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Occurrence, Origin, and Fate
and
Source-Monitoring Recommendations

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ORGANIC CONSTITUENTS OF OIL-SHALE PROCESS STREAMS:

Occurrence, Origin, and Fate and Source-Monitoring Recommendations

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CONTENTS

Table:

Figure:

ABSTRACT

This report is the first attempt at presenting a unified overview of the organic compounds produced by the retorting (thermal pyrolysis) of raw oil shale. The emphasis is on the secondary, minor, and trace organic constituents of the process streams rather than on the major components of the crude shale oil. All of the well-characterized organic constituents of oil-shale process streams are discussed with respect to their occurrence and abundance. The origin and fate of each chemical class during retorting is also discussed; much of this discussion includes conjectures based on known chemical reactions. Brief discussions are also included when environmental/health effects may be important. Conjectures are made with respect to compounds that may be present in process streams (esp. retort waters) but have yet to be identified because of limitations in methods of chemical analysis. The major objective of this unified approach was to suggest a way in which predictions could be made regarding the composition of oil shale process streams, which to date remain largely uncharacterized. An approach is suggested with which this information could be used in developing environmental monitoring plans for commercial-scale oil shale facilities. A major conclusion of this report is that most organic compounds produced during oil-shale retorting have multiple origins; many originate from either direct liquid extraction or mild pyrolysis of the kerogen (or secondary pyrolysis reactions) as well as from complex intermolecular chemical reactions of simple precursors (esp. aldehydes, amines, ammonia, and pyrite). Almost all of the compounds produced are not only products of other synfuel processes (e.g., tar sands and coal gasification) and petroleum refining, but they also occur ubiquitously in the environment (from either biogenic or anthropogenic sources).

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I. Analytical Considerations Pertinent to Oil Shale Process Streams

Although the chemical characterization of waste and product streams from oil shale retorting has received much attention, the extraordinary complexity of their chemical matrices has thwarted all attempts at thorough characterization of the organic constituents. In addition to the overall problem presented by the presence of numerous classes of compounds, together with their associated types, homologs, and isomers, several other general analytical problems are pervasive to these samples.

The major analytical approaches that have been employed during the last two decades rely heavily on gas chromatography (GC). This is the foremost separation technique in use today, and furthermore, it readily lends itself to interfacing with mass spectrometry (MS) for molecular structure identification (speciation). With the prevalence of GC and GC/MS, however, it is important to recognize their shortcomings. These include the following.

(1) Pre-separation/fractionation of organic constituents of aqueous and solid samples is almost always required prior to chromatographic analytical separation. Most often this is achieved by liquid-liquid extractions with organic/halogenated solvents; preparative high-performance liquid chromatography (HPLC) is also used sometimes. Although HPLC has few of the limitations of liquid extraction (except for irreversible retention by the stationary-phase of certain compounds), it is much more time consuming and not as frequently employed. Aqueous samples frequently involve a preseparation before HPLC can be used, and organic extracts of solids can only be used for nonaqueous reverse-phase separations. For liquid extraction, only those compounds with favorable partition coefficients will be extracted and amenable to subsequent chromatographic analysis. Of this portion, only those that are sufficiently volatile will chromatograph. Compounds that boil much above 400°C will not elute from most columns. These include compounds of high molecular weight and those of low molecular weight that have multiple functional groups or heteroatoms. The latter are often highly polar and have a propensity to hydrogen-bond and adsorb. This latter group of compounds, which will occur primarily in the retort waters, may comprise numerous compounds present at low or high concentrations that have yet to be identified. The higher-molecular-weight compounds will be associated mainly with particulates and product oil, although low concentrations will exist in the process waters. An additional factor concerning those compounds that are chromatographable is thermal stability. Heat-labile compounds (e.g., some of those formed in reactions occurring after retorting) may degrade in the injection port on the column, and the associated products would therefore contribute to unidentified artifact.

(2) Although GC/MS has facilitated the identification of numerous compound types, its major limitation is in distinguishing members of positional, structural, or molecular-formula isomers. For example, the fragmentation patterns for the structural isomers methyl-ethyl- and propyl-pyridine or for quinolines and isoquinolines may not be distinguishable without reference standards of the same compounds run under the same conditions; this is a time-consuming and very expensive task. Compounds of the same molecular formula but having totally different structures can also be difficult to distinguish. This is extremely important with regard to the azaarenes and aromatic primary amines (e.g., Felice 1982; Schmitter et al. 1984). The latter must usually have their amino groups derivatized to distinguish them from the azaarenes (e.g., alkylquinolines versus alkylnaphthylamines). Furthermore, amino azaarenes with even numbers of nitrogen atoms are difficult to identify because of the lack of the characteristic odd-numbered parent ion (e.g., Wilson et al. 1983). Structural assignments, therefore, are often limited to isomeric forms (e.g., C_3-pyridine) or sometimes to alternative classes (e.g., C_2-pyridine/C_1-aniline). Much of the published literature that reports separation of numerous unspeciated isomers is therefore useless for identification of individual compounds (e.g., Gebhart and McKown 1980; Wingender,

Harrison, and Raphaelian 1981). Only if an authentic reference standard is available, can retention indices possibly be used to augment structure confirmation. The general problem of the unavailability of analytical reference standards for aromatics, hydroaromatics, and heteroaromatics has been discussed (Wozniak and Hites 1985a). This problem is severe with regard to the alkylated heterocycles, which are prevalent in retort waters. For example, there are 654 possible structural isomers for the C_0-C_6 alkylpyridines alone (Wingender et al. 1981). Furthermore, even though most GC/MS studies show numerous well-resolved components, these almost always fall within a large, unresolved envelope of unidentified materials; this is a limitation even of ultra-high-efficiency fused-silica capillary columns and can occur despite prefractionation procedures. Even if most of these compounds were separated and detected by GC/MS, identifications could only be assigned for a small portion of the heterocycles. The published reports of the individual compounds that have been identified are perhaps biased as a result of all of these reasons. That is, those compounds that have been identified tend to be those for which reference standards are commercially available or have been independently synthesized and purified (an expensive undertaking). Many of these limitations can be overcome with the advent of more widespread use of tandem mass spectrometry (MS/MS) (e.g., Hunt et al. 1985).

(3) Another limitation of GC/MS analysis of complex samples is quantification of individual components. Since it is not feasible to quantify each compound by using a separate standard curve, much of the reported research concentrates only on identification. In many publications, compounds are merely reported as being present, or at best they are "quantified" in terms of "total ion current" from the mass spectrometer. It is therefore not possible to even infer relative concentrations. These data, although in some instances extensive (e.g., Conditt et al. 1983; Fox et al. 1984), are of little use in establishing which representatives from particular chemical classes may be most abundant in a process stream. "Semiquantitative" work can be done by using an internal standard and by assuming equal normalized responses for all components. Another approach uses indicator (selective) ion monitoring. All of these points directly relate to the problem of reviewing published data to choose compounds that (1) have the highest probability of occurring (i.e., frequency) and (2) occur at the highest concentrations. Therefore, it is important to assess the available characterization data in conjunction with what is known about retorting chemistry, an approach that will be more thoroughly discussed in subsequent sections.

(4) Nearly all process streams analyzed to date have been from noncommercial-scale facilities and have been stored for various time periods under a range of conditions with little attention to potential, ambient chemical alterations or volatilization. Not only may the compositions of these waste streams not be representative of those produced by near-commercial facilities such as the Union B process, but portions of extremely volatile solutes may have escaped during sample collection/storage. Further losses are inevitable during the numerous types of sample fractionation schemes that are used prior to analytical separations. Large portions of very volatile compounds, therefore, have possibly escaped detection, and oxygen sensitive compounds (e.g., pi-excessive N-heterocycles such as pyrroles) may have oxidized or polymerized. A further consideration is microbial transformation. It is well known that microbial growth can easily be established in certain retort waters (Farrier et al. 1977; Healy, Jr., Langlois, and Daughton 1985). This is of unknown significance, however, because of the low phosphate concentrations of these waters. For example, the phosphate concentration in Oxy-6 retort water is 0.032 mM, while organic carbon is about 2.9 M (Jones et al. 1982). The approximate molar ratios for C:N:P required in microbial catabolism of organic substrates are 300:25:1, respectively (Cook, Daughton, and Alexander 1978); only trace amounts of sulfur are required (Cook, Daughton, and Alexander 1980). Ammoniac-N and sulfide- and sulfate-S would be in excess but phosphate would rapidly become limiting. Growth would therefore be minimal and could not begin again without the addition of phosphate. Regardless of these considerations, the samples that have

been analyzed to date are not necessarily representative of real-time samples generated at the site. In particular, one could expect the possible emission of higher amounts of volatile compounds than the current literature may indicate. The sampling points for which current characterization data are least useful would therefore include fugitive air emissions from shale quenching and retort offgas.

II. Characterization of Organic Constituents

The organic material of oil shales is probably combined with a complex inorganic matrix of mineral assemblages in a variety of structures whose characteristics still remain to be resolved. This organic material is traditionally categorized as comprising two components: (1) kerogen, an amorphous high-molecular-weight heterogeneous, polymeric assemblage (defined as insoluble in CS_2) and (2) bitumen, a lower-molecular-weight, oligomeric material (defined as soluble in CS_2). The bitumen is generally viewed as being dispersed within but not covalently bonded with the kerogen, perhaps representing a geologically later stage of kerogen maturation. Crude shale oil is the combination of distillable, unaltered endogenous organic material (i.e., lower-melecular-weight materials) and condensed, volatile pyrolytic products (also known as pyrobitumen). Any compounds that evolve during the retorting process will partition into one of four phases: solid (retorted shale or particulates), vapor, oil. and aqueous phases.

The composition of these phases varies greatly depending on the type of process (in-situ vs. above-ground) and mode of retorting (direct vs. indirect heating). In-situ processes can yield more dilute process waters because of steam injection and mine-drainage water. Shales resulting from indirect modes of retorting have more residual organic material. It is therefore only possible to give general ranges in concentrations for major organic parameters such as organic carbon, nitrogen, and sulfur. This is especially true for tne raw and retorted shales for which it is extremely difficult to distinguish organic forms of carbon, nitrogen, and sulfur from inorganic forms. For Green River shales the organic carbon content ranges up to 20%, and the total contents of N and S are generally below 0.5% and 1%, respectively (e.g., Maase 1980). For noncombusted retorted shales (e.g., Tosco II, Union B), the organic carbon content is less than 10% (probably between 0.5 and 3%), and total N and S are less than 0.5% and 0.85%, respectively (e.g., Maase 1980; Pereira and Rostad 1983). Crude shale oils (Tosco II, Union B) have C, N, and S contents of 85, <1.9, and <0.9%, respectively (Maase 1980); these values probably represent organic forms exclusively. For process waters, organic carbon can range from 200 to 45,000 mg/L (Langlois et al. 1984) and organic nitrogen can range from 10 to 5,000 mg/L (Daughton, Jones, and Sakaji 1985); organic sulfur contents have not been determined. Retort offgases vary tremendously in composition.

The traditional definition of kerogen/bitumen is based purely on operational terms, dictated by the conditions used for extraction (i.e., type of solvent and temperature); the percentage of extractables necessarily increases with increasing temperature. It has therefore been recently proposed that this classification scheme merely serves to obfuscate the probability that kerogen is not a single hetero-polymeric structure (and bitumen a distinctly different class of compounds), but rather, kerogen and bitumen are structurally the same, comprising a complex mixture of compounds whose molecular weights typically range from 600-800; lower and higher (>1200) molecular-weight compounds are also present (McKay 1982). Most of these compounds require thermal degradation before distillation can ensue; this begins around 250-350°C. For simplification, therefore, the term "bitumen" will not be used in this report.

In addition to discussing the research on characterization of the process waters and gas streams themselves, it is important to consider the extensive published literature on the composition of the product oil because these data can give valuable insight into the spectrum of compounds that can potentially occur in the other streams. More extensive characterizations have been completed on the oil than other by-products, mainly because it is the primary economic product. Another reason, however, is that the oils are much more amenable to chemical analysis, a result of their nonpolar nature and the extremely high concentrations of many of their components. These qualities allow for the immediate application of classical separation methods (e.g., normal-phase column chromatography) and the collection of large masses of fractions. Analysis of oils is more in the realm of formulation analysis, while the characterization of the retort waters, gas condensates, and offgases requires the application of the countless varieties of trace analysis. For example, some of the older literature has established more complete identifications of isomers in shale oil because the large-scale fractionation and identification procedures were very straightforward, although labor intensive (e.g., Van Meter et al. 1952).

Even though most of the nonpolar compounds in oil (e.g., aliphatics) would be expected only in low concentrations in the aqueous phases, they could reside in the particulate/colloidal/suspended fractions of these streams. In contrast, compounds present in the oil in trace concentrations could occur in higher concentrations in the aqueous streams; this would be especially true of compounds that have polar functionalities (esp. polyfunctional compounds such as hydroxyacids). Amphiphatic compounds (i.e., those having intramolecular, separated aliphatic and polar moieties) would be expected in both phases. These compounds could occur at extremely high concentrations at oil-water interfaces in product-oil separator tanks or in analytical extraction devices; interface materials are extremely difficult to analyze. These compounds (e.g., fatty acids) would also be partly responsible for enhancing the solubility of less-polar compounds in the aqueous phases. In general, the relative concentrations of the spectrum of compounds in each of these two phases will mirror that of the other phase in an inverse manner.

Considerable effort has been focused on characterization of the organic constituents in retort process waters, but the spectrum of compounds identified is by no means complete, mainly for reasons previously discussed. The thorough analyses that have been completed have accounted only for at most one-half of the total organic carbon present (Leenheer, Noyes, and Stuber 1982; Raphaelian and Harrison 1981; Dobson et al. 1985). Most of the unidentified compounds are probably hydrophilic or higher molecular weight, a result of their being less amenable to the usual separation/identification methods that are used (i.e., gas chromatography). Polyfunctional aliphatics/aromatics/heterocycles and their associated polymers probably comprise much of this material (Leenheer et al. 1982). This problem is universal in the analysis of any aqueous sample (e.g., Giabbai et al. 1983). It is also possible that this unidentified fraction could be composed of countless homologs and isomers, each present at a concentration sufficiently low as to confound their separation and identification. In contrast, the percentage of organic carbon accounted for by compounds that have been identified in volatile emissions from process waters (i.e., headspace samples) is much higher (66-87%) (Hawthorne and Sievers 1984). This, however, is merely a reflection of the tool of analysis (i.e., gas chromatography).

The available data, being incomplete and possibly not representative are not sufficient for justifying the selection of compounds that should be included in an environmental monitoring plan (e.g., indicator compounds). These data therefore need to be supplemented by other rationale. Without initiating extensive, fundamental characterization research on the process streams under study, additional information for establishing a list of key indicator compounds can be obtained by review of literature that is directly and indirectly related to the organic chemistry of oil shale retorting. The importance of this approach is described below and it is implemented in Section III, where specific process-stream characterization data are discussed.

The ability to predict the assemblage of compounds that could occur in oil shale process streams from different retort technologies and rock sources is not an unreasonable objective, but it will not be tenable for years to come. A thorough understanding of several diverse fields will first be required. These include (i) geochemistry (for understanding the origin, composition, and variability of kerogen and how it is physically associated with the mineral assemblages in different shales), (ii) pyrolysis (for understanding the initial thermolytic processes in the breakdown of the shale organic matter), and (iii) organic chemistry of the initial pyrolytic products (for understanding the origin and possible fates of the pyrolysis products as they engage in the countless secondary chemical reactions associated with retorting). This task will require an integration of effort by geo-, organic-, physical-, and analytical-chemists. Only with these lines of research will the occurrence of compounds in the process streams be understood and a framework be in place for predicting their concentrations.

The Retort Environment.

Most research has focused on the geochemical aspects of oil shale, a result of it being a long-established field of research with much knowledge being transported from what is known about other petrolithic rocks. The least is known about the organic chemistry associated with the retorting process. The overall problem of characterizing the organic composition of oil shale process streams is complicated by the nature of the numerous reactions that occur during the formation of the complex assemblage of these organic compounds. Many of the products are simply unaltered, direct reflections of the chemical nature of the parent kerogen (e.g., alkanes, alkylbenzenes, and carboxylic acids). These compounds are simply distilled or leached directly from the kerogen/shale matrix. Many other compounds, however, result from the direct pyrolysis (thermal degradation or cracking) of the nonvolatile, higher-molecular-weight moieties of the shale (e.g., pyrroles). Still more compounds result from primary chemical reactions (additions, aromatization, isomerization, cracking) involving the distilled, leached, or pyrolyzed products. Many of these reactions are catalyzed in the liquid- or gas-phase surrounding the mineral assemblages of the shale (Regtop et al. 1985), but others occur simply because of the high reactivity of some of the pyrolysis products (esp. carbonyl compounds). Combustive (oxidative) chemistry can also be associated with the pyrolysis of the kerogen (e.g., direct-mode retorting). Finally, many products can be formed later, during exposure of the waste/product streams to oxygen or light or simply after sufficient time has passed for significant completion of slower reactions.

The organic constituents of oil shale are a result of complex biochemical (synthetic and degradative), chemical, and physical (thermal) reactions occurring over geologic time (e.g., diagenesis). Shales differ greatly in their degrees of maturation, and this greatly influences the properties of the kerogen; in general, the thermodynamic tendency is to reduce the abundance of functional groups (i.e., approach a pure hydrocarbon state). Many of the same chemical reactions, which occurred over geologic time, occur again during retorting; the primary difference is that the variable of time is replaced by that of temperature. In the discussion that follows, these routes of newly created compounds will be referred to as "de novo" synthesis. The retorting process can be simplified as an extremely fast replay of many of the same reactions that occurred during the diagenesis of the kerogen. This means that many (if not most) of the chemical classes that occur in the process streams have multiple origins (i.e., from the kerogen and from multiple de novo synthetic routes occurring within the retort).

It is important to understand that the chemistry associated with the production of these process streams is further complicated because it is one of dynamics; chemical equilibria are established only after storage of samples under constant conditions. All of the reactions that occur during retorting take place in an ever-changing four-phase environment -- one of solids, gas, oil, and water. The reactions that can occur in each phase can be distinctly different because of properties unique to each phase (e.g., hydroxide ion in the aqueous phase, organic radicals in the gas phase, and catalytic surfaces of the solid phase). The products of any reaction immediately distribute among these four phases as dictated by their physico-chemical properties, which include: molecular weight, size, and functional groups, all of which in turn determine polarity (dipole moments, hydrogen bonding, water solubility, etc.) and volatility (vapor pressure and Henry's Law constant).

The dynamics of the process are amplified by spatial and temporal effects. Although some compounds may be produced in relatively high abundance from the initial pyrolytic/combustive process of retorting, the more reactive ones (esp. aldehydes, ketones, and alkyl amines) will be found in correspondingly lower concentrations as the stream becomes further removed (spatially and temporally) from the origin of production (i.e., zone of retorting). Similarly, those compounds formed in lower abundances during the primary reactions but created by the secondary reactions of the major pyrolytic products will increase in concentrations as the waste streams age (e.g., hydantoins, cycloalkanones, and phenolic/pyrrolic polymeric material). These temporal- and spatial-dependent phenomena are generally responsible for the seemingly contradictory results that are sometimes reported by different researchers. That is, most samples have varied greatly in where they were obtained from the retort process flow, how they were collected and stored (e.g., presence/absence of air; refrigerated/ambient), and how long they were stored prior to analysis. Much of the data that have been reported, therefore, are possibly not relevant to freshly produced process streams. These streams have not reached chemical equilibrium and could have totally different relative abundances of certain chemical classes. Little literature is available on the analysis of freshly generated samples, other than those from lab-scale retorts.

Summary of General Conclusions and Organization of Report.

A major conclusion of this report, which has been substantiated by some current research (e.g., Regtop et al. 1985), is that many (if not most) of the heterogeneous spectrum of compounds, whose occurrence in oil shale process streams can be explained as resulting directly from kerogen, can also result from reactions undergone by some of the simple aliphatic pyrolytic products of retorting. Most of the compounds that have been identified, therefore, arise from at least two (if not a multitude) of sources. Similarly, compounds that disappear (as reactants) during certain phases of retorting may reappear as products from totally different reactions when entering other retort zones or during cracking. The reaction pathways are all interrelated.

The composition of a shale oil is not necessarily a direct reflection of the structure of kerogen. Indeed, remarkable parallelisms exist in the process streams from all synfuel and petroleum processes. In simplistic terms, the chemistry of retorting can be described as a function of three concurrent processes: (1) direct distillation of endogenous volatile components or of simple pyrolysis products (e.g., radical disproportionations) of chemical classes endogenous to the kerogen, (2) de novo synthesis of many of these same classes from simple aliphatic pyrolytic products and inorganic gases via reaction pathways analogous to those that occurred over geologic time in the biosynthesis and diagenesis of the kerogen, and (3) extraction of ionic or polar constituents from the kerogen-shale matrix. The resulting compounds are simply those that are most thermodynamically favored.

Inorganic or simple organic forms of oxygen, sulfur, and nitrogen (e.g., molecular oxygen, hydrogen sulfide, and ammonia; carbonyl compounds, alkylthiols, and alkyl amines) are responsible for driving much of the subsequent primary chemistry that occurs during retorting; the fact that the organic forms are major reactants is reflected by their correspondingly low concentrations in the process streams. Reaction of these species (among others) with compounds containing carbonyl moieties favors the de novo synthesis of the respective heterocyclic analogs: furans, pyridines/pyrroles, and thiophenes. Pyrolysis of these compounds, in turn, produces the respective fused-ring, benzo derivatives.

Finally, it is helpful to point out some of the parallelisms that exist regarding the origin of some of the seemingly unrelated compounds produced by destructive reactions that occur during retorting. These parallel origins are all destructive pathways resulting from heterocycle cracking. Hydrogenation and cracking can occur (uncontrolled) to various degrees during retorting and they are actively promoted during oil upgrading. Many of the possible reactions have been discussed in numerous articles (e.g., Green et al. 1985). In general, hydrocracking of multi-ring N-, S-, and O-heterocycles (e.g., indoles/quinolines, benzo[b]thiophenes, and benzo[b]furans) can yield the respective functionalized arene analogs: anilines, thiophenols, and phenols. Further hydrocracking of these yields the respective aliphatic analogs: alkylamines, alkylthiols, and alcohols; alkyl substituents on the arene carbon adjacent to the functional group hinders cracking. These latter products are then available for participating in numerous de novo synthetic reactions (during retorting) or are further cracked to yield the inorganic forms of the heteroatoms: ammonia, hydrogen sulfide, and carbon monoxide. In an analogous manner, hydrocracking of the iso-heterocyclic analogs (i.e., isoindoles/isoquinolines, benzo[c]thiophenes, and benzo[c]furans) would yield the respective benzyl amines (alpha-amino toluenes), aralkylthiols and sulfides, and benzyl alcohols; most of the five-membered iso-derivatives are unstable, however, and probably of lessor importance in retorting. In general, the azaarenes are amenable to hydrogenation but are less susceptible to cracking than are the thia- and oxa-arenes (Green et al. 1985).

The compounds produced in these pyrolytic and chemical reactions that can occur during retorting are ubiquitous products of pyrolysis processes in general and can be derived from most naturally occurring materials (many occur in thermally processed foods). For this reason, most of these compounds are also either naturally occurring or are ubiquitous, anthropogenic-derived environmental contaminants With the exception of some of the heterocycles (esp. azaarenes), cyanides (esp. nitriles), and amino-substituted arenes and azaarenes, almost all of the compound classes that have been identified in oil shale process streams (and many of those in this report that are proposed to exist) have been identified in thorough characterization studies of environmental samples of urban storm water runoff (Eaganhouse, Simoneit, and Kaplan 1981; Hoffman et al. 1984), urban rain water (Kawamura and Kaplan 1983), and atmospheric aerosols (Broddin, Cautreels, and van Cauwenberghe 1980). Extensive discussions are included in these references concerning anthropogenic versus natural sources for the origin of each chemical class; perhaps the major single source for all of the classes identified relates to the processing and use of petroleum. It would also be safe to surmise that all of the compounds that have been or will be identified in oil shale process streams also occur in process streams from other synfuel or petroleum refining processes. Any unique chemical signatures of a particular oil shale process, or for that matter synfuel processes in general, will probably result from different relative abundances among the individual chemical classes. For example, the acidic class in oil shale products is predominated by carboxylic acids, while the hydroxybenzenes dominate in the streams from coal gasification (e.g., cp. Leenheer et al. 1982 vs. Giabbai et al. 1985). There appear to be no compounds that are unique to oil shale processing. Furthermore, only a few of the compounds whose existence is probable pose much environmental concern: the alkylpyridines and thiols (severe malodor) and aromatic and heterocyclic primary amines (potent mutagens).

The following is a summary of specific generalizations (derived from Section III) directly relevant to the organic compounds produced by oil shale processing.

- Organic compounds from retorting originate from (i) liquid extraction of hot, raw shale by process waters and oil (e.g., carboxylic acids), (ii) direct distillation or mild thermolysis of endogenous kerogen constituents (e.g., aliphatics, alkylbenzenes, pyrroles), (iii) thorough pyrolysis/cracking (e.g., amines, thiols), and (iv) de novo intra- and inter-molecular chemical reactions (e.g., alkylcyanides, cycloalkanones, alkylpyridines, amides, hydantoins), and (v) combustive reactions during direct-mode retorting (e.g., oxygenated species such as sulfoxides, sulfones, sulfonic acids, nitrated PAHs, nitrosated amines).

- Many compounds have multiple origins (from endogenous kerogen constituents and from de novo synthesis). These include pyridines, pyrroles, thiophenes, and thiols.
- Individual chemical classes preferentially partition to one of four phases during retorting as a function of (i) polarity: nonpolar compounds (aliphatics) to oil, and polar compounds (nitrogen/oxygen functional groups) to retort waters, and (ii) volatility: nonvolatile/polar compounds to retort waters, high-molecular-weight aliphatics/aromatics to oil and shale, volatile (low-molecular-weight neutrals) to gas condensates and offgases.
- The pH of retort waters and gas condensates is high because of high ammonia and carbonate concentrations.
- Gas condensates comprise compounds that are steam distillable at high pH (e.g., alkylpyridines), those that are volatile only while in the gas phase and before contacting retort waters (e.g., thiols, hydroxybenzenes), as well as those compounds that are not volatile at any pH, but which originate from de novo synthesis from volatile precursors (e.g., possibly hydantoins).
- Retort waters comprise compounds that are nonvolatile (e.g., carboxylates, amides) as well as those compounds which in their protonated forms are volatile but are ionized at the high pH (e.g., hydroxybenzenes, thiophenols, thiols).
- Major portions of the organic compounds in retort waters have not been characterized. These are highly functionalized compounds (i.e., containing various combinations of carbonyl, hydroxyl, or amino substituents), and most probably contain nitrogen.
- The two single most abundant classes from retorting are the alkanes (the major constituent of the crude oil) and the carboxylic acids (the single most abundant class in the retort waters).
- The compounds identified in oil shale process streams are generally the same as those known to result from other synfuel processes (e.g., tar sands and coal processing) and from petroleum refining. Many of the compounds that could potentially be released to the environment are already significant ambient constituents of natural waters and air, and they have both biogenic and anthropogenic origins.
- The major features distinguishing oil shale process streams from those of other synfuel processes (and petroleum refining) is the much lower concentrations of hydroxybenzenes and the much higher concentrations of carboxylic acids and organonitrogen compounds.
- Organic-nitrogen is associated with numerous chemical classes, including: amides (alkylamides, lactams, urea); alkyl- and arylamines; heterocycles (mainly pyrroles and pyridines together with numerous benzologs and countless variations of alkyl and hydroxyl substituents); cyanides (hydrogen cyanide, alkyl nitriles, benzonitriles); and thiocyanate. Numerous multi- and mixed-heteroaromatics are also possibly present, such as hydantoins.

- Alkylpyridines are the most abundant organonitrogen species in retort waters and cyanides are the most abundant in offgases and gas condensates.
- In contrast to organic-nitrogen, organic-sulfur is present in only a few forms, including: heterocyclic thiophenes and their benzologs (including alkyl substituents); thioalcohols; alkyl sulfides; and carbonyl sulfide.
- Heterocyclic forms of oxygen are minor (mainly furans and their benzologs).
- Arylamines are relatively minor organonitrogen constituents in retort process streams, but they can be major constituents if hydrocracking has occurred during retorting or when oil is upgraded.
- Malodor could be a major problem at a retort site. For the individual process streams, malodor will be determined primarily by alkylpyridines (retort and oil-upgrading waters), hydroxybenzenes (gas condensates), and thiols/sulfides (scrubber offgases).
- Coloration of retort waters is caused by oligomers and polymers formed mainly from pyrroles and anilines and secondarily by hydroxybenzenes; the association of color with high-molecular-weight substances is evidenced by the removal of color by sub-micron filtration. Color therefore comprises nonpolar, organonitrogen compounds.
- Of all the carbon-containing compounds identified, the acute toxicity of none is as great as that of hydrogen cyanide (retort process waters or offgases) or of metal carbonyls (possibly present in offgases from retorting or oil upgrading), both of which are also common, regulated byproducts of other fossil-fuel based industries.
- Aminated derivatives of polycyclic aromatic hydrocarbons and of aza- and thia-arenes have the highest mutagenic potential of any compounds identified in raw (i.e., unrefined) crude oils from synfuel processes. These primary amines probably account for much of raw shale oil's mutagenic activity, which is low in comparision with that of other syncrudes.
- Compounds produced by retorting that do not occur ubiquitously in the environment but which could be emitted include: 1-alkenes, aromatic and azaarene primary amines, alkylpyridines (esp. oxo-derivatives), and alkyl- and benzonitriles.
- Compounds produced in large amounts during retorting but which play crucial roles in secondary reactions (their transient concentrations in the process streams are therefore often low) include: aldehydes, aliphatic ketones, and possibly alcohols.
- Metals and metalloids associated with organic structures will be associated primarily with the oils (as porphyrin and non-porphyrin ligands and as cyanide complexes) and will play crucial roles during oil upgrading. Raw shale mercury is converted almost exclusively to alkylated forms and emitted in the offgases. The retort chemistry of most metal/organic compounds is poorly understood, however.

Objectives and Organization of Report.

The major classes of organic compounds that have been identified in oil shale process streams (oil and by-products) will be discussed in the following section. It should be noted that for a truly critical, in-depth understanding of the composition of these waste streams, a thorough review of the geochemical and chemical analysis literature would be required not only for oil shale processing, but also for all other synfuel processes. This would be an enormous undertaking. So for each chemical class, only brief discussions will be included of their possible or known origins (geochemical or de novo synthesis) as well as the possible or known reactions that they can undergo during and after retorting. "Name" or "type" reactions will be mentioned parenthetically where appropriate or for illustrative purposes; some of these reactions are invoked merely to show that the reaction is possible, while others are presented as the actual route of de novo synthesis within the retort. Most of these reactions can be found in standard references (e.g., The Merck Index 1983).

The discussions of the possible reactions occurring during the retorting process are in no way intended to be comprehensive. They are presented to illustrate the complexity of retort chemistry and to impart some continuity to the seemingly unrelated, vast array of reactions and products. Discussion will be limited to those chemical classes that are known to occur and those whose occurrence is possible in oil shale process streams. The objectives will be an attempt to (1) integrate the chemical reactions that have occurred during the production of these streams and identify the major constituents and (2) predict the possible compounds that remain unidentified. The latter will be particularly important with respect to those compounds that are not extractable with organic solvents or that are not sufficiently volatile to be identified with gas chromatography. In the discussion below, those compounds that could be representatives of these unidentified classes will be flagged as "possible unidentified components" (PUCs). It should be noted that although the reactivity of many of these compounds often leads to products whose existence could be ascribed solely to the isolation procedure used during analysis, the same reactions could also occur during process stream storage/disposal or in the environment. It cannot be overemphasized that even though some clear generalities can be made with respect to the probable occurrence of some of the individual compounds (or chemical classes) that have been conclusively and consistently identified in shale products, these are mainly the more volatile constituents. The major polar constituents may have yet to be identified. Most of these polyfunctional compounds, which would reside almost exclusively in the process waters, are probably insignificant toxicologically. One class, however, the aminated/hydroxylated polyaromatic and heterocyclic compounds, may be the single most important constituent with respect to mutagenic potential.

The discussion in Section III is organized under individual chemical classes that have been identified in oil shale process streams. Within each class, an attempt was made to include the following information when it was relevant or important: (1) the general occurrence or origin of the class in the environment (i.e., natural [biogenic/terrigenic] or man-made [anthropogenic]) and environmental/toxicological significance, (2) occurrence in the retorting process with respect to raw shale, oil, waters, gases, spent shale, and particulates (class members that occur most frequently or in highest concentrations are emphasized), (3) origin (direct products of kerogen distillation or routes of de novo synthesis), and (4) fate (major reactions undergone within the retort, including conjectures on PUCs, or reactions that could occur after process-stream storage, disposal, or discharge to the environment).

Finally, with respect to each of these areas of discussion, the reader may want to refer to the following, relevant summary Tables and Figure while reading this report.

Table I: Chemical nomenclature relevant to each chemical class (synonyms, jargon, alternative nomenclature, examples, etc.).

Table II: The relative abundance (contributions to the loading of organic carbon, nitrogen, and sulfur) of each chemical class in each type of process stream.

Table III: The primary chemical-class contributors to organic C, N, and S for each process stream.

Table IV: The most abundant or frequently occurring compounds within each class.

Table VI: A compilation of the compounds and compound types that have been postulated as "possibly occurring" (PUCs).

Figure 1. A generalized scheme of the chemical reaction pathways for the origin and fate of each chemical class during retorting. These are compiled from the relevant discussions of retort chemistry in Section III. The chemistry of the retort process is divided into four sections, all of which ultimately relate back to constituents endogenous of the kerogen/bitumen matrix. The first section lists endogenous, raw-shale constituents. The second lists products of direct extraction, distillation, or pyrolysis. The third shows the classes that could result from further pyrolysis or secondary chemical reactions (e.g., oxidation, condensation). The fourth lists the classes that are further removed from retorting per se -- those that result from tertiary chemical reactions; many of these reactions can occur outside the retort environment.

III. Chemical Classes and Constituent Organic Compounds

MAJOR INORGANIC REACTANTS

Any discussion involving retort chemistry of organic compounds must necessarily involve mention of inorganic reactants. The major inorganic reactants are gaseous (H_2S, NH_3, CO_2, CO, and H_2) and will only be briefly discussed here. The inorganic solids either serve as sources of the gases or as catalysts for reactions of organic compounds.

Hydrogen sulfide has both organic and inorganic origins during retorting (Wong, Crawford, and Burnham 1984). The major inorganic source is from reaction of pyrite (FeS_2) with hydrogen, yielding pyrrhotite (FeS) and H_2S. Hydrogen sulfide is by far the major contributor to sulfur in retort offgases (e.g., Wong et al. 1984).

Retorting produces large quantities of ammonia, which is the most abundant form of inorganic-N in the offgases (e.g., Ondov et al. 1982). Ammonia concentrations in the process waters probably can exceed 25 g/L (Daughton, Sakaji, and Langlois in press). The origin of the ammonia is still unclear. Recently, evidence has been presented that major portions (e.g., one half) of the total nitrogen in raw shales can be contributed by inorganic sources, primarily ammonium-silicate mineral assemblages (e.g., ammonium feldspar, or buddingtonite) (Cooper and Evans 1983). This potential source appears to be unreactive, however, because at temperatures less than 500°C (under anoxic conditions), buddingtonite is stable (Taylor et al. 1985). It is therefore possible that the gaseous ammonia results from ultimate cracking of organonitrogen compounds (e.g., primary amines). Buddingtonite has been shown to be a possible source of nitric oxide (Taylor et al. 1985). The concentrations of NH_3 and H_2S are, of course, greatly increased during oil upgrading (hydrocracking). Ammonia is a major contributor to the alkalinity of process waters.

Other major reactants include carbon dioxide and carbon monoxide. These gases can evolve at both low and high temperatures (e.g., 150°C and >500°C) depending on the shale, indicating both organic and inorganic (carbonate) origins (Ekstrom, Hurst, and Randall 1983). Any CO_2 emitted during retorting, however, tends to dissolve in the process waters (if contact is made) because of their high pH (i.e., generally >8); inorganic carbon concentrations range from hundreds to thousands of milligrams per liter (Langlois et al. 1984). Hydrogen probably results from dehydrogenation of organic reactants. Finally, numerous metals and metalloids on exposed shale surfaces can act as catalysts (Regtop et al. 1985) and thereby promote cracking.

HYDROCARBONS

The hydrocarbons of oil shale processing comprise mainly alkanes, alkenes, alkylbenzenes, and polycyclic aromatic hydrocarbons (PAHs), in the respective order of abundance. The alkenes are susceptible to hydrogenation, giving the homologous alkane, and in the presence of a suitable catalytic surface, they can be hydrated to alkanols; acetylene is too reactive to remain, but it is partly responsible for formation (via polymerization) of other products (esp. PAHs). The lower relative abundance of aromatic compounds from oil shale processing, as compared with other fossil-fuel processing, is a direct reflection of the predominantly aliphatic nature of the polymeric, amorphous kerogen. Because of their low water solubilities (order of magnitude reduction for each additional ring; Maase 1980), PAHs would be almost exclusively associated with the oil and solid phases, including particulate and vapor emissions. The waters generally have only fractional ppm concentrations of alkanes and alkylbenzenes (e.g., Raphaelian and Harrison 1981; Dobson et al. 1985; Pellizzari et al. 1979). In retort water that has contacted the crude oil for long periods (e.g., Paraho), however, a series of normal and branched alkanes have been reported (C_{11}-C_{25}) (Gebhart and McKown 1980); this is probably a result of physico and biological emulsification.

Alkanes/Alkenes.

Solvent extracts of raw shales have shown a homologous series of C_{13}-C_{37} n-alkanes (Vitorovic and Saban 1983). The most abundant center around C_{21}. Odd carbon-numbered homologs predominate in the C_{25}-C_{37} range. The branched alkanes are mainly isoprenoids (esp. phytane and pristane) (Vitorovic and Saban 1983). Cyclic alkanes include polycyclic isoprenoids, mainly C_{27}-C_{29} steranes and terpanes. The branched alkanes (esp. 2-methylalkanes) are probably endogenous shale constituents (e.g., from biological waxes; Rovere et al. 1983). The alkylcyclopentanes and cyclohexanes are probably endogenous shale constituents from cyclization of unsaturated fatty acids during diagenesis (Rovere et al. 1983). In the process streams, therefore, these classes may origin from direct distillation of kerogen constituents.

From low-temperature pyrolysis, the largest class of aliphatics in crude shale oil are olefins (mainly 1-alkenes, esp. 1-pristene) and saturated n-alkanes (C_7-C_{35}), branched alkanes (esp. isoprenoidal) (Vitorovic and Saban 1983), and alicyclics (Harvey, Matheson, and Pratt 1984; DiSanzo, Uden, and Siggla 1979; Rovere et al. 1983), all of which occur in homologous series. Recently, a series of linear dienes were identified in shale oil (Rovere et al. 1983). The lower and higher alkanes probably originate from disproportionation of alkyl radicals generated by the thermal cracking of C-C bonds of the aliphatic chains of algal and plant hydrocarbons (respectively), which are the major constituents of the kerogen. Alkanes of less than C_{15} may result from catalytic cracking of longer-chain alkanes by shale-matrix minerals (Crisp et al. 1986; Regtop et al. 1985). The 1-alkenes could result from cleavage of the phytyl ester side-chain of the porphyrin, chlorophyll (Pereira et al. 1981); the pristanes and pristenes, however, probably come from another precursor (i.e., tocopheryl moieties) (Crisp et al. 1986). The major origin of the 1-alkenes, however, is from disproportionation (cracking) of alkyl radicals (Regtop et al. 1985).

Pyrolysis of alkanes in the presence of shale leads to various degrees of dehydrogenation and cyclodehydrogenation: alkenes and highly substituted alkylbenzenes ($<400^oC$) and less substituted alkylbenzenes and naphthalenes ($>400^oC$) (Regtop et al. 1985). With alkenes, similar products result, with the addition of isomerization and hydrogenation reactions (Regtop et al. 1985).

The aliphatics occur only in low concentrations in process waters (e.g., Raphaelian and Harrison 1981). They preferentially partition to the particulate phase. For example, major components of the particulate phase of Oxy-6 retort water are the higher alkanes; the alkenes are notably absent (Raphaelian and Harrison 1981), perhaps because of hydration of the unsaturated bond.

In retort offgases, C_1-C_{18} alkanes/alkenes, branched homologs, and mono-/di-unsaturates have been identified (Fruchter et al. 1982; Ondov et al. 1981; Rinaldi 1981; Sklarew et al. 1984). The alkanes (and cycloalkanes) and alkenes are the major and secondary organic constituents in offgas, respectively (Ondov et al. 1981). The distribution of the alkanes/alkenes in offgas seems to be bimodal; this may be a result of the sampling methods that were used. Methane, ethane, and propane predominate (Fruchter et al. 1982; Ondov et al. 1981; Rinaldi 1981), with the secondary abundance distributed around n-decane (i.e., nonane and undecane) and their homologous 1-alkenes (Ondov et al. 1981; Rinaldi 1981). For the light alkanes that would comprise offgas, comparison of Paraho (direct) and Tosco crudes showed that Tosco had the greatest proportion of C_7-C_{11} alkanes, probably because it had not been stored as long as Paraho. Tosco's most prevalent alkane was C_9, while Paraho's was C_{12} (DiSanzo et al. 1979); the lower alkanes had probably been lost to volatilization during storage of the Paraho sample. Retort offgas particulates (after venturi scrubbing) contain mainly higher alkanes ($C>15$) and cycloalkanes/alkenes (Rinaldi 1981).

In weathered retorted shale (Pereira et al. 1981), the following were found: C_{10}-C_{35} n-alkanes, C_{13}-C_{18}/C_{20}-C_{22} 1-alkenes, and isoprenoids (esp. pristane and phytane). The latter are probably from diagenesis of chlorophyll. The 1-alkenes have been proposed as tracers of shale-oil contamination of sediments/particulates (Riley et al. 1982). Branched and alicyclic aliphatics would be more susceptible to vaporization from particulates than the analogous alkanes (Eaganhouse et al. 1981). In Tosco II, Union, and Paraho retorted shales, C_{11}-C_{30} alkanes have been reported in benzene extracts (Maase 1980).

The alkanes are ubiquitous in the environment (e.g., Eaganhouse et al. 1981), but the 1-alkenes are unique (although unstable) products of retorting (e.g., Riley et al. 1982). The alkanes, and especially the alkenes, are of environmental significance as precursors to photochemical smog.

Alkylbenzenes (phenylalkanes).

Alkylbenzenes are associated predominantly with the oils, particulates (Rinaldi 1981), retorted shale (Maase 1980; Pereira et al. 1981), condensates, and offgases (C_1-C_4) (Fruchter et al. 1982; Ondov et al. 1982; Rinaldi et al. 1981; Sklarew et al. 1984). They probably result from pyrolysis of kerogenic carotenoids (Pereira et al. 1981) and from aromatization of alkenes (Regtop et al. 1985). The degree of alkylation is usually limited to three substituents; higher substitution is thermodynamically unstable (Linton and Turnbull 1984), probably leading to condensation (cyclization) to diaromatics and PAHs (Maase 1980). Another origin may be from alkylated biphenyls occurring in raw shale (Vitorovic and Saban 1983).

The oils contain a homologous series of n-alkylbenzenes (C_1-C_{28}) (DiSanzo et al. 1979; Harvey et al. 1984; Rovere et al. 1983) and their methyl and dimethyl derivatives (Rovere et al. 1983). Although lower-molecular-weight alkylbenzenes occur in retorted shale (e.g., Maase 1980), only the higher n-alkylbenzenes ($>C_{10}$) are found in weathered retorted shale (Pereira et al. 1981). The lower homologs probably volatilize.

In the offgas, xylenes are common (Ondov et al. 1982). The alkylbenzenes are secondary components of offgas, being present at concentrations similar to the alkenes; in offgas particulates (after venturi scrubbing), they are the third major component (Rinaldi 1981).

Although the relative concentrations of these compounds are low (sub-ppm) in most process waters (Dobson et al. 1985; Pellizzari et al. 1979; Raphaelian and Harrison 1981), they have been reported to be the major constituents of the static headspace of freshly collected process waters (Hawthorne and Sievers 1984). This means that they rapidly volatilize. These would be the major compounds in the headspace over nonexposed process waters such as in water reuse sumps. The high headspace concentrations of these compounds is because of high vapor pressures as opposed to high concentrations in the waters. The major species of organic compounds in static process-water headspace are benzene and toluene (Hawthorne and Sievers 1984). These data conflict, however, with another study which showed that most of the compounds in the static headspaces from a series of eight process waters were nitrogen-containing (Hunter, Persoff, and Daughton in press); these latter samples, however, had been stored for various numbers of years, probably leading to volatilization of the alkylbenzenes. Benzene, toluene, and all three xylene isomers were the most common benzenes in water from the LLL retort (Gebhart and McKown 1980) and Omega-9 (Pellizzari et al. 1979).

Linear alkylbenzenes occur in the environment from anthropogenic sources (e.g., sulfonate detergent manufacturing). Although these are easily metabolized by bacteria via omega-oxidation and successive beta-cleavage, eventually yielding benzoic acids, they can persist in anoxic environments (e.g., Eaganhouse, Blumfield, and Kaplan 1983). Similar persistence could be expected for certain ground waters.

Small amounts of biphenyl (phenylbenzene) and unidentified methyl derivatives have been reported in shale oil (Pelroy and Petersen 1979) and process water (Wildung et al. 1978).

Diaromatics (Naphthalenes) and Polycyclic Aromatic Hydrocarbons (PAHs).

Although alkylated diaromatics and certain polycyclic aromatic hydrocarbons (PAHs) are endogenous constituents of oil shale (Radke, Willsch, and Welte 1984; Vitorovic and Saban 1983), most probably result from condensation/polymerization of the acetylene and olefin radicals produced during pyrolysis of the kerogen (Pereira et al. 1981), particularly at higher temperatures (Wen et al. 1984). Molecular hydrogen serves to terminate radical condensation reactions by "capping"; this explains why conversion of aliphatics to aromatics is blocked by hydrogen (Burnham and Happe 1984). PAHs also result from ring cyclization of the respective, lower benzologs that have excessive alkylation. This explains the low degree of alkylation of the "steady-state" products, which are usually limited to methyl groups. These compounds are associated mainly with the oil, particulates, and retorted shale (Carpenter, Jr. 1978; Fruchter et al. 1982; Pereira et al. 1981).

PAHs in oil are generally secondary to the aliphatics and benzenes. They include diaromatics (e.g., C_1-C_6 1- and 2-substituted naphthalenes), fused-ring aromatics (e.g., phenanthrene and anthracene), nonbenzoidal hydroaromatics (e.g., indans, tetralins, fluorene, acenaphthenes), and alkyl polyaromatics (characterized by having only short side chains) (DiSanzo et al. 1979; Harvey et al. 1984; Robbins and Blum 1981; Rovere et al. 1983). Only recently has it been possible to identify some of the higher-molecular-weight PAHs (up to 10 rings); this was done for a solvent-refined coal liquid (Novotny, Hirose, and Wiesler 1984). In shale oil, however, the PAHs seem to mainly comprise fewer than five rings (Novotny, Hirose, and Wiesler 1984); this probably results from inhibition of condensation reactions because of the low degree of alkylation (Wilson, Lambert, and Collin 1984).

In process waters, the PAHs are probably associated mainly with particulates; over 80% of those present in coal gasification waters are associated with the filterable residue (Walters and Luthy 1984). In Omega-9 water, naphthalenes and acenaphthene were the only species identified (Pellizzari et al. 1979). The major reason for the low aqueous-phase concentrations is preferential sorption to the retorted shale. Numerous PAHs (up to at least 5-ring members) occur in the retorted shale (e.g., Maase 1980), phenanthrene being most common (ca. 100-200 ppb), and they can be the major form of organic carbon in retorted shale (e.g., Burnham and Happe 1984). Aqueous extracts of the retorted shale, however, yield dissolved concentrations less than 1% of maximum solubilities (Maase 1980). PAHs are resistant to biodegradation. The major mechanism for chemical transformation in shale-disposal piles would be photodegradation; this process is a function of the adsorbent surface (e.g., organic content and color) and can vary widely in effectiveness (Behymer and Hites 1985; Yokley et al. 1986).

Only small portions of PAHs partition to the vapor phase of offgases (Fruchter et al. 1982; Ondov et al. 1982); most are associated with the vapor-phase particulates. Alkyl indans and indenes are the major PAHs of offgas vapor phase (Ondov et al. 1982R51). PAHs will probably comprise a major portion of the carbonaceous residue that escapes incineration, however, especially that which is adsorbed to respirable particulates (Fruchter et al. 1982). This is partly a result of their further formation by low-temperature incineration, which is used to minimized creation of NO_x from nitrogen gas. PAHs identified in Rio Blanco Retort 0 offgas were mainly anthracene, pyrene, benzo(a)anthracene, and chrysene (in descending order) (Fruchter et al. 1982). Incinerated offgas, in comparison, comprised numerous PAHs, including acenaphthene, 9-methylanthracene, and benzo(e)pyrene (Fruchter et al. 1982). A significant feature of the distributions and concentrations of the PAHs in the offgas is that they vary wildly during retorting (Fruchter et al. 1982). This will make any monitoring attempts extremely difficult. It would perhaps be best to measure them as a class, without individual speciation. This approach could be used for all waste streams but the methodologies would be different for each.

In the atmosphere, as in the shale piles, phototransformations (direct and indirect) could be of significance. An important class of products that can be produced by the indirect mechanism (night-time reaction of nitrogen oxide radicals) is the nitroarenes (Pitts et al. 1985); these compounds, such as 1-nitropyrene, are extremely mutagenic. The formation of these compounds is known to be enhanced during stack sampling when NO_x is present (Brorstrom-Lunden and Lindskog 1985). This presents profound problems for characterization studies because of the inability to discern whether the nitro derivatives were created in situ or whether they are sampling artifacts (Brorstrom-Lunden and Lindskog 1985).

For many years, much attention has been focused on the mutagenicity of PAHs. Although these compounds are of unquestionable importance in this regard, it has recently been recognized that the functionalized PAHs may be much more important (e.g., Ho, Guerin, and Buchanan 1983). Of particular importance are the polycyclic aromatic ketones (PAKs), which are potential offgas constituents (see "PAKs"), and amino-substituted PAHs (see "Arylamines"); the latter have higher water solubilities than their PAH analogs. Hyroxylated PAHs are much more polar, and they are not particularly mutagenic; they are also less persistent in the environment since they are intermediates to dihydrodiols during biooxidation.

Hydroaromatics.

Hydrogenation of PAHs yields partially hydrogenated (nonbenzoidal or hydroaromatic) derivatives which are more volatile than the parent PAHs. This class (e.g., indans and tetralins) has not been well characterized until recently because of a lack of reference standards (Wozniak and Hites 1985a), but they are present in shale oils (e.g., Harvey et al. 1984). Hydrogenation can occur within the retort and is actively promoted during hydrocracking. This process is regioselective, being a function of catalyst type (Wozniak and Hites 1985a). In some direct-mode retorting processes, reductive and oxidative conditions can alternate for a particular molecule as it vaporizes and recondenses through the different zones. Severe hydrocracking yields lower, homologous-ring alkylated hydroaromatics, indicating loss of carbon in the form of lower alkanes; compounds with five-membered rings (indans) are most susceptible to ring opening (Wosniak and Hites 1985b), and cata-condensed PAHs (i.e., containing no "internal carbon") are more susceptible than peri-condensed PAHs (i.e., containing "internal carbon") (Wosziak and Hites 1985b). The diaromatics are more easily hydrogenated and cracked than the PAHs (Green et al. 1985), yielding alkylbenzenes; the latter are relatively resistant to further hydrogenation and therefore are enriched in the product oil (Green et al. 1985). The chemistry of hydroaromatics with respect to coal-derived synfuels has been discussed (Wosniak and Hites 1985b). Analogous chemistry undoubtedly occurs in retorting, but it has not been investigated thoroughly because the aromatics comprise a smaller (less important) portion of hydrocarbons in crude shale oil.

HYDROXYLATED DERIVATIVES

Alkanols (aliphatic alcohols).

Although alkanols are probably produced in significant amounts during retorting (cp. Fischer-Tropsch Synthesis), they have been reported only in low concentrations (with the exception of 2-propanol). Because of their volatility, they occur mainly in gas condensate (Leenheer et al. 1982). Relatively high concentrations of methanol were reported from some of the time-course aqueous samples from the LLL retort (Gebhart and McKown 1980). If present, they are only trace constituents of volatile emissions from retort water and gas condensate (Hawthorne and Sievers 1984, 1985).

Alkanols probably result from surface-catalyzed hydration of alkenes. For the most part, the alkanols are probably consumed in secondary reactions involving their alkoxide ions. For example, hemiacetals (1-alkoxy alkanols) (PUCs) are formed by their reaction with aldehydes. Pyrolysis of alkanols in the presence of retorted shale yields alkanes, alkenes, and 2-alkanones (Regtop et al. 1985). Kerogen pyrolysis and subsequent alkaline hydrolysis of entrapped glycerides would release the corresponding polyhydric alcohols (PUC), together with fatty acids; for example, triglycerides would yield glycerol. These are high-boiling and very polar compounds, which means that they would be expected only in retort waters.

Hydroxybenzenes (phenols and naphthols).

There are numerous alkyl derivatives of mono- and poly-hydroxylated benzenes. There are also numerous terminologies used for their categorization, including nondescriptive common names (see Table I). As a class, the monoaromatic derivatives are referred to as phenols and the diaromatic derivatives are termed naphthols. Phenols are endogenous constituents of oil shale, probably in the form of lignins and tannins. The lower abundance of these materials in kerogen, compared with coal, explains the much lower abundance of phenols in oil shale process streams; this is a major distinguishing feature of shale and coal products. Some of the hydroxybenzenes, however, probably result from direct oxidation of the alkylbenzenes (e.g., phenol from toluene; cresols from xylenes); benzene could not serve as a precursor for phenol, because the oxidative conditions would necessarily be sufficiently stringent to destroy any resulting phenol. Another origin is from cyclodehydrogenation of 2-alkenols and 2-alkenones, whose pyrolysis yield C_0-C_2 phenols (Regtop et al. 1985). Still another origin is from cracking of aromatic cyclic ethers, such as benzofurans (Green et al. 1985). Mono- and dihydroxybenzenes are known to undergo complex polymerization reactions (Green et al. 1985). The darkening of coal-gasification condensate waters upon exposure to oxygen is probably a result of these reactions (Mohr 1983). For oil shale process waters, these processes are probably secondary to those involving N-heterocycles in developing the brownish colorations. For coal-gasification waters, polymerization can be minimized by collecting samples under inert gas and by acidifying the sample. For retort waters, however, acidification could cause pyrrolic polymers to form.

The major fate of alkylated phenols during pyrolysis is dealkylation, eventually to phenol itself. Phenols can also react with formaldehyde in the presence of base to give 2-hydroxymethylphenols (PUC), which can polymerize (e.g., Baekeland Process). Various cyclic and linear oligomers are known products (Ludwig and Bailie, Jr. 1984). They also react with carbon dioxide in base to give 4-hydroxyaromatic acids (PUC) (Kolbe-Schmitt). Phenol also reacts with arsenic acid to give 4-hydroxyphenylarsonic acid (Bechamp Reaction). Although phenylarsonic acid has been identified in retort waters, its origin was not hypothesized (Fish, Brinckman, and Jewett 1982), and it may result from similar reactions.

In the crude oil, hydroxybenzenes exist in the acidic-polar fraction. They are primarily unsubstituted phenol and alkylphenolic homologs ($<C_7$), especially 2,4-dimethyl-, 2-methyl-, 4-methyl-, 2-methyl-4-ethyl-, and 2,3,5-trimethylphenol (Bett et al. 1983; Gallegos 1984; Uden et al. 1979; Van Meter et al. 1952). Indanols ($<C_3$) (Bett et al. 1983) and naphthols ($<C_2$) have also been identified in shale oil; they comprised less than 7% of the total phenol concentration (Bett et al. 1983). Phenol and 2-hydroxytoluene have been reported at over 300 ppm each in a 150-Ton shale oil (Hertz et al. 1980). 2-Hydroxytoluene was the primary phenolic reported in the acidic fraction of NTU-retorted Green River shale (Van Meter et al. 1952). The 2-alkyl phenols (o-cresols) predominate probably because they are the most resistant to dehydroxylation via hydrogenation (Green et al. 1985); this is because of hindrance by the alkyl group.

Phenols that have been identified in the process waters are primarily unsubstituted phenol and the cresols (primarily 3- and 4-hydroxy derivatives since these have higher solubilities than the 2-hydroxy cresols) (Bell, Greenfield, and Nicklin 1983; Gebhart and McKnown 1980; Hawthorne and Sievers 1984; Ho, Clark, and Guerin 1976; Leenheer et al. 1982; Pellizzari et al. 1979). Dimethylhydroxybenzenes (xylenols) have also been reported (Leenheer et al. 1982), especially in headspace samples (Hawthorne and Sievers 1984). In general, the phenols would be expected to occur in the process waters at much higher concentrations than the alkylbenzenes because of their higher water solubilities. They would also not partition to particulates in the process waters because they would be ionized under these alkaline conditions. Their ionization would also prevent their effective removal from process waters by steam stripping (e.g., Conditt 1984). Their preponderance in gas condensates is probably a result not just of distillation of the small fraction of neutral forms, but also a result of de novo synthesis from volatile precursors (e.g., alkylbenzenes, 2-alkanones). They become major constituents of gas condensates and process-water headspace (Hawthorne and Sievers 1984; Leenheer et al. 1982; Pellizzari et al. 1979). Hydroxybenzenes are probably major contributors to the odor of retort gas condensates, but much less of a factor for retort waters, whose odors are predominated by alkylpyridines.

In the atmosphere, hydroxybenzenes would be expected to partition almost exclusively to the gas phase (because of high vapor pressures) and to be easily scavenged by precipitation (because of low Henry's Law constants) (Leuenberger, Ligocki, and Pankow 1985).

Phenols are generally not constituents of retorted shales (e.g., Carpenter, Jr. 1978). In retorted shale codisposed with process waters (esp. untreated waters), phenols would be expected to readily volatilize or leach. They could therefore be expected in ground- or surface-waters (e.g., Stuermer, Ng, and Morris 1982); most of them are easily biodegraded, however.

CARBONYL DERIVATIVES

The carbonyl compounds are probably responsible for driving many of the secondary reactions that occur during retorting. Many of these reactions involve enolate anions. Although the origins of many of these compounds are from unique, endogenous kerogen constituents, all of the lower simple carbonyl compounds can be produced by oxidation of hydroxylated compounds such as phenols (e.g., Conditt and Sievers 1984).

Aldehydes.

alkanals (acyclic). Aliphatic aldehydes are probably major direct products of pyrolysis (cp. Fischer-Tropsch Synthesis). Acetaldehyde (ethanal) probably derives from addition of water to acetylene through an unstable alkenal intermediate. Because of their reactivity (esp. formaldehyde and acetaldehyde), however, they are also probably the key constituents that initiate and participate in many of the numerous secondary reactions during and after retorting. Few would long survive the alkaline thermal conditions of shale retorting, especially in the presence of so many other reactive species. Indeed, this has been demonstrated by documenting the rapid consumption of formaldehyde when added to Oxy-6 process waters at ambient temperature (Leenheer et al. 1982). Aldehyde-amine reactions are major aspects of retort chemistry, especially in the formation of N-heterocycles (Sprung 1940). These reactions (aldol-like condensations) will be discussed later. Some of the reactions that involve only aldehydes are discussed here.

Aldehydes that lack a hydrogen at the 2-position (such as formaldehyde) undergo self-oxidation/reduction in the presence of base and heat to yield the homologous alcohol and acid (Cannizzaro Reaction). Formaldehyde could react with methanol to give heat-labile oligomers of poly(oxymethylene)glycols (PUCs) and their methyl ethers (Utterback, Millington, and Gold 1984). Aldol condensations (additions involving the carbonyl double bond) would be major reaction pathways. Aldehydes can condense in the presence of base to give aldols (3-hydroxycarbonyls). For example, 2 molecules of acetaldehyde condense to give 3-hydroxybutanal (PUC); unlike aldehydes can also condense to give higher aldols (PUC) (Crossed Aldol Condensation). The aldols can be dehydrated to give 2-alkenals. Other important aldol condensations yield 1,5-diones, which can dehydrate to give pyrans (PUC).

Other key reactions undoubtedly involve ammonia, especially since it is present at high concentrations. Adducts (inclusion complexes: unbonded, associated molecules) of aldehyde-ammonia (PUCs) form readily (Sprung 1940); for example, acetaldehyde-ammonia (1-aminoethanol) (PUC) would result from acetaldehyde. These adducts would subsequently revert or dehydrate and polymerize because of their instability. Formaldehyde and ammonia, however, form hexamethylenetetramine (methenamine) (PUC) (Sprung 1940), a very water-soluble, nonvolatile tricyclic triazine. Although never reported, alpha-amino acids (PUC) are possible constituents of the process waters. These could be produced from the reaction of hydrogen cyanide and ammonia with aldehydes (Strecker Amino Acid Synthesis).

The high chemical reactivity of aldehydes overall, and not their absence, is probably the major reason for their reported low occurrence in process waters (e.g., Hawthorne and Sievers 1984, 1985; Pellizzari et al. 1979); instead, they are important transient intermediates of secondary reactions during retorting. Recently, however, high concentrations of formaldehyde, among other aldehydes, were reported in a 150-Ton retort water (Richard and Junk 1984).

Some of the reactions involving aldehydes with other chemical classes are listed here and are discussed further under the relevant chemical class.

- polymerization of phenols (Baekeland Process)
- polymerization of pyrroles (Rothemund Reaction)
- decarboxylation of picolinic acids (Hammick Reaction)
- N-methylation of primary/secondary amines (Eschweiler-Clarke Reaction)
- N-alkylation of anilines (Eschweiler-Clarke Reaction)
- formation of alkyl pyridines, quinolines, and pyrroles (Chichibabin [Tschitschibabin] and Hantzsch Pyridine Syntheses, Paal-Knorr Pyrrole Synthesis)
- formation of nitriles
- formation of pyridylstilbazoles
- formation of hydroxymethylpyridines
- formation of 3-alkylaminoindoles (Mannich reaction)

aromatic aldehydes. Benzaldehyde would derive from oxidation of alkylmethylbenzenes. Exposure to air, however, would result in further oxidation to the benzoic acid derivative. This may be why aromatic aldehydes are not usually identified in retort waters. In general, however, benzaldehydes are less reactive than the alkanals.

Aromatic aldehydes can condense with aliphatic aldehydes in the presence of base to give 1,2-unsaturated aldehydes (Claisen-Schmidt Condensation). For example, benzaldehyde condenses with acetaldehyde to give 3-phenyl-2-propenal (cinnamaldehyde) (PUC). Aromatic aldehydes can also react with aqueous ammonia to give hydrobenzamides (PUC) (Sprung 1940); when heated, these in turn can cyclize to various imidazoles (PUCs). Although reported in some retort waters, benzaldehyde in the aqueous phase would primarily undergo base-catalyzed dismutation to benzoate and benzylalcohol (Cannizzaro Reaction). Despite these possible reactions, benzaldehydes were the only aldehydes detected in ground water from a coal-gasification facility (Stuermer et al. 1982); this indicates the potential for their persistence.

In the troposphere, under the action of sunlight, benzaldehyde is a direct precursor of peroxybenzoyl nitrate, a very powerful eye irritant.

Ketones.

Some of the simple alkanones are probably direct products of pyrolysis (cp. Fischer-Tropsch Synthesis); some may derive from addition of water to alkynes. They are generally not as reactive as aldehydes, but they too are probably major constituents that initiate and participate in many of the numerous secondary reactions. Among the alkanones in process waters, methyl ketones (2-alkanones) occur most frequently, indicating that they may derive directly from the kerogen, where they had been incorporated as esters after beta-oxidation of alkanoic acids, followed by decarboxylation (Pereira et al. 1981). The unsaturated 2-alkenones are highly stable and are probably diagenesis moieties of kerogen. In solvent extracts of raw shale, C_{13}-C_{14} alkyl methyl ketones have been identified, along with isoprenoid ketones (Vitorovic and Saban 1983). 2-Alkanones are also major products from pyrolysis of carboxylic acids (Regtop et al. 1985). Some relevant reactions in which ketones are the major reactants are discussed below.

alkanones (acyclic). Aliphatic ketones are known to react sequentially with ammonia, cyanides, and carbon dioxide to give the multiheteroaromatic hydantoins (PUC) (Bucherer-Bergs) (Diehl, Olson, and Worman 1985). These compounds (in particular 5,5'-dimethylhydantoin, which would result from acetone) have been identified as major polar constituents of coal-gasification wastes (Giabbai et al. 1985; Mohr and King 1985; Olson, Diehl, and Miller 1983), and their presence seems probable for oil shale process streams; amino nitriles (PUCs) are intermediates in this process. 1,4-Diketones when heated under pressure, with ammonia or primary amines, form 2,5-dialkylpyrroles (Paal-Knorr Pyrrole Synthesis). The unsaturates (e.g., methylvinylketone) are particularly reactive. Methyl ketones can undergo oxidation in base because of the unsaturated nature of the enol tautomer. Ketones also could be involved in the formation of pyridylcarbinols (PUC) (Emmert Reaction).

2-Methyl ketones (C_7-C_{31}) have been identified in the neutral-polar fraction of shale oil (Harvey et al. 1984; Rovere et al. 1983; Uden et al. 1979). The odd carbon-number homologs predominate over the nearest even-carbon-number homologs, corroborating that they result from endogenous 2-keto acids in the raw shale (Rovere et al. 1983). A series of 3-alkanones is also present, but at much lower concentrations (Rovere et al. 1983). Acetone and 2-butanone are major constituents of the headspace of both retort waters and gas condensates (Day and Rawlings 1981; Gebhart and McKnown 1980; Hawthorne and Sievers

1984; Pellizzari et al. 1979), but they comprise only a small fraction of the compounds that can be volatilized when the headspace is continually purged.

cycloalkanones. The cyclic pentanones, pentenones, hexanones, and hexenones have been identified in several different waters (Bell et al. 1983; Dobson et al. 1985; Fox et al. 1984; Gebhart and McKown 1980; Hawthorne and Sievers 1979; Pellizzari et al. 1979); concentrations have ranged up to 100 ppm (Dobson et al. 1985; Gebhart and McKown 1980). The abundance of cyclic ketones in the process waters is always less than the carboxylic acids and generally greater than the N-heterocycles. The alicyclics probably result from the cyclization/decarboxylation of C_6 and C_7 dicarboxylic acids by heating (Blanc Reaction; Ruzicka Large-Ring Synthesis). This is possibly corroborated by the high concentrations of cycloalkanones in coal gasification waters (Chong and McKay 1984), which have correspondingly low dicarboxylic acid concentrations. Alkylated derivatives would result from branched dicarboxylic acids; 3-methylcyclopentanone is prevalent in a LLL retort water (Gebhart and McKown 1980). Because of the reduced steric hindrance at the carbonyl carbon, the unsubstituted cyclic ketones are more reactive than their alkylated derivatives. Cyclopentanone is not stable; it can easily polymerize. In spite of this, concentrations as high as 50 ppm have been reported in retort water (Dobson et al. 1985). These compounds are volatile and are major constituents of gas condensates (Fox et al. 1984). Cycloheptanone (PUC) would result from octanedioic acid; it has been tentatively identified in a Rundle-shale retort water (Bell et al. 1983). Since it is not soluble in water, it would partition to the oil. The corresponding cyclopentenones and hexenones that have been reported could perhaps come from dehydrogenation of the saturates, but another route is that they form from the aldol condensation of diketones. Alternatively, they may result from cyclic aldol condensation of diketones with subsequent dehydration to the enone form. Other cyclic ketones can be formed by the condensation of cyclopentanones or cyclohexanones with vinyl ketones (Robinson Annelation Reaction).

In shale oil, cyclopentanone and cyclohexanone with substituents ortho to the carbonyl reside in the neutral-polar fraction (Uden et al. 1979). The unsaturated analogs have also been found in shale oil (Harvey et al. 1984). Small amounts of phenylketones have also been found (Harvey et al. 1984; Uden et al. 1979).

Cyclic ketones could be especially important with regard to air quality because their photochemical alteration easily yields radicals, which are precursors to photochemical smog.

polycyclic aromatic ketones (PAKs). Polycyclic aromatic hydrocarbons that contain a ring(s) with a singly bonded carbon are subject to rapid oxidation during combustion at this methylene carbon ($-CH_2-$), giving polycyclic aromatic ketones (PAKs) (Ramdahl 1983). Oxidation of 6-membered hydro rings gives highly unstable PAKs that have not been isolated in the environment; those containing 5-membered rings (e.g., 9<u>H</u>-fluoren-1-one) have been isolated because of greater stability (Ramdahl 1983). PAKs could occur in combusted retort offgases (PUCs). Their contribution to mutagenic activity of the neutral fraction of shale oil could be substantial (Ramdahl 1983; Wilson et al. 1983). PAKs subjected to the reductive retort atmosphere would be reduced to their hydro-derivatives (Wozniak and Hites 1985a). Little is known about the occurrence of PAKs in oil shale process streams.

Carboxylic Acids

Carboxylate salts in Green River oil shale have been studied extensively (e.g., Burlingame and Simoneit 1968, 1969; Chong and McKay 1984). Perhaps up to 40% of the oxygen in Green River oil shale kerogen is present as carboxyl groups, and the associated compounds may comprise at least 3.5% of the total organic matter (Chong and McKay 1984). These compounds are primarily aliphatic (normal and branched) alkanoic and alkanedioc acid salts, but aromatic acid salts are also present (Chong and McKay 1984). Many of these compounds exist in their free forms in the kerogen/inorganic shale matrix and are extracted by process liquids (i.e., water and perhaps oil) during retorting. These are the major organic constituents of retort waters.

alkanoic (monocarboxylic) and lactones. Some of the aliphatic monocarboxylic acids in the process streams probably result from mild pyrolysis of endogenous constituents of the parent kerogen (e.g., Chong and McKay 1984; Fish, Newton, and Babbitt 1982), incorporated as triglycerides and sitosterol esters from algal/plant material. Most result from direct extraction of unaltered acids entrapped in the kerogen in their free forms (Chong and McKay 1984; Vitorovic and Saban 1983). These would probably be associated with sodium (Chong and McKay 1984) or ammonium ions (e.g., buddingtonite). Solvent extracts of raw Green River shale have yielded C_{11}-C_{34} *n*-alkanoic acids (Chong and McKay 1984; Vitorovic and Saban 1983), with an even-odd carbon-number predominance. In these solvent extracts, the carboxylates were present almost exclusively as their sodium salts (with minor amounts of silicon and aluminum). These alkanoic acids represented over 50% of the total acids that could be made volatile by methylation and chromatographed (Chong and McKay 1984). Branched alkanoics composed 13% of the volatile acids; these were isoprenoid (C_{15}-C_{22} and nonisoprenoid (C_{14}-C_{19}). Many of the higher fatty acid homologs (e.g., >C_{16}) probably undergo thermolysis during retorting to yield the lower homologs.

In oil shale process waters, these acids would all be present as their nonvolatile anions (free carboxylate salts) because the process streams are always alkaline. Even though they seem to be conspicuously absent from reductive-retorted oils (e.g., Tosco II) (Carpenter, Jr. 1978; Uden et al. 1979), their presence has been repeatedly noted in oils (concentrations being less than for the phenols; e.g., Van Meter et al. 1952). It is surprising that the higher homologs are not found more frequently and in higher concentrations in the oils; this may be a result of the oil/water separation processes, where these amphiphatic compounds would be concentrated at the interface of the two phases and therefore difficult to isolate. In retort processes that use combustion, another origin of these acids would be the oxidation of alkanes during retorting.

The homologous series of branched and olefinic acids also probably occur together with the alkanoic acids, but at lower concentrations (Dobson et al. 1985). The acids are found only in small concentrations in gas condensate waters (e.g., Day and Rawlings 1981; Hawthorne and Sievers 1985; Leenheer et al. 1982; Wingender et al. 1981) because they exist in their nonvolatile ionized forms. It is important to recognize, however, that contact of the retort waters with hot containment-vessel surfaces could result in protonation of the acids and their subsequent volatilization. This has been demonstrated by the contact of retort water with hot glass, where the emission of high levels of short-chain fatty acids was shown (Hawthorne and Sievers 1985). Therefore, although the very large concentrations of alkanoic acids would present no malodor problem at a retort facility, the potential for this problem should be recognized. Aliphatic (C_1-C_{10}) acids are ambient constituents of the atmospheric vapor phase (Kawamure, Ng, and Kaplan 1985), originating from fuel combustion, biogenic emissions, and photooxidation of aldehydes.

In the retort waters or even within the shale, a portion of these acids probably react with ammonia to give aliphatic amides, which subsequently dehydrate to yield the analogous aliphatic nitriles; nitriles are major trace-organonitrogen species in both the product waters and in the offgases and can be major constituents of the oils (discussed under "Cyanides"). Evidence for this was recently obtained from the pyrolysis of decanoic acid in the presence of shale minerals and ammonia (Regtop et al. 1985). All of these reactions would be reversible in the heated, alkaline atmosphere of the retort; the amides would be favored in a reducing atmosphere (e.g., Tosco II, Union B) and the carboxylic acids favored in an oxidizing atmosphere (e.g., Paraho direct). This would account for the absence of alkanoic acids in Tosco II retorted shale and their presence in Paraho shale (Pereira and Rostad 1983); these acids have been quantified, however, as major components of other samples of Tosco retorted shale (Wapensky 1976). An alternative nitrile synthesis from carboxylic acids is from potassium thiocyanate (Letts Nitrile Synthesis); this reaction yields cyanate and sulfide as by-products. Monocarboxylic acids are also known to pyrolyze to acyl and alkyl radicals, which couple to give long-chain ketones. The latter undergoes beta-homolysis (preferred because of resonance stabilization) to give 2-methyl ketones (Regtop et al. 1985).

For the process waters, alkanoic acids were first identified in Tosco II retort water (Cook 1971). They comprise a major portion of the DOC of retort waters from reductive and combustive processes (12%-42%) (Dobson et al. 1985; Leenheer et al. 1982; Richard and Junk 1984; Rogers et al. 1981) and nearly all of the acid fraction of some waters (Cook 1971; Dobson et al. 1985; Ho et al. 1976; Torpy, Luthy, and Raphaelian 1982). They are the major constituents of retort waters and the major constituents of the acid fraction of retort waters (Bell et al. 1983; Fish, Newton, and Babbitt 1982; Leenheer et al. 182). These are among the most commonly identified components in characterization studies. Because of the isolation schemes that are used, however, the lower homologs are often lost. From the numerous studies that have been completed, the aliphatic series (C_1-C_{14}) seems to have a bimodal distribution. The most prevalent seem to be the C_1-C_3 followed by the C_7-C_9 (Bell et al. 1983; Cook 1971; Day and Rawlings 1981; Dobson et al. 1985; Fish, Newton, and Babbitt 1982; Ho et al. 1976; Raphaelian and Harrison 1981; Richard and Junk 1984; Riley et al. 1979; Rogers et al. 1981); of these, the most prevalent are ethanoic and heptanoic/octanoic, respectively. The only exception to this distribution seems to be for some of the time-course retort-water samples from the LLL retort, where nonanoic (C_9) followed by decanoic (C_{10}) were most prevalent (Gebhart and McKown 1980); these were mainly generated during the earlier parts of the run. Nonanoic acid was also the most prevalent in Omega-9 retort water (Pellizzari et al. 1979).

Although alkanoic acids are readily metabolized by many bacteria (i.e., via beta-oxidation or methanogenesis), the higher homologs ($>C_7$) have proved to be more resistant to activated sludge in a study of tar-sands wastewater (Torpy, Raphaelian, and Luthy 1981). These compounds should pose no problem to treatment systems, however. Use of untreated retort waters for shale codisposal, however, could impose high oxygen demands (or cause the production of much methane) in surface/ground waters or in shale piles.

The amphiphatic character (i.e., containing both highly polar and nonpolar ends; detergent-like) of alkanoic acids is probably responsible for increasing the concentrations of many oil-soluble components in the retort waters. Also because of this property, these compounds can create micelles and cause emulsification and foaming problems during solvent extraction or gas purging.

The n-alkanoic (C_9-C_{32}), isoprenoid, and unsaturated acids are the major constituents (after aliphatic hydrocarbons) that have been identified in weathered, combusted retorted shales (Pereira et al. 1981; Wapensky 1976). These probably remain from incomplete extraction by the process liquids during retorting.

Polyfunctional monocarboxylic acids may be major constituents of the endogenous acid fraction of raw shale. For example, in a study of methylated carboxylic acids from Green River shale, up to 45% of the compounds that were extracted were insufficiently volatile to chromatograph (Chong and McKay 1984). These probably were hydroxy- or keto-substituted acids, although evidence was presented that some were pyridyl and thiophenic aliphatic acids. The 2,3-unsaturated acids (e.g., acrylic [2-propenoic] acid) undergo hydration to yield the 3-hydroxyalkanoic acids. These hydroxy acids (PUC), among many others, are probably major constituents of the process waters, even though heat can drive the reaction back to the olefinic acids; in retorted shale, 3-hydroxyalkanoic acids have been identified (Wapensky 1976). Alternatively, heating of 4- and 5-hydroxy acids causes internal esterification to yield the 5- and 6-membered lactones, respectively. Recently, raw shale was shown to contain delta-lactones and C_6-C_{16} and alicyclic gamma-lactones (Vitorovic and Saban 1983); these are presumably of biolipid origin, but they may also result from diagenesis of hydroxyalkanoic acids in the shale. Heating of the 2-hydroxyacids causes bimolecular esterification to give lactide. Lactones can also result from internal addition of the carbonyl group to the double bond of alkenoic acids. The lactones and lactides should be ephemeral products because they readily hydrolyze back to the hydroxy acids, especially in hot alkaline water. In spite of this, both butyro- and valerolactones have been identified in Oxy-6 process waters (Leenheer et al. 1982).

alkanedioc (dicarboxylic). Solvent extracts of raw shale have shown the presence of C_{11}-C_{29} n-alkanedioc acids, present as free salts (Chong and McKay 1984; Vitorovic and Saban 1983). These are all terminal (alpha, omega) dicarboxylic acids and are probably extracted from the shale as their salts by contact with the process water during retorting. Of the acids that are extractable from Green River oil shale and methylated for chromatography, 20% are alkanediocs (Chong and McKay 1984). In direct-heated retorts, many of the dicarboxylic acids are also probably secondary products from retorting (i.e., oxidation of monocarboxylic acids). Because of their higher water solubilities than the monocarboxylic acid analogs, higher homologs are found in the product waters.

By way of the Blanc Reaction (or Ruzicka Large-Ring Synthesis), some of these acids probably cyclize to give the aliphatic cyclic ketones. In particular, because of minimized ring strain, hexanedioc acid (adipic) and heptanedioc acid (pimelic) upon heating yield cyclopentanone and cyclohexanones, respectively; this was recently corroborated by the pyrolysis of heptanedioc acid in the presence of shale minerals to yield cyclohexanone (Regtop et al. 1985). These are the two major cyclic ketones reported in the process waters (Hawthorne and Sievers 1984). This also explains why the concentrations of these two diacids are usually reported as low relative to the others in the homologous series that have been identified (Fish, Newton, and Babbitt 1982; Riley et al. 1979, 1981; Rogers et al. 1981). Butanedioic (succinic acid) and pentanedioic (glutaric acid) would form strained rings. These instead give 5- and 6-membered cyclic anhydrides. In retort water, however, succinic anhydride would probably react with ammonia, and, when heated, form the cyclic imide, succinimide (PUC); evidence does exist for the presence of this compound in retort water (Yen 1981). The lower diacid homologs, propanedioc (malonic acid) and ethanedioic (oxalic acid) are simply decarboxylated upon heating to yield acetic and formic acids, respectively.

Succinic acid in base can react with sulfides to give thiophene (Volhard-Erdmann Cyclization); 2-, or 3-branched succinates would yield 3- and 4-alkylthiophenes. In an analogous manner, succinate when heated with ammonia can give pyrrole (Paal-Knorr Pyrrole Synthesis).

The dicarboxylic acids generally occur in much lower concentrations than the monocarboxylic acids in the process waters (e.g., Fish, Newton, and Babbitt 1982). This is a direct reflection of their relative abundance in the raw shale (Chong and McKay 1984). They are also lost during retorting because of cracking, yielding lower alkanoic acids. As salts, they are not volatile enough to partition to the gas condensate (Leenheer et al. 1982). In retort waters from direct-combustion retort processes (e.g., Paraho), large concentrations of alkanedioc acids have been reported (Dobson et al. 1985; Riley et al. 1979; Rogers et al. 1981). This could reflect their synthesis from more thorough oxidation of the kerogen or of the fatty acids, or alternatively, it could reflect a lower incidence of cracking. Like the mono acids, the dicarboxylic acids have a bimodal distribution. This distribution, however, seems to be shifted to favor the higher homologs (C_4-C_5 and C_9-C_{11}) (Dobson et al. 1985; Leenheer et al. 1982; Riley et al. 1979). The most common are perhaps pentanedioc and octanedioc. Hexanedioc and heptanedioc are at conspicuously lower concentrations (Dobson et al. 1985; Fish, Newton, and Babbitt 1982; Rogers et al. 1981; Leenheer et al. 1982) probably because of alicyclic ketone formation. The shift in the abundance distribution for the mono and diacids implies that the dicarboxylics are thermally decarboxylated (cracked) to yield successively lower monocarboxylic homologs. This would explain the lower concentration of alkanedioc acids in reductive retorting processes. Dicarboxylic acids are prevalent, however, in retorted shale from the Tosco II process (Wapensky 1976).

aromatic (benzoic acids). Solvent extracts of raw shale have shown the presence of numerous aromatic acids, including mono-, di-, and tricarboxylic benzoic acids with hydroxy, methoxy, and methyl substituents (Vitorovic and Saban 1983); naphthoic acids also occur (Chong and McKay 1984). Like the aliphatic acids, these are extracted from the shale during retorting. In process streams from direct-mode retorts, the alkylbenzoic acid homologs could also result from direct oxidation of one or more side chains of the alkylbenzenes. Benzoic acid, for example, would come from toluene, and the toluic acids from the xylenes. Despite their water solubilities, these acids are most prevalent in retorted shales, where they can be major organic constituents (Wapenskyy 1976). In spent-shale leachate, benzoic acid was the most prevalent acid from Paraho retorted shale, while 3,5-dimethylbenzoic acid was the major species from Tosco II retorted shale (Pereira and Rostad 1983); naphthoic acids were also observed in the Tosco shale. Benzoic acid can be present in concentrations similar to the alkanedioc acids in retort waters (e.g., Fish, Newton, and Babbitt 1982; Rogers et al. 1981) The benzene dicarboxylic acids (i.e., phthalic acids) have been reported only in low concentrations in retort waters. These benzene poly acids occur in the raw shale, but they probably undergo decarboxylation during retorting.

Esters.

Esters have not been definitively established as endogenous constituents of oil shale, although evidence exists. Methyl esters of C_4-C_{25} alkanoic acids have been reported in certain shales (Vitorovic and Saban 1983), but their origin is unknown. Fatty-acid esters such as triglycerides would be likely origins. Phthalic acid esters (ubiquitous anthropogenic environmental pollutants) have been tentatively identified in Tosco II retorted shale (Carpenter, Jr. 1978); sample contamination was ruled out, however, implying that they originated from the shale. In general, esters would be thermally labile during retorting, especially under the alkaline conditions. Hydrolysis to the corresponding acids and alcohols would occur.

Amides.

aliphatic amides. Aliphatic amides (acylamines) are functional derivatives of alkanoic acids and probably result from the reaction of alkanoic acids and ammonia or primary amines. This has recently been demonstrated for ammonia (Regtop et al. 1985), which yields primary acylamines. Reaction of alkanoic acids with alkyl amines would yield secondary (N-alkyl) and tertiary (N,N-dialkyl) acylamines; these have not been reported in any process stream. Reaction with ammonia would be preferred because of its higher concentration than alkyl amines. An alternative route to acyl amines would be gas-phase reaction of ketene (ethenone, CH_2CO; from thermal disproportionation of acetyl radicals generated from 2-alkanones) with ammonia or primary amines. Hydrolysis of amides in base to return the acid is slow, but their dehydration to yield nitriles is probably significant. The formation of nitriles is probably the major reason that nitriles and amides are often reported in oils in widely different relative abundances (cp. Harvey et al. 1984; Rovere et al. 1983 with Holmes and Thompson 1981).

Because of their nonvolatile/polar nature, they have been identified only in low concentrations in gas condensates or in the headspace from process waters (Hawthorne and Sievers 1984; Leenheer et al. 1982). Large concentrations probably exist in the retort waters, if they have not undergone further reaction. Alkyl (C_1-C_4) amides (esp. acetamide) have been identified in Oxy-6 retort water (Leenheer et al. 1982) and 150-Ton retort water (Ho et al. 1976). Their transient occurrence is also inferred when aliphatic nitrile concentrations are high (e.g., Rovere et al. 1983). Amides probably serve as intermediates in numerous other reactions other than nitrile formation. For example, heating of formamide and ammonia can yield purine (PUC) (Newcome and Paudler 1982). Alkyl(benzyl)carboxamides (PUC) are major polar substituents in crude shale oils (Holmes and Thompson 1981; Shue and Yen 1981) and possible occur in the process waters.

lactams. The other major form of aliphatic amides reported in the process waters are cyclic amides, or cyclized amino acids (lactams) (e.g., Torpy et al. 1982), especially delta-valerolactam (2-piperidone) and gamma-butyrolactam (2-pyrrolidone). Various alkyl and N-methyl derivatives have also been reported (Bell et al. 1983; Dobson et al. 1985). Cyclization/dehydration of gamma- and delta-amino acids (PUCs) is possibly the major source of these 2-substituted, fully reduced N-heterocycles. Cyclic amides have also been reported in hydrotreated shale oil (Green et al. 1985); the mechanism of formation is unknown, but oxygen is not required. The 3- and 4-isomers (alicyclic amino ketones) would result from hydrogenation of the respective oxo pyridines and pyrroles. The latter route via hydrogenation is probably minor, however, since only the saturated 2-oxo forms (lactams) have been found (e.g., Fox et al. 1984; Bell et al. 1983; Dobson et al. 1985). In fact, the major base reported in Fischer-retorted Rundle shale was 1-methyl-2-pyrrolidone (Bell et al. 1983); 1-methyl- and 1,6-dimethyl-2-piperidone were also reported (Dobson et al. 1985). Maleimides (keto lactams) have been reported in retort waters (Yen 1981). These probably result from oxidation of pyrroles on exposure to heat and air (Katritsky and Lagowski 1968, p 116). Subsequent hydrolysis of the lactams would return the delta- and gamma-aminoacids.

urea. Urea (carbamide) probably comes from the reaction of carbon dioxide and ammonia (Bosch-Meiser Urea Process) and/or the heating of aqueous ammonium cyanate (Wohler Synthesis). The latter is more probable since moderate concentrations of urea have been reported for retort water but not for the gas condensate (Leenheer et al. 1982). The analogous reaction with ammonium thiocyanate should yield thiourea (thiocarbamide) (PUC).

AMINES (primary alkyl and aryl)

Except for pyrroles, lactams, and piperidines, few secondary and tertiary amines have been reported to exist in shale products. The major exception are N-alkyl- and N-dialkyl-arylamines (e.g., Bett et al. 1983; Wildung et al. 1978). Secondary and tertiary nonaromatic alkyl derivatives have been reported very infrequently; for example, tributylamines have been tentatively identified in Paraho retort water (Wildung et al. 1978).

The alkyl and aryl amines probably both derive from the same pathways of N-heterocycle hydrocracking (Holmes and Thompson 1981). The aryl amines are initial cracking products, and the alkyl amines are simply the penultimate products of cracking; they subsequently undergo C-N bond scission to yield ammonia as a final product. Cracking of N-heterocycles occurs preferentially at the heterocyclic C-N bond. This means that six-membered heterocycles such as quinolines could only yield aromatic primary amines; further cracking (of the aromatic C-C bonds) would yield monoalkylamines; isoquinolines could conceivably yield aralkylamines. In contrast, five-membered heterocycles such as indoles can potentially yield (in addition to arylamines) dialkylamines or alkylarylamines, if the heterocyclic nitrogen has an alkyl substituent. For example, the secondary amine, N-diphenylamine was reported for a retort water (Wildung et al. 1978); this could derive from cracking of the biphenyl bridge of carbazole. Similarly, the tertiary amine, N-methyldiphenylamine was reported in a shale oil (Shue and Yen 1981); this could derive from scission of the biphenyl bridge of N-methylcarbazole. Cracking of the heterocycle C-C bonds of indoles and quinolines can yield N-alkylanilines, and the similar reaction for isoindoles and isoquinolines yields the aralkylamine. In general, N-substituted indoles and carbazoles are resistant to cracking. Therefore, cracking eventually favors monoalkylamine formation over di- or trialkylamine formation.

Most of the mutagenic activity of shale oil resides in its polar-basic fraction. For this fraction, most of the activity is believed to derive from polyaromatic and azaarene primary amines. The significance of these compounds in synfuel liquids has been discussed in a number of reports (e.g., see Mahlum, Gray, and Felix 1981) (also see "Benzothiophenes" and "Fused-Ring N-Heterocycles"). These aromatic primary amines are possibly the most important of the organic constituents in synfuel process streams with respect to mutagenic potential (e.g., Ho et al. 1983). Hydrotreatment substantially reduces this activity, despite its tendency to produce greater amounts of PAHs (Ho et al. 1983); this is presumably because of deamination.

Alkylamines (aliphatic amines).

In general, the aliphatic primary amines (esp. methyl and ethylamine) have only been identified in retort waters recently (Avery and Junk 1985; Richard and Junk 1984). This is probably because the lower homologs are extremely volatile under alkaline conditions, and they react (e.g., with carbonyls) after initial synthesis in the retorting process. They are probably present only in low transient concentrations in crude shale oil (Carpenter, Jr. 1978; Van Meter et al. 1952). Neither primary, secondary, nor tertiary amines were found in samples of retort offgas (Sklarew and Hayes 1984).

Alkylamines would be major reactants in many of the secondary retort reactions. They are particularly reactive with aldehydes, yielding a plethora of products (esp. methlyolamines and N-heterocycles), and they undergo dehydrogenation to give nitriles (Regtop et al. 1985). Alkylamines can also react with carboxylic acids to form N-alkylamides (or lactams) and with carbon disulfide to give alkylthiocyanates (PUCs). Primary amines can also react with 1,4-dicarbonyl compounds to give N-alkylpyrroles (Paal-Knorr Synthesis) or undergo reductive methylation with formaldehyde and formic acid to give methyl- and dimethyl-secondary and tertiary amines (PUC) (Eschweiler-Clarke Reaction). Heat can cause the elimination of ammonia from alkylamines; this represents the final reaction in hydrodenitrogenation (HDN).

Arylamines (amino benzenes).

Alkylated arylamines (e.g., alkylanilines) are difficult to distinguish from alkylpyridines solely on the basis of their electron-impact mass-fragmentation patterns (Felice 1982; Schmitter et al. 1984). So without authentic standards available for many of these compounds, confusion has inevitably resulted regarding their presence in the process streams. Derivatization can obviate this problem if GC/MS is to be used (Felice 1982).

Partly for this reason, the literature is often contradictory about the occurrence of amino-substituted aromatics in process waters. A further reason is that these compounds are most likely the result of minor cracking reactions during the retorting process; in retorting, these reactions are uncontrolled and erratic and probably are catalyzed by metals in the raw and retorted shale. For example, anilines and alkylanilines usually are present only in low concentrations in the crude oil (e.g., Bett et al. 1983; Van Meter et al. 1952), but they are produced in large amounts during refining by the process of hydrodenitrogenation (HDN) (Schmitter et al. 1984). They result from reduction of the hetero rings and cleavage of the aliphatic hetero-ring C-N bond of indoles and quinolines (and their benzologs). In an analogous manner, cleavage of the benzoid C-N bond results in the aralkylamines. and further benzoid C-C bond cleavage gives the alkylamines. Aralkylamines would preferentially be formed from isoheterocycle cracking. For example, benzylamine has been reported in process waters (Pellizzari et al. 1979; Pellizzari and Castillo 1980) and retort offgas (Fruchter et al. 1982); this is possibly a product of isoquinoline cracking. These routes of aniline formation by cracking are probable, especially in light of the numerous reverse syntheses of alkylquinolines from anilines (e.g., Doebner-von Miller Reaction; Friedlaender Synthesis). More severe hydrotreatment (e.g., multi-stage HDN), however, results in scission of the remaining C-N bond (hydrogenolysis) and therefore complete deamination and removal of arylamines (Thompson and Holmes 1985) Hydrogenolysis of the aryl amino group is most impeded by the presence of adjacent alkyl groups (Schmitter et al. 1984). Since cracking of azaarenes necessarily yields 2-alkylarylamines, many of the alkylated arylamines in shale oil should be relatively persistent products of cracking.

Arylamines could therefore be expected in waters from an upgrade plant, depending on the effectiveness of the HDN process. Anilines accounted for a third of the base fraction of a hydrocracked oil (Brown et al. 1970); almost all were alpha-substituted, mainly 2-ethyl- and 2-propylaniline (probably from scission of indoles and quinolines, respectively. 2-Alkyl anilines could therefore be expected as major contaminants of upgrade process waters, but probably not in retort waters. For this reason, they are abundant in the sour condensate from refining Occidental shale oil (Wingender et al. 1981), but usually occur only in low levels in the retort waters (Hawthorne and Sievers 1984, 1985; Raphaelian and Harrison 1981). When present in retort waters, unsubstituted aniline is the major arylamine reported (Conditt 1984; Hawthorne and Sievers 1984, 1985; Leenheer et al. 1982; Pellizzari et al. 1979). Its concentration is generally much less than the 2-alkylpyridines, but it can be more concentrated (e.g., Conditt 1984; Pellizzari et al. 1979) when cracking of quinoline has been suspected, such as in in-situ retorting, where temperatures can rise substantially. Alternative routes of aniline synthesis, however, could explain its occurrence in retort waters. Recently, for example, aniline was shown to be a product of heptanedioic acid pyrolysis when ammonia was present (Regtop et al. 1985).

Anilines are very water soluble because of hydrogen bonding by the amino group. For this reason, their vapor pressures tend to be low. Volatility increases, however, within any series of positional alkyl isomers as the amino group becomes more hindered (i.e., N-alkyl or alpha-alkyl). These are amenable to removal by steam stripping (e.g., Conditt 1984); those with greater than C_2-substitution, however, cannot be completely removed. In some process waters, anilines probably contribute to color formation by polymerizing (i.e., "aniline blacks"); for example, air oxidation can lead to polymer precursors such as the dimer, azobenzene (Conditt 1984).

In an manner analogous to the cracking reactions for aniline formation, fused-ring primary amines (amino-PAHs) would result from cracking the heterocyclic ring of fused-ring N-heterocycles. For example, 1-napthylamine (Bell et al. 1983; Dobson et al. 1985) has been identified in process waters. It could result from benzo(h)quinoline. 2-Napthylamine (PUC) (a much more potent carcinogen) would result from benzo(f)quinoline.

Hydrogenation of aromatic amines yields the corresponding saturated, alicyclic amines. For example, anilines would yield the corresponding cyclohexylamines (PUC); these would partition to the oil and particulates because of limited water solubility. Anilines can also undergo reductive methylation with formaldehyde/formic acid to give their N-alkyl, secondary amine derivatives (Eschweiler-Clarke Reaction). N-Methylaniline in shale-oil refining condensate water was a major product (Wingender et al. 1981), but probably results from C-C bond scission during quinoline or N-methylpyrrole cracking. Aromatic primary amines also undergo numerous reactions with formaldehyde, giving darkly colored polymeric materials (Sprung 1940); many of these reactions are catalyzed by acid and therefore may not account for color formation in retort waters. These reactions are probably responsible, however, for some of the polymeric material created during separation/fractionation procedures used in oil analysis (e.g., Rovere et al. 1983).

HETEROCYCLES

More than one-half of the compounds synthesized in nature have heterocyclic components. Most of these are N-heterocycles, and many are physiologically active (e.g., alkaloids). Many other man-made N-heterocycles (and aromatic primary amines) have been the basis of countless drugs and pesticides as well as dyestuffs (anilines), plastics (melamine), rubber (piperidine), and antioxidants (morpholine). Pyridines and pyrroles have been known as constituents of shale oil since the mid 1800s (see Van Meter et al. 1952). The prominence of these components in the liquid products from retorting presents numerous problems with regard to oil upgrading (catalyst poisoning; refractory to hydrodenitrogenation; poor storage stability), the environment/work site (malodor; precursors to NO_x formation via combustion; possible carcinogens), and biotreatment (relatively refractory to degradation; highly volatile alkylamines can be end-products of successful degradation). Formation of NO_x is important not only in the generation of photochemical smog but also in its vapor-phase reactions with PAHs and hydroxybenzenes to yield highly toxic nitrated derivatives. Despite these problems, the recovery and purification of the numerous N-heterocycles from the oil and waste streams should eventually be considered as a rich and economical source of these compounds as feedstocks for commercial chemical syntheses.

Although all of the heterocycles known to exist in oil shale process streams probably have definite origins from similar parent structures in the kerogen (with the possible exception of the pyridines), all of them can, and probably do, also result from pyrolysis of simple aliphatic precursors in the presence of H_2S, NH_3, or CO. The fate of heterocycles during retorting is intimately tied to the extremely complex chemistry of hydrogenation and cracking (see "Arylamines"), which occurs to various degrees depending on the partial pressure of molecular hydrogen and the presence of catalytic shale surfaces. An excellent investigation of hydrotreatment summarizes many of the reactions that may also be relevant to retorting as well as to shale oil upgrading (Green et al. 1985).

Since most of the benzo derivatives of heterocycles are relatively nonvolatile, if they are released to the environment, they would partition to the terrestrial and groundwater compartments. Biodegradation would be a major transformation process; metabolism of N-heterocycles has been reviewed (Callely 1978). Volatilization of N-heterocycles (esp. nonbenzoid derivatives) is enhanced when the nitrogen is hindered by alkyl substituents. For example, ortho-alkylpyridines and N-alkypyrroles have lower boiling points than other positional isomers because intermolecular hydrogen bonding via the nitrogen is impeded or prevented. These isomers can be expected, therefore, to be enriched in gas-phases in contact with liquids or solids containing a mixture of isomers. The benzo- and fused-ring derivatives would be expected to partition mainly to the oil phase.

pi-Excessive Heterocycles (aza, thia, and oxa derivatives of the cyclopentadienyl carbanion)

Five-membered carbocyclic heterocycles (pyrroles, thiophenes, and furans) have six pi-electrons distributed over five carbon atoms, exceeding the neutral density of benzene. These compounds easily undergo electrophilic substitutions and oxidation, and they are unstable in acidic solution (commonly encountered during chemical characterization procedures). For the aza derivatives (pyrroles), the nitrogen is able to covalently bond with another carbon (usually an alkyl group); this is in contrast to the pi-deficient N-heterocycles (e.g., pyridines) and has ramifications with respect to ring cracking. The reactivity of pi-excessive heterocycles is reflected by their often low and usually erratic concentrations in oil shale process streams. Although directly related in their de novo synthetic pathways (e.g., Paal-Knorr type syntheses), pyrroles, thiophenes, and furans can also have totally different origins as direct pyrolysis products of endogenous constituents of kerogen. All of them therefore have multiple origins.

Pyrroles.

Many of the pyrroles that have been identified in the oils and waters undoubtedly result from the pyrolysis of petroporphyrins (tetrapyrroles), such as chlorophylls, by reduction to the hexahydroporphyrinogen followed by fragmentation and demetallation. This would create a preponderance of N-alkyl-, 2-methyl-, and 2,5-dimethylpyrroles. Pyrroles can be major constituents (e.g., 2,3,4,5-tetramethyl- and 2,4,5,-trimethyl-3-ethyl-pyrrole) of the basic-polar fraction of shale oils (Van Meter et al. 1952), but most of the recent characterizations (e.g., Rovere et al. 1983) find low concentrations probably because either the oil is old (slow reactions have reached completion) or the fractionation techniques expose the sample to oxygen. Indeed, in a recent (and very extensive) shale-oil characterization study, large amounts of nitrogenous polymeric materials were formed during column chromatography (Rovere et al. 1983); this was probably the cause for the much lower abundance of these compounds with respect to the nitriles.

Synthetic routes to alkylpyrroles almost always favor substitution at the 2-position (Katritsky and Lagowsky 1968). Pyrroles (again with 2- or 2,5-substitution) can be formed also by heating 1,4-dicarbonyl compounds such as butanedioc acid (succinate) with ammonia (Paal-Knorr Pyrrole Synthesis). Indirect evidence for this route is the report of butanedioc acid as the least prevalent alkanedioc acid in certain retort waters (e.g., Leenheer et al. 1982). Pyrroles are also known to be products from the pyrolysis of alkylamines (Regtop et al. 1985). N-Methylpyrroles when heated rearrange to 2- and 3-methylpyrroles (Newcome and Paudler 1982). Some alkylpyrroles undergo direct alkylation in alkali by alkoxy ions (Newcome and Paudler 1982).

Large amounts of pyrroles are probably created during retorting, but the reactivity of pyrroles leaves the transient concentrations low. For example, the reverse synthesis to porphyrins is accomplished in the presence of aldehydes (Rothemund Reaction). In the presence of air, "pyrrole blacks" are formed as polymeric products. In their separation from shale oil, the initially colorless pyrroles darken after only several hours of exposure to air (Van Meter et al. 1952). These polymers, along with others (e.g., those from phenols), are probably responsible for much of the color associated with retort waters; because these polymers are nonvolatile, much less color is associated with gas condensates.

Pyrroles are a case in point for the importance of the sequence of pH adjustments used in various liquid-extraction and adsorption fractionation schemes that are performed; in the presence of mineral acids, pyrroles easily polymerize (Necome and Paudler 1982). In general, the abundance of pyrroles would decrease both with time and with exposure of a sample to oxygen. In one of the few studies that took care to collect and store a retort water and gas condensate from a retort run (150-Ton run 20) without exposure to air, alkylpyrroles were found to be emitted to the headspace during simulation of codisposal (Hawthorne and Sievers 1985); these were mainly 2-methylpyrroles. Similarly, in water from the LLL retort, 2,5-dimethylpyrrole (and possibly 2-methylpyrrole) were the only pyrroles detected (Gebhart and McKown 1980).

Oxo- and Hydroxy-Pyrroles (pyrrolidones).

Hydroxylated pyrroles (pyrrolidones) can also exist in their keto (oxo) forms depending on position of the hydroxyl group. The 2-hydroxypyrroles exist mainly in their oxo form; the 2-oxo derivative is a lactam, and the 3-oxo derivative is an alicyclic amino ketone. For oil shale process streams, the only oxo- or hydroxy-derivatives reported have been in the process waters. These have been the saturated pyrrolidones, mainly alkyl 2-pyrrolidones (Bell et al. 1983; Dobson et al. 1985; Fox et al. 1984; Torpy et al. 1982); the origin of these compounds is discussed under lactams. The 5-unsubstituted 2-pyrrolidones can react with aldehydes/ketones to form 5-substituted methene products (Katritsky and Lagowski 1968).

Benzopyrroles.

Benzopyrroles can be major nitrogenous constituents of shale oil (e.g., Bett et al. 1983). Monobenzopyrroles (indoles) probably result from pyrrolic condensation reactions as well as from hydrocracking of fused-ring compounds such as carbazole; the latter would yield 2- and 3-alkyl derivatives. Indoles can also be formed from aromatic amines, for example, toluidines (e.g., Madelung Indole Synthesis). In contrast to pyrroles, synthetic routes to indoles almost always favor substitution in the 3-position. Like pyrroles, indoles tend to polymerize under acid conditions, and they are easily oxidized in the presence of heat and air. Iso-indoles (analogs of six-membered iso-quinolines) tautomerize to the isoindolenines, and they are very unstable (polymerizing readily in air) (Newcome and Paudler 1982). Aminoindoles may arise from reaction of indole with formaldehyde and ammonia (Mannich Reaction; 3-methylaminoindoles should predominate). Indeed, aminoindoles were tentatively identified as major constituents of Oxy-6 retort water (Raphaelian and Harrison 1981).

Carbazoles and benzocarbazoles can be major N-heterocycles in shale oil (Robbins and Blum 1981), and as expected, N-alkylcarbazoles are the most resistant compounds during hydrodenitrogenation (Holmes et al. 1982). Hydroxycarbazoles (PUC) were recently identified as major constituents of the oxo-N-heterocycles in coal liquid (Nishioka, Campbell, Lee et al. 1985), but they have not been identified in shale products.

Thiophenes.

The reaction of succinic acid in base with sulfides gives thiophene (Volhard-Erdmann Cyclization). This could be a major source of thiophenes in process waters. The 2- or 3-alkyl succinates would yield 3- and 4-alkylthiophenes. The 2- and 3-methylthiophenes are easily oxidized to their thiophenic carboxylic acids (PUC) (Newcome and Paudler 1982). Another major source of the thiophenes, however, is probably directly from thiophenic polymers in the kerogen; in offgas, almost all thiophenes evolve at 300-450°C, implying an organic origin (Wong et al. 1984). Simple thiophenes probably do not occur in raw shale (Bissell 1983). These polymers are formed by higher plants by addition of sulfides to 1,3,-diacetylenes (Newcome and Paudler 1982). Their pyrolysis should yield mainly 2,5-dialkyl thiophenes. Direct formation from thiophenic polymers is more probable than de novo synthesis (with H_2S) because of competitive reactions of ammonia with the diketones. Thiophenes can be easily formed, however, by the pyrolysis of aliphatic compounds in the presence of a sulfur source such as pyrite or thiols (Jeong and Patzer II 1983; Regtop et al. 1985). Thiophenes, therefore, probably have an origin different from that of other organosulfur compounds.

In an early study of shale oil, alkylthiophenes (C_1-C_4) were found to predominate. Of the total sulfur in the crude shale oil, 80% was reported to be thiophenic (Kinney, Jr., Smith, and Ball 1952); two-thirds of these were represented by only 17 of the possible 122 isomers (for this boiling range). Of the mono-, di-, and tri-substitutes, 2-, 2,5-, and 2,3,5-alkyls predominate. The C_3-C_4's are more frequent than the C_1-C_2's; 2-methyl-5-ethyl- and 2-methyl-5-isopropylthiophene are the most abundant.

Generally, unsubstituted thiophene is reported in retort waters (Day and Rawlings 1981; Gebhart and McKown 1980; Pellizzari et al. 1979) and offgases (Sklarew et al. 1984; Wong et al. 1984). Unidentified methyl-, ethyl-, and propylthiophene isomers have also been reported in offgas (Ondov et al. 1982; Sklarew et al. 1984; Wong et al. 1984); of all the thiophenes, unidentified methylthiophenes seem to dominate in offgas (Wong et al. 1984). In water from the LLL retort, 2,5-dimethylthiophene was tentatively identified (Gebhart and McKown 1980). In Oxy-7&8 gas condensate and Rio Blanco 1 retort water, 2-methylthiophene was a dominant isomer (Hawthorne and Sievers 1984). The thiophenes are more thermally stable than the organic sulfides and thiols, and therefore they may be expected to be present at higher concentrations, especially in offgases, where they are secondary to alkylbenzenes (Ondov et al. 1982). With the exception of the thiols, these compounds seem to be the most abundant form of organosulfur, especially in the offgases (Wong et al. 1984), and can contribute substantially to the total offgas sulfur content, which is mainly hydrogen sulfide. Real-time determination of thiophene concentrations in the offgases would probably be much higher, but the concentrations actually measured (<1% of total gaseous sulfur) are low because of immediate losses to condensation in sampling equipment (Wong et al. 1984).

Benzothiophenes (thianaphthalenes). Although benzothiophenes are endogenous constituents of raw shale (Radke et al. 1984), pyrolysis of the thiophenes themselves is reported to produce benzo(b)thiophene. Benzo(c)thiophenes (isobenzothiophenes) (PUCs) are S-analogs of isoindoles. They have not been reported in oil shale process streams (e.g., Kong et al. 1984), and little is known about them (Newcome and Paudler 1982). "Benzothiophene" usually refers to the b-isomer. In an Occidental oil shale, thiophene were found with up to four rings (Kong et al. 1984); dibenzo(b)thiophene was the most abundant species, with various amounts of C_1-C_4 alkyl derivatives. Recently, various hydroxy-substituted isomers of phenyl- and mono- and dibenzothiophenes (PUC) have been identified in a coal liquid (Nishioka, Lee, Kudo et al. 1985). The phenylthiophenes probably result from reaction of the thiophene with phenyl radical (Newcome and Paudler 1982). This mainly yields the 2-phenyl isomer. In one study of retorted shales, dibenzothiophene was more prevalent than most PAHs (Maase 1980). More significantly, however, is the possible occurrence of aminodibenzothiophenes (PUC) and alkylated derivatives. These have been identified in a coal liquid (Nishioka, Campbell, West et al. 1985). The 2- and 3-amino isomers are potent mutagens (orders of magnitude greater than benzo[a]pyrene in the Ames assay) (Nishioka, Campbell, West et al. 1985). Aminothiophenes can in turn react with methylvinylketone to produce methylthienopyridines (PUC), the latter of which have been identified in shale oil (Newcome and Paudler 1982).

During hydrocracking, the thiophenes do not undergo reduction as easily as pyrroles and furans. The products are dihydro derivatives (some of which easily polymerize) and perhydro derivatives (thiolanes). The latter have been tentatively identified in water from the LLL retort (Gebhart and McKown 1980), in particular, 2-methylthiacyclopentane. These are more prevalent in sour waters from hydrotreatment (Wingender et al. 1981). Thiolane can undergo hydrolysis to yield terminal butenethiols (PUCs) (Clark, Hyne, and Tyrer 1984), which pyrolyze to H_2S and butene. Hydrotreatment can also cause heterocyclic C-S bond scission of benzothiophenes with concomitant reduction of the unsaturated substituent ortho to the sulfur of the resulting thiophenol. For example, dibenzothiophene and benzothiophene would give o-cyclohexyl- and o-ethyl-thiophenols (PUCs), respectively (Wood et al. 1985); in the absence of ring-hydrogenation, scission of the biphenyl bridge bond in dibenzothiophenes would yield diphenylsulfides (PUCs). Thiophenols (benzenethiols) are high-boiling and water insoluble; they would therefore partition to the oil. They also easily oxidize in air to give the diphenyldisulfide. Cleavage of the benzoidal thiophenic C-S bond would yield alkylthiols (mercaptans), and cleavage of the aromatic C-C bonds would yield dialkylsulfides (thioethers).

Furans.

Furans are more reactive than the pyrroles. In general, only small amounts of alkylfurans (Raphaelian and Harrison 1981) and dibenzofuran (Pellizzari et al. 1979) have been reported in retort water. Benzo(b)furan has been reported in shale oil (Van Meter et al. 1952). Benzo(c)furans (isobenzofurans) (O-analogs of isoindoles) have not been reported, and they are very reactive towards oxygen (Newcome and Paudler 1982).

The furans probably result from Paal-Knorr type reactions, but the preponderance of ammonia would effectively compete and lead to pyrroles. Kerogen may also contain furan constituents. An alternative route of synthesis could be from dehydrogenation of the cyclized oxolane produced by autooxidation of alkanes (Zinbo and Jensen 1985). Even if present or produced during retorting, however, furans could be effectively reduced (hydrogenated) to their alicyclic ethers (oxolanes).

Pi-Deficient N-Heterocycles (aza derivatives of benzene).

In six-membered heterocylic compounds, the hetero atom, being more electronegative than carbon, lowers the electron density for the ring carbons, leaving the ring less electron-rich than benzene and therefore subject to nucleophilic reactions.

The oxygen six-membered rings occur primarily as their oxo derivatives (i.e., 2- or 4-pyrone) or as the dihydropyrans (2H- or 4H-pyran). The latter have been reported in retort water only at low concentrations (Gebhart and McKown 1980). As with the furans, their origin from 1,5-dione dehydration/cyclization is probably competitively blocked by the high concentrations of ammonia, which would yield the dihydropyridine. Only the aza derivatives (pyridine and its benzene congeners), therefore, are of significance in retort process waters and will be discussed below.

Pyridines.

Although alkylpyridines occur infrequently in nature, they are common products of pyrolysis when nitrogenous materials are involved. For example, numerous alkylpyridines result from the pyrolysis of alanine and beta-alanine (Lien and Nawar 1974) and from pyrolysis of alkylamines (Regtop et al. 1985). Their occurrence in thermally processed foods, as opposed to unprocessed foods, is further evidence of this (Maga 1981). Commercially, pyridines are derived from coal-tar distillates.

Pyridines are a relatively minor component of shale oil, although they are major contributors to total nitrogen (e.g., Bett et al. 1983). They also are probably the major contributors to the odor of the crude oil. The predominant isomers have short alkyl chain lengths ($<C_3$) and total alkyl carbons of C_1-C_6 (Bett et al. 1983; Uden et al. 1979). The dialkyl- and trialkyl-derivatives are common (e.g., 2,3- and 3,5-dimethyl, and 2,4-dimethyl-6-ethyl- and 2,4,6-trimethylpyridine) (Bett et al. 1983; Van Meter et al. 1952); 2,4,6-trimethylpyridine is the most frequently encountered and abundant isomer (e.g., 1000 mg/L; Hertz et al. 1980).

The pyridines are also a major contributor of organic nitrogen in the process waters, but not in offgases. Again, the trimethyl isomers (esp. 2,4,6-trimethylpyridine) are the most frequently encountered and most abundant (e.g., Conditt 1984; Day and Rawlings 1981). For some waters, 2,4,6-trimethylpyridine can represent over one-third of the total pyridines (e.g., Leenheer et al. 1982). It also comprises more mass than any other compound when fully volatilized from the process waters (Hawthorne and Sievers 1984). The concentrations of these compounds are higher in the aqueous process streams than would be expected on the basis of their solubilities alone. Their partitioning from oil is probably enhanced by ligand association with metal ions (e.g., ferric ion) (Stanley and Sievers 1985; Stetter, Stamoudis, and Jorgensen 1985). The other most commonly reported isomers are 2-alkyl- and 2,4- and 2,6-dialkylpyridines, especially 2,4-dimethylpyridine (Bell et al. 1983; Conditt 1984; Hawthorne and Sievers 1984; Richard and Junk 1984) and 2-methylpyridine (Bell et al. 1983). The 3-alkylpyridines occur in low concentrations (Bell et al. 1983; Conditt 1984; Hawthorne and Sievers 1984).

Alkylpyridines can be the major organic constituents of gas condensates (Hawthorne and Sievers 1984), and they readily steam strip from water (e.g., Conditt 1984); volatility increases within a series of positional isomers as the nitrogen becomes more shielded (i.e., 2-alkyl and 2,6-dialkyl). Because of the volatility of the alkylpyridines, they are also the major class of compounds in the vapor phase of thoroughly purged process waters (Hawthorne and Sievers 1984, 1985). In a study of eight process waters, most of the compounds emitted to the headspace were found to contain nitrogen (Hunter et al. in press); the majority of these compounds were found to be common to each of these eight waters, and all of these were alkylpyridines.

The prevalency of alkylpyridines in oil shale process streams together with a number of their properties makes these compounds candidates for tracers, indicative of oil-shale processing contamination of surface and subsurface waters (Riley et al. 1981); a trimethylpyridine was one of the few compounds found in well water at Anvil Points, Colorado (Gebhart and McKown 1980). These compounds occur in only low concentrations in petroleum processing, they have low affinity for retorted shale (Riley et al. 1981), and they are catabolized much more slowly in nature than are the more prevalent aliphatic acids. Pyridine and its derivatives can be biorefractory (Sims and Sommers 1985), and they can migrate through soil (Leenheer and Stuber 1981) as demonstrated by their occurrence in groundwater samples (Stuermer et al. 1982). In general, their affinity to solid surfaces is probably related to their polarity. For example, their retention by soil is directly related to their retention in reverse-phase liquid chromatography (Leenheer and Stuber 1981).

The natural occurrence of alkylpyridines in thermally processed foods has led to the inclusion of some of these compounds on the FDA GRAS List (food additives "Generally Recognized As Safe"). Of those that have FEMA registry numbers, some occur in retort waste streams: pyridine, 3-ethylpyridine, 2,6-dimethylpyridine, and 5-ethyl-2-methylpyridine (Maga 1981). Of these, 2,6-dimethylpyridine can be added to foods at concentrations up to 10 ppm. All alkylpyridines, however, have offensive or off odors, most impart off flavors, and many have low odor thresholds. For example, 2-pentylpyridine has a fatty (tallowy-like) odor with a threshold of 0.6 ppm (Maga 1981). The aesthetic problem of malodor may indeed be a major problem of any retort facility, and alkylpyridines would be the major contributors. These are the major contributors to the odor of retort waters, but secondary contributors for gas condensates; alkylpyridines could be major contributors to the odor of condensate waters from upgrading. That they are major causes of malodor in retort waters is even more impressive in view of the extremely high concentrations of dissolved ammonia gas, whose odor they totally mask (Daughton et al. in press; Daughton et al. 1985).

Recent evidence indicates that one origin of alkylpyridines in shale oil may be from isoprenoidal-alkylpyridines present in the kerogen (Gallegos 1984). Pyridine alkyl substituents of over 20 carbons have been found in the oil (Gallegos 1984; Shue and Yen 1981). This does not discount the occurrence of de novo synthesis, however, since these same, long-chain alkylpyridines could result from long-chain aldehydes in a Chichibabin-type synthesis. In shale oil products, therefore, these compounds could also result from Chichibabin (or Hantzsch) Pyridine Synthesis reactions involving aldehydes and ammonia or alkylamines (Sprung 1940). The Chichibabin Synthesis preferentially gives 2-, 3-, and 5-alkyl substituents, while the Hantzsch gives 2-, 4-, and 6-alkyl substituents. For example, the reaction of ammonia with acetaldehyde, propionaldehyde, and butyraldehyde preferentially yields 2-methyl-, 2-ethyl-3,5-dimethyl- and 2-propyl-3,5-dimethylpyridine, respectively (Sprung 1940); numerous other methyl- and ethyl-substituted products also result.

Alkylpyridines are also probably formed by quinoline hydrocracking that can occur during retorting. The products of cracking are enriched with hindered alkylpyridines (i.e., 2- and 2,6-alkylpyridines) because the nitrogen is least hindered from catalyst interaction (and further cracking) in the 3-alkylpyridines. For this reason, hindered alkylpyridines are the most prevalent organonitrogen compounds in refined oil (Bett et al. 1983; Brown et al. 1970; Holmes et al. 1982). In turn, cracking of alkylpyridines yields ammonia, polymeric material, and hydropyridines. Likewise, the synthetic routes favor the 2- and 4-positions for nucleophilic substitution. Overall, 3-alkylpyridines would be the least favored to be formed by de novo synthesis and the most favored to undergo cracking. This would imply that their concentrations would necessarily be low. Indeed, few 3-alkylpyridines were found in a cracked shale oil (Brown et al. 1970). All of these reactions generally yield relatively short alkyl chain-lengths.

Pyridine can react with amide ion in the presence of ammonia to give 2-aminopyridine (PUC) (Chichibabin Amination). Although aminopyridines have not been identified in oil shale products, their mass spectra could possibly be confused with alkyl pyrazoles, which have been tentatively identified in retort water (Raphaelian and Harrison 1981). Amino pyridines are the most refractory of the pyridines to biodegradation and would therefore be expected to persist after biotreatment or transport to the environment. Among the substituted pyridines, degradability increases in the following order: amino- < alkyl- < oxo- < carboxylic-pyridines (Sims and Sommers 1985).

Alkylpyridines when reacting with amide ion and ammonia can also yield their respective carbanions, which then react with carbon dioxide to give the corresponding pyridine carboxylic acids (Newcome and Paudler 1982). Alkylpyridines can also oxidize to 2-, 3-, and 4-pyridenecarboxylic acids, which can react with aldehydes to give hydroxyalkylpyridines (PUC) (Hammick Reaction). The pyridine carboxylic acids are unstable to heat and can decarboxylate to return the alkylpyridines and pyridine; 3-picolinic acid (nicotinic), however, is more resistant. These scenarios are corroborated by the occurrence of low concentrations of pyridinecarboxylic acids in retort waters, while 3-picolinic acid is the most common (Leenheer et al. 1982).

When heated, 2-methylpyridine recombines to yield benzonitrile (Hurd and Simon 1962). This is possibly the major source of benzonitrile in shale products, having an origin distinct from the alkylnitriles. Alkylpyridines react with aromatic aldehydes in the presence of base to give 2- and 4-stilbazoles (PUCs); these compounds would be high boiling and nonpolar. Methylpyridines undergo vapor-phase oxidation to give pyridinecarboxaldehydes (PUCs). Condensation of pyridine with ketones yields 2-pyridyldialkylcarbinols (PUCs) (Emmert Reaction). 3-Hydroxypyridine reacts with formaldehyde to give 2-hydroxymethyl-3-hydroxypyridine (PUC) (Katritsky and Lagowski 1968); pyridinols have been tentatively identified in shale oil (Toste, Sklarew, and Pelroy 1982).

The reduced pyridines (dihydro and perhydro isomers) are easily formed de novo (e.g., 1,5-dione cyclization) or by pyridine hydrogenation (Thompson and Holmes 1985). The low concentrations of the perhydro derivative (piperidine) (e.g., Dobson et al. 1985) is probably a result, however, of the reactivity of these less-reduced intermediates, which can easily oxidize back to pyridines or polymerize. Piperidines, being secondary amines, also undergo alkylamine-type reactions. For example, they react with formaldehyde to give N-methylol derivatives (PUCs) (Sprung 1940).

Oxo- and Hydroxy-Pyridines (pyridones).

When retort water characterizations have focused on the polar solutes, the oxo (hydroxy) pyridines have been found in significant concentrations. The most abundant derivatives are 2-pyridones, especially unsubstituted 2-pyridone (Leenheer et al. 1982). These compounds have much lower volatilities (because of higher water solubilities) than the alkylpyridines, and they therefore are encountered mainly in the retort waters. Since these compounds are distinctive to oil shale processing, they have been proposed as conservative tracers for retort-water contamination of surface and groundwaters; because of their characteristic absorbance maxima around 300 nm, they can be easily monitored by high-performance liquid chromatography (Leenheer et al. 1982).

Oxo-pyridines are probably major products of secondary reactions of alkylpyridines within the retort. Alkylpyridines readily form pyridyl carbanions because of the stabilization afforded by the pi-deficient ring. These reactive species probably undergo numerous reactions during retorting. Among the more likely reactions include those that form numerous oxo-derivatives, especially in the presence of hydroxide, air, and heat. In aqueous solution, the 2- and 4-hydroxypyridines exist primarily in their oxo (keto) forms (pyridones); in contrast, 3-hydroxypyridine behaves primarily as a phenol. Pyridine itself reacts mainly to give 2-pyridone; the prevalence of both unsubstituted pyridine and unsubstituted 2-pyridone in retort waters implies that the latter does result from the former.

When hydrogenated, the oxo-pyridines could yield piperidones. These are major base-neutral constituents of Oxy-6 retort water, accounting for 50% of the identified compounds in this fraction (Torpy et al. 1982). 2-Piperidone is a lactam (see "Amides: lactams"), which could result from amino acids or from hydrogenation of 2-pyridone; this saturated compound can hydrolyze back to the amino acid. In contrast, 3-piperidone is a cyclic amino ketone and should be more stable. Presumably, N-alkylation of the lactams inhibits hydrolysis. This explains the preponderance of N-methyl-2-oxo-piperidones and pyrrolidones that are sometimes reported (Dobson et al. 1985).

Naphthyridines (Quinolines/Isoquinolines).

The quinolines (benzopyridines), like the alkylpyridines, probably result from both synthetic and destructive reactions. Their origin from synthetic reactions probably parallels those for pyridines (e.g., Chichibabin-type reactions). In turn, they would also result from cracking of fused-ring heterocycles, such as acridines. The synthetic route is probable, especially in light of their occurring in pyrolysis products from pyridines (Hurd and Simon 1962). Evidence for the destructive route is that their concentration in shale oil increases substantially with respect to the pyridines at higher retorting temperatures (Wen et al. 1984), suggesting that they would be expected more in products from in-situ processing. In oil shale process waters, unsubstituted quinoline and isoquinoline (Conditt 1984; Conditt et al. 1983; Hawthorne and Sievers 1984; Leenheer et al. 1982; Pellizzari et al. 1979) are the most common, but they occur at much lower concentrations than the respective alkylpyridines because of limited water solubility. The alkylnaphthyridines proved very refractory to removal by activated sludge in an evaluation of tar-sand wastewater (Torpy et al. 1981). Both quinoline and 6-methylquinoline are on the FDA GRAS list (0.5 ppm usage) (Maga 1981).

Unsubstituted and alkyl (C_1-C_2) quinolines/isoquinolines are also major constituents of the basic fraction of shale oil (Bett et al. 1983; Rovere et al. 1983). Analogous to the formation of alkylpyridines from cracking of quinolines, the 2-alkylquinolines would result from cracking of the higher fused-ring analogs (e.g., acridine). These hindered quinolines are very resistant to hydrocracking (Schmitter et al. 1984). The cracking of quinolines and isoquinolines yields, in turn, 2-alkylanilines and aralkylamines, respectively. With respect to the latter, benzylamine has been tentatively identified in the offgas from Rio Blanco 0 and 1 (Fruchter et al. 1982), and high levels have been found in Omega-9 retort water (Pellizzari and Castillo 1980).

The oxo-derivatives of quinoline are formed more readily than those of pyridine because of the aromatic ring. Products from quinoline and isoquinoline would be 2-quinolone (PUC) and 1-isoquinolone (PUC), respectively. Among others, these have recently been identified in coal liquid (Nishioka, Campbell, Lee et al. 1985).

Fused-Ring pi-Deficient N-Heterocycles.

Benzo derivatives of quinolines and isoquinolines (e.g., acridines; N-PAHs) can be major organonitrogen species of shale oil (e.g., Bett et al. 1983; Shue and Yen 1981). Most have fewer than 4 rings. Alkyl substitution decreases from C_3-C_6 to C_0-C_2 with increasing pyrolysis temperature (Robbins and Blum 1981). As discussed previously, these compounds undergo cracking reactions to yield the corresponding fused-ring 2-alkylarylamines and aralkylamines. The fused-ring N-heterocycles would associate predominantly with the particulates and oil. Only low concentrations are found in the waters (e.g., acridine; Conditt 1984).

The amino-substituted N-PAHs (amino-azaarenes), like the other aromatic primary amines, probably contribute substantially to the mutagenicity of the polar-basic fraction of shale oil. Their characterization has been impeded, however, since compounds with even-numbers of nitrogen atoms are difficult to distinguish by GC/MS because of the absence of the characteristic odd-integer molecular ions (Wilson et al. 1983).

Multi- and Mixed-Hetero Aromatics.

Although these more complex heterocycles, those having multiple or mixed heteroatoms, have seldom been reported in shale products (e.g., alkylpyrazoles, Pellizzari et al. 1979; alkylthiazoles, Raphaelian and Harrison 1981), their identification is hampered by the unavailability of reference standards and difficulties in analysis (Wilson et al. 1983). Thiazoles, thiazenes, and oxazenes occur in coal-derived liquids (Wilson et al. 1983), but they are of unknown significance in shale products.

It has already been mentioned that purine, and its amino derivative adenine, could be possible products of retorting. Other, more complex heterocycles could easily account for many of the unidentified compounds of retort waters. Some of these could derive from natural products present in the kerogen matrix (e.g., pteridines; PUC), and others could be synthesized de novo during retorting (e.g, pyrazines; PUC). The pyrazines are of particular interest since they are formed in abundance by thermal processing of foods (Maga 1982). The precursors in foods are sugars and ammonia; these reactants could easily be replaced by alpha-amino acids (formed from cyanides, aldehydes, and ammonia; Strecker Amino Acid Synthesis). In spite of these scenarios, many of these multi-heteroaromatic compounds were not found in process waters from Oxy-6 (Leenheer et al. 1982). Imidazoles were not present in Omega-9 retort water (Pellizzari et al. 1979).

Hydantoins (PUC) (2,4-imidazolidinediones) are formed from the low-temperature reaction (<100°C) of aliphatic ketones, cyanides, and ammonium carbonate (Bucherer-Bergs). These are very polar/nonvolatile compounds, but they could also be formed in the vapor phase (since the reactants are volatile) and therefore appear in gas condensates. A major fraction of the polar constituents of coal-gasification condensate waters has been identified as a series of alkyl hydantoins (in particular 5,5'-dimethylhydantoin, probably resulting from acetone) (Diehl et al. 1985; Giabbai et al. 1985; Mohr and King 1985; Olson et al. 1983); after the phenols, they appear to be the most abundant constituent in these coal-process waters (Giabbai et al. 1985). Their presence in oil shale process waters would seem probable. These compounds are known to continue to form after sample collection when the alkaline waters are not acidified; immediate freezing of gasification condensate completely inhibited their formation (Olson et al. 1983). Hydantoins hydrolyze in water to give the corresponding hydantoic acids (PUC), related compounds that also occur in coal-gasification waters (Mohr 1983); hydantoins also appear to be resistant to biotreatment (Mohr 1983). Other imidazoles can result from reactions of benzaldehydes and ammonia (Sprung 1940).

Mixed-heteroaromatics such as alkylthiazoles (Raphaelian and Harrison 1981) have been reported in retort water, but their concentrations were low and the isomers were unidentified. They could easily be direct pyrolytic products of naturally occurring compounds in the kerogen matrix (e.g., thiamine).

Other Aza Heterocycles.

Aziridines (ethylenimines; azacyclopropanes) and azetidines (trimethylenimines; azacyclobutanes) have been tentatively identified in leachates from gas condensate/retorted shale codisposal (Fox et al. 1984), but not in the parent process water. If these compounds are indeed formed, they are only intermediates since their ring strain leads to hydrolysis, yielding hydroxyalkylamines.

CYANIDES

Hydrogen Cyanide.

Molecular hydrogen cyanide has been reported in concentrations equivalent to nitriles in retort offgas (Fruchter et al. 1982; Sklarew and Hayes 1984). In water, dissociated hydrogen cyanide (cyanide ion) complexes with metal ions (esp. iron); these complexes would tend to partition to the oil. Cyanide ion in the process waters is very difficult to determine because of the numerous reactions that it can undergo. Any cyanide or metal cyanides that remain in the alkaline process waters or in codisposed shale piles would be in their nonvolatile forms because of the high pH. This is especially true for the metal cyanides having very low dissociation constants (e.g., ferro- and ferri-cyanides). Speciation of cyanides is extremely difficult, and for this reason, very little is known about their occurrence in oil shale process streams. It is very important to note, however, that co-mingling of retort waters and domestic waters should be avoided. Any residual chlorine in the latter could convert cyanides (and thiocyanates) into cyanogen chloride (CNCl), an extremely poisonous gas; alkaline conditions, however, would promote hydrolysis of cyanogen chloride to cyanate ion. The chemistry and analysis of cyanides has been reviewed (ASTM 1985).

An extremely toxic gas, HCN can result from reaction of ammonia, methane, and oxygen (Andrussov Oxidation). More likely sources during retorting are from catalytic decomposition of formamide, nitrile cracking, or reaction of ammonia with methyl radical. In some of these pathways, cyanogen (ethanedinitrile) is probably involved; cyanogen can hydrolyze in water to oxalic acid and ammonia or polymerize. Most of the HCN would probably undergo immediate reaction. For example, hydrogen cyanide and sulfur compounds can yield hydrogen thiocyanate, the major cyanate species in retort waters (Leenheer et al. 1982); this reaction is enhanced at high pH. Hydrogen cyanide adds to aldehydes and ketones under base catalysis to give alpha-cyanoalkanols (cyanohydrins) (PUCs); oxidants can drive this reaction backwards, returning the cyanide. Hydrogen cyanide also reacts with ketones, ammonia, and carbon dioxide to give hydantoins (Bucherer-Bergs) (PUCs) (Diehl et al. 1985). Hydrogen cyanide can react with ammonia to yield adenine (PUC) (Newcome and Paudler 1982), and it also reacts with ammonia and aldehydes to give alpha-amino acids (PUCs) (Strecker Amino Acid Synthesis).

Alkylcyanides (aliphatic nitriles).

The aliphatic cyanides (nitriles), although prevalent in shale oil (e.g., Rovere et al. 1983), have not been detected in kerogen. They probably result from dehydration of amides, which are formed from carboxylic acids and ammonia. These reactions are reversible; amides can result from the hydrolysis of nitriles, and in turn can be converted back to carboxylic acids. This route of de novo nitrile synthesis was recently demonstrated by the pyrolysis of alkanoic acids in the presence of ammonia (Regtop et al. 1985). The alkaline conditions of retorting would explain the low concentrations of these compounds in the retort waters. In the presence of base, nitriles react with each other to yield imines, which tautomerize with their enamine forms (PUCs) (Thorpe Reaction).

An alternative, and probably concurrent, pathway of nitrile formation is by high-temperature pyrolytic ring-scission of pyridines (Hurd and Simon 1962). For example, cracking/hydrogenation of pyridine would yield pentanenitrile.

In shale oil are found C_8-C_{30} aliphatic nitriles (Harvey et al. 1984; Rovere et al. 1983; Uden et al. 1979). The relative abundances increase with chain length, with a notable preponderance of even carbon-number over the two nearest odd carbon numbers (Rovere et al. 1983). This suggests that they do indeed result from alkanoic acids, which have biosynthetic origins (Rovere et al. 1983). Nitrile concentrations in shale oils vary widely. The lower, more polar and volatile nitriles (acetonitrile followed by propionitrile) are the most prevalent nitriles in both process water and offgas samples (Day and Rawlings 1981; Hawthorne and Sievers 1984; Leenheer et al. 1982; Sklarew and Hayes 1984). In retort offgas, the aliphatic nitriles comprised 1-2% of the total N contributed by ammonia (Sklarew and Hayes 1984). They therefore represent major potential sources of NO_x from offgas combustion.

Although nitriles are minor constituents of retort waters, they are major headspace components (esp. acetonitrile), and they are about the third most prevalent constituent of gas condensate because of their volatility (Leenheer et al. 1982).

Arylcyanides (benzonitriles).

Benzonitrile probably results from the pyrolytic recombining of 2-methylpyridine (Hurd and Simon 1962). This is corroborated by the fact that alkylbenzonitriles (2- and 3-methyl) become more prevalent than the pyridines in shale oils cracked at high temperature (Wen et al. 1984). Unsubstituted benzonitrile is more prevalent in many process water/offgas samples (Day and Rawlings 1981; Leenheer et al. 1982) and recycle gas condensate (Gebhart and McKown 1980) than some of the higher aliphatic nitriles. Sometimes it is the major nitrile (Pellizzari et al. 1979), and this was reflected by the correspondingly low concentration of 2-methylpyridine.

CYANATES

Hydrogen Cyanate.

Hydrogen cyanate (cyanic acid) would probably be a labile intermediate during retorting since it decomposes to carbon dioxide and ammonia. Heating in the presence of ammonia, however, can produce urea (Wohler Synthesis). Like cyanide ion, free cyanate is also difficult to determine chemically. Evidence does exist, however, for its occurrence at high concentrations in coal gasification water (Farzam, Felder, and Ferrell 1985).

Thiocyanate.

In contrast to cyanate, thiocyanate (a tautomer with isothiocyanate) has been reported in both retort water (in high concentrations) and the gas condensate from Oxy-6 (Leenheer et al. 1982), even though it is a nonvolatile anion. This reaffirms that it probably is formed from the reaction of volatile HCN and sulfide species, the latter of which must first undergo partial oxidation to polysulfides (Luthy et al. 1979). These reactions are probably responsible for keeping the aqueous cyanide ion concentration low (Stuber, Leenheer, and Farrier 1978). Analogous to cyanate, heating of thiocyanate with ammonia could produce thiourea (PUC). Thiocyanate has been proposed as a conservative tracer of retort contamination of aquifers because of its high concentrations, stability, and resistance to biodegradation (Stuber et al. 1978). Although nontoxic, thiocyanate is responsible for severe corrosion problems with steel (Luthy et al. 1979).

The alkylthiocyanates are only slightly soluble in water and would therefore partition to the oil. They are highly toxic but none has been reported in oil shale process streams. The alkylisothiocyanates are less toxic. They can result from reaction of carbon disulfide and alkyl amines, but none has been reported in oil shale process streams.

ORGANOSULFUR (nonthiophenic)

Although the main sulfur-containing compound in retort offgases (contributing up to 98% of the vapor-phase sulfur) is hydrogen sulfide (Hester, Mester, and Wang 1983; Ondov et al. 1982; Sklarew et al. 1984; Wong et al. 1984) and the main organosulfur compounds are thiophenes, other organosulfur compounds could be extremely important in retort offgases. Even though they comprise only a small percentage of total sulfur in retort offgases (<2-20% together with thiophenes), their potential conversion to SO_2 during offgas combustion would increase the burden placed on achieving extremely high H_2S removal efficiencies prior to offgas incineration. These sulfur emissions, in contrast to those of the thiophenes, mainly reflect the pyritic sulfur content of the raw shale, which undoubtedly is the major origin of the hydrogen sulfide (Sklarew et al. 1984; Wong et al. 1984); hydrogen sulfide does have a secondary, organic origin, being emitted at 250-450°C (Wong et al. 1984). For this reason, the concentrations of these secondary organosulfur compounds (together with hydrogen sulfide) in retort offgases seem to correlate positively with each other (Sklarew et al. 1984; Wong et al. 1984). Indeed, if secondary reactions and condensation were eliminated, quantification of just one sulfur compound would allow prediction of the others (Wong et al. 1984). The absolute concentrations of these gases varies widely, however, as a result of different conversion efficiencies of sulfur in different shales (e.g., $8 \pm 7\%$) (Wong et al. 1984).

Carbonyl sulfide, carbon disulfide, dialkylsulfides (thioethers) and methane-, ethane-, and propanethiol (methyl-, ethyl-, and propylmercaptan) have been identified in offgas (Hester et al. 1983; Sklarew et al. 1984; Wong et al. 1984). The first two sulfides have only pyritic origins (since they parallel high-temperature H_2S emissions) and probably result from reaction of H_2S with carbon dioxide and methane, respectively. The lower thiols have both organic and pyritic origins (Wong et al. 1984); the latter origin is probably from reaction of hydrogen sulfide with methylene and ethylene radicals. The thiols and sulfides also are major products of thiophene hydrocracking, resulting from C-S and C-C bond cleavage, respectively; this is probably their origin from the shale as well as from hydrocracking, especially since organic thiols may not exist in raw shale (Bissell 1983). Preference for C-S bond scission explains why the thiols are more common than the alkylsulfides; this is analogous to the preferential formation of primary alkyl amines versus secondary or tertiary amines from N-heterocycles (see "Amines"). The higher thioalcohols ($>C_3$) and thioethers (dialkylsulfides) are for the most part notably absent from offgas (Hester et al. 1983; Sklarew et al. 1984; Wong et al. 1984), probably because of their reactivity. During the hydrotreatment of shale oil, many open-chain and cyclic sulfides (e.g., thiolanes) are produced. These have been noted in sour-water condensate (Wingender et al. 1981). Thiophenolates could possibly result from hydrocracking of benzothiophenes (Wood et al. 1985), and diphenylsulfide could result from dibenzothiophene (see "Benzothiophenes"). The thiols and sulfides could be major contributors to odor in offgases that have been scrubbed for H_2S. Their contact with process waters, however, would cause ionization.

The most thorough sulfur-gas characterization study to date (Wong et al. 1984), which achieved mass-balance closures around sulfur, verifies the difficulties in offgas analysis. Much of the variability in inter-comparisons probably is caused by the difficulty in collecting and storing sulfur gases because of their adsorption, condensation, or reaction with any available surface; this is especially true for hydrogen sulfide (Wong et al. 1984).

No organosulfur characterization has been done for the process waters, but the potential reactions are well established. Not surprisingly, hydrogen sulfide is not found in process waters that have been stored (e.g., Stuber et al. 1978; Wallace and Alden 1984); this is a result of its high reactivity with functionalized organic solutes. The thiols (in particular thioalkanols) would form insoluble salts with any heavy metals (esp. mercury); this may be a major explanation for the extremely low mercury concentrations in the waters. These mercaptides can undergo nucleophilic displacement reactions to yield thioethers. Thiols can also react with alkanoic acids, alkanals, and alkanones to give thioesters, dithioacetals, and dithioketals, respectively (PUCs). But for the most part, thiols are easily oxidized to disulfides, and under vigorous oxidative conditions, these oxidize to sulfoninc acids (PUCs); sulfonates can also result from the addition of bisulfite to aldehydes and methyl- and cycloalkanones. The dialkylsulfides oxidize to sulfoxides; for example, dimethylsulfide gives dimethylsulfoxide (PUC). Many of these oxygenated sulfur species could be present in offgas plumes or combusted offgases.

All of the gaseous sulfur products identified in retort offgases also occur naturally in the troposphere (Adams et al. 1981). All of these have biological origins, primarily from bacterial metabolic processes in soils and sediments (Jorgensen and Okholm-Hansen 1985). These biogenic inputs together with all anthropogenic inputs are believed to be of equal magnitude (Jorgensen and Okholm-Hansen 1985). In the atmosphere, photochemical reactions of dialkylsulfides and alkylthiols result in aldehydes and alkylnitrates (in the gas phase) and alkanesulfonic acids (in the particulate phase) (Grosjean 1984); the latter is a contributor to acid deposition.

METAL- AND METALLOID-CONTAINING ORGANIC COMPOUNDS

The association of metal ions with organic structures confers greater solubility in organic solvents (i.e., reduces the effective polarity of the metal). These associations can be classified in a number of ways, falling into two broad categories: (1) organometallics, which have metal-carbon covalent bonds, and (2) metallo-organics, which have no metal-carbon covalent bond. The analogous metalloids incorporate the metal-like elements, such as arsenic and selenium. The reduced polarity of these structures and other aspects of their organic nature can have several important consequences when compared with the characteristics of the inorganic, ionized forms. These include: (1) increased bioavailability and toxicity (because of enhanced membrane permeability), (2) higher volatility (leading to enhanced environmental transport and exposure via inhalation), and (3) enhanced solubility in product oil (causing fouling of catalysts used in upgrading). The inorganic species, such as mercuric and arsenate ion, can also be made volatile by reduction to their elemental or hydride forms (e.g., Hg^0 and AsH_3).

The biogeochemistry and retort chemistry of these compounds with respect to their origins from within the shale and de novo synthesis is a field that is just emerging (e.g., Brinckman and Fish 1981). Because of the complexity of these topics, only a few aspects relevant to oil shale processing will be summarized.

Perhaps the simplest means of estimating the portions of various elements that are associated with organic structures is by various partitioning schemes. For example, "lipid-soluble" metallics (i.e., soluble in nonpolar solvents) have been investigated for a coal-gasification water (Dahl and Weissman 1982), and metallic compounds retained by reverse-phase chromatography have been examined in a cursory manner for retort waters (Olsen et al. 1981). In the latter report, of the few elements studied, only zinc, molybdenum, and iron were found to partition with less-polar materials; these were possibly porphyrin complexes. In general, the metal organic compounds are probably much more important with respect to the oils and the offgases.

Because of the numerous types of metal/metalloid associations with organic moieties, structural speciation is required for understanding how these elements fit into the scheme of kerogen structure and retort chemistry. The literature regarding molecular speciation is summarized below.

Organometallics and Metalloids.

The two major elements that have undergone the most research are mercury and arsenic. As with most of the other organic compounds identified in oil shale process streams, the organic forms of these two elements probably have concurrent and distinct origins (i.e., by direct derivation from the kerogen and by de novo synthesis).

mercury. Dialkylmercury homologs are the major forms of mercury that have been identified in process streams. These include dimethyl-, diethyl-, di-n-propyl-, and methylethylmercury (Olsen et al. 1985). Because of their volatilities, these compounds are found almost exclusively in offgas and their contributions to total mercury can account for almost all of the mercury in the raw shale (Olsen et al. 1985). In the process waters, the only organomercury species present would probably be alkylmercury cations. These, however, have not been reported. Methylation of mercury is a well-documented detoxification mechanism used by bacteria (Wood and Wang 1983) and could account for endogenous levels of methylated forms in raw shale. Mercury more likely exists in the raw shale in the form of mercaptides or associated with pyritic sulfur. The occurrence of the higher alkyl homologs in the offgases is evidence for de novo synthesis, probably by reaction of alkyl radicals with elemental or ionized mercury. This is further supported by the fact that evolution of elemental mercury in offgas precedes the evolution of organomercury as the retort temperature increases (Olsen et al. 1985).

Other retort chemistry involving mercury undoubtedly involves the thioalkanols (mercaptans) (see "Organosulfur").

arsenic. Organoarsonic acids are the major forms that have been identified in process streams. These include mainly methyl- and phenylarsonic acids (Fish, Brinckman, and Jewett 1982). Because these compounds would be ionized under the alkaline conditions of retorting, they probably do not occur in offgases or condensates. Because of its higher relative polarity, methylarsonic acid probably partitions mainly to the retort waters; concentrations up to 2 mg/L have been reported in various retort waters (Fish, Brinckman, and Jewett 1982). In contrast, the less-polar phenylarsonic acid may partition more to the oil; evidence for its presence in Paraho oil has recently been obtained (Jeong and Montagna, submitted). Recently, evidence has been presented that both species may be endogenous constituents of Green River oil shale (Fish et al. 1983). The diagenesis of lipids, where aliphatic arsonates are purposefully or fortuitously synthesized as analogs of phosphonolipids (Irgolic et al. 1981) could explain the occurrence of methylarsonates, but arylarsonates are not known products of biosynthesis. Alkyl and arylarsonates could easily be produced during retorting, however, by the reaction of any number of organic radicals with arsenic ion (e.g., Brinckman and Fish 1981, p. 321).

Most of the arsenic (90%) remains in the shale after retorting (Olsen et al. 1985), implying that in contrast to mercury, de novo synthesis may be a minor aspect to arsenic retort chemistry. Indeed, most of the arsenic in raw shale may be inorganic and associated with macromolecular or pyritic iron (Jeong and Montagna, submitted). The mobilization (e.g., biomethylation) of arsenic in retorted shale and its implications for the leaching or volatilization (e.g., trimethylarsine) of arsenic from disposal piles have undergone preliminary investigation (Hassler, Klein, and Meglen 1984). Availability of nutrients, carbon (energy), and phosphate have positive influences on the various mobilization processes. Anaerobic conditions, which could evolve within a disposal pile, were inhibitory to the processes (Hassler et al. 1984). Methyl- and phenylarsonic acids have much less affinity for retorted shale than does arsenic acid (Conditt 1984).

In addition to methyl- and phenylarsonic acids, more-polar arsenic-containing compounds may also be present in process waters as indicated by their shorter retention times during reverse-phase chromatography (Fish, Brinckman, and Jewett 1982; Fish et al. 1983). These could be hydroxy- and amino-substituted phenylarsonates. For example, phenol or aniline can react with arsenic acid (Bechamp Reaction) to give 4-hydroxy- or 4-amino-phenylarsonic acid (PUCs), respectively. These reactions could also occur during retorting.

metal carbonyls. Metal carbonyls can form when carbon monoxide passes over elemental metals at high temperature. The carbonyl of most significance for petroleum refining is nickel carbonyl (nickel tetracarbonyl), a highly toxic and volatile compound that readily oxidizes; iron and cobalt carbonyls are also prevalent in petroleum refining. Although the formation of metal carbonyls is enhanced by the presence of abundant metal catalysts during oil upgrading, they could also result from the endogenous minerals of shale during retorting. These compounds are of unknown significance in oil shale processing.

organo hydrides. Hydrides of lead, tin, and arsenic can form with alkyl radicals. These are volatile and relatively stable. They are of unknown significance in oil shale retorting.

Metallo-Organics and Metalloids.

Non-covalently bonded metals associated with organic structures comprise the coordination complexes (i.e., ligand chelates, in particular the prophyrins) and pi-electron complexes such as arene carbonyls and metallocenes (e.g., the cyclopentadienyl iron complex, ferrocene). Speciation of these metal complexes in any of the process streams is an extremely difficult task, the study of which has only begun (Stanley and Sievers 1985).

porphyrins. Alkylated petroporhyrins are presumed to derive from diagenesis of chlorophylls. It has been suggested, however, that these compounds more likely result from bacterial synthesis rather than from chlorophyll diagenesis (Sugihara and Branthaver 1976). They occur in petroleum source rock as chelates of numerous metals, in particular vanadium, nickel, copper, and iron. The vadanium chelate is the most common because it is the most stable. Metalloporphyrins are probably a major source of pyrroles during pyrolysis. Any porphyrins that survive pyrolysis would partition to the oil because of their lipophilic nature. Their occurrence in significant concentrations in crude oil, however, is controversial because they are difficult to analyze, especially since the metals (i.e., nickel and vanadium) associate mainly with the heavy N-heterocycle distillates. Most metal may indeed be associated with non-porphyrin ligands (Fish, Komlenic, and Wines 1984). A nickel porphyrin was recently isolated from shale oil but not from retort water (Olsen et al. 1981).

non-porphyrin ligands. As mentioned previously, metal ions probably play critical roles in solubilizing organic ligands within the aqueous phase. This is especially true for the N-heterocycles and aromatic primary amines (Stetter, Stamoudis, and Jorgensen 1985); ferric ion would be a major factor (Jorgensen and Stetter 1982; Stanley and Sievers 1985). Pyrroles also form salts with alkali metals. Indeed, metal association with polyfunctional (hydroxyl, sulfhydryl, and carbonylic) organic solutes may be one of the factors impeding the identification of these polar organic compounds (Peterson et al. 1984). The preponderance of organonitrogen compounds, many of which are potential ligands, may also play a significant role in the mobilization and transport of metals from retorted shale (e.g., Stanley and Sievers 1985). High-molecular-weight N-heterocycles may be responsible for chelating most of the metals that occur in oil.

MISCELLANEOUS

Organohalogens.

There have been a few reports of trihalomethanes or other halogenated alkanes in oil shale process streams. For example, dichloromethane, chloroform, and trichloroethane were reported in retort water from the LLL simulated MIS retort (Gebhart and McKown 1980). A possible source of these compounds could be from the use of chlorinated water at the retort. All of these compounds, however, are ubiquitous environmental constituents and have both natural and anthropogenic sources.

There are several possible sources for these compounds in retorting, including (1) pyrolytic products from low levels of halogenated compounds introduced or contacted with any portion of the retort process (e.g., poly[vinylchloride] pipe), (2) pyrolysis products of halogenated organic compounds that are endogenous constituents of the kerogen (microbial halophytes are capable of synthesizing countless chlorinated and brominated compounds), (3) formation by chlorination of pyrolysis products after introduction of reuse water that has been chlorinated, (4) formation by the still-debated mechanism of high-temperature reaction of chloride ion (which is common in retort water) with suitable organic precursors, and (5) sample contamination by vapors from laboratory solvents during analysis.

The last of these possibilities is very probable since the most commonly reported compound is dichloromethane (methylene chloride), a very frequently used laboratory solvent; proper sampling and analysis blanks can control for this possibility. The first point could also be a source since poly(vinylchloride) polymers are used so extensively. The second point is of unknown significance since nothing is known about endogenous halogenated constituents in oil shale; these could easily be endogenous constituents, but their existence has never been investigated. The third point would mainly be responsible for trihalomethanes, especially chloroform; dihydroxybenzenes, among other retort process constituents, readily react with chlorine, especially at pH 8-10 (Boyce and Hornig 1983). The fourth possibility, reaction at high temperature with chloride ion, has been put forth as a mechanism of polychlorinated dibenzofurans and benzenes, but it is still highly questionable (Fink 1983).

Other Nitrogenous Compounds.

Small amounts of nitro- and nitroso-phenols have been reported for the water from the LLL retort (Gebhart and McKown 1980). N-Nitroso and hydrazine compounds have also been reported for coal-gasification gas condensates (see Yen 1981). These reports are of unknown significance, but nitroso derivatives are well known mutagens. These compounds could result from gas-phase reactions with nitrous acid (e.g., Haugen, Peak, and Reilly, Jr. 1981) and therefore could be important during offgas combustion; a parallel problem of formation of nitrated polycyclic aromatic hydrocarbons has been discussed (see "PAHs"). Recently, it has been found that nitrosation of secondary amines (e.g., diphenylamine and N-alkyl anilines) can be effected in aqueous solution under alkaline conditions during biotreatment with activated carbon (DiGiano, Carrier, and Dietrich 1984).

IV. Chemical-Class Indicator Compounds and Relationships of Reaction Pathways

The literature review presented in Section III on the occurrence, origin, and fate of organic compounds in the retort process should provide a better understanding of retort chemistry. This information could be used for developing an environmental monitoring plan for a commercial-scale facility. Such a process is outlined in this section.

The extraordinary complexity of oil shale process streams would necessarily mean that complete chemical characterization of process emissions would not be practically or economically feasible. It would therefore be necessary to choose or predict those compounds that would serve as a limited but representative spectrum of the composite whole. This process could obviously be facilitated if a complete computerized data base existed for the published compositions of all process streams from oil shale processes; pattern recognition techniques could then be used to extract the suite of compounds that served as the "principal components" (i.e., the minimum set of compounds whose presence and quantitation could be used to calculate the occurrence/concentration of the remaining, unidentified/unquantified set). Since this latter approach is not currently possible, the information presented in Section III will be used to rationalize a suitable set of compounds for an environmental monitoring program. This problem has already received some attention (Henschel and Stemmle 1983), but the data used in that study were very limited and the approach was generic, being intended for synfuel facilities in general.

Any decision process for choosing a compound or chemical class to be monitored in a given process stream should be based on at least one of the following considerations. The compound or chemical class should:

(1) Represent a distinct chemical class or subclass.

(2) Originate during retorting from origins distinct from those of other chemical classes, whether these origins are from raw shale extraction, distillation/mild pyrolysis of kerogen, severe pyrolysis/cracking, or secondary chemical reactions.

(3) Occur at a high concentration within its class.

(4) Possess significant properties with respect to potential health effects (e.g., acute toxicity or mutagenic potential) or nuisance (e.g., malodor, atmospheric haze).

(5) Possess significant potential for environmental effects, including (i) persistence (resistant to chemical, photochemical, biological transformations, or subject to bioaccumulation) or (ii) easily transformed, causing indirect problems (e.g., photochemical pollution, oxygen demand in ground- or surface-waters).

(6) Belong to a list of regulated compounds (e.g., EPA priority pollutants).

The first two points refer to the concept of "principal components". A major objective is to eliminate redundancy. Compounds of the same chemical class generally share the same pathways of formation from kerogen or of de novo synthesis. Only the most abundant need to be monitored; in some instances, however, compounds of seemingly related natures may have totally different origins. Compounds from seemingly unrelated classes, however, can also share the same pathways of formation. For these classes, a decision to include or exclude one or the other can be based on environmental/health significance.

The relatedness or unrelatedness of the chemical classes relevant to retorting can be visualized by constructing a flow chart of reaction pathways. From the discussions of retort chemistry in Section III, a generalized scheme can be devised for the origin and fate of each chemical class within the retort. Such a scheme comprises the dendrograms in Figure 1. The chemistry of the retort process is divided into four sections, all of which ultimately relate back to constituents endogenous to the kerogen/shale matrix. The first section comprises those structures that are mostly ill-defined, unaltered endogenous constituents of kerogen, such as fatty acid salts, porphyrins, and algal hydrocarbons. The second section comprises the compounds that result from thermally induced liquid extraction of the raw shale or direct distillation/mild thermolysis of kerogen constituents. The third section is those classes that originate from more severe pyrolysis of the initial distillate/pyrolysate or from reaction of these compounds with inorganic minerals or gases. Compounds of the fourth section represent products of even latter chemical/pyrolytic reactions; many of these can occur outside the immediate environment of the retort. It should be remembered that many of the compounds that are shown in these pathways may be produced in significant quantities but their instantaneous, transient concentrations in a process stream may be low because of their reactivity (e.g., alkanals, alkanones, alkenes, acetylene, hydrogen, ammonia, hydrogen sulfide). Many of these compounds represent the driving force for the de novo synthesis of many of the compounds that are found in the retort waste streams. These latter compounds are secondary products; they do not necessarily directly reflect the structure of kerogen. Many of these are stable end-products but some lead to tertiary products upon exposure to molecular oxygen or even higher temperatures (cracking), such as those often occurring in in-situ retorts or at oil upgrade facilities. Some of these tertiary reactions can occur both within and outside the retort (i.e., in the environment).

It is clearer from the dendrograms of Figure 1 as to which classes or subclasses have common and which have distinctly different pathways of origination. Those seemingly related subclasses that have distinct origins include representatives from the following classes:

(1) ketones:	alkanones (kerogen, aldehydes, alkanoic acids) cycloalkanones (alkanedioc acids)
(2) hydrocarbons:	alkanes (kerogenic algal/plant hydrocarbons) alkenes (kerogenic chlorophyll phytyl) alkylbenzenes (kerogenic carotenoids) PAHs (acetylene, alkylaromatics)
(3) cyanides:	hydrogen cyanide (ammonia and methane) alkylnitriles (acylamines) benzonitriles (2-methylpyridines)
(4) acids:	alkanoic (kerogenic constituents, e.g., glycerides) alkanedioc (kerogenic constituents; entrapped) benzoic (kerogenic constituents; alkylbenzenes)
(5) aromatics:	alkylbenzenes (kerogenic carotenoids) PAHs (acetylene; alkylaromatics) fused-ring heterocycles (aldehydes and amines).

Those seemingly unrelated classes that can result from common origins include:

(1) benzoic acids and hydroxybenzenes: (alkylbenzenes)

(2) alkenes and pyrroles: (porphyrins)

(3) oxo-pyridines, benzonitriles, and alkylamines: (alkylpyridines.)

(4) acylamines, alkylnitriles, and alkanoic acids (all interrelated)

The chemical classes that have been repeatedly identified in oil shale process streams and summarized in Section III are compiled in Table II. For each of various process streams from all types of retort processes, the relative contributions to the organic forms of carbon, sulfur, and nitrogen are listed for each chemical class. It must be emphasized that these relative abundances are in many cases extremely rough estimates. This is mainly because there are few studies that have quantified many classes at once (e.g., Bell et al. 1983; Dobson et al. 1985; Leenheer et al. 1982; Pellizzari et al. 1979; Raphaelian and Harrison 1981; Rovere et al. 1983) and none that has extensively quantified polar/nonvolatile and volatile solutes at the same time. In general, the abundances are shown in Table II only where the contributions from a particular class are known to be significant or known to be of no significance; when information was not available, the field was left blank. These abundances also reflect the maximum possible contributions for a particular class. For example, the relative proportions of nitriles and amides can vary widely, and aromatic and alkyl amines are strict functions of whether cracking has occurred. With these abundance frequencies, one could deduce whether to monitor for a particular chemical class in a particular process stream. Included in the last column of Table II are rough indications as to whether the class is volatile or steam strippable under the alkaline conditions of retorting; some compounds that are normally volatile in the neutral forms (e.g., alkanoic acids, thiols, phenols) may not be volatile when present in the retort waters or retorted shales. These data can be used to deduce whether a class is to be expected in the headspace that contacts a particular stream (e.g., volatilize from storage ponds or retorted shale piles) or whether a class would be effectively removed by steam stripping. The primary contributors to organic carbon, nitrogen, and sulfur in each stream or phase have been taken from Table II and summarized in Table III.

The one or two most abundant or frequently occurring compounds of each chemical class that have been identified in oil-shale process streams are listed in Table IV; priority pollutants are also indicated where appropriate.

With Figure I and Tables I-IV, a rationale can be presented for minimizing the number of classes and compounds that would suffice for representative source monitoring; ideally, these compounds would constitute a unique signature for oil shale processing as opposed to other synfuel processes. These compounds, would be those occurring at high concentrations and which have unique origins and present possible environmental/health hazards. An illustrative attempt at deriving such a list of "key indicator compounds" is indicated by the asterisks (*) in Table IV. By ignoring those compounds that have common origins, redundancy could be minimized. The occurrence of a particular, chemical-class representative would therefore signal the presence of its associated relatives. The rationales for choosing each of these (and for excluding the remainder) are summarized in Table V. These indicator compounds were chosen on the basis of unique origins, toxicity, potential for environmental/health consequences, or whether they were unique to shale processing. Some could be chosen as indicators of the occurrence of cracking or oxidation during retorting (i.e., aryl-/alkyl-amines, arylcyanides, and thiolanes). Those that were excluded were as a result of redundancy in their origination or fate or of insignificant toxicological/environmental consequences. It should be noted that almost all of the recommended compounds are volatile (Table II). This means that they will be found in the headspace that contacts any stream in which they are present; their chance of occurring in fugitive emissions is therefore maximized. This also means, however, that monitoring is facilitated since gas chromatography can be used. Some of the recommended classes represent redundant origins; these are usually required for compliance monitoring (e.g., COS, CS_2, thioalcohols).

In the example presented above, the number of organic compounds required for monitoring retort process-stream emissions has been minimized for several reasons. The central issue is that even an extensive monitoring program that measures several representatives from each subclass would still not account for major portions of organic carbon. This is especially true for the retort waters, which contain high concentrations of polar organic compounds. Representatives of the subclasses that could account for at least some of these unidentified organic compounds were flagged in Section III as "possible unidentified components" (PUCs). These are summarized in Table VI. From this list of PUCs, one can surmise that certain of these may comprise major portions of the unidentified organic carbon. This is especially true of the polyfunctional compounds and others that are hydroxylated or aminated; this would make them much more polar/nonvolatile and therefore difficult to analyze. The most likely to occur or most toxicologically significant compounds or subclasses are denoted by asterisks (*) (Table VI) Of these, the aldols, aldehyde-ammonia-adducts and polymers, polyhydric alkanols, and hydroxyalkanoic acids may be of particular significance with respect to overall contributions to organic carbon. Others, such as hydroxycarbazoles, aminoindoles, hydantoins, amino acids, cyanohydrins, and ammonia-aldehyde adducts, may be significant contributors to organic nitrogen; the presence of large numbers of these kinds of compounds would account for the large amounts of organonitrogen in retort process waters (e.g., Daughton et al. 1985). One class of PUCs, the aminated PAHs and aminated azaarenes (e.g., aminodibenzothiophenes), although possibly present only at low concentrations in the process waters, may be responsible for much of the mutagenicity of the oils and particulates.

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130 DAUGHTON C G
ORGANIC CONSTITUENTS OF OIL SHALE PROCESS STREAMS: OCCURRENCE, ORI

VI. TABLES AND FIGURES

Table I. Chemical Nomenclature[a] Relevant to Oil Shale Process Streams

Substituent Groups and Positions

- **alkyl group** (alkane radical): conceptual group remaining after removal of one H from an alkane (abbrev. "R"); methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl.
- **aryl group** (phenyl radical): conceptual group remaining after removal of a hydrogen from benzene (abbrev. "Ar").
- **functional groups**: atom(s) other than carbon occurring in place of a hydrogen atom in a hydrocarbon, often conferring reactiveness.
- **positional isomers**:
  - di-substitution positions on six-membered rings are referred to as ortho (o-), meta (m-), and para (p-) depending on whether they are adjacent (1,2-), have one intervening carbon (1,3-), or are opposite (1,4-), respectively.
  - substitutions with respect to a functional group are termed alpha-, beta-, gamma-, or omega-, if the substituent is bonded adjacent to, one carbon removed, two carbons removed, or at the opposite end, respectively.

HYDROCARBONS (contain only C and H)

Aliphatic/Olefinic
- occur in homologous series (homologs). **Homologs** differ by only one methylene ($-CH_2-$) unit.

Alkanes (aliphatic; paraffins); - methane -
- · **acyclic** (not cyclic) and saturated (fully reduced or hydrogenated)
- · **branched** and **normal** (n-; straight chains): C_nH_{2n+2}
- - homologous series starting with methane include: ethane, propane, butane, pentane, hexane, heptane, octane, nonane, decane

Cycloalkanes (alicyclic); - cyclopentane -
- · saturated hydrocarbons containing a ring

Alkenes (olefins; unsaturated hydrocarbons); - ethene -
- · contain at least one C=C double bond

Cycloalkenes; - cyclopentene -
- · cyclic hydrocarbons containing one C=C double bond

Arenes (aromatic hydrocarbons)
- occur in homologous series (benzologs). **Benzologs** differ by only one benzene ring ($-C_4H_4-$).

Alkylbenzenes (phenylalkanes) (e.g., toluene, xylenes, and isomers and homologs): $Ar-R_n$
- -methylbenzenes: - toluene -
- -dimethylbenzenes: - xylenes -
- -trimethylbenzenes: e.g., - mesitylene (1,3,5-)-

Diaromatics (naphthalenes); - naphthalene -

Polycyclic Aromatic Hydrocarbons (PAHs)
- - fused aromatic rings, having two carbon atoms common to at least two rings
- · polynuclear aromatics (PNAs); - anthracene -

Hydroaromatics; - tetralin - (1,2,3,4-tetrahydronaphthalene)
- - aromatics with at least one partly or fully reduced (hydrogenated) ring

Table I (continued)

HYDROXYLATED DERIVATIVES (H replaced by hydroxyl, -OH)

Alkanols (alcohols): R-OH; - methanol -
Hydroxybenzenes ("phenols", "naphthols", and alkyl homologs)
- monohydroxybenzenes: Ar-OH; - phenol -
- methylphenols (cresols): CH_3-Ar-OH; - (o-, m-, p-cresols -
- dimethylphenols (xylenols; six isomers): $(CH_3)_2$-Ar-OH
- dihydroxybenzenes (benzenediols): Ar-$(OH)_2$
  - o-dihydroxybenzene: - pyrocatechol -
  - m-dihydroxybenzene: - resorcinol -
  - p-dihydroxybenzene: - hydroquinone -

Hemiacetals
- result from addition of alcohols to carbonyl of aldehydes: R-CH(OH)(OR); e.g., 1-isopropoxyethanol

CARBONYL DERIVATIVES (oxygen atom doubly bonded to a carbon atom): -C(O)-

- **keto-enol** isomers (reversible hydrogen transfer from carbon adjacent to carbonyl group to the carbonyl oxygen), e.g., R-C(H)O <> R=C(H)OH

Aldols: beta-hydroxycarbonyl compounds: R-HC(OH)O
Aldehydes
- acyclic (alkanals; aliphatic aldehydes): R-C(H)O; - formaldehyde -
- cyclic (alicyclic and aromatic): Ar-C(H)O; - benzaldehyde -

Ketones
- acyclic (**alkanones**; aliphatic ketones): R-C(O)-R; - acetone -
- cyclic: Ar=O; - cyclopentanone -

Acids
- **alkanoic**
  - aliphatic monocarboxylic acids: R-C(O)OH; - formic acid -
  - homologous series starting with formic acid include: acetic, propionic, butyric, valeric, caproic, enanthic, caprylic, pelargonic, and capric
- **alkanedioc**
  - aliphatic dicarboxylic acids: R-$[C(O)OH]_2$; - oxalic acid -
  - homologous series starting with oxalic acid include: malonic, succinic, glutaric, adipic, pimelic, suberic, azaleic, and sebacic
- **aromatic**
  - benzoic acids and alkyl derivatives: R_n-Ar-C(O)OH; - benzoic acid -
  - methyl benzoic acids: CH_3-Ar-C(O)OH; - toluic acid -
  - benzene dicarboxylic acids: Ar-$[C(O)OH]_2$; - phthalic acid -

Anhydrides: cyclized derivatives formed by elimination of water; e.g., succinic anhydride

Table I (continued)

Esters
- hydroxyl group of carboxylic acid replaced by -OR; R-C(O)-OR; - ethylacetate -
- **lactones** (intramolecular, cyclized esters); - butyrolactone -
  - formed by dehydration of an hydroxyl and carbonyl group

Amides (amino derivatives of carboxylic acids; alkanoic acid amines)
- aliphatic: R-C(O)NH_2; - formamide -
- **lactams** (intramolecular cyclized amides); - 2-pyrrolidones, 2-piperidones, 2-pyridone -
  - formed by dehydration of an amino and carboxy group
- urea: NH_2-C(O)-NH_2

AMINES
- primary: H replaced by -NH_2); secondary: $(R)_2$-NH; tertiary: $(R)_3$-N

Alkyl amines; mono-, di-, and trimethyl amines
Aryl amines (anilines, aminobenzenes): Ar-NH_2; - aniline -
- nitrogen occurs exo to benzenoid system
- methyl anilines (toluidines)
- dimethyl anilines (xylidines; six isomers)

Aralkyl: Ar-R-NH_2; - benzylamine -
Fused-Ring Aromatic and Heteroaromatic: - naphthylamine -

HETEROCYCLES
- **heteroaromatic compounds**; one or more ring carbons replaced by a hetero atom, esp. aza (N), oxa (O), or thia (S)

HETEROCYCLES **(pi-electron excessive)**
- aza, oxa, and thia derivatives of cyclopentadienyl carbanion)
- 5-membered heteroatom rings with more delocalized pi-electrons than atoms over which they are delocalized
- "iso" derivatives of benzo derivatives have one carbon separating the heteroatom from the benzoid system (referred to as benzo[c] derivatives as opposed to benzo[b] derivatives)

Pyrroles (aza derivatives of cyclopentadienyl anion); - pyrrole -
- reduced forms are cyclic, secondary amines; - pyrrolidine -

Oxo-Pyrroles (2-oxopyrroles are synonymous with lactams); - pyrrolid(in)ones -
Benzopyrroles (indoles, isoindoles); - indole -
Thiophenes (thia derivatives); - thiophene -
- reduced forms are alicyclic sulfides; - thiacyclopentane (thiolane) -

Benzothiophenes (aromatic derivatives); - benzo(b)thiophene -
Furans (oxa derivatives); - furan -
- reduced forms are alicyclic ethers (thiolanes); - tetrahydrofuran -

Benzofurans (aromatic derivatives); - benzofuran -
Fused-Ring (heterocyclic arene analogs); - carbazole -

Table I (continued)

HETEROCYCLES (**pi-electron deficient**); aza, thia, and oxa derivatives of benzene
- heteroaromatics, esp. 6-membered rings, in which pi-electron density is less than that of aromatics

Pyran (oxa derivative)
Pyridines (aza derivatives); - pyridine -
  - methylpyridines (picolines)
  - ethylpyridines (lutidines)
  - ethylmethylpyridines (collidines)

Pyridine carboxylic acids
  - o-, m-, and p-derivatives are picolinic, nicotinic, and isonicotinic acids, respectively

Oxo-Pyridines (3-hydroxypyridines; 2- and 4-pyridones); - 2-pyridone -
Naphthyridines (benzopyridines; quinolines, isoquinolines); - quinoline -
  - 4-methylquinolines (lepidines)
  - 2-methylquinolines (quinaldines)

Fused-Ring (heterocyclic analogs of arenes); - acridine -
Multi-Hetero Aromatics
  · contain at least two occurrences of same hetero atom; e.g., hydantoins

Mixed-Hetero Aromatics
  · contain at least two dissimilar hetero atoms; e.g., thiazoles

Other Aza-Heterocycles
  · 3- and 4-membered rings; e.g., azetidines, aziridines

CYANIDES (terminal nitrogen atom triply bonded to carbon)

· Hydrogen cyanide (hydrocyanic acid); HCN
· Alkyl (**alkanenitriles**); R-CN; - acetonitrile - (ethanenitrile; methylcyanide)
· Aryl (phenylcyanides; cyanobenzenes; **benzonitriles**); Ar-CN; - benzonitrile -
· **Cyanohydrins**
  - result from addition of HCN to carbonyl of aldehyde; RCH(OH)(CN);
  - acetocyanohydrin - (2-hydroxy-2-methyl-propanenitrile)

CYANATES/THIOCYANTES (H replaced by -O-CN or -S-CN)
· **Cyanate ion**; $CN\text{-}O^-$ (cyanic acid)
· **Thiocyanate ion**; ^-SCN (tautomer with isothiocyanate; $^-N=C=S$)

ORGANOSULFUR (nonthiophenic)

· Carbonyl sulfide; O=C=S
· **Thiols** (H replaced by a mercapto group, -SH; analogs of alcohols)
  - **thioalcohols** (mercaptans); R-SH; - methane thiol (methyl mercaptan) -
  - **thiophenols**; Ar-SH; - thiophenol -

· **Sulfides** (dialkylsulfides)
  - H replaced by -SR; thioethers; R-S-R; - dimethylsulfide -

· **Sulfoxides**
  - sulfide sulfur atom bonded to one oxygen atom; R-S(O)-R; - dimethylsulfoxide -

· **Sulfones**
  - sulfide sulfur atom bonded to two oxygen atoms; $R\text{-}S(O)_2\text{-}R$

· **Sulfonic acids**
  - H replaced by sulfo group, $-S(O_2)OH$; $R\text{-}S(O)_2OH$

· **Sulfonates**
  - esters of sulfonic acids; $RS(O_2)OR$

Table I (continued)

METAL ORGANIC

- **Organometallics** (contain metal-carbon covalent bond); e.g., R_2Hg
- **Metal Organics** (metals associated with functionalized organic compounds (coordination complexes; chelates; ligands)

- **Alkylarsonates**
  - contain C-As bond; $R\text{-}AsO_3$; - methylarsonic acid -
- **Mercaptides**; water-insoluble mercury salts of thiols
- **Alkylmercurials**; R_2Hg; - dimethyl mercury -
- **Porphyrins**; tetrahydropyrrole ligands of vanadyl, nickel, etc.

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[a] Chemical classes are listed only when relevant to oil shale processing. Synonyms are given in parentheses. Simplest member for each chemical class is given as an example (underlined). Key words used in report are highlighted in boldface.

Table II. Chemical-Class Contributions to Relative Abundance of Organic Forms of Carbon, Nitrogen, and Sulfur Identified in Process Streams [a]

Chemical Class	Oil (crude)	Oil (hydrotreated)	Retorted (spent)	Particulates aqueous-phase	Particulates vapor-phase	Water (retort)	Water (condensate) retort	Water (condensate) refining	Retort Offgas	Head-space[b]
HYDROCARBONS										
Alkanes	C*	C*	C*	C*	C*	C'	C'	C'	C*	yes
Alkenes	C+	C'	C+	.	C+				C+	yes
Alkylbenzenes	C+	C'		C*	C+	C'	C*	C+	C+	yes
Diaromatics/PAHs	C+	C*	C+	C'	C*	--	C'	--	C'	no
HYDROXYLS										
Alkanols		--				C'	C*			yes
Hydroxybenzenes	C'	C'				C+	C*	C'	C'	no/yes
CARBONYLS										
Alkanals	C'	--				C'	C'	--	--	yes
Alkanones	C'					C'	C*	C'	--	yes
Cycloalkanones		--				C+	C+		--	yes
Alkanoic acids	C'	--	C+	C+		C*	C'	--	--	no
Alkanedioic acids	--	--	C"			C+	--	--	--	no
Aromatic acids	--	--	C+			C*	--	--	--	no
Amides (acyl)	C'N+	--				C"N+	C'N"		--	no/yes
Amides (lactams)	C'N+	C'N'				C"N+			--	no/yes
Urea						C'N"				no
AMINES (primary)										
Alkylamines	C'N'	C'N+				C'N'			--	yes
Arylamines	C'N'	C'N+				C"N+		C+N+	--	yes/no
HETEROCYCLES (pi-excessive)										
Pyrroles	C'N"	C'N'				C'N"	C'N'	--	--	yes
Oxo-pyrroles (see lactams)										
Benzopyrroles	C'N"	C'N+						C+N+		no
Thiophenes	C' S"	C' S"				C' S*	C' S*		C" S*	yes
Furans		--				C'			--	yes
HETEROCYCLES (pi-deficient)										
Pyridines	C"N*	C'N"	--			C+N*	C+N+	C"N*	C'N'	yes
Oxo-pyridines	C'N+					C'N+	--	--	--	no
Naphthyridines	C'N"	C'N+		C"N"		C+N"	C'N'	C"N"		yes/no
Fused-ring	C'N"	C'N"	C'N"	C'N+	C'N"	--		C+N+		no
Multi- & Mixed-						C'N'S*				no
CYANIDES										
Cyanide (hydrogen)								C'N"	C'N+	yes
Alkylcyanides	C"N"	--				C'N"	C+N*		C'N*	yes
Arylcyanides		--				C'N"	C+N+			yes
CYANATES										
Cyanate						C'N'	C'N'			
Thiocyanate						C'N"S+	C'N'S"			no
ORGANOSULFUR (nonthiophenic)										
Carbonyl sulfide									C' S+	yes
Thioalcohols	C' S"	C' S"							C' S+	yes
Thioethers (thiolanes)	C' S+	C' S+						C" S"		yes
ORGANOMETAL(LOID)S										
Alkylmercury									C' Hg+	yes
Methylarsonate						C' As+				no

[a] (*) = major source, (+) = secondary, (") = minor, (') = trace, (--) = not present; blanks mean that relevant information has not been reported. [b] Voaltile under the alkaline conditions of retorting; this means that the compounds could be present in headspace that contacts a process stream or that the compounds could be removed by steam stripping.

Table III. Primary Contributors to C, N, and S in Oil Shale Process Streams

Stream	Carbon	Nitrogen	Sulfur
crude oil	alkanes (>C_{10})	alkylpridines	thiophenes
hydrotreated oil	alkanes (>C_{10})	alkylpyridines/ aryl- & alkylamines	thiols
retorted shale	alkanes/PAHs	fused-ring N-heterocycles	fused-ring S-heterocycles
retort water	alkanoic acids	alkylpyridines	thiophenes/ thiocyanate
retort gas-condensate	hydroxybenzenes	alkylcyanides/ alkylpyridines	thiophenes
upgrade gas-condensate	alkylpyridines	alkylpyridines	thiophenes/ thiols
retort offgas	alkanes (<C_{10})	alkylcyanides	thiophenes
lquid-phase particulates	alkanes	naphthyridines	fused-ring S-heterocycles
gas-phase particulates	alkanes	fused-ring N-heterocycles	

Table IV. Most Abundant or Frequently Occurring Compounds from Each Chemical Class [a]

Chemical Class	Indicator Compound
Hydrocarbons	
alkanes	methane; n-decane
* alkenes	n-1-decene; 1-pristene
* alkylbenzenes	benzene; o-xylene; (toluene; ethylbenzene) [b]
* diaromatics/PAHs	(naphthalene); acenaphthene
Hydroxyls	
alkanols	2-propanol
* hydroxybenzenes	(phenol); 2-hydroxytoluene (o-cresol)
Carbonyls	
alkanals	formaldehyde; acetaldehyde
* alkanones	acetone; 2-butanone
* cycloalkanones	cyclohexanone
alkanoic acids	heptanoic acid
alkanedioc acids	pentanedioc acid
aromatic acids	benzoic acid; 2-methylbenzoic acid
amides (acylamines)	acetamide
* amides (lactams)	1-methyl-2-pyrrolidone; 2-piperidone
urea	urea
Amines (primary)	
alkylamines	methylamine
* arylamines	aniline; 2-ethylaniline
Heterocycles (pi-excessive)	
pyrroles	pyrrole; 2,5-dimethylpyrrole
benzopyrroles	indole; N-methylcarbazole
* thiophenes	thiophene; 2,5-dimethylthiophene
furans	benzofuran
Heterocycles (pi-deficient)	
* pyridines	2-methylpyridine; 2,4,6-trimethylpyridine
oxo-pyridines	2-pyridone
naphthyridines	quinoline; 2-methylquinoline
fused-ring	benzoquinoline; acridine
muti- and mixed-	5,5'-dimethylhydantoin (PUC)
Cyanides	
* hydrogen cyanide	hydrogen cyanide
* alkylcyanides	acetonitrile
arylcyanides	benzonitrile
Cyanates	
* thiocyanate	thiocyanate ion

Table IV (continued)

Organosulfur (nonthiophenic)	
* oxo	carbonylsulfide
* thiols	methanethiol
* disulfides	CS_2
sulfides (thiolanes)	dimethylsulfide
Organometal(loid)s	
* alkylmercury	dimethylmercury
alkylarsonates	methylarsonate

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[a] Asterisks denote classes to be monitored; see Table V for rationale. [b] Compounds in parentheses are EPA priority pollutants or required by compliance monitoring.

Table V. Monitoring-Program Rationale for Including (Excluding) Each Chemical Class [a]

Chemical Class	Unique or (Redundant) Origination/Fate	Retort Cracking/ Oxidation Indicator	Toxicological Significance	Environmental Significance	Oil Shale Process Specific[b]
HYDROCARBONS					
Alkanes	(kerogenic HCs)			(major C source in oil & solids)	no
Alkenes*	chorophyll (phytyl)			tropospheric free radicals	yes
Alkylbenzenes*	carotenoids		chronic; respired	priority pollutants	no
Diaromatics/PAHs*	acetylene condensation		chronic; respired	major C in retorted shale; persistent	no
HYDROXYLS					
Alkanols	(alkenes)			(short-lived; minor emissions)	no
Hydroxybenzenes*	alkylbenzenes		chronic/acute extremely malodorous	priority pollutants; major C source in retort condensates	no
CARBONYLS					
Alkanals	(kerogenic HCs)			(short-lived; major reactants)	no
Alkanones*	alkenes, fatty acids			short-lived; major reactants	no
Cycloalkanones*	alkanedioc acids		chronic		no
Alkanoic acids	(kerogen matrix)		(not significant)	(short-lived)	no
Alkanedioc acids	(cycloalkenones)		(not significant)	(short-lived)	no
Aromatic acids	(alkylbenzenes)		(not significant)	(short-lived)	no
Amides (acylamines)	(alkanoic acids, HCN)				yes
Amides (lactams)*	amino acids; oxo-pyridines and pyrroles		unknown	major N source in waters, oils	yes
Urea	(cyanide/ammonia)		(not significant)	(short-lived)	no
AMINES (primary)					
Alkylamines	(alkylpyridines)	(cracking)		(minor emissions)	no
Arylamines*	benzo heterocycles	cracking	chronic/acute mutagenic	biorefractory; major N source in sour waters	yes
HETEROCYCLES (pi-excessive)					
Pyrroles	(porphyrins)		(minor)	(short-lived; polymerization)	no
Benzopyrroles	(pyrroles)		(minor)	(short-lived; polymerization)	no
Thiophenes*	thiophanic biopolymers			major S source in offgas, waters, oil	no
Furans	(aldehydes)			(trace concentrations)	no
HETEROCYCLES (pi-deficient)					
Pyridines*	aldehydes and amines		extremely malodorous	major N source in waters, oil	yes
Oxo-pyridines	(alkylpyridines)			(monitor in ground water)	yes
Naphthyridines	(alkylpyridines)				yes
Fused-ring	(naphthyridines)				no
Multi- & Mixed-	varied		unknown		no
Aza-primary amines			extremely mutagenic		yes
CYANIDES					
Cyanide (HCN)*	ammonia and methane		acute		no
Alkylcyanides*	acylamines		acute	biorefractory; major N in offgas	yes
Arylcyanides	(alkylpyridines)	(cracking)			yes
CYANATES					
Thiocyanate*	sulfide and HCN			persistent; metal corrosion	yes
ORGANOSULFUR (nonthiophenic)					
COS*	H_2S and CO_2		acute; respired	major trace S in offgas	no
Thioalcohols*	organic thiols		extremely malodorous	compliance monitoring	no
Disulfides*	H_2S and CH_4		extremely malodorous		no
Thioethers	(thiophenes)		extremely malodorous	compliance monitoring	no
(thiolanes)	(thiophenes)	(cracking)			no
ORGANOMETAL(LOID)S					
Alkylmercury*	Hg + organic radicals		acute		yes
(Methylarsonate)	(arsenolipids)		(minor)	(trace concentrations)	no

[a] Classes to be monitored are in bold face and followed by asterisks (*); rationale for exclusion of a particular class are given in parentheses. [b] unique to oil shale retorting or present at significantly higher relative abundance than encountered in other synfuel processes; not ubiquitous in the environment.

Table VI. Possibly Unidentified Organic Compounds (PUCs) of Oil Shale Processing [a]

Hydroxyl Compounds

* polyhydric alcohols; glycerol
* poly(oxymethylene)glycols
* higher aldols (3-hydroxycarbonyls; e.g., 3-hydroxybutanal)
* hydroxy alkanoic acids
* hemiacetals

4-hydroxyaromatic acids
2-hydroxymethylphenols
hydroxyalkylpyridines; 2-hydroxymethyl-3-hydroxypyridine
pyridylcarbinols; 2-pyridyldialkylcarbinols
2-quinolone; 1-isoquinolone

* hydroxycarbazoles
* hydroxybenzothiophenes

Aldehydes

3-phenyl-2-propenal (cinnamaldehyde)
pyridinecarboxaldehydes

Ketones

cycloheptanone

* polycyclic aromatic ketones (PAKs)

quinolones

Acids

* hydroxy alkanoic acids

thiophenic carboxylic acids

Amides

* alkyl(benzyl)carboxamides (water streams)

hydrobenzamides
succinimide
thiourea

Amino Compounds

* 2-, 4-, and 5-aminoacids
* aldehyde-ammonia adducts (e.g., 1-aminoethanol; polymers)

cyclohexylamines
aralkylamines

* 2-naphthylamine

2-aminopyridine

* aminoindoles
* aminodibenzothiophenes

methyl- and dimethyl-secondary and tertiary amines
methylolamines
aminonitriles
aminodibenzothiophenes

Table VI (continued)

Heterocycles

- * metheamine
- pyrans
- 2- and 4-pyridine stilbazoles
- * hydantoins (e.g., 5,5'-dimethylhydantoin); hydantoic acids
- imidazoles
- benzo(*b*)thiophene
- * phenyl- and mono- and dibenzothiophenes
- methylthienopyridines
- pyrazines
- pteridines
- purine
- adenine

Other Organonitrogen Compounds

- nitroarenes (nitro-PAHs)
- nitroso compounds

Other Organosulfur Compounds

- mercaptides
- thioesters, dithioacetals, dithioketals
- butenethiols
- diphenylsulfides
- sulfonic acids
- sulfoxides; dimethylsulfoxide
- *o*-alkyl- and *o*-alicyclicthiophenols
- thiophenic carboxylic acids
- benzo(*c*)thiophenes
- alkylthiocyanates

Metal Organics

- 4-hydroxyphenyl- and 4-aminophenylarsonic acids
- metal carbonyls

Cyanides

- * cyanohydrins
- aminonitriles

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[a] These compounds and chemical subclasses have not been identified in any process stream or in a particular stream, but their existence is inferred from reactions possible within the retort process. Asterisks (*) indicate those compounds or classes that may comprise major portions of unidentified organic carbon or have toxicological importance.

TABLE FILMED

IN SECTIONS

Kerogen Constituents		Extraction/Distillation/ Mild Pyrolysis Products		Secondary Pyrolysis, Oxidation, and Condensation		Tertiary Reactions
algal/plant hydrocarbons	$\xrightarrow[\text{(disproportionation)}]{}$	alkanes + 1-alkenes	$\longrightarrow$	alkene isomers		
			$\longrightarrow$	alkylbenzenes/naphthalenes		
	$\longrightarrow$	2-methylalkanes; cycloalkanes				
	$\longrightarrow$	acetylene	$\xrightarrow[\text{high temp.}]{}$	PAHs		
	$\longrightarrow$	aldehydes	$\longrightarrow$	aldols*; 1,5-diones*		
			$\longrightarrow$	furans, pyrans (from diones)	$\xrightarrow[\text{H}_2]{}$	alicyclic ethers (PUCs)
			$\xrightarrow[\text{pyridines}]{}$	naphthyridines	$\longrightarrow$	2-alkyl arylamines
					$\longrightarrow$	aralkylamines
			$\xrightarrow[\text{NH}_3]{}$	alkylpyridines	$\xrightarrow[\text{OH}^-]{}$	oxo-pyridines
					$\xleftrightarrow[\text{H}_2]{}$	piperidines
					$\xrightarrow[\text{RCHO}]{}$	pyridinols (PUCs)
					$\longrightarrow$	benzonitriles
					$\longrightarrow$	alkylamines
			$\xrightarrow[\text{NH}_3]{}$	aldehyde-ammonia adducts*	$\longrightarrow$	polymers* (PUCs)
			$\xrightarrow[\text{NH}_3]{}$	hexamethylenetetramine (PUC)		
			$\xrightarrow[\text{NH}_3\text{ + HCN}]{}$	amino acids* (PUCs)	$\longleftrightarrow$	lactams
pyridyl isoprenoids	$\longrightarrow$	alkylpyridines				
glycerides	$\longrightarrow$	lower alkanoic acids	$\xrightarrow[\text{O}_2]{}$	alkanedioc acids	$\longrightarrow$	cycloalkanones
			$\xleftrightarrow[\text{NH}_3]{}$	acylamines	$\longleftrightarrow$	aliphatic nitriles
			$\rightarrow$	2-alkanones		
	$\longrightarrow$	alkenoic acids	$\xleftrightarrow[\text{H}_2\text{O}]{}$	hydroxyalkanoic acids*	$\longleftrightarrow$	lactones
	$\longrightarrow$	polyhydric alkanols*	$\longrightarrow$	hydroxyalkanoic acids	$\longleftrightarrow$	lactones
entrapped (endogenous)	$\longrightarrow$	higher alkanoic acids	$\rightarrow$	lower alkanoic acids		
	$\longrightarrow$	alkanedioc acids	$\longrightarrow$	cycloalkanones		
			$\xrightarrow[\text{NH}_3]{}$	succinimide		
			$\xrightarrow[\text{RNH}_2]{}$	pyrroles		
			$\longrightarrow$	lower alkanoic acids		
			$\xrightarrow[\text{RSR}]{}$	thiophenes		
fatty acid diagenesis	$\longrightarrow$	2-alkanones	$\xrightarrow[\text{HCN + NH}_3]{}$	hydantoins* (PUCs)	$\xrightarrow[\text{H}_2\text{O}]{}$	hydantoic acids* (PUCs)
			$\xrightarrow[\text{high temp.}]{}$	ketenes	$\xrightarrow[\text{RNH}_2]{}$	acylamines
	$\longrightarrow$	1,[illegible]-diketones	$\xrightarrow[\text{RNH}_2]{}$	1,2,5-alkylpyrroles		
			$\xrightarrow[\text{heat + NH}_3]{}$	acylamines		
carotenoids	$\longrightarrow$	alkylbenzenes	$\longrightarrow$	benzoic acids		
			$\longrightarrow$	hydroxybenzenes	$\longrightarrow$	polymers* (PUCs)
			$\longrightarrow$	naphthalenes		
porphyrins (chlorophyll)	$\longrightarrow$	alkenes (1-alkenes)	$\xleftrightarrow[\text{H}_2\text{O}]{}$	alkanols	$\xrightarrow[\text{RCHO}]{}$	hemiacetals (PUCs)
			$\longrightarrow$	alkanes		
porphyrins	$\longrightarrow$	pyrroles	$\longrightarrow$	benzopyrroles	$\longrightarrow$	2-alkyl arylamines
					$\longrightarrow$	aralkylamines
					$\xrightarrow[\text{HCHO + NH}_3]{}$	aminoindoles* (PUC)
			$\xrightarrow[\text{O}_2]{}$	polymeric blacks* (PUCs)		

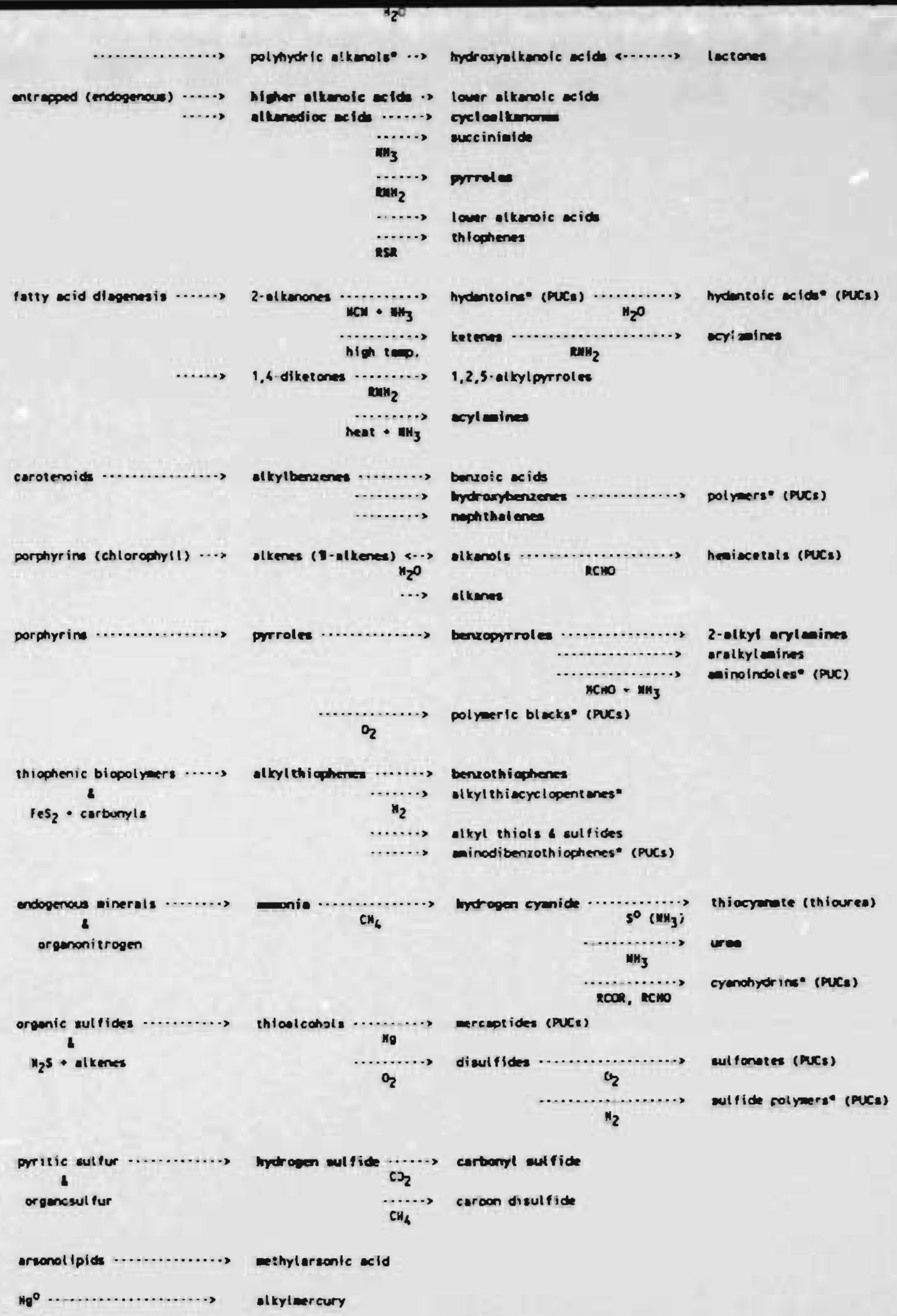

Figure 1. Origins and Fates of Organic-Compound Classes Associated with Shale Oil Production. PUCs refer to "possible unidentified components". Classes that occur at high frequency or concentrations are in bold face. Unidentified classes that may occur at high or significant concentrations are followed by an asterisk (*).

END OF

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