed. This presentation is taken from Sullivan, et al, 1978. The paper is 42 pages long and has 15 tables and 5 figures.

Sullivan, R.F. and B. E. Strangeland. "Converting Green River Shale Oil to Transportation Fuels," in 11th Oil Shale Symposium Proceedings, Colorado School of Mines, Golden, CO. April 12-14, 1978.

The removal of nitrogen, oxygen and heavy metals from crude shale oil is a major consideration in the catalytic conversion of shale oil to transportation fuels. Hydrotreating can remove substantially all of these elements, while coking only removes most of the heavy metals. Pilot plant data for three processing schemes were generated during the course of this study: hydrotreating followed by hydrocracking; hydrotreating followed by fluid catalytic cracking; and delayed coking, followed by hydrotreating. Yields and product inspections are presented for these three cases. Schematic flow diagrams are also given. The paper has 15 pages, 17 tables, and 4 figures.

Sullivan, R.F. et al. "Refining and Upgrading of Synfuels from Coal and Oil Shales by Advanced Catalytic Processes." 1st Interim Report to U.S. DOE. Processing of Paraho Shale Oil FE-2315-25 Dist. Category. UC-90d. April, 1978.

Part I - Laboratory and Pilot Plant Studies

Chevron Research Company conducted extensive laboratory, pilot plant, and engineering studies to demonstrate the feasibility and estimate costs for refining of surface-retorted Paraho shale oil. These studies showed that raw shale oil can be conventionally refined using advanced, commercialized petroleum technology to produce finished transportation fuels, primarily motor gasoline, kerosene jet fuel, and diesel fuel.

Three alternative refining routes were evaluated: (1) hydrotreating followed by hydrocracking, (2) hydrotreating followed by fluid catalytic cracking, and (3) coking followed by hydrotreating. In addition, a fourth alternative was evaluated where raw shale oil was hydrotreated to produce a synthetic crude suitable for processing in an existing refinery.

The technical accomplishments are described by task:

Task 1 - Feedstock Analysis and Feed Preparation

Task 2 - Whole Oil Hydrotreating

Task 2A - Alternate to Whole Oil Hydrotreating Coking of Whole Shale Oil, Hydrofinishing of Coker Distillate

Task 3 - Middle Distillate Hydrotreating
Task 4 - Extinction Recycle Hydrocracking
Task 4A - Alternate Processing of 650°F+ Hydrofined Shale Oil:FCC
Task 5 - Catalytic Reforming
Task 6 - Final Process Design (summarized in Part II)
Task 7 - Reports
Task 8 - Distillate Shale Oil Hydrotreating

A list of quarterly reports and papers covering portions of this contract is included.

Areas for future study also were identified. None of these appears to represent a major problem. Rather, most involve second-order process refinements that will be incorporated in future commercial projects which are based on specific product slates. Part I is 174 pages in length with 79 tables and 39 figures.

Part II. Engineering Design Studies and Estimated Processing Costs

Screening-type process designs and estimated refining costs were developed for each of the three process routes listed above based on producing (1) 50,000 BPCD of transportation products from a "grass roots" refinery in a remote Rocky Mountain location and (2) 100,000 BPCD of transportation products from a "grass roots" refinery located near a Rocky Mountain or Mid-Continent urban center. The costs for hydroprocessing to produce a synthetic crude were estimated both for a "grass roots" site near the shale oil retorting facilities and for location at a typical existing Mid-Continent refinery. All refineries were designed with facilities to meet present environmental requirements and anticipated near-term environmental and enery conservation regulations. Part II contains 51 pages, 28 tables, and 10 figures.

Sullivan, R.F. et al. "Refining Shale Oil." API Preprint No. 25-78. Presented at API Refining Dept. 43rd Midyear Meeting, Conserving Petroleum - New Feedstocks and Fuels for Refineries, Toronto, Ontario, Canada. May 10, 1978.

A pilot plant refining study on surface retorted Paraho shale oil was recently completed by Chevron Research Company. Three basic shale oil processing samples, Fischer assay, particle size distribution, refractive index of retort oils, ASTM methods, molecular weight, simulated distillation, solvent fractionation, true boiling point distillation plus blending of fractions, hydrocarbon types on lighter fractions, hydrocarbon separation and mass spec analysis of heavier fractions, trace elements in retort oils, methods used for radionuclides analysis by Controls for Environmental Pollution, Inc. (CEP), and major analytical instrumentation used for radionuclides analyses. Section II is composed of detailed tables from the analytical data obtained. The figures include electron photomicrographs and qualitative x-ray data, and TBP and simulated distillation of shale oil.

The first report contains 93 pages, 52 tables and 16 figures. The revised report has 100 pages with 66 tables and 24 figures.

Winward, M.R. and L. W. Burdett. "Comprehensive Analyses of Shale Oil Products: Second Study." Union Oil Co. of Calif., Science and Technology Division, Project Report No. 79-39 to Am. Pet. Ins. Nov. 27, 1979.

Winward, M.R. and L. W. Burdett. "Comprehensive Analysis of Shale Oil Products: Second Study - Final." Union Oil Co. of Calif., Science and Technology Division, Project Report No. 79-39 to Am. Pet. Ins. 1979.

Section I lists the samples analyzed, discusses the sampling handling and preparation, and the analytical methods. The analytical methods are divided into physical properties and chemical analysis. The physical properties include refractive index, molecular weight, ASTM methods, solvent fractionation, simulated distillation, and true boiling point distillation plus blending of fractions. The chemical analysis is based on elemental analyses, trace elements, and hydrocarbon types. Section II is organized into detailed tables and charts of the physical properties and chemical analyses data.

The second study report contains 71 pages, 43 tables, and 16 figures. The second study - final report has 74 pages, 46 tables, and 16 figures.

7.4.6 Industrial Hygiene

The industrial hygiene studies performed on shale oil and its end products were not availabe for review.

routes for the production of transportation fuels were studied: hydrotreating followed by hydrocracking, hydrotreating followed by fluid catalytic cracking (FCC), and severe coking followed by hydrotreating. Also, a fourth alternate was evaluated in which raw shale oil was hydrotreated to produce a synthetic crude suitable for processing in an existing refinery. In this paper, product yields, product properties, and estimated process costs derived from these studies are presented. It is concluded that shale oil can be refined to high quality transportation fuels via modern state-of-the-art refining technology and that it can serve as a substitute for crude oil in a refinery equipped with modern hydrotreating facilities.

7.4.4 Petrochemicals

Glidden, H.J. and C. F. King. "Light Olefins from Shale Oil Distillates," presented at Symposium: Feedstock Alternatives I - New Technologies for the Production of Chemical Feedstocks from Unconventional Resources. Philadelphia, PA. 1980.

This study evaluates the commercial potential for production of olefins from shale oil. The sample analysis and preparation, process studies, pyrolysis results, and commercial unit projections are discussed; and the conclusions are given. The paper is 13 pages long, with 6 tables.

7.4.5 Material Properties

Robbins, W.K. "Analysis of Shale Oil Products." Exxon Research and Engineering Company, Final Report to Am. Pet. Ins. March 4, 1980.

Model compound studies were used to determine separation characteristics of the 14-N-PNA's (polynuclear aromatic N-heterocyclics) of silicic acid columns and in N-methyl pyrrolidone/cyclohexane extractions. These data were utilized in the development of a general scheme for the isolation of PNA and N-PNA from shale oil liquids. Six samples of shale oil liquids were analyzed for PNA and N-PNA by the GC/UV procedure after the separation. Three ring PNA's were found in diesel fuel marine (DFM) precursor and product samples. The higher boiling samples contained 4-7 ring PNA's as well. Only a few N-PNA's were detected in all but the crude shale oil sample. The most commonly encountered species were carbazoles and benzcarbazoles. Qualitative analyses on the isolated N-PNA fractions by high resolution mass spectrometry suggest the presence of numerous unidentified N-PNA which do not correspond to the available reference compounds. The GC/UV data are listed in tables; the separation scheme and the N-analogs of anthracene and phenanthrene are shown in figures. The paper contains 33 pages, 16 tables, and 2 figures.

Robbins, W.K. and S. C. Blum. "Analysis of Shale Oil Liquids for Polynuclear Aromatic Hydrocarbons and their N-Heterocyclic Analogs," in Proceedings of the Symposium on Health Effects Investigation of Oil Shale Development. Gatlinburg, Tenn. June 23-24, 1980.

Six shale oil liquids have been analyzed for PNAs and selected N-PNAs. These samples were found to contain PNAs at levels similar to those in comparable petroleum fractions. Few of the selected acridines, carbazoles or benzo analogs which could be measured by the GC/UV procedure were detected. However, elemental analysis and LV/HR/MS (Low Voltage/High Resolution/Mass Spec.) demonstrate that numerous N-containing compounds are isolated in the fractions which would contain N-PNAs. Qualitatively, the LV/HR/MS data suggest that the bulk of the N is associated with highly substituted or partially hydrogenated multi-ring heterocyclics. The GC/MS and LV/HR/MS data are presented in tables, the separation scheme are N-analogs of anthracene and phenanthrene and are shown in figures. The paper has 31 pages, 18 tables, and 2 figures.

Burdett, L.W. "Comprehensive Analyses of Shale Oil Products." Union Oil Co. of Calif., Research Dept. Project Report No. 78-75 to Am. Pet. Ins. Jan. 31, 1978.

Burdett, L.W. "Comprehensive Analysis of Shale Oil Products (Revised)." Union Oil Co. of Calif., Research Dept. Project Report No. 78-75 to Am. Pet. Ins. Sept. 1, 1978.

Section I of the reports lists the samples analyzed, describes sampling handling and analytical methods. The analytical methods described and used include minerals, scanning electron microscopy and photomicrographs, sample preparation, micrographs and interpretation, surface area, benzene extractables followed by specific analyses, elemental analyses of whole samples, chemical analysis for major constituents of whole shale samples, trace elements in whole

Task 3 - Middle Distillate Hydrotreating
Task 4 - Extinction Recycle Hydrocracking
Task 4A - Alternate Processing of 650°F+ Hydrofined Shale Oil:FCC
Task 5 - Catalytic Reforming
Task 6 - Final Process Design (summarized in Part II)
Task 7 - Reports
Task 8 - Distillate Shale Oil Hydrotreating

A list of quarterly reports and papers covering portions of this contract is included.

Areas for future study also were identified. None of these appears to represent a major problem. Rather, most involve second-order process refinements that will be incorporated in future commercial projects which are based on specific product slates. Part I is 174 pages in length with 79 tables and 39 figures.

Part II. Engineering Design Studies and Estimated Processing Costs

Screening-type process designs and estimated refining costs were developed for each of the three process routes listed above based on producing (1) 50,000 BPCD of transportation products from a "grass roots" refinery in a remote Rocky Mountain location and (2) 100,000 BPCD of transportation products from a "grass roots" refinery located near a Rocky Mountain or Mid-Continent urban center. The costs for hydroprocessing to produce a synthetic crude were estimated both for a "grass roots" site near the shale oil retorting facilities and for location at a typical existing Mid-Continent refinery. All refineries were designed with facilities to meet present environmental requirements and anticipated near-term environmental and enery conservation regulations. Part II contains 51 pages, 28 tables, and 10 figures.

Sullivan, R.F. et al. "Refining Shale Oil." API Preprint No. 25-78. Presented at API Refining Dept. 43rd Midyear Meeting, Conserving Petroleum - New Feedstocks and Fuels for Refineries, Toronto, Ontario, Canada. May 10, 1978.

A pilot plant refining study on surface retorted Paraho shale oil was recently completed by Chevron Research Company. Three basic shale oil processing samples, Fischer assay, particle size distribution, refractive index of retort oils, ASTM methods, molecular weight, simulated distillation, solvent fractionation, true boiling point distillation plus blending of fractions, hydrocarbon types on lighter fractions, hydrocarbon separation and mass spec analysis of heavier fractions, trace elements in retort oils, methods used for radionuclides analysis by Controls for Environmental Pollution, Inc. (CEP), and major analytical instrumentation used for radionuclides analyses. Section II is composed of detailed tables from the analytical data obtained. The figures include electron photomicrographs and qualitative x-ray data, and TBP and simulated distillation of shale oil.

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Winward, M.R. and L. W. Burdett. "Comprehensive Analyses of Shale Oil Products: Second Study." Union Oil Co. of Calif., Science and Technology Division, Project Report No. 79-39 to Am. Pet. Ins. Nov. 27, 1979.

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7.4.6 Industrial Hygiene

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7.4.7 Biological Testing References of Shale Oil Products

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