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QUARTERLY TECHNICAL PROGRESS REPORT

April - June 1993

OIL SHALE

TAR SAND

COAL RESEARCH

ADVANCED EXPLORATORY PROCESS TECHNOLOGY

JOINTLY SPONSORED RESEARCH

MASTER

Under Cooperative Agreement DE-FC21-86MC11076

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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 complete the analysis of the products, evaluate the data, and initiate preparation of the milestone report.

Accomplishments. Determination of the distillate range of selected products was completed, the data were evaluated, and preparation of the milestone report was initiated.

Procedures. The distillate range of selected products from the tubing bomb and hydrogenation experiments was determined using ASTM Method D 2887.

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. An additional increase was noted for tests performed at 797°F (425°C).

As reported last quarter, increasing the residence time also increased the conversion for tests made at 707 and 752°F (375 and 400°C). However, data from tests run at 797°F (425°C) did not show the increase with increasing time. While a large increase was noted between the 5 and 10 minute residence times, the conversion remained the same for tests with tetralin as a hydrogen donor solvent. Tests using the middle distillate as a donor solvent show marked decreases when the tests at 797°F (425°C) were run for 20 minutes. While no tests were run at higher temperatures, the decreases in organic carbon conversion would probably be even more pronounced.

Also reported last quarter, using tetralin as a hydrogen donor solvent did not appear to show an increase in conversion when compared to tests using an eastern shale oil distillate as the donor solvent. For tests run at 797°F (425°C), about 15% more organic conversion was observed when tetralin was used as the donor solvent. Data for the middle distillate tests indicated the solid-to-oil ratio did not appear to affect the organic conversion. There was some scatter in the data and no real trend could be determined.

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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 submitted and reviewed by 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 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 were consistent with those reported earlier that were based on the preliminary analysis of the data: that western subbituminous 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 objective for the quarter was to complete the preparation and in-house review of the milestone report.

Accomplishments. A draft of the milestone report was prepared and reviewed in-house. Final revisions were being made to the report.

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 prepare the experimental plan, 3.4.1A.

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

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 complete 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.

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.

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 objectives for the quarter were to complete the designed experiments and begin preparation of the milestone report.

Accomplishments. The experimental testing program has been completed and a draft of the milestone report is being prepared.

Procedures. Eleven one-dimensional displacement tests were 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 were run for validation purposes. Contaminated soil samples obtained from Midwest Gas were used as the test material.

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 evaluate data from the first block test and conduct the second of the two block tests.

Accomplishments. Data from the first block test were evaluated and the second block test was started.

Procedures. The second test was initiated in late June but was suspended temporarily because of a leak in the reactor box. The box has been repaired and the test will be conducted the first week of July.

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 build directional permeability capabilities into the thermal code and to continue to test the model.

Accomplishments. The ability to describe directional permeabilities was added to the thermal code and tested. The model's ability to partition flow correctly between layers at source (well) term locations was verified.

Procedures. The model is capable of describing permeability variations in the x-, y-, or z-directions. In addition, for ease of history matching, the user may specify a transmissibility variation of the form: (a * T) + b, where a and b are specified in the model's input file over a range of calculational blocks or grids. (Transmissibility is the product of absolute permeability and the cross-sectional area to flow divided by block length in the direction of flow.)

Results. The model has been used to help develop the experimental design for CROW tests. Under these conditions of stratified water and oil layers, the models centered-difference differentiation technique continues to perform in a stable manner.

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 work towards approval of the work plan for the full-scale demonstration test.

Accomplishments. Based on meetings and discussions with the Minnesota Pollution Control Administration (MPCA), modifications to the detailed work plan for the full-scale demonstration have been made and resubmitted for review and approval. The permitting approvals have delayed the project significantly. A letter proposal is being prepared to request carryover of the project into the new JSR cooperative agreement as a new task.

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. The modified work plan has been tentatively accepted by the MPCA.

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 obtain ASTM approval of precision and bias statements on the new method and complete the DOE final report.

Accomplishments. Precision and bias statements on the sequential batch extraction method were approved by ASTM in concurrent balloting at the subcommittee and main committee levels. The final report to DOE was completed and submitted. This task is completed.

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 $\pm$ 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.

5.8 PGI Demonstration Project

Objective. The objective for the quarter was to confirm continued financial support of the project by the cosponsor.

Accomplishments. A poster presentation, "Development and Demonstration of a Wood-Fired Gas Turbine System," was prepared and given at the METC Coal-Fired Power Systems 93 -- Advances in IGCC and PFBC Review Meeting in Morgantown, West Virginia. Continued financial support of the project by the cosponsor has not occurred. A request was submitted to redirect the remaining DOE funds to other tasks.

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 ir 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 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 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 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 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 preparation of the final project reports to the various sponsors.

Accomplishments. 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 nuclear magnetic resonance (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 Mesaverde Group, Greater Green River Basin, Wyoming. The objectives for the quarter were: to evaluate 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 to prepare the final report on the project.

Accomplishments. Results of the NMR measurements have been evaluated and a draft of the final report has been written and reviewed in-house.

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. In general, the maturation trends observed by NMR for the naturally and artificially matured samples were in agreement with results obtained from other geochemical analyses. The NMR spectra of the naturally matured shale samples showed only a small aliphatic component at depths greater than about 12,000 ft, indicating little capacity for hydrocarbon generation at depths greater than this. Vitrinite reflectance measurements placed the oil window at between 4,500 and 14,500 ft. NMR measurements of the hydrous pyrolysis residues showed a clear loss of aliphatic carbon, relative to the aromatic carbon, with temperature. For the residue obtained from the highest temperature studied (360°C, 680°F) there was a 60% depletion of the hydrocarbon-producing aliphatic components. The trends in loss of aliphatic carbon with temperature suggested a means of defining a geochemical transformation ratio in terms of the loss of the aliphatic carbon fraction. A good correlation was found between the NMR transformation ratio and the production index determined by Rock-Eval pyrolysis measurements.

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 and apply them for characterization of petroleum residua from industry participants. The objectives for the quarter were to complete the separations, to perform characterization work on residua D, E, and F, and begin preparation of the final report.

Accomplishments. Residuum F was deasphaltened. The maltenes from residuum D and E were separated into saturate, aromatic, and polar fractions on silica gel. The asphaltenes from residua E and F were separated into four fractions by preparative size exclusion chromatography (SEC). Physical, elemental, and metals analyses were completed on all the fractions. Work was started on a draft of the final report.

Procedures. The procedures developed include each residuum being deasphaltened 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.

Results. Insufficient asphaltenes were obtained from residuum E to do the preparative SEC. Additional separation work was done on residuum E to obtain sufficient asphaltenes. Because additional work was required for this, the structural feature calculations from the nuclear magnetic resonance (NMR) spectra for the six residua may not be done.

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 evaluate the collected field test data, and begin preparation of the final report.

Accomplishments. The data were evaluated and preparation of the final report was initiated.

Procedures. Production data, gas samples, and temperature data were collected during the test. Injection of air into the formation has been terminated. All wells have been shut-in. Abandonment of the wells will not proceed until the final report is prepared.

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 final report was prepared and submitted. This task is completed.

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, was prepared. 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 project on thermal maturation in areas of steep thermal gradient. The objective for the quarter was to complete sample measurements and prepare the final report.

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. A final summary report has been prepared and submitted. This task is completed.

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. Solid-state ^{13}C NMR measurements were made on a suite of whole rock and kerogen concentrate samples derived from sedimentary deposits obtained from Leg 139 of the Ocean Drilling Program. Carbon aromaticity measurements obtained by NMR correlate with the maturity of the sediments. For situations where the sediments have been, or are being heated by hydrothermal flow, there is a noticeable loss of the aliphatic component of the kerogen, and the remaining organic material is almost exclusively aromatic.

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 an oil field waste problem and thereby develop an energy resource that is currently being wasted, discarded, or destroyed. The objectives for the quarter were to complete the detailed process design and begin procurement of equipment.

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 have been prepared. Equipment procurement has been initiated.

Procedures. Based on previous laboratory simulation results, a field-scale unit is being designed and constructed. It will be 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. Experimental work on the extraction of diesel fuel from contaminated

soils using non fluorocarbon solvents continued. Several solvent systems were tested. Some initial experiments were performed to evaluate possible configurations for a device to measure volatile organic compounds in groundwater. A study continued to look for indicators for surface enhanced resonance Raman spectroscopy for determining pH.

The cooperative agreement funding this 30-month effort is due to expire on September 30, 1993, 11 months into the project. A proposal to complete the project as a new task under the new JSR cooperative agreement was submitted.

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

Results. In the diesel fuel extraction work, one solvent system showed promise in selectively extracting the hydrocarbons. In the study looking for indicators for surface enhanced resonance Raman spectroscopy for determining pH, several indicators for use with an inexpensive red diode laser were evaluated. None of them has met all of the requirements. Evaluation of the Lab-in-a-Bag showed that this is a good tool for measuring gasoline, but has limited application for less volatile diesel fuel. The evaluation also found that a higher and more uniform signal is obtained by analyzing soils with no water added.

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 objective for this quarter was to satisfy permitting requirements so that the construction and operation can proceed.

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 earlier. 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.

Progress on the project has been slowed because of problems encountered in the recharacterization of the site as requested by the EPA. The recharacterization was completed in late June and the work on the field demonstration has resumed. The permitting approvals have delayed the project significantly. A letter proposal is being prepared to request carryover of the project into the new JSR cooperative agreement as a new task.

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 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 perform preliminary work for the NMR measurements.

Accomplishments. Some new NMR pulse programs are being tested in preparation for the NMR measurements on the Mowry samples. These programs are designed to minimize signals from the NMR probe during recording of signal averages over long periods of time on samples with low levels of carbon.

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 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 evaluate NMR measurements on source rock samples.

Accomplishments. Data from the hydrous pyrolysis are being analyzed for inclusion in the first year report. A four page summary was submitted for publication in the Proceedings of the International Conference on Coal Science to be held September 12-18, 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.

NMR measurements were made on residue samples from hydrous pyrolysis experiments conducted at temperatures from 290 to 360°C (554 to 680°F) for 72 hr. The aliphatic resonance band was deconvoluted into resonances due to methylene carbons (30 ppm), methyl groups attached to aromatic rings (~20 ppm) and terminal methyl groups on side chains (~16 ppm) using curve-fitting procedures. This provides a further discrimination of carbon functionalities that are prone to produce oil and gas.

Results. During oil generation, the major changes in the aliphatic components are the disappearance of the methylene carbons (30 ppm) and the relative increase in the number of methyl groups attached to aromatic rings.

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 preparation of the final report.

Accomplishments. In previous quarters, 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. Preparation of the final report was initiated.

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 blowdown 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 CC/gram/cycle.

END

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