



Project Summary

Components Identified in Energy-Related Wastes and Effluents

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The results of an analysis of effluent samples obtained from seven energy-related activities are presented. The energy-related processes included coal strip mining, oil refineries, oil shale operations, coal-fired power plants, coal liquefaction operations, coal gasification processes, and geothermal energy production. Chemical analyses were performed on solid and liquid effluents associated with each of these activities to identify organic and inorganic components. Organic compounds were identified and quantified by gas chromatography/mass spectrometry/data system techniques. Sample preparation methods permitted determination of purgeable (volatile) and extractable (semivolatile) organics. Samples were analyzed for mercury using a cold vapor atomic absorption spectrophotometric procedure. Approximately 70 other elements were determined in the samples by spark source mass spectrometry.

Because much relevant data were being generated concurrently with this research effort, a state-of-the-art review,* was updated regularly. The reliability of the data reviewed was evaluated according to preselected criteria of sample source, sampling and analytical methodology, and data source. Information gathered during

the review was used to identify gaps in existing data on characterization of energy-related wastes and effluents and thereby serves as a guide to selection of sites for the samples analyzed in this research effort.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The need for energy sources that are both reliable and safe, coupled with the national goal of energy independence, has generated increasing activity in the technology of energy production. Technologies are being developed and used to exploit this country's reserves of oil, coal, and geothermal fluids and gases. Energy production processes must be assessed from the standpoint of cost effectiveness and of potential health and environmental effects.

Use of domestic oil supplies is increasing as a matter of policy and economics. Fuel generated from refining conventional crude oil feed stocks will continue to be an important source of energy for some years to come. Much emphasis, however, has been placed on coal conversion processes because United States coal reserves are estimated to comprise more than 80 percent of the total available coal, oil, and gas. Furthermore, these supplies are sufficient to

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support production of a large amount of synthetic fuels. Over 230 billion tons of coal are accessible to conventional mining techniques. Technological advances are increasing the total amount of usable coal and making additional reserves available in the form of oil shale and tar sands. Development of geothermal resource areas offers the potential for the extraction of thermal and electrical energy.

The nature and extent of the controls that may be required for energy-related production processes are based on a knowledge of the constituents in the crude fuel feedstocks, an understanding of the conditions and chemical reactions involved in the finished fuel producing processes, and a knowledge of the components in the process streams from these activities. Generation of such data could also result in identification of potentially useful by-products of the fuel producing technologies.

Sample Site Selection

Although the state-of-the-art review and site selection for sample collection were conducted concurrently, information gathered during the review was used to identify gaps in existing data on characterization of energy-related wastes and effluents and to identify operations from which solid and liquid waste samples might be obtained. In choosing sites for sample collection, priority was given to the energy-related activities of the Western Energy Resource Development (WERD) sector of the United States. Attempts were also made to obtain samples from operations on which some data had been generated by other research efforts. In this manner, those investigations would be complemented by this program.

Difficulties were encountered in obtaining solid samples from several of the energy-related activities. Some of the processes simply did not generate significant quantities of solid wastes (e.g., geothermal sources), and some operations were not equipped with a mechanism for collecting samples of this type (e.g., *in situ* gasification). When these problems arose, additional liquid samples were obtained. It was not always possible to arrange cooperative agreements to obtain samples from commercial operations. Therefore, most of the analyses carried out were samples collected from operations supported or sponsored by a governmental agency.

All samples were collected in a manner to insure that they were representative of the process stream or effluent being characterized. Precautions were taken in preserving and shipping the samples to guarantee their integrity.

Results

Table 1 presents an overview of the classes of organic compounds identified in the effluents of each energy-related activity surveyed in this program.

Coal Strip Mining

The mercury levels in the aqueous effluent obtained from coal mining operations were, in general, fairly low. Of the 20 mines whose wastes were sampled and analyzed, only one was shown to contain mercury at a level higher than 10 ppb. This mine is located in West Virginia. The effluents of other mines located in this area contained smaller amounts of this metal. Other metals determined to be present in these samples at moderate or high (>1 ppm) concentrations included the alkali and alkali earth metals. In some samples, calcium and magnesium concentrations exceeded 10 ppm. Significant levels of strontium, sulfur, silicon, chlorine and fluorine, were also present in most of these samples. The concentrations of toxic metals (e.g., lead, arsenic, selenium, and calcium) in general were less than 10 ppm.

The most significant component of the purgeable fraction of the coal mining effluents was methylene chloride, usually present at the parts-per-million level. The identification of other halogenated volatile materials such as chloroform, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane suggests either that these effluents had been chlorinated as a treatment procedure prior to discharge or that a chlorinating agent was used in some phase of the coal mining process. The compounds most frequently detected in the semivolatile fractions of these samples were phthalates.

Oil Refineries

In general, concentrations of mercury and other elements determined in the oil refinery effluents were low. Major components (>1 ppm) in these samples included calcium, chlorine, fluorine, magnesium, phosphorus, potassium, strontium, and sulfur. None of these materials, however, was determined to be present at levels that constituted an environmental hazard.

Organic compounds identified in the purgeable fractions of these effluent samples were present at relatively low levels. Among them were trihalomethanes, cyclohexane, benzene, and toluene. Several sulfur-containing compounds were tentatively identified. However, standards were not available to confirm these identifications. The major semivolatile organic components identified in these effluents included phenols and normal alkanes. With the exception of phenol and p-cresol in one sample, all extractable organic compounds were determined to be present at levels less than 100 ppb.

Oil Shale Operations

Mercury levels determined in effluents from the Paraho oil shale retorting process were less than 1 ppb, with the exception of one sample of process water that was less than 5 ppb. Other elements detected at moderate to high levels in these samples included sodium, potassium, calcium, magnesium, iron, sulfur, and strontium. It is of interest that the three samples of this set that were most representative of the process discharge also contained arsenic, at concentrations approaching or exceeding 1 ppm. The levels of the other toxic metals, however, were fairly low.

Organic compounds identified in the purgeable fractions of these samples included significant levels of halogenated compounds including methylene chloride, chloroform, carbon tetrachloride, bromodichloromethane, dibromochloromethane, and trichloroethane. The presence of these compounds may be due to the use of chlorination as a treatment method for the wastes or because the process water had already been chlorinated in the retorting process. The product water samples contained thiophene, alkyl-substituted thiophenes, benzene, and alkyl-substituted benzenes. The recycle gas condensate sample contained a number of compounds at levels greater than 1 ppm including nitriles, thiophene and alkyl-substituted thiophenes, benzene and substituted benzenes, ketones and substituted pyridines. The semivolatile fractions of these samples were found to contain carboxylic acids and alkyl substituted pyridines in the acid and base/neutral extracts, respectively. Components of the product water also included the homologous series of normal alkanes from n-undecane (C₁₁) to pentacosane (C₂₅) at levels in the parts-per-million range.

Table 1. Organic Compounds Identified in Effluents from Energy-Related Activities

	Coal Strip Mining	Oils Refineries	Oil Shale Processing	Coal-Fired Power Plants	Coal Liquefaction	Coal Gasification	Geothermal
Alkanes	X	X	X	X	X	X	
Alkenes & Alkynes			X			X	
Benzene & Alkyl Benzenes	X	X	X	X	X	X	X
Polynuclear Aromatic Hydrocarbons			X	X		X	
Ethers & Heterocyclic Oxygen Compounds	X						
Amines							
Alcohols			X				
Esters	X	X		X	X	X	
Aldehydes							
Ketones			X	X		X	
Nitro Compounds							
Amines			X				X
Phenols & Naphthols	X	X	X		X		X
Carboxylic Acids			X				
Nitrogen Compounds			X				
Sulfur Compounds			X				

In the samples collected during the operation of the oil shale retort of Lawrence Livermore Laboratory, the mercury levels increased with time into experiment (TIE). The concentration of this metal determined in the earlier samples was approximately 1 ppb. As the retorting process proceeded, the amount of mercury in the effluent increased until, in the final sample collected, it reached 58 ppb. Although the concentration of the other elements in these samples, as determined by spark source mass spectrometry, was somewhat higher than in the effluents of other energy-related activities, there was no obvious trend of concentration increasing with TIE.

The results of the analysis of the latter samples for organics indicated that they were heavily contaminated with volatile compounds. Among the purgeable organic components identified were normal alkanes, thiophene and alkyl-substituted thiophene, benzene and alkyl-substituted benzenes, ketones, substituted pyridines, substituted pyrroles, and, possibly, substituted cycloalkanes. In general, levels of these components increased as retorting proceeded. These effluents also contained a wide variety of semivolatile organic compounds including substituted phenols, a homologous series of alkanic acids, substituted pyridines, and alkane series up to dotriacontane (C₃₂), an alkene series up to heptacosene (C₂₇), and a variety of ketones. Again, the number of components in these effluents and their concentrations increased with retort progress.

It is probable that the increase in all types of contaminants in these samples as a retorting experiment progressed was in part due to leaching of contaminants from spent shale and subsequent transport of these materials down the retort. In assessing data generated by analyses of these effluent samples, it must be noted that these wastes were sampled prior to any clean-up or pollution abatement treatment. This is in contrast to many other samples analyzed under this program that were final effluents collected after treatment.

Coal-Fired Power Plants

The levels of mercury determined in the aqueous effluents from coal-fired power plants were generally low. There was no apparent difference in the mercury concentration in these samples from one geographical area to another. In these samples the alkali and alkali earth metals were shown to be present at concentrations exceeding 1 ppm. Strontium and sulfur were also found at significant levels in many of these samples.

The purgeable fractions of many of these aqueous waste samples contained very high levels of methylene chloride. Other volatile components identified in the coal-fired power plant effluents included chloroform, benzene, toluene, trichloroethylene, and bromoform. Organic compounds identified in the extractable fractions of these samples primarily included phthalates and alkanes.

The concentrations of mercury determined in the fly ash and scrubber sludge

samples obtained from coal-fired power plants were also determined to be relatively low. Other elements, however, were determined to be present at very high levels. Antimony, arsenic, cadmium, lead, copper, manganese, and sulfur were present at levels exceeding 10 ppm in all cases and greater than 100 ppm in several of the samples.

A wide variety of organic compounds were thermally desorbed from the solid waste samples. These compounds included a number of ketones, alcohols, and ethers. Only phthalates were determined to be present in the semivolatile fractions at significant levels, however, probably because these samples were collected from the final discharge of a treatment process.

Coal Liquefaction

The purgeable fractions of the effluents obtained from the coal liquefaction operation contained a number of organic compounds at relatively high concentrations, including alkyl benzenes, a variety of unsaturated hydrocarbons, and chlorinated materials including methylene chloride, chloroform, and trichloroethylene. Many of these materials were determined to be present at levels exceeding 100 ppb; some at concentrations greater than 1000 ppb.

These samples were also found to be highly contaminated with extractable organic compounds, the major components being alkyl phenols. Alkyl phenols from phenol through isomers of C₈ alkyl phenol were determined to be present at concentrations exceeding 1000 ppb.

Several higher molecular weight normal alkanes were also present.

Coal Gasification

The gasifier solid samples obtained from Pittsburgh Energy Technology Center were found to contain only low levels of mercury. Other elements including cerium, chromium, copper, and zirconium were determined to be present, however, at concentrations exceeding 100 ppm. Major organic components identified in these samples included methylene chloride, chloroform, isopropyl alcohol, carbon tetrachloride, ethyl acetate, and several low molecular weight alkanes.

The concentrations of mercury in the samples obtained from the underground coal gasification process operated by the Laramie Energy Technology Center were also quite low. Elements in significant concentrations in these samples included calcium, iron, magnesium, phosphorus, potassium, sulfur, and, in some cases, strontium.

In the samples obtained from wells in the Hanna III site prior to gasification, the number of organic components and their concentrations were relatively low. Compounds identified in the purgeable fractions of these samples included methylene chloride, dichloroethylene, and traces of benzene and toluene. Semivolatile compounds that were present included low levels of phthalates and normal hydrocarbons. Samples obtained from the same wells during the gasification contained more purgeable organic components than the pre-burn samples, including thiols, ethers, and substituted amines. Organic compounds identified in extractable fractions were primarily phthalates and normal hydrocarbons. Samples of the product water obtained from the Hanna III test during gasification contained a large number of organic compounds in very high concentrations. Among the components identified in the purgeable fractions were nitriles, ketones, thiophenes, pyridines, and alkyl benzenes. Extractable organic components included a variety of alkyl phenols, alkyl naphthalenes, and normal alkanes at concentrations exceeding 10 ppm.

In the samples obtained from wells in the Hanna III site some time after the gasification operation had been completed, both the number and concentration of organic components were significantly lower. In the purgeable fractions of many of these samples only traces of benzene, carbon disulfide, and

toluene were determined. In the extractable fractions, alkyl phenols, carboxylic acids, and normal alkanes were identified.

Mercury levels determined in the product tar and product liquor samples obtained from the lignite gasification operation of Grand Forks Energy Research were less than 1 ppm. High concentrations of a number of other elements were determined in these samples, particularly in the product tar. Very high levels of a number of organic compounds were detected. Among the organic components identified were alkyl phenols, carboxylic acids, normal alkanes, and phthalates. The product tar was the more heavily contaminated of the two samples and also contained a number of alkenes and polynuclear aromatics.

In the aqueous samples obtained from wells in the Hoe Creek II experimental site prior to gasification, the number of components identified and the concentrations at which they were determined were quite low. After the experimental burn was conducted, the number and amount of material found in these samples increased significantly. Immediately after the gasification experiment, samples obtained from wells closest to the burn zone showed the greatest increase in types and levels of contaminant. As time passed, wells further from the burn zone began to show the effect of leaching of the spent fuel by the natural movement of groundwater. Prior to gasification, calcium and magnesium were the only elements found in these samples at concentrations exceeding 10 ppm. After gasification, iron, potassium, sulfur, titanium, and strontium were also determined to be major components of these effluents. Of the organics, only alkanes and phthalates were determined in the samples collected before the test burn. After gasification, however, the classes of compounds identified in these samples included alkanes, alkenes, alkyl phenols, alkyl benzenes, alkyl thiophenes, alkyl anilines, alkyl pyridines, and polynuclear aromatics.

Several aspects of this research effort should be continued in an effort to characterize the components of energy-related wastes and effluents. First, the state-of-the-art summary of completed programs and research in progress should be continued. The collection of this information provides a valuable data base for researchers to use in the design of additional analytical studies. Second, there should be continued and expanded efforts to characterize effluents

and wastes from energy-related processes. The inclusion of nonvolatile and nonextractable materials in these characterization schemes should be considered. Specifically, it would be of interest to sample and analyze the process streams and final effluents of those technologies that are approaching commercial scale-up. This would provide valuable information on the efficacy of the waste treatment procedures. Finally, there is need for the involvement of the life sciences, particularly toxicology, in these programs. Total characterization of the wastes and effluents from energy-related activities is an important effort when very little is known about the nature of these liquid and solid byproducts. As more information is generated, however, it should be possible to identify specific compounds or classes of compounds related to certain energy producing activities that, because of their stability or toxicity, represent a potential threat to the environment and/or the health of a given population. Then, monitoring the effluents of a certain process for only important materials known to result from that process could be accomplished in a timely and cost-effective manner.

Geothermal Energy Production

Because the samples obtained from geothermal energy production activities were collected as part of a round-robin analytical effort, additional data were available on the characterization of these samples. The levels of mercury and most other elements were relatively low. Elements found to be present at concentrations exceeding 1 ppm included arsenic, barium, calcium, cesium, chlorine, fluorine, iron, lead, lithium, magnesium, manganese, molybdenum, phosphorus, potassium, rubidium, silicon, sodium, strontium, sulfur, titanium, and zinc.

Few organic compounds were identified in either the purgeable or the semivolatile fractions of these samples. Low levels of methylene chloride, chloroform, benzene, and toluene were determined in the purgeable fractions. Small amounts of phenol were found in the semivolatile fractions.

Conclusions and Recommendations

The data collected during the state-of-the-art review were evaluated according to the following criteria: 1) sample source, 2) completeness of sampling

design, 3) sampling procedures, 4) sample preparation procedures, 5) analytical procedures, and 6) completeness of analysis. Information gathered in this review indicates that characterization of the inorganic components of energy-related wastes has received more attention than the identification of the organic components. The research conducted to date on the analysis of these effluents, however, is insufficient to assess the efficiency of these energy-related processes or the potential environmental impact.

Analysis of the waste and effluent samples collected from the seven energy-related activities surveyed in this program revealed their extreme complexity. It became evident that analysis of these samples required high resolution glass capillary gas chromatography/mass spectrometry/data system analysis. In some cases derivatization techniques were required to obtain acceptable separation of the individual organic compounds.

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The complete report, entitled "Components Identified in Energy-Related Wastes and Effluents," (Order No. PB 82-236 985; Cost: \$49.50, subject to change) will be available only from:

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