WESTERN RESEARCH INSTITUTE

QUARTERLY TECHNICAL PROGRESS REPORT

January - March 1993

OIL SHALE

TAR SAND

COAL RESEARCH

ADVANCED EXPLORATORY PROCESS TECHNOLOGY

JOINTLY SPONSORED RESEARCH

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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 evaluate the effect of temperature, residence time, and liquid-to-solid ratio on the thermal conversion of Sunbury eastern oil shale; and to evaluate the effects of temperature, pressure, and residence time for regeneration of the recycle oil.

Accomplishments. Thermal conversion experiments were conducted on the Sunbury shale and a series of hydrotreating tests were performed on spent hydrogen donor solvent to evaluate the best conditions to regenerate the donor solvent. Data for the two sets of experiments are being collected and evaluation of the data is in the preliminary stages.

Procedures. Thermal conversion experiments were conducted in tubing bombs. The tubing bombs were heated in a sand bath set at the desired temperature for the prescribed length of time. The experiments were conducted at 707 and 752°F (375 and 400°C). Tests including three residence times (5, 10, and 20 minutes) and two oil-to-solid ratios were completed at each temperature.

A large sample of spent hydrogen donor recycle solvent was generated by thermally extracting an equal amount of Sunbury shale oil in a 1-liter batch autoclave. This sample was then hydrogenated at various temperatures and pressures. Liquid hourly space velocities of 1 and 2 were also examined. These tests were run at 525, 550, 575, and 600°F (274, 288, 302, and 316°C) at three pressures (1500, 1700, and 1900 psig).

Results. Preliminary results from the thermal conversion with a hydrogen donor present indicate that temperature had the greatest effect on the conversion of the Sunbury shale. Increasing the temperature from 707 to 752°F (375 to 400°C) nearly doubled the conversion of the organic carbon for most residence times. Similarly, increasing the residence time also increased the conversion. Using tetralin as a hydrogen donor solvent did not appear to increase the conversion when compared to tests using an eastern shale oil distillate as the donor solvent.

Preliminary results from the hydrotreating experiments suggest that the best conditions for regenerating the shale oil distillate are similar to those predicted from the model compound study. The best temperature appears to be between 550 and

575°F (288 and 302°C). Pressure did not affect the regeneration of the donor solvent as much as the temperature did. However, tests performed at 1900 psig did appear to introduce more hydrogen into the sample. Increasing the liquid hourly space velocity from 1 to 2 decreased the hydrogen uptake by approximately two-thirds.

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 complete the final milestone report on the study.

Accomplishments. Milestone 1.2.4C, report on energies of interactions correlated with observed stabilities and rheological properties of asphalt-aggregate mixtures, was completed, submitted, and approved. This task has been completed.

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 was to design and initiate fabrication of a modified 6-inch bench-scale unit that included 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 was 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. Milestone report 2.2.1B has been completed, reviewed by LFTB, and submitted to METC. Milestone report 2.2.1C has been completed and reviewed by LFTB. Final revisions are being made to the report.

3.0 COAL RESEARCH

3.2 Coal Combustion

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 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 that is associated with each of the three subtasks and to initiate preparation of the milestone report.

Accomplishments. The experimental series associated with each of the three subtasks was completed. For the milestone report, 3.3.4B, two of the three subtasks have been written in draft form and are in review.

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. The results of subtask 1 are being evaluated as the preparation of this portion of the report progresses. For subtask 2, four modified catalysts were prepared from Amocat 1A and evaluated with respect to coal liquefaction. Overall performance of the modified catalysts did not differ significantly from the original catalyst. However, differences in conversion yield do exist between the modified catalysts and with Amocat 1A. The conversion yields obtained using cobalt/moly catalyst containing a coating of titania deposited by the impregnation method is comparable to Amocat 1A. Use of the other three catalysts in coal liquefaction result in lower conversion yields than Amocat 1A, with the use of cobalt/moly catalyst containing a coating of titania deposited by the deposition method of Fogar and Anderson having the lowest conversion yield. The use of cobalt/moly catalyst containing a coating of zirconia deposited by the impregnation method and a catalyst containing a coating of carbon deposited by pyrolysis of cyclohexene resulted in conversion yields that were intermediate with respect to the other two modified catalysts.

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. The milestone report (not for publication) was completed, reviewed by LFTB, and submitted to METC. This task has been completed.

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 being prepared.

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.

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 three-dimensional reservoir simulator.

Accomplishments. The horizontal well algorithm has been installed in the three-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.

4.1.9 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 objective for this quarter was to conduct laboratory simulation tests using blocking agents.

Accomplishments. Screening of the potential blocking agents to be tested has been completed. Core flood tests to evaluate the selected blocking agents to ensure proper functioning prior to use in the three dimensional simulations were completed and the report on these tests is being prepared.

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

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.

Results. In the physical simulation study, the Shannon sandstone block samples have been saturated. Core floods using the identified blocking agents have been 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 supplier and other suppliers to identify the nonperformance problems and to identify better agents. Testing of the modifications and new materials has been completed.

4.2 Advanced Mitigation Concepts

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 objective for the quarter was to conduct the designed experiments.

Accomplishments. The experimental testing program is under way and is 85% 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.

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 complete the milestone report on the research.

Accomplishments. Comments on the report were received and the report is being modified.

4.3 Oil and Gas Technology

4.3.1 Enhanced Oil Recovery (FY 1992)

Objectives. The original objective of this research task was to determine the enhancement of oil recovery using steamflooding in conjunction with chemicals or gases and horizontal wells. The approved experimental plan for this task has eliminated the use of horizontal wells. The objectives for this quarter were to complete the experimental plan and to conduct the first block test.

Accomplishments. The experimental plan has been reviewed by DOE and the DOE comments have been addressed. The revised experimental plan has been accepted. The first block test has been conducted.

Procedures. The test used the horizontally fractured block with surfactant as the blocking agent. Preliminary evaluation of the test will be completed prior to beginning the second test.

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.

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

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 continue refining the capabilities of the three-dimensional, thermal code and to evaluate the performance of the code by comparing model results with literature results.

Accomplishments. The major accomplishment for this quarter was to resolve a convergence difficulty encountered when modeling problems with asymptotic-approach, saturation changes.

Procedures. In the model's previous configuration, conditions of asymptotic approach caused the model's convergence routines to make large numbers of iterations, each successive iteration making extremely small improvements in the saturation estimate. The problem of slow convergence was solved by implementing a centered-difference differentiation technique (order ΔX^2 accuracy) in the model's solution routines in place of the previously used (order ΔX accuracy) forward difference scheme.

Results. The improvements in speed with the new technique have been significant. The model can currently solve these type of problems in 15 minutes, rather than the previously required 5 days. Further enhancements made to the code during this quarter include: numerous changes to solution and source-term routines to reduce memory storage and simplify operation, refinement to the constant flow-term routines to permit gravity-head pressure gradients and to allocate flow to individual layers based on implicitly calculated reservoir and fluid properties, and inclusion of new output routines that generate data saves for injection and production wells in reservoir engineering field units.

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 CROWTM Field Demonstration with Bell Lumber and Pole

Objectives. The objective of this task is to design, construct, and operate a field demonstration of the CROWTM process technology to treat a site contaminated with organic wastes from the wood treatment process. The objectives for the quarter were to work towards approval of the work plan for the full-scale demonstration test and submit a revised report for the two-well test.

Accomplishments. Based on meetings and discussions with the Minnesota Pollution Control Administration, modifications to the detailed work plan for the full-scale demonstration have been made and resubmitted for review and approval. The revised report for the two-well test has 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 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, 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) prepare precision and bias statements on the sequential batch extraction method for ASTM balloting, (2) complete the final report for the Institute for Standards Research (ISR) cosponsors, (3) prepare the ASTM research report, and (4) begin work on the DOE final report.

Accomplishments. Precision and bias statements on the sequential batch extraction method were prepared and sent to ASTM for concurrent balloting at the subcommittee and main committee levels. These are being balloted as additions to the new ASTM method, D5284-92. The report for the ISR project cosponsors was finalized and sent to ISR for distribution. The ASTM research report was started; however, ASTM has decided that the ISR final report can replace the research report for this project. As a result, the ISR report will be referenced in the precision and bias statements that are added to the method. Work was also started on the final report for DOE.

Procedures. The precision and bias statements on the new method are being balloted concurrently within ASTM Subcommittee D34.02 on Physical and Chemical Characterization and ASTM Main Committee D34 on Waste Management. The balloting is expected to close on April 13, 1993. Contact with ASTM headquarters is being maintained to keep abreast of the voting results.

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- μm versus 0.8- μm , 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 ± 0.05 and the dilute acid solution standards having a pH of 5.0 ± 0.05 was less than desired, based on the criterion given in ASTM Practice D-2777.

At this time, one negative vote on the precision and bias statements has been received. The negative voter feels that too much information is presented in the precision and bias statements. This item and any other negative votes will be addressed by ASTM Task Group D34.02.01 on Waste Leaching Techniques at its meeting in May.

5.8 PGI Demonstration Project

Objective. The objective for the quarter was to continue preparation of equipment specifications and the detailed design of the system.

Accomplishments. Detailed design and preparation of bid packages continued. A pre-design meeting with representatives from NREL, Fossil Energy, LFTB, PGI, VTT, and WRI was held in early March.

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 CO₂ 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 fluid 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 fluid samples have been taken from the field tests of the CO₂ 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 fluid 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.

Results. Preliminary well responses show mixed results as to the success of the CO₂ stimulations. The single well tracer tests have been shown to be invaluable in determining the potential of candidate wells for the CO₂ 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 objectives for the quarter were to finish laboratory testing of various soils, fly ash, and aggregates as related to fly ash stabilization and CTB, and to initiate preparation of the final project reports to the various sponsors.

Accomplishments. All laboratory testing has been completed and preparation of the final reports is under way.

Procedures. Three reports will cover the testing and demonstration activities.

(1) Laboratory testing of soils, fly ash, and aggregate samples that was concluded under subcontract to the University of Wyoming, Department of Civil Engineering. Fly ash stabilization of unpaved roads laboratory testing examined three additional soils ranging from AASHTO soil types A-1b to A-6 (RS-1, RS-2, RS-5, and RS-7) with two additional fly ashes (Naughton and Laramie River). The results of the durability tests provided an evaluation of whether or not sufficient strength and durability can be realized at these low dosages under the climatic conditions of the Rocky Mountain region. A report covering the CTB testing has been completed by the subcontractor and has been submitted to WRI for review and incorporation into a WRI final report.

(2) Laboratory testing for CTB applications using a scoria aggregate from Reno Junction, Type II portland cement from Mountain Cement and the above mentioned three fly ashes (Dave Johnston, Naughton, and Laramie River). The fly ash replacement of the portland cement ranged from 20% to 75%. Approximately 8% portland cement or cement plus fly ash is used in the CTB mixes. A report covering the CTB testing has been completed by the subcontractor and has been submitted to WRI for review and incorporation into the WRI final report.

(3) Field demonstration of the fly ash treatment of unpaved roads. An interim report covering the fly ash treatment of unpaved roads and, in particular, the demonstration test section in Converse County had been submitted to DOE, PacifiCorp, and STEA for review and approval. It is now being converted into a final technical report on the Glenrock Demonstration.

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 ^1H NMR spectra were obtained using cross polarization with magic-angle (CP/MAS) and combined rotation and multiple pulse spectroscopy (CRAMPS). The ^{13}C measurements were made at a frequency of 25 MHz, and the ^1H 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 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 in the previous quarter. Revisions are being made to address review comments and complete the report.

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 begin analysis on new samples received from the cosponsor.

Accomplishments. Methods were established and characterization was completed on residua samples provided by the cosponsor in previous quarters. Analyses were begun on sample Residua D and E.

Procedures. The procedures developed include each residuum being deasphalted in heptane, and the heptane-soluble materials separated into saturate, aromatic, and polar fractions on activated silica gel. The asphaltenes are separated into four fractions according to apparent molecular size by preparative size exclusion chromatography (SEC). The whole residua are 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 are 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 are evaluated for sulfur content, molecular weight, and trace metals content.

Residua D and E were deasphalted. The maltenes from Residua D and E were separated into saturate, aromatic, and polar fractions on silica gel. The asphaltenes from Residuum D were separated into four fractions by preparative SEC.

Results. Insufficient asphaltenes were obtained from Residuum E to do the preparative SEC. Additional effort was undertaken to separate additional Residuum E to obtain sufficient asphaltenes. This is in progress.

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 complete the field test at the Chetopa Townsite oil field site, evaluate the collected data, and begin preparation of the final report.

Accomplishments. The test has been terminated and the data are being evaluated for preparation of the final report.

Procedures. Production data, gas samples, and temperature data were collected during the test. Injection of air into the formation has been terminated. At the present time, all wells have been shut-in. Abandonment of the wells will not proceed until the final report is prepared. A simulation test (Nelson and McNeil, "Thermal Methods Provide Three Ways to Improve Oil Recovery," Oil and Gas Journal, January 1959) has been run. A physical simulation test that will evaluate gravity drainage in one dimension will be performed using the most feasible enhanced oil recovery process.

Results. Temperature increases in the horizontal production wells were not observed during the air injection phase. Injection of air has been terminated due to the economics of the project. A total of 40 barrels of reservoir crude oil was produced.

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 objectives for the quarter were to continue the scale-up design and prepare a preliminary report on the reservoir characterization, physical simulations, and scale-up to field scale.

Accomplishments. 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 is nearly completed. The preliminary report, covering the first five phases of the project, is also nearly completed. A copy of the report will be sent to 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.

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 (JOI) project on thermal maturation in areas of steep thermal gradient. The objective for the quarter was to continue making measurements on the samples.

Accomplishments. Solid-state ^{13}C NMR aromaticity measurements have been made on all the samples sent to WRI from the Woods Hole Oceanographic Institution. The NMR results have been included in the Woods Hole project report on the time and temperature histories of sediments from Leg 139 of the Ocean Drilling Program.

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 (CP/MAS) spinning. 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. The NMR analyses are now complete, and the results are being assembled into a brief summary report. The NMR results for samples affected by the hydrothermal flow in the study area show the organic matter to be almost exclusively aromatic carbon functionalities. These results are in agreement with maturity measurements based on vitrinite reflectance.

5.23 Menu Driven Access to the WDEQ Hydrologic Data Management System

This task was completed in previous quarters.

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 the detailed 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 was developed. From the preliminary process schematic, detailed construction drawings and equipment specifications are being prepared.

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 continue the literature and marketing studies to define the technologies that will be pursued for instrument and method development work and to continue the experimental work.

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

Experimental work on the extraction of diesel fuel from contaminated soils using non fluorocarbon solvents continued. Several solvent systems were tested.

A visit was made to Carnegie-Mellon Research Institute in Pittsburgh to discuss solid-state sensor technology.

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. This will not decrease or constrain the objectives or planned accomplishments of this project.

A field analysis product, Lab-in-a-Bag, is being evaluated for its response to diesel fuel and weathered gasoline in sand, silt, and clay soil matrices.

A subcontract was initiated to look for indicators for surface enhanced resonance Raman spectroscopy for determining pH. Several indicators were evaluated. None of them has met all of the requirements.

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 CROWTM 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 objective for this quarter was to prepare a 30% design of the field installation and operating scheme.

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

A 30% design of the field installation and operating scheme was 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 U.S. 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 complete NMR measurements on source rock samples.

Accomplishments. NMR measurements were completed on 22 samples of coals, shales, and hydrous pyrolysis residues that have been received for analysis. An abstract has been approved to present a paper at the International Conference on Coal Science to be held September. 12-18, 1993 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. The NMR data are being fit using computer software to provide further discrimination of carbon functional groups. In particular, the aliphatic carbon functionality is being deconvoluted into methylene carbons and carbons in methyl groups attached to aromatic rings and terminating aliphatic chains. Results of this analysis will be useful for modeling the kinetics of oil generation during hydrous pyrolysis.

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 investigate the effect of various adsorption cycle parameters in the separation of a mixture of methane and nitrogen by pressure swing adsorption.

Accomplishments. The effects of pressurization rate, depressurization rate, shut-in time between pressurization and depressurization, purge rate and volume, purge and blow-down direction (cocurrent or countercurrent) have been investigated. The use of a 100% methane purge has also been investigated.

Procedures. A small laboratory adsorption column was loaded with molecular sieve carbon and degassed under vacuum. The sieve is a 5 angstrom carbon molecular sieve manufactured by the Takeda Chemical Company of Japan. For a typical test, the column is pressurized at a predetermined rate with a mixed gas consisting of 30% nitrogen and 70% methane, allowed to depressurize, and purged with the feed gas mixture. The effluent from the column is collected and its volume is measured by water displacement. The effluent is collected in increments corresponding to various column pressure ranges and the increments are analyzed by gas chromatography. Product purity, product recovery, and sorbent productivity are calculated from the collected data.

Results. Little effect on separation performance resulted from changing pressurization and depressurization rates or the length of shut-in between pressure changes. Purge rate is not as significant as purge volume. Countercurrent blow-down and purge both result in minor improvement for this separation. The 100% methane purge resulted in a lower recovery of methane from the feed, with no improvement in product purity. The best conditions observed so far result in a product purity of 87%, 61.5% methane recovery, and a sorbent productivity of 12.2 cm³/gram/cycle.

END

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