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# WESTERN RESEARCH INSTITUTE

## QUARTERLY TECHNICAL PROGRESS REPORT

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**October - December 1992**

**OIL SHALE**

**TAR SAND**

**COAL RESEARCH**

**ADVANCED EXPLORATORY PROCESS TECHNOLOGY**

**JOINTLY SPONSORED RESEARCH**



**Under Cooperative Agreement DE-FC21-86MC11076**

# 1.0 OIL SHALE

## 1.2 Oil Shale Process Studies

### 1.2.2 Process Studies (FY 1991 Mod.)

Objectives. The objective of this task is to investigate the use of a shale oil-derived, recycle oil to mediate the transfer of hydrogen to eastern oil shale. This task is composed of three subtasks: (1) the evaluation of a distillate from eastern shale oil as a recycle oil to mediate hydrogen transfer, (2) the determination of the catalytic hydrogenation conditions necessary to regenerate the recycle oil, and (3) the evaluation of the chemical and physical properties of the liquid products from the process to determine their appropriateness as feedstocks for the production of transportation fuels. The objectives for this quarter were to run and evaluate the results of a series of hydrogenation experiments that were conducted on the solution of model compounds.

Accomplishments. The suite of samples that were produced as a result of the series of hydrogenation experiments were analyzed by gas chromatographic/mass spectral (GC/MS) analysis and the results were evaluated.

Procedures. A series of model compounds (phenol, toluene, naphthalene, 1-octene, 1,3-pentadiene, cyclohexene, pyridine, and thiophene) were hydrotreated using the Chemical Data Systems reaction system. Approximately 2 wt % of each compound was dissolved in hexane. The sample was then treated at several different temperatures (204, 218, 232, 246, 260, 274, 288, 302, and 316°C / 400, 425, 450, 475, 500, 525, 550, 575, and 600°F) and pressures (1200, 1700, and 1900 psi). The product from each test was analyzed by GC/MS analysis to obtain qualitative and quantitative information.

Results. The olefins (1-octene and 1,3-pentadiene) were the easiest to convert to their corresponding saturated hydrocarbon. Reactor temperatures above 220°C (428°F) converted most of the olefins, regardless of the pressure.

A significant amount of cyclohexene was converted at temperatures of 246°C (475°F) and above. As the pressure was increased from 1200 to 1900 psi the conversion to cyclohexane increased. However, only about 50% of the cyclohexene was converted to cyclohexane at 1900 psi. The remaining cyclohexene was apparently cracked to smaller compounds.

Naphthalene was almost completely converted to products at 288°C (550°F), regardless of the operating pressure. At 1700 and 1900 psi, almost all of the naphthalene could be accounted for by addition of the three main products (trans-decalin, cis-decalin, and tetralin). At 1200 psi only about 75% of the naphthalene and its products could be accounted for. Of these products only the tetralin is useful as a hydrogen transfer solvent. Once the naphthalene is converted to one of the decalins it cannot be used as a hydrogen transfer solvent, and thus, converted back to naphthalene for recycle. The best conditions for maximizing the conversion of naphthalene to tetralin appears to be at 270°C (518°F) and 1700 psi. No pressures between 1700 and 1200 psi were tested. Pressures between these two need to be examined to determine the lowest pressure that can be used with the current catalyst without loss of the desired tetralin due to cracking.

Toluene was quite resistant to hydrotreating at most of the conditions tested. At 1200 psi very little conversion of the toluene could be noted. At 1700 and 1900 psi conversion of toluene started at 316°C (600°F) with about one third of the toluene being converted at 328°C (622°F).

The removal of the heteroatom from phenol, pyridine, and thiophene was accomplished at fairly mild conditions and was insensitive to pressure. The removal of oxygen from phenol began at 204°C (400°F) and oxygen was completely gone at 288°C (550°F). The removal of nitrogen from pyridine began at 204°C (400°F) and nitrogen was not detected above this temperature. The removal of sulfur from thiophene began at 218°C (425°F) and sulfur was completely gone at 288°C (550°F). These three compounds were converted into low-molecular-weight compounds and gas.

The reactor pressure did not appear to affect the temperature at which conversion took place. However, the pressure was important with respect to the type of reaction taking place. At pressures of 1700 and above the conversion of the model compounds appeared to be mainly hydrogenation of the unsaturated bonds. At 1200 psi cracking appeared to become more prevalent, with loss of the main product.

### 1.2.4 Product Utilization Studies (FY 1992)

Objectives. The objective of this research is to determine unique applications of oil shale-derived products that have high market values. The research is concentrated toward development of highly specialized products for roadway pavement applications. The two areas being investigated are pavement joint and crack fillers and interactions of asphalt, including shale oil modified asphalt, with aggregate. The objective for the quarter was to prepare the two milestone reports to complete the study.

Accomplishments. Milestone 1.2.4B, report on the evaluation of shale oil products as joint and crack filler materials, was completed, submitted, and approved. Milestone 1.2.4C, report on energies of interactions correlated with observed stabilities and rheological properties of asphalt-aggregate mixtures, was completed in draft form and is in review.

# 2.0 TAR SAND

## 2.2 Process Development

### 2.2.1 Recycle Oil Pyrolysis and Extraction (ROPE™) Process (FY 1991)

Objectives. The first objective of this task is to design and initiate fabrication of a modified 6-inch bench-scale unit that includes a twin-screw conveyor and a new feed system. This system permits long runs required to evaluate the application of the ROPE™ process to tar sands. The second objective is to develop a process for the treatment of petroleum production wastes commonly termed tank bottom wastes. These wastes are a combination of oil, water, and solids with a water and solids content too high for refinery acceptance of the oil. The objective for the quarter was to prepare milestone reports 2.2.1B, results of two long-term tests of the modified 6-inch ROPE units, and 2.2.1C, results of tests on tank bottoms.

Accomplishments. Evaluation of data from the tests has been completed and preparation of the reports continued. Milestone report 2.2.1B has been completed in draft form and is in review. Milestone report 2.2.1C has nearly been completed in draft form. The work on tank bottoms has resulted in funding from a private source, the state of Wyoming, and the JSR program for further development of the process.

# 3.0 COAL RESEARCH

## 3.2 Coal Combustion

### 3.2.2 Combustion of Low-Rank Coals and Industrial Wastes (FY 1991)

The request to eliminate milestone 3.2.2C has been approved. This task is completed.

### 3.2.3 Gasification and Cogeneration (FY 1992)

Objectives. The objective of this research is to select and develop a combustor design and hot-gas cleanup system suitable for use with low-sulfur coal. The objective for this quarter was to complete the milestone report.

Accomplishments. The milestone report is being prepared.

Procedures. The Western Research Institute (WRI) 6-inch fluidized bed reactor was used as an air-blown gasifier. Bed depths used were in the 8- to 13-inch range.

Results. Findings are consistent with those reported earlier that were based on the preliminary analysis of the data: that western sub-bituminous coals can be partially gasified at temperatures low enough that some of the contaminants, such as alkali compounds deleterious to downstream components in 2GPFBC systems, are not volatilized, remaining in the char. As a result, the hot-gas stream cleanup requirements for the overall system are reduced.

## 3.3 Integrated Coal Processing Concepts

### 3.3.4 Coal Coprocessing (FY 1992)

Objectives. The objectives of this research are to define more closely coprocessing conditions that improve the liquid yield through more efficient dispersion of iron-based catalysts and to characterize the acid sites on supported catalysts and their impact on the formation of coke. The objectives for the quarter were to complete the experimental series involving pretreatment prior to coal/heavy oil coprocessing, to continue the assembly and evaluation of various catalysts for testing using solid-state nuclear magnetic resonance (NMR) spectroscopic analysis, and to complete the analysis of the products obtained from commercial organizations regarding hydrogen utilization.

Accomplishments. Comments received on the previously submitted experimental plan were discussed with DOE personnel and a revised plan was submitted. The experimental series involving pretreatment prior to coal/heavy oil coprocessing was completed, and the data are being evaluated. The analysis of the products obtained from commercial organizations regarding hydrogen utilization was completed.

Procedures. Carbon-13 NMR spectroscopic analysis using cross polarization/magic angle spinning were conducted on four spent catalysts that possessed a coating of coked material. The spent catalysts include: (1) alumina support modified by titania via liquid impregnation, (2) alumina support modified by titania via vapor deposition, (3) alumina support modified by zirconia via liquid impregnation, and (4) alumina support modified by carbon via vapor decomposition. The promoter metals are cobalt and molybdenum. NMR dephasing experiments will be conducted next on the four spent catalysts to obtain data regarding the quaternary carbons in the coke structure. It will then be possible to calculate the cluster size of the coked material and nine carbon structural parameters of the coked material.

Results. Preliminary evaluation indicates that the UOP bench-scale process utilizes more hydrogen for the production of hydrocarbon gases (60%) than does the Wilsonville process (25%). In addition, the UOP process liberates hydrogen derived from condensation reactions during the process ($\Delta H_{matrix}$ is negative); while in the Wilsonville process hydrogen is liberated only during the first stage of the process, and hydrogen is consumed by cracking reactions in the second stage of the process ($\Delta H_{matrix}$ is positive).

### 3.3.5 Agglomerating and Stabilizing Dried Coal (FY 1992)

Objectives. The objective of this task is to develop and test concepts for stabilizing dried Wyodak coal from the Powder River Basin. The objective for this quarter was to complete the milestone report.

Accomplishments. A draft of the milestone report was completed and the report is in internal review.

### 3.3.6 High-Heating-Rate Process Studies (FY 1992)

Objectives. The objective of this research task is to determine oil yields from the rapid pyrolysis of coal in an entrained flow reactor. The objective for the quarter was to prepare the milestone report.

Accomplishments. The milestone report is nearly completed.

## 3.4 Solid Waste Management

### 3.4.1 Use of Solid Waste for Chemical Stabilization (FY 1991 and FY 1992)

Objectives. The objective of this research is to determine a use for fly ash, such as that produced as waste during operations at the Dave Johnston Steam Electric Project, that would be economically and environmentally reasonable. Dave Johnston fly ash has been shown to have some affinity for selected organic compounds that have created problems in the environment. The objectives for the quarter were to continue evaluation of the data and to work on preparation of the experimental plan, 3.4.1A.

Accomplishments. Evaluation of the mass spectrometric data is continuing and the experimental plan is nearly completed.

3.4.2 Use of Solid Waste for Physical Stabilization (FY 1991 and FY 1992)

Objectives. The objectives of this research were: (1) to develop an understanding of the key properties of fly ash that are responsible for cementation and stabilization, (2) to study sodium and calcium wastes generated from clean coal technology in an effort to develop waste disposal technologies that result in stable land fills, (3) to provide detailed information on potentially toxic compounds from cemented fly ash and to evaluate the use of fly ash to enhance stabilization of hazardous materials placed in landfill sites, and (4) to develop methods to separate organic selenium species that may be found in coal fly ash materials. The objective for this quarter was to complete the report on coal fly ash and soil stabilization mechanisms (FY 1991 milestone 3.4.2C).

Accomplishments. The FY 1991 milestone report 3.4.2C was completed and submitted. The request to eliminate FY 1991 milestone 3.4.2A and FY 1992 milestone 3.4.2B was approved. This task is completed.

# 4.0 ADVANCED EXPLORATORY PROCESS TECHNOLOGY

## 4.1 Advanced Process Concepts

### 4.1.7 In Situ Model of Pyrolysis (FY 1990)

Objectives. The objectives of this research effort are to predict solute transport and develop new control concepts that incorporate some of the more recent geochemical data obtained from research projects. The objective for the quarter was to make modifications to the 3-dimensional reservoir simulator.

Accomplishments. The horizontal well algorithm has been installed in the 3-dimensional reservoir simulator. It has been mechanistically checked for proper performance. The request to combine milestone 4.1.7A with milestone 4.3.3A has been approved.

Procedures. Implementation of the horizontal well algorithm allows the user to orient the well in either the x- or y-direction and to "complete" the well in a single block or through several blocks. The single well completion may be useful for the simulation of slant injection or production wells.

### 4.1.8 APT Method Development (FY 1990)

The request to eliminate milestone 4.1.8B has been approved. This task is completed.

### 4.1.9 In Situ Process Modeling (FY 1991)

Objectives. The objectives of this research task are to conduct laboratory simulations and develop a numerical model for the simulation of the steamflood process in fractured reservoirs. The objectives for this quarter were to conduct laboratory simulation tests using blocking agents and to modify the thermal process portion of the model.

Accomplishments. Screening of the potential blocking agents to be tested has been completed. Core flood tests to evaluate the selected blocking agents were initiated to ensure proper functioning prior to use in the three dimensional simulations. The core flood tests are nearing completion.

A test plan for the physical simulations was developed and approved by the DOE. Modification of the original test plan has been proposed and submitted to the LFTB for comment. This modification is included in the test plan for task 4.3.1.

Validation studies were performed on two new features that were added to the thermal model.

Procedures. Procedures for the physical simulation tests are: (1) determine the appropriate blocking agent to use for steamflooding the Shannon formation, (2) conduct two three-dimensional physical simulations of the steamflood process with a blocking agent in samples containing either a vertical or horizontal fracture, and (3) transfer the data and results for numerical simulations.

Two new features were added to the thermal model. These are a point-centered grid system and the ability to use nonuniform grids. The point-centered grid is useful when performing symmetrical pattern studies and the nonuniform grid is useful in refining grids in regions where flow characteristics are rapidly changing, such as in the vicinity of fractures.

Results. In the physical simulation study, the Shannon sandstone block samples have been saturated. Core floods using the identified blocking agents are being conducted. The tests have not validated the projected performance as stated by the supplier of the commercially available blocking agent. Discussions have been held with the suppliers and other suppliers to identify the nonperformance problems and to identify better agents. Testing of the modifications and new materials is under way.

In the modeling study, validation of the two additions to the thermal model is proceeding very well, at least through waterflooding. UTCOMP has been used to provide another answer to the problem for use in comparison of these features. The thermal model should be able to solve problems unsolvable by UTCOMP because it is fully implicit, as opposed to the IMPES(Implicit Pressure, Explicit Saturation) formulation in UTCOMP. Some trouble has been encountered in getting the thermal model to run faster. This problem is still under investigation. During the checkout of the thermal model, a new method for handling wells in numerical models was developed, a method that should be of much interest to government and industry.

## 4.2 Advanced Mitigation Concepts

### 4.2.1 Treatment of Oil and Gas Product Waters (FY 1991)

Objective. The objective for the quarter was to complete the milestone report.

Accomplishments. The report was completed and submitted. This task is completed.

### 4.2.3 CROW™ Development (FY 1992)

Objectives. The objective of this research is to obtain baseline data that show the effectiveness and environmentally safe use of chemicals to enhance the CROW process. The objectives for the quarter were to complete and submit milestone 4.2.3A, the experimental plan, and to begin the experiments.

Accomplishments. The experimental plan was completed and submitted. Comments received on the plan have been addressed. The experimental testing program has been initiated and is 75% completed.

Procedures. Eleven one-dimensional displacement tests are being conducted to investigate the effect of three chemical concentrations (0, 0.5, and 1.0 vol %) at three temperatures (ambient, the projected optimum temperature, and 40°F [4°C] below the optimum temperature). Two duplicate tests are run for validation purposes. Contaminated soil samples obtained from Midwest Gas are being used as the test material.

Results. The initial tests are being evaluated to determine the conditions for the remaining tests.

### 4.2.4 Environmental Treatment of Process Gases (FY 1992)

Objectives. The objective of this research is to optimize vortex combustor design to obtain maximum thermal destruction efficiency at selected temperatures and retention times. The objective for the quarter was to prepare the milestone report on completed research.

Accomplishments. The report was completed and submitted. This task is completed.

## 4.3 Oil and Gas Technology

### 4.3.1 Enhanced Oil Recovery (FY 1992)

Objectives. The objective of this research task is to determine the enhancement of oil recovery using steamflooding in conjunction with chemicals or gases and horizontal wells. The objectives for this quarter were to complete preparation of the experimental plan, milestone 4.3.1A, and submit it for approval.

Accomplishments. The experimental plan was completed and has been submitted to the LFTB for review.

### 4.3.2 Natural Gas Cleanup (FY 1992)

Objectives. The objective of this work is to investigate a less complex and more cost effective method for gas cleanup. The method is based on pressure swing adsorption. The objective for this quarter was to prepare the milestone report on the findings of the series of completed experiments to evaluate the pressure swing adsorption process and the regeneration of the adsorbent.

Accomplishments. A draft of the milestone report was completed and is being reviewed.

Results. Findings of the study were that microwave energy can be used successfully to regenerate a zeolite adsorbent (chabazite); but excessive heating of the zeolite makes the concept impractical for application to natural gas upgrading, in this case, the separation of nitrogen from methane. However, microwave-assisted desorption during the regeneration portion of the pressure swing cycle may prove useful in adsorptive purification processes where recovery of the sorbate with minimal dilution is required.

### 4.3.3 Thermal Reservoir Simulation (FY 1992)

Objectives. The objective of this research effort is to improve the capabilities of WRI's thermal reservoir simulation model. The objectives for the quarter were to conduct model verification studies to confirm correct fluid movement (Darcy flow) in 2- and 3-spacial dimensions and to add thermal and compositional capabilities to the 3-dimensional simulator.

Accomplishments. Verification studies were performed and thermal and compositional capabilities were added to the simulator. Approval was received to combine the milestone report for this task with the milestone report, 4.1.7A, on in situ modeling of pyrolysis products.

Procedures. The correct prediction of fluid movement was verified by comparing model results with analytical results. Simulation results of linear flow and five-spot pattern flow (2-D & 3-D) were compared with the analytical results of Muskat. Simulations were conducted with the model configured for: cell-centered, fixed-grid; point-centered, fixed-grid; and point-centered, variable-grid formulations. Additional water flood studies were conducted in 2-D mode to verify the model's ability to predict areal sweep. Several thermal and compositional capabilities of the 3-D simulator were activated.

Results. For linear flow problems, the cell-centered configuration yields virtually exact agreement with Muskat. For the cases studied, the point-centered formulations differ by a minimum of 5% (from Muskat), with the error increasing with increased grid size. It appears that the inaccuracy for linear flow is caused by the method's specifying grid pressure at the boundary instead of average cell pressure.

For five-spot pattern studies, the point-centered formulations are within 0.5% of the Muskat rates. The cell-centered formulations are significantly in error. The best approach to Muskat were 30%, with increased errors at increased cell size.

Results from the study of water flood simulations were in good agreement with data from the literature.

With the thermal and compositional capabilities of the 3-D simulator activated, the model is now capable, in concept, of simulating the injection of hot fluids (including steam). The model can partition components into vapor or liquid phases using equilibrium coefficients that are calculated in the model as a function of temperature and pressure.

## 5.0 JOINTLY SPONSORED RESEARCH

### 5.1 Occidental Oil Shale, Inc. Demonstration Program Support

This task was completed in previous quarters.

### 5.2 Investigation of ROPE Process Performed on Sunnyside Tar Sand

This task was completed in previous quarters.

### 5.3 Organic and Inorganic Hazardous Waste Stabilization

Objective. The objective for this quarter was to continue evaluation of data generated in simulated weathering experiments.

Accomplishments. Analysis and data reduction continued for samples obtained from weathering experiments. In the previous quarter, discussions were held with the EPRI representative regarding redirection of the remaining work, and a proposal for redirection of the final work was submitted.

### 5.4 Optimization of Product Yields for the CHARFUEL Process

This task was completed in previous quarters.

### 5.5 Cold Flow Injector Mixer Project for the CHARFUEL Project

This task was completed in previous quarters.

### 5.6 CROW™ Field Demonstration with Bell Lumber and Pole

Objectives. The objective of this task is to design, construct, and operate a field demonstration of the CROW™ process technology to treat a site contaminated with organic wastes from the wood treatment process. The objective for the quarter was to complete and submit a detailed work plan for the full-scale demonstration test.

Accomplishments. Review comments were received on the previously submitted technical progress report. The report is being revised for resubmittal. A detailed work plan for the full-scale demonstration has been completed and submitted to the Minnesota Pollution Control Administration for review and approval. A copy of the work plan has also been submitted to DOE.

Procedures. The activities being carried out to accomplish this research task include: review and analyze available site data; develop design parameters from site data and one-dimensional physical simulations of the process using site materials; develop process flow diagrams of surface and subsurface systems; assist in the development and submittal of all project permits required by local, state, and federal agencies; conduct a two-well test to provide additional information on organic displacement and hydraulic confinement; develop detailed design for all injection, production, and water treatment systems; assist in the purchase or lease of all required equipment; monitor the facilities construction; assist in the monitoring of the displacement operations; and evaluate and report on the performance of the displacement process.

Results. The two-well pilot test was successful. Activities are proceeding to complete the design and obtain all required permits for the full-scale test.

## 5.7 Development and Validation of a Standard Test Method for Sequential Batch Extraction Fluid

Objectives. The objectives of this task are to develop a sequential batch extraction procedure using acidic extraction fluid simulating acid rain, as a modification of ASTM Method D4793-88, to determine the precision of the method, and to ballot the method within ASTM so that a new standard is approved. The objectives for this quarter were to (1) report the status of this project at the meetings of ASTM Task Group D34.02.01 on Waste Leaching Techniques and ASTM Subcommittee D34.02 on Physical and Chemical Characterization, (2) complete the statistical evaluation of the collaborative study data, and (3) prepare the final report for the Institute for Standards Research (ISR) cosponsors.

Accomplishments. The statistical evaluation of the collaborative study data was completed and a draft on the final report for the ISR sponsors was prepared. The report is in review. The status of the project was reported at the meetings of ASTM Task Group D34.02.01 on Waste Leaching Techniques and ASTM Subcommittee D34.02 on Physical and Chemical Characterization.

Procedures. Statistical evaluation of the collaborative study data was performed as specified by ASTM Practice D-2777, Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water. The multiple-laboratory and single-operator precision of the sequential batch extraction method were estimated. Data from the collaborative study were also evaluated to determine the effects of filter pore size and digestion versus nondigestion on the elemental concentrations in the extracts from the spray dryer waste and composite mining waste. In addition, analytical bias evaluations, evaluations involving baseline (water as the extraction fluid) versus collaborative study data (acidic extraction fluid), and bias evaluations examining the effects of stopping the sequential batch extraction method over the weekend on the elemental concentrations were performed.

Results. The data generated in this study are specific to the test materials used in the study, the elements of interest, and the pH values of the extraction fluids used. For other materials, elements, and pH values, these data may not apply. As a result, general precision and bias statements that cover all wastes, elements, and extraction fluid pH values cannot be prepared. However, the data generated in this study give the user information on both the multiple-laboratory and single-operator estimated precision of the extraction procedure when it is applied to two different waste materials using two different extraction fluid pH values. The data also provide information to aid the user in making decisions concerning filtering the extraction slurries and analyzing the extracts.

Conclusions that can be made based on the results of this study include the following:

- The estimated precision of the sequential batch extraction method using acidic extraction fluid varies with the type of waste being tested and the element of interest.

- Filter pore size, 0.45-$\mu$m versus 0.8-$\mu$m, and digestion versus nondigestion affect certain elemental concentrations determined in the extracts of the spray dryer waste and composite mining waste. The effects of these variables on the elemental concentrations are waste and element specific.

- The effect of using an acidic extraction fluid versus water depends on the material being tested, the pH of the extraction fluid, the element or parameter(s) of interest, and the extraction number in the sequence of the sequential batch extraction.

- In the collaborative study, the level of analytical accuracy for certain elements of interest in the dilute acid solution standards having a pH of $4.3 \pm 0.05$ and the dilute acid solution standards having a pH of $5.0 \pm 0.05$ was less than desired, based on the criterion given in ASTM Practice D-2777.

Precision and bias sections, based on the results of this study, are being prepared and will be balloted as a modification to ASTM Method D-5284-92. The precision and bias sections will contain information on the details of the collaborative study and statistical evaluation.

## 5.8 PGI Demonstration Project

Objectives. The objectives for the quarter were: to commence detailed and procurement design; to commence preparation of bid packages, including specifications; and to update and refine the project critical path schedule.

Accomplishments. Detailed and procurement design specifications were commenced. Meetings between PGI and WRI were conducted to further refine the project schedule and participant responsibilities and activities.

## 5.9 Mild Gasification of Usibelli Coal

This task was completed in previous quarters.

## 5.10 Real-Time In-Situ Remote-Sensor Development

This task was completed in previous quarters.

## 5.11 Enhanced Gravity Drainage in the North Tisdale Reservoir Using Horizontal Wells

This task was completed in previous quarters.

## 5.12 Solid State NMR Analysis of Powder River Basin Shales

This task was completed in previous quarters.

## 5.13 Operation and Evaluation of the $CO_2$ HUFF-N-PUFF Process

Objectives. The objectives of this task are to (1) conduct in situ residual oil saturation determinations; (2) assist in the design, operation, and monitoring of well tests; (3) determine the characteristics of collected liquid samples; (4) assist in the development of phase equilibrium relationships with chemical and thermodynamic properties of selected crude oils; (5) assist in the development of a predictive numerical process model; and (6) assist in the analysis, reporting, and dissemination of collected data. The objective for this quarter was to continue preparation of the final report.

Accomplishments. All testing has been completed and all field samples have been collected and analyzed. The basic numerical model is operational and special functions that incorporate hysteresis, viscous fingering, and wettability and surface tension changes were used in evaluations. Analysis of samples collected for development of phase equilibrium relationships have been completed. The final report is being prepared.

Procedures. Over 1,867 gas and 1,418 liquid samples have been taken from the field tests of the $CO_2$ Huff-n-Puff process. Routine gas analysis has been performed on approximately 1,675 of the gas samples. Oil-water separation has been completed on approximately 1,418 of the liquid samples with further analysis on approximately 275 of these samples.

Modifications to incorporate hysteresis, viscous fingering, and wettability and surface tension changes into the numerical model have been made and the model is operational.

The collected samples represent 21 fields in four of the major producing basins of Wyoming. Seven of the fields are part of the programs sponsored by the state of Wyoming; the remaining fields are being sampled for future analysis if funding permits. These additional fields will permit a more comprehensive analysis of the $CO_2$ Huff-n-Puff process.

Results. Preliminary well responses show mixed results as to the success of the $CO_2$ stimulations. The single well tracer tests have been shown to be invaluable in determining the potential of candidate wells for the $CO_2$ cyclic stimulation.

## 5.14 Fly Ash Binder for Unsurfaced Road Aggregates

Objectives. The objectives are to develop and demonstrate the use of Wyoming fly ash in two construction techniques: (1) fly ash stabilization of soils as applied to unpaved roads and (2) fly ash replacement of portland cement in conventional cement treated bases (CTB). The use of fly ash in these construction technologies could potentially result in lower cost construction techniques and provide the ash generators new or expanded markets for Wyoming coal fly ash. The development of commercial enterprises, based on these technologies for the enhanced use of coal power plant fly ash in construction applications, therefore represents both a business and an environmentally attractive option for the state of Wyoming. The objective for the quarter was to continue laboratory testing of various soils and fly ashes as related to fly ash stabilization.

Accomplishments. Laboratory testing was concluded on the fly ash stabilized soil study. Testing for the quarter focused on the durability and resilient modulus of soil/fly ash mixtures.

Procedures. Two fly ashes, (Laramie River and Naughton) and four soil types, A-1b to A-6 (e.g., RS-1, RS-2, RS-5, and RS-7) were used in the testing.

The durability requirements for pavement construction includes the survival of the cement/soil mixture under 12 cycles of freezing and thawing, as well as less than 14% weight loss under wet/dry cycling. Mixtures of 25% fly ash and 75% soil were compacted to maximum density and 'optimum' moisture content in soil-cement molds, cured 7 days at 70°F and 100% relative humidity, and subjected to wet/dry cycles and freeze/thaw cycles according to ASTM D 559 and ASTM D560, respectively. All of the mixtures survived the twelve freeze/thaw cycles, but none of the mixtures met the less than 14 wt % loss requirement under wet/dry cycles. None of the soil alone mixtures were able to survive three wet/dry cycles, indicating that the fly ash treatment is improving the durability performance of the soils. It should be noted that these ASTM specifications were established for soil cement, which is a soil stabilized with portland cement for specific applications. The applicability of this criteria for fly ash stabilized soils has not been established.

Results. The resilient modulus is a measure of the stiffness of a subgrade soil for conditions that represent the stresses in pavements subjected to moving wheel loads. The resilient modulus test describes the resilient, or elastic, response of the subgrade material to repeated axial deviator stress of a fixed magnitude, frequency, and load duration when applied under triaxial pressure. Resilient modulus has been selected by AASHTO (1986) as the definitive material property to characterize roadbed soils for pavement design. Resilient modulus values of the fly ash treated specimens range from 121 to 904 k psi. Preliminary testing of the soils without fly ash indicate values in the range of 5 to 10 k psi. The data indicate that the relationship of resilient modulus is both fly ash sensitive and soil type sensitive. The behavior of Naughton compared to Laramie River material varies by up to a factor of five, with the Naughton showing higher resilient modulus values for soils RS-1, RS-2, RS-5. However, for the RS-7 soil (more clay), the response is the reverse, with the Laramie River material showing the higher values, by a factor of two.

## 5.15 Evaluation of Products Recovered from Scrap Tires for Use as Asphalt Modifiers

This task was completed in previous quarters.

## 5.16 Solid State NMR Analysis of Mesaverde Group, Greater Green River Basin, Tight Gas Sands

Objectives. The objectives of this study are to apply solid-state $^{13}C$ NMR to measure changes in the organic structure of petroleum source rocks (kerogens) brought about by laboratory hydrous pyrolysis experiments and by maturation in the natural geologic environment as a result of depth of burial. These data, in conjunction with other analyses and kinetic measurements, will be used by the University of Wyoming, Department of Geology and Geophysics to develop an innovative exploration and production strategy that will optimize the efficient exploitation of tight gas resources in the Mesa Verde Group, Greater Green River Basin, Wyoming. The objectives for the quarter were: (1) to complete NMR measurements of changes in the organic structure of petroleum source rocks brought about by laboratory hydrous pyrolysis experiments and by maturation in the natural geologic environment as a result of depth of burial and (2) to evaluate the results of the measurements.

Accomplishments. The NMR measurements have been completed and the results are being evaluated.

Procedures. Solid-state $^{13}C$ NMR measurements were performed on coal samples from the Lance and Almond coal groups that were subjected to laboratory hydrous pyrolysis experiments in the temperature range of 290-360°C (554-680°F). The NMR measurements were made on a Chemagnetics CMX 100/200 solids NMR spectrometer. $^{13}C$ and $^{1}H$ NMR spectra were obtained using cross polarization with magic-angle spinning (CP/MAS) and combined rotation and multiple pulse spectroscopy (CRAMPS). The $^{13}C$ measurements were made at a frequency of 25 MHz, and the $^{1}H$ measurements were made at 200 MHz.

Results. Plots of the different aliphatic carbon functionalities as a function of temperature have been made. The data show the expected decrease in the methylene carbons with temperature as oil is produced during the hydrous pyrolysis experiments. In addition, an increase in the concentration of methyl carbons attached to aromatic rings was noted. Presumably, these are the result of free radical capping during oil generation.

## 5.17 Flow-Loop Testing of Double-Wall Pipe for Thermal Applications

Objectives. The objectives of this research effort are: to develop a numerical model that will predict down-hole steam quality, steam pressure, and temperature; to evaluate InterMountain Pipe Company's double-wall pipe for thermal application; and to provide future industrial clients with a fully instrumented flow loop. The objective for the quarter was to complete the final report.

Accomplishments. The final report was completed and submitted. This task is completed.

## 5.18 Characterization of Petroleum Residua

Objectives. The objectives of this effort are to develop methods for and characterize petroleum residua from industry participants. The objective for the quarter was to wait for additional samples and authorization from the cosponsor to proceed with analyses.

Accomplishments. Methods were established and characterization was completed on residua samples provided by the cosponsor in previous quarters. Samples of residua D and E were received from the cosponsor.

Procedures. All experimental work with the residua designated A, B, and C, was completed in the previous quarter. Each residuum was deasphaltened in heptane, and the heptane-soluble materials were separated into saturate, aromatic, and polar fractions on activated silica gel. The asphaltenes were separated into four fractions according to apparent molecular size by preparative size exclusion chromatography (SEC). The whole residua were evaluated for elemental composition, trace metals content, carbon residue, simulated distillation profile, specific gravity, pour point, and rheological profile. The asphaltenes and silica gel chromatographic fractions were evaluated for elemental composition, trace metals content, molecular weight, carbon residue, analytical SEC profiles, and aromaticity by nuclear magnetic resonance (NMR) spectroscopy. The preparative SEC fractions from the asphaltenes were evaluated for sulfur content, molecular weight, and trace metals content.

The toluene solutions for the preparative size exclusion fractions from residuum C asphaltenes for molecular weight determinations had to be made above 40°C (104°F) to maintain clear solutions. This had no detrimental effect on the vapor-phase osmometry measurements, which were made as usual at 60°C (140°F).

Results. Material balances show that the data obtained on the fractions account for the data obtained on the original material. This indicates that the contributions of the properties of the fractions can be studied and related to properties of the whole material.

## 5.19 Shallow Oil Production Using Horizontal Wells with Enhanced Oil Recovery Techniques

Objectives. The objectives of this task are to demonstrate that enhanced oil recovery techniques can be successfully used with horizontal wells in shallow reservoirs to increase oil production significantly, to validate a numerical model with the use of physical simulations using an implemented enhanced oil recovery process with horizontal wells, and to provide the technical expertise and supervision for the implementation of a pilot test that will use the information generated in the study. The objectives for the quarter were to initiate and monitor the field test at the Chetopa Townsite oil field site.

Accomplishments. The redesigned ignitor was used successfully to start combustion in the field. Process parameters are being monitored and evaluated as the test proceeds.

Procedures. As reported last quarter, attempts to position the originally designed and fabricated down-hole ignitor in the ground were unsuccessful because the drilling contractor down-sized the ignition well casing from specifications. A new gas (propane-air) burner was fabricated and tested for slim-hole applications. The burner was fueled with a premixed propane-air mixture, which was ignited with a flame rod. The flame rod uses electricity to produce a 6000 volt spark to ignite the mixture. Electricity is supplied to the rod with the use of a cable and a 110 volt transformer.

Production data, gas samples, and temperature data are being collected and evaluated as the test proceeds.

Results. Reservoir ignition in the Chetopa field was obtained after a 48-hour period of heat injection. Gas analysis and temperature profiles indicate that combustion is being sustained.

## 5.20 "B" Series Pilot-Plant Tests

Objectives. The objective of this study is to conduct and evaluate tests using the K-Fuel® Series B pilot plant on selected western coals. The objective for the quarter was to report on the additional tests conducted using a different coal resource.

Accomplishments. The additional tests were evaluated and a supplement to the existing report was prepared. The supplement is being reviewed by the cosponsor.

## 5.21 Surface Process Study for Oil Recovery Using a Thermal Extraction Process

Objectives. The objective of this task is to develop an economic process for shallow oil resources which are not being utilized. The objective for the quarter was to initiate research on the DOE portion of the task.

Accomplishments. All accomplishments to date have been completed under the funding of the cosponsor. The reservoir has been characterized, and the physical simulations of the thermal process and the gravity drainage process have been completed. The process and product evaluations have been completed and the scale-up of the process to field scale has been initiated.

A preliminary report covering the first five phases is presently being drafted for submittal to the cosponsor. A copy of the report will be sent to DOE.

Obligation of funds has not been received from DOE.

Procedures. The phases of the project are: (1) characterization of the preselected target reservoir, (2) physical simulation of the thermal process using reservoir material, (3) physical simulations of the gravity drainage process, (4) process and product evaluation, (5) scale-up of the process to a field-pilot, (6) field demonstration of the process, and (7) project reporting. Thermal processing of reservoir material will be evaluated using existing equipment at WRI. Based on the laboratory simulations, a field-scale demonstration unit will be designed, constructed, and operated at a field location.

Results. Laboratory simulations of two thermal processes were conducted. The processes evaluated were the ROPE process and a vertical fluidized bed. For scale-up reasons, the vertical fluidized bed was selected as the system to be constructed for the field demonstration.

## 5.22 NMR Analysis of Samples from the Ocean Drilling Program

Objectives. The objective of this study is to apply solid-state $^{13}C$ NMR to study samples collected from leg 139 of the Joint Oceanographic Institute project on thermal maturation in areas of steep thermal gradient. The objective for the quarter was to continue making measurements on the samples.

Accomplishments. Ten additional kerogen concentrates and seven whole rock samples were received for NMR analysis. Solid-state $^{13}C$ NMR measurements were made on seven whole rock samples and two kerogen concentrates.

Procedures. Solid-state NMR measurements were made on a Chemagnetics CMX 100/200 solids NMR spectrometer. $^{13}C$ spectra were obtained at 25 MHz using cross polarization with magic-angle spinning (CP/MAS). A large-volume spinner was used for analysis of whole rock samples.

Results. CP/MAS $^{13}C$ NMR spectra were acquired on samples received from the Woods Hole Oceanographic Institution. However, because of the low levels of organic matter in the sediments, a large-volume spinner was used whenever possible to obtain useful NMR spectra. Even for these samples, 12 to 18 hours of signal averaging was required to obtain decent spectra. The spectra were compromised by background signals from the probe. As a result, the probe background signals were recorded under different conditions and subtracted from the sample spectra to determine the carbon aromaticities of the sedimentary material.

## 5.23 Menu Driven Access to the WDEQ Hydrologic Data Management System

Objectives. The objective of this study is to develop an enhancement to the Wyoming Department of Environmental Quality Data Management System that will provide menu-driven access. The objective for this quarter was to complete the documentation report.

Accomplishments. The documentation report was prepared, submitted, and approved. This task is completed.

## 5.24 Oil Field Waste Cleanup Using Tank Bottom Recovery Process

Objectives. The objective of this task is to remediate a waste problem and thereby develop an energy resource which is currently being wasted, discarded, or destroyed. The objective for the quarter was to prepare a preliminary process design.

Accomplishments. Preliminary evaluation of the process was accomplished under another program. Based on results of the previous project, a preliminary process schematic and material balance have been developed. From the preliminary process schematic, detailed construction drawings and equipment specifications are being made.

Procedures. Based on previous laboratory simulation results, a field-scale unit will be designed, constructed, and operated in the field.

## 5.25 Remote Chemical Sensor Development

Objectives. The objectives of this research effort are to design, test, and construct prototype field instrumentation for in situ qualitative identification and quantitative determination of selected groundwater pollutants. The objectives for this quarter were to begin the literature and marketing studies to define the technologies that will be pursued for instrument and method development work and to initiate the experimental work.

Accomplishments. Work began on the literature and marketing studies to define the technologies that will be pursued for instrument and method development work. These technologies will not be limited to Raman spectroscopy probes, based on the results of the above studies.

Experimental work on the extraction of diesel fuel from contaminated soils using non-fluorocarbon solvents was initiated. Several solvent systems were identified for testing.

A visit was made to Mike Angel at Lawrence Livermore National Laboratory to discuss Raman sensor technology. A visit was also made to the Technology Transfer Division at UCLA to discuss proprietary technologies that might be applicable to sensor or field test kit development.

Procedures. Due to a contract that the University of Wyoming (UW) has with the Electric Power Research Institute on the development of surface enhanced Raman spectroscopy probes for determining a limited number of organic species, UW's participation in the JSR project will be very limited, if at all. This will not decrease or constrain the objectives or planned accomplishments of this project. A letter describing the changes and redirection in the approach will be submitted soon.

## 5.26 In Situ Treatment of Manufactured Gas Plant Contaminated Soils Demonstration Program

Objectives. The objectives of this task are to demonstrate and evaluate the CROW™ process and bioremediation to remediate a site contaminated with a dense organic fluid. Hopefully, treatment levels in the field will achieve results that are comparable to prior laboratory findings. The objectives for this quarter were to prepare and submit a field demonstration work plan and to initiate preparation of a 30% design of the field installation and operating scheme.

Accomplishments. The work plan for the field demonstration has been drafted and submitted to the U.S. Environmental Protection Agency (EPA), Region 3 office for approval. All environmental and construction permits have been identified and the permitting phase is underway.

A 30% design of the field installation and operating scheme is being prepared for submittal to the EPA Region 3 office as part of the EPA site requirements. The Pennsylvania Department of Environmental Resources is also being included in the design, review, and operational requirements of the project.

Procedures. The overall task procedures are: (1) develop and submit a detailed work plan, (2) identify all required construction and environmental permits, (3) apply for all permits, (4) prepare and submit for approval a 30% complete design for the field layout and operation, (5) prepare and submit a prefinal design for the field layout and operation (all equipment, well construction, and operating routines will be fully specified), (6) prepare a final project design based on the review comments from the prefinal design submission, (7) procure all required equipment and construct the field facilities, (8) operate the field demonstration test, (9) dismantle the field facility, and (10) analyze the data from the field demonstration and report the results to the DOE, EPA, and the cosponsors.

The laboratory results that are being used to design this project are from a completed project sponsored by the EPA's Emerging Technologies Program.

## 5.27 Solid State NMR Analysis of Mowry Formation Shale From Different Sedimentary Basins

Objectives. The objective of this task is to apply the solid-state $^{13}C$ NMR techniques of cross polarization with magic-angle spinning (CP/MAS) to measure changes in organic carbon structure of kerogens brought about by laboratory hydrous pyrolysis experiments and by maturation in the natural geologic environment as a result of depth of burial. These data, in conjunction with other analyses and kinetic measurements will be used to construct a model for reconstructing the diagenetic and maturational history of pressure chambers. Ultimately, this information will become a framework for seismic detection of these pressure chambers. The objective for the quarter was to begin planning for the research effort.

Accomplishments. Plans have been formulated and work will begin in the next quarter.

Procedures. Solid-state NMR measurements will be made on a Chemagnetics CMX 100/200 solids NMR spectrometer. $^{13}C$ NMR spectra will be obtained using CP/MAS. The $^{13}C$ measurements will be made at a frequency of 25 MHz.

## 5.28 Solid State NMR Analysis of Naturally and Artificially Matured Kerogens

Objectives. The objective of this research effort is to apply solid-state $^{13}C$ NMR techniques of cross polarization with magic-angle spinning (CP/MAS) to measure changes in the organic carbon structure of the kerogen in petroleum source rocks brought about by maturation in the natural environment and by artificial maturation in laboratory environments. These data in conjunction with other geochemical analyses and kinetic measurements will be used to establish the basic information required for calculating kinetic parameters used in the modeling of the generation of critical compounds in diagenetic systems. The objective for the quarter was to begin NMR measurements on source rock samples.

Accomplishments. NMR measurements are in progress on 22 samples of coals, shales, and hydrous pyrolysis residues that have been received for analysis. An abstract has been submitted to DOE for approval to present a paper at the International Conference on Coal Science to be held September 12-18, in Banff, Alberta, Canada.

Procedures. Solid-state NMR measurements are made on a Chemagnetics CMX 100/200 solids NMR spectrometer. $^{13}C$ NMR spectra are obtained using CP/MAS. The $^{13}C$ measurements are made at a frequency of 25 MHz.

## 5.29 Development of an Effective Method for the Clean-Up of Natural Gas

Objectives. The objective of this task is to evaluate the feasibility of using a molecular sieve carbon that is manufactured by the Takeda Chemical Company of Japan as the solid adsorbent in a pressure swing adsorption (PSA) cycle to separate nitrogen from natural gas. Development of a less complex and more cost-effective method for upgrading low-quality natural gas by the use of physical separation processes will require an adsorbent that can function in a simple pressure swing cycle, instead of the pressure/vacuum swing cycle used in currently available physical separation processes. The objective for this quarter was to begin planning for the research effort.

Accomplishments. Plans have been formulated and work will begin in the next quarter.

# END

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4/7/93