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**Research Investigations in Oil Shale, Tar Sand,
Coal Research, Advanced Exploratory Process
Technology, and Advanced Fuels Research
Volume II -- Jointly Sponsored Research Program**

**Final Report
October 1986 - September 1993**

Verne E. Smith

September 1994

Work Performed Under Contract No.: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Wyoming Research Corporation
Laramie, Wyoming

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FOREWORD

This report summarizes the major research investigations conducted by the Western Research Institute (WRI) under Cooperative Agreement DE-FC21-86MC11076 with the U.S. Department of Energy (DOE) over the period October 1986 through September 1993. In 1989 a Jointly Sponsored Research Program (JSRP) was incorporated into the agreement whereby some of the investigations were conducted as part of the Base Program and some were undertaken with cosponsorship from the commercial sector or other government agencies in the JSRP.

This report is divided into two volumes: Volume I consists of 28 summaries that describe the principal research efforts conducted under the Base Program in five principal topic areas. Volume II describes tasks performed within the JSRP. Research conducted under this agreement has resulted in technology transfer of a variety of energy-related research information. A listing of related publications and presentations is given at the end of each research topic summary. More specific and detailed information is provided in the topical reports referenced in the related publications listings.

ACKNOWLEDGEMENTS

Funding for this research has been provided under U.S. Department of Energy Cooperative Agreement DE-FC21-86MC11076 and by numerous JSRP cosponsors. In addition to the efforts of the authors who prepared the topic summaries, the considerable efforts of the many researchers and support people at Western Research Institute (WRI) who provided essential assistance in the design, conduct, and reporting of the work are greatly appreciated. Special thanks is due the individuals in DOE who have provided input and direction to the research studies and for their review and comments on completed studies.

EXECUTIVE SUMMARY

Numerous studies have been conducted under Cooperative Agreement DE-FC21-86MC11076 since its initiation in October 1986. During the time of the agreement, the most significant change occurred in 1989 when the agreement was redefined as a Base Program and a Jointly Sponsored Research Program (JSRP). Research topics within the Base Program continued, with an emphasis given to exploratory research that might lead to further development under the JSRP.

The JSRP was initiated to foster participation between WRI, industry, and DOE in areas of high industrial interest. With joint funding of tasks, greater levels of effort were carried out, resulting in more significant findings, for each participant's contribution. Under the program, 29 tasks were performed in topics of coal processing, enhanced oil recovery, recovery of oil from tank bottoms, in situ cleanup of organic materials, utilization of coal fly ash for road stabilization and waste containment, natural gas cleanup, oil shale processing, tar sand processing, development of instruments for in situ measurements, nuclear magnetic resonance (NMR) measurement of organic material in sedimentary rocks, development of methods for characterization of petroleum residuals and for leachate extraction, evaluation of materials derived from processing scrap tires as asphalt modifiers, cogeneration from wood-derived fuels or coal, and development of a hydrologic data base system for coal mines. Several of these technologies show good promise for commercialization.

A very promising process developed by WRI for application to environmental mitigation problems is the Contained Recovery of Oily Wastes (CROWTM) process. From development in the laboratory, the process is being used in two field demonstration projects. The first site is a wood treating plant in Minnesota where creosote and pentachlorophenol have contaminated the aquifer. A two-well pilot test that injected hot water to displace and recover contaminants was successful. Preparations are proceeding for the full-scale test. The second location is an old manufactured gas plant site in Pennsylvania where the soil is contaminated. Designs and permitting have been completed so the demonstration can proceed. Laboratory testing indicates that up to 90% of the contaminating material may be removed. Both studies have taken longer than anticipated because of the time required to obtain permits.

Another promising process under development at WRI is Tank Bottom Recovery and Remediation (TaBoRRTM). This process consists of preheating, flashing, distilling, and pyrolysis of oil-water materials associated with petroleum products. Process modeling was done using data collected from a candidate field site. The modeling results were used to design and fabricate a demonstration unit capable of producing 200 bbl/day of salable material. This unit will be tested in the field. If successful, the process could be used to recover oil and clean up material that is accumulating in this country at the rate of 2,000,000 bbl/year.

An evaluation was made of the potential increase in production that could be obtained from oil wells in Wyoming using the CO₂ huff-n-puff process. Selection criteria were developed and applied to Wyoming oil fields, resulting in the selection of 11 study wells. Cyclic CO₂ stimulations were carried out on the wells and product samples were collected and analyzed. Eight of the study wells were found to be successful in increasing oil production.

Enhanced oil recovery techniques were evaluated for application to a horizontal gravity-drained reservoir. It was determined from a screening of possible methods that waterflooding or steamflooding had the most potential for successful application. Numerical modeling of the two processes indicated that waterflooding would provide a better sweep of the reservoir, but steamflooding would give slightly better recovery. Physical simulations of the two processes

were conducted using blocks of material from the reservoir formation. The steamflood test yielded 80% more oil than did the waterflood test, indicating that steamflooding may be the best approach, depending on the costs related to steam generation and distribution.

Several processes were studied to determine a method of oil production from minable oil resources. Water extraction and solvent extraction were found to have drawbacks in comparison to thermal processing. From bench-scale tests of two thermal processes, fluidized-bed processing was determined to have the most likely potential for success. A pilot unit was designed, constructed, and tested at a site in Wyoming. Although problems were encountered in the field demonstration, fluidized-bed technology can be used on near-surface oil reserves.

A shallow oil field, containing high viscosity oil, was evaluated for the application of enhanced oil recovery techniques. Horizontal wells had previously been drilled in the Chetopa field in Kansas. Screening of possible techniques led to the conclusion that in situ combustion was the most feasible process for the site. Two bench-scale tests were run to help define the field test conditions. Poor recovery was obtained in the field test. This is attributed to positive pressure in the production well and low heat transfer from the burn zone.

A steam injection system for enhanced oil recovery using a double-walled tubular product has been privately developed to reduce heat losses between the steam source and the oil reservoir. A flow loop was constructed and tested by WRI to evaluate the system. It was found that annular insulation very significantly reduced heat loss. Heat losses at couplings was high, indicating the need for using thermal-resistant materials or redesigning the couplings. A new numerical model was developed for simulating the thermal hydraulics of saturated steam in wellbore configurations. The model provides more accurate predictions than previously developed models.

Nitrogen contaminates a significant amount of available natural gas resources, requiring its removal for the natural gas to be saleable. A series of experiments was run to evaluate molecular sieve carbon as a pressure swing adsorbent for nitrogen removal. Results of the tests indicated that such a system is technically feasible, but further study is needed to determine if it would be economically viable.

Although many techniques exist for characterization of petroleum residua, there is little established systematic methodology. An analytical scheme was developed in which asphaltenes were removed prior to fractionation and then analyzed for chemical and physical characteristics. The procedure was successfully applied to residua from six different heavy crude oils.

WRI has been developing an inclined fluidized-bed process for drying and stabilization of coal. A series of tests was conducted on coal from the Usibelli Coal Mine. Evaluation of the products indicated that the process could be used successfully with this coal.

A technical evaluation was made on the K-Fuel® Series B Process. This process removes moisture, decarboxylates, and removes some sulfur-containing compounds from coal, resulting in a dry, improved heating value, low-sulfur coal. Batch tests run on four coals substantiated the results of earlier testing.

A wood-fired gas turbine system is being developed for cogeneration purposes. A series of preliminary tests was run in a wood-fired combustor to obtain information on the entrained ash and on the fate of alkali and other materials that might cause deposition and corrosion problems. It was found that particulates present in the gas are likely to deposit and there is a

potential for alkali corrosion. Conventional treatment, such as washing or nut shelling and alkali gettering, can alleviate these problems.

A concern in modified in situ retorting of oil shale is the release of chemical compounds in local groundwater. Laboratory-scale simulations were conducted to evaluate methods for post-retorting control of impacts on groundwater. Combinations of quenching, deluge, and reverse combustion were applied after retorting. Reverse combustion was found to be the most effective method for removing organic material in the simulated retorts.

The Recycle Oil Pyrolysis and Extraction (ROPE™) process developed by WRI was applied to Sunnyside tar sand. The tests were conducted with no major operational difficulties and the product oils could be used as blending stock for diesel fuel.

As part of the development of a process for recovering useful products from scrap tires, WRI evaluated the solid residue from processing scrap tires as asphalt modifier. Asphalt cements modified with residue had greater viscosities, less elasticity, and better performance in freeze-thaw cycle tests.

Development of reliable instruments to detect and monitor groundwater contaminants is needed for environmental management. To this end, a prototype field test kit for determining diesel and other fuel types in soil has been built and tested. Also, initial experimental work was done on methods to measure volatile organic compounds in groundwater.

Established methods exist for characterizing materials leached from solid wastes. However, they are based on a single extraction procedure. More meaningful information can be derived from sequential batch extractions. WRI developed such a method that has been independently tested and established as a standard test method by the ASTM.

Definition of the organic carbon structure of hydrocarbon source rocks is essential to modeling the nature of hydrocarbon resources. Solid-state NMR measurements were made on coal and shale samples from several sedimentary basins to provide information on the maturity and generative capacity of the organic material.

The utilization of ash from coal combustion can provide beneficial applications while reducing solid waste disposal requirements. Fly ash materials were tested in the laboratory for soil stabilization and cement replacement applications. These tests indicated that the fly ash materials have good potential for such applications if carefully processed in the construction phase. A field demonstration study was conducted in which fly ash was mixed with existing road material on a section of unpaved road. Performance was quite good on the segments of roadway in which the mixing and wetting were properly done. Poorly mixed areas soon formed washboards and had other deterioration.

Solid waste materials generated by clean coal technologies could have application for hazardous waste stabilization. Four clean coal technology materials were evaluated for their ability to stabilize four hazardous organic or inorganic wastes. In some cases, the waste mixtures were too complex to evaluate. However, the clean coal technology solid wastes did appear to be effective in containing certain metals and organic materials from hazardous wastes.

A hydrologic data management system was improved by the development of menu-driven access to the data and data entry forms. The system provides hydrologic information on surface coal mines in Wyoming.

PILOT TEST OF THE CROW™ PROCESS AT THE BELL LUMBER AND POLE SITE

**L. John Fahy
Lyle A. Johnson, Jr.**

Background

Beginning in 1990, efforts were initiated in conjunction with the Bell Lumber and Pole Company to implement an in situ remediation project to address the creosote and pentachlorophenol (PCP) contaminated surficial aquifer at the Bell Pole site. The remediation project involves the application of the Contained Recovery of Oily Wastes (CROW™) process which consists of hot-water injection to displace and recover non-aqueous phase liquids (NAPL).

Wood treating activities began in 1923 at the Bell Pole site in New Brighton, Minnesota. Wood treating activities have included the use of creosote and PCP in a fuel oil carrier. Creosote was used as a wood preservative from 1923 to 1958. A 5 to 6% mixture of PCP in fuel oil was used as a wood preservative from 1952 to the present.

Characterization of the contaminated area at the Bell Pole site has been ongoing for several years. The two uppermost geologic formations identified beneath the Bell Pole site include the New Brighton and Twin Cities Formations. The contaminated New Brighton Formation contains a 23-47 ft thick, surficial aquifer consisting of uniform silty, fine to medium, gravel/sand. This formation is recharged through precipitation and by percolation, with groundwater flowing primarily to the southwest and discharging to a county drainage ditch. The Twin Cities Formation is a till material which creates an effective aquitard, separating the New Brighton Formation from lower aquifers.

As an interim response action, a two-well pilot test of the CROW process was conducted. The test consisted of injecting hot, potable water into the NAPL saturated area of the aquifer, producing groundwater

(and NAPL) from an existing production well, PW1, and treating the produced water for sanitary sewer discharge.

Objectives

The objectives of the pilot test were to compare predicted injection and production rates with actual field data, demonstrate the ability to heat the aquifer to the 49 to 60°C (120 to 140°F) range, demonstrate the ability to hydraulically control the injected water to prevent spreading contamination, confirm treatment system effectiveness in reducing PCP and polynuclear aromatic hydrocarbons (PAHs) prior to sanitary sewer discharge and predict anticipated operating conditions for a full-scale CROW application.

Procedures

The pilot-test location was selected based on the NAPL isopach mapping and the location of the existing production well, PW1. The injection and production wells were located in the area that contains high NAPL accumulations.

The pilot test began on September 24, 1991. Over the entire test, the pumping rate of PW1 averaged 6.5 gpm. The hot-water injection rate averaged 4.5 gpm. The pumping rate was consistently higher than the injection rate throughout the test. Water levels and temperatures in the aquifer were monitored throughout the test. Wellhead injection and production temperatures and the downhole temperatures were continuously recorded for certain monitor wells. Manual temperature readings were also taken daily.

Results

Early temperature data indicated that the hot water might be having a tendency to override and travel predominantly across

the top of the aquifer. But by the end of the test the highest temperatures were more toward the center of the zone, indicating that the hot water was not just traveling across the top of the zone but was heating the entire interval uniformly. In all cases, a temperature equal to or greater than the targeted 60°C (140°F) was achieved in the interior monitor wells. Downhole temperature measurements also indicated that 66°C (150°F) fluids had reached the production well prior to the conclusion of the hot-water injection phase.

NAPL arrival at the production well was noted by increased levels of floating oil at the top of the water table, only 6 days before breakthrough of the hot-water front. After the test was concluded, two boreholes were drilled to estimate the amount of oil remaining after hot-water injection. The post-test coring data indicated that, after the first 20 pore volumes of water were injected, the process efficiency declined drastically. Additional pore volumes of water injected will displace increasingly smaller amounts of NAPL.

Two samples were chosen from the soil samples for PCP analysis. One sample was taken from the injection well core in an area containing the highest NAPL saturation. A corresponding sample was taken from the closer borehole, at the same depth, to represent post-test conditions. Before hot-water injection, the PCP concentration was 2,100 mg/kg. After hot-water injection, the PCP concentration was reduced to approximately 3.6 mg/kg, greater than a 500 fold decrease in concentration.

Conclusions

The pilot test provided sufficient hydraulic information to design the full-scale CROW remediation system. The pumping test portion of the pilot test indicated uniform aquifer properties. The entire thickness of the aquifer reached the target temperature range and containment of the injected hot water was achieved. Pretest injection and production rate predictions were achieved.

The post-test soil boring data indicated hot-water injection displaced greater than 80% of the NAPL near the injection well. The data indicates that a NAPL saturation of approximately 19% (pore volume basis) and a 500 fold decrease in PCP concentration can be achieved with 20 pore volumes of flushing.

The treatment system used during the pilot test was effective in reducing PCP and PAH compounds to concentrations acceptable for sanitary sewer discharge. The microbial assay of the post-test samples found an encouraging increase in microbial population compared to earlier data collected before the pilot test.

Related Publications, Presentations, and Patents

Publications

Conestoga-Rovers and Associates Limited and Western Research Institute, 1990, Interim Response Action Work Plan Bell Lumber and Pole Company Site. New Brighton, MN, Unpublished Report, 40 p.

Fahy, L.J. and L.A. Johnson, 1992, Bell Pole Pilot Test Evaluation. Laramie, WY, WRI-92-R033

Presentations

Fahy, L.J., L.A. Johnson Jr., D.V. Sola, S.G. Horn, and J.L. Christofferson, 1992, Bell Pole Pilot Test Evaluation. Presented at the Colorado Hazardous Waste Management Society Annual Conference, October 1992, Denver, CO.

Patents

Johnson, L.A., and B.C. Sudduth, Contained Recovery of Oily Waste, July 18, 1989, U.S. Patent No. 4,848,460. Western Research Institute, Laramie, WY.

IN SITU TREATMENT OF MANUFACTURED GAS PLANT CONTAMINATED SOILS, DEMONSTRATION PROGRAM

Lyle A. Johnson, Jr.

Background

The Contained Recovery of Oily Wastes (CROW™) process removes organic contaminants from the subsurface by adaptation of technology used for secondary and heavy oil recovery (Johnson and Leuschner 1992). The CROW technology has been successfully tested in the laboratory as part of a project for the U.S. Environmental Protection Agency (EPA) SITE Program's Emerging Technology Program (Johnson and Guffey 1990). The development consisted of several one- and three-dimensional physical simulations of the process. The preliminary testing has shown that hot-water flushing could reduce

contaminant content by approximately 60 wt %. Additional testing with totally biodegradable chemicals indicated that the removal rate could be increased to approximately 90%, as shown in Figure 1. Based on the laboratory performance of the process, the EPA advanced the process to the SITE Demonstration Program.

Further development of the process has included the completion of a pilot test at an active wood treatment facility. The pilot test provided additional information for the design of a field-scale remediation effort, in addition to verifying several of the pre-pilot design specifications and predictions.

Figure 1. One-Dimensional CROW™ Tests

Verified by the pilot test were the ability to: (1) establish and maintain desired injection and production rates, (2) heat the test area to the desired temperature, (3) achieve non-aqueous phase liquid removal rates equivalent to laboratory rates, and (4) show that the produced fluid can be easily treated for reinjection or disposal (Fahy et al. 1992).

Objective

The objective of this study is to demonstrate and evaluate the CROW process and bioremediation to remediate a site contaminated with a dense organic fluid. The goal is to achieve treatment levels in the field that are comparable to prior laboratory studies.

Procedures

The following procedures will be followed to conduct the project:

- Develop and submit a detailed work plan.
- Identify and secure all required construction and environmental permits.
- Prepare and submit for approval a 30% complete design for the field layout and operation.
- Prepare and submit a 95% design for the field layout and operation. All equipment, well construction, and operating routines will be fully specified.
- Prepare a final project design based on the review comments from the 95% design submission.
- Procure all required equipment and construct the field facilities.
- Operate the field demonstration.
- Dismantle the field facility.
- Analyze the data from the field demonstration and report the results to the DOE, EPA, and cosponsors.

The site selected for this demonstration project is a former manufactured gas plant site located in Stroudsburg, Pennsylvania. The site is a Superfund site owned by Pennsylvania Power and Light. The funding support for the project is provided by the U.S. Department of Energy, Pennsylvania Power and Light, Gas Research Institute, and Electric Power Research Institute.

Western Research Institute (WRI) in conjunction with Remediation Technologies Inc., is designing and operating the project. Other participants working at the site include Atlantic Environmental Services Inc. (site characterization), Michigan Biotechnical Institute (water treatment for disposal), and the U.S. EPA SITE Demonstration Program (process monitoring, analysis, and evaluation).

The work plan for the field demonstration submitted to and approved by the EPA Region 3 office included a three-step system design and approval sequence. Also identified were all the environmental and construction permits required.

Results

The 30% design and the 95% design of the field installation and operating scheme have been prepared and submitted to the EPA Region 3 office as part of the EPA site requirements. The Pennsylvania Department of Environmental Resources (PADER) was also included in the review of the design and operational requirements of the project. Review comments on both design phases have been received and addressed. The final design has been prepared based on the comments to the prior design phases and has been submitted to EPA and PADER. Procurement of long lead-time equipment for the site operations has been completed.

The present schedule for the project is for drilling and construction to begin at the site about June 1, 1994. Operation of the facility should begin around August 15, 1994.

Conclusions

The progress of the project has been slowed because of problems encountered in the recharacterization of the site as requested by the EPA, and the lengthy and complex EPA design and approval protocol. Planning of future field tests, whether for environmental or energy production projects, should include sufficient time for the proper environmental permitting of the project.

OPERATION AND EVALUATION OF THE CO₂ HUFF-N-PUFF PROCESS

**Lyle A. Johnson, Jr.
Robert M. Satchwell
Harry A. Deans
Kenneth P. Thomas**

Background

Two basic types of carbon dioxide injection processes are used for enhanced oil recovery. These processes are termed immiscible and miscible displacement processes, depending on the solubility of the CO₂ in the crude oil. Several variations of the immiscible process have been tried, including continuous CO₂ injection, carbonated water injection, a variation of the water-alternating-gas process, and the CO₂ cyclic stimulation (huff-n-puff) process. In the cyclic stimulation process, a slug of carbon dioxide is injected, allowed to soak, thereby allowing the production mechanisms to develop, and then produced back into the injection well. Commonly, this cyclic process is repeated as oil production decreases.

Although Wyoming is ranked sixth in oil production in the United States, production is declining at a rate of about 10% per year. Under present market conditions, there is little incentive to develop new production. Based on the type of oil and the reservoir size, miscible flooding, particularly with CO₂, probably has the widest potential applicability for enhanced oil recovery in Wyoming reservoirs. Also, a large supply of CO₂ is available for oil field use from the Madison Formation in southwest Wyoming.

A number of reservoirs with good potential for CO₂ flooding have been defined in the major producing basins of Wyoming. An average CO₂ utilization factor of 7,000 standard cubic feet per barrel of oil recovered has been quoted for Permian Basin CO₂ flooding. If 350 mmcsfd of CO₂ from southwest Wyoming can be put to work at this same efficiency, 50,000 bbl of oil per day are potentially available from

Wyoming fields by the late 1990s. This would amount to more than 25% of the state's production by that time.

The Enhanced Oil Recovery Institute (EORI) of the University of Wyoming (UW) performed a CO₂ cyclic stimulation as a demonstration, to develop interest in supporting research on the process. With technical assistance from WRI, support was obtained for the program from the Wyoming Legislature and the Science, Technology, and Energy Authority (STEA) of Wyoming. Significant in-kind contributions were also provided by the operators of wells in the form of workovers required for the tests, separation and testing equipment, daily sampling of the wells, and other expenses associated with performing the stimulations.

Objective

The program developed by WRI and UW had the objective of evaluating the potential of cyclic CO₂ stimulation of marginal oil wells in Wyoming for increased oil production.

Procedures

Solicitation for candidate wells was accomplished by sending a letter and information form to essentially all operators of wells in Wyoming. The operators were requested to propose one or more wells for the program. The information received on potential study wells was reviewed and the candidate wells were selected by a panel made up of individuals from UW, STEA, EORI, and WRI.

The criteria for designing the cyclic stimulation was based on previous tests reported in the literature, and on limited laboratory/simulation results.

The essential elements of the design were: CO₂ should penetrate between 50 and 200 ft into the target formation; the CO₂ phase would occupy about 50% of the pore space; injection of CO₂ should be at the highest practical rate; the liquid CO₂ would be heated, after being pumped to injection pressure, to at least 4°C (40°F); and a shut-in (soak) period, between the end of injection and the start of production, in the range of 2 to 4 weeks would be used.

Single-well chemical tracer (SWCT) tests were performed in the candidate wells for CO₂ injection. The SWCT tests were used to provide information concerning reservoir flow characteristics, as well as the residual oil saturations in the target zones, prior to the CO₂ injection. In order to estimate the amount of remaining oil which will be contacted by CO₂ during a cyclic treatment, it is necessary to know the remaining oil saturation in the target formation. The wells chosen for the demonstration program were all stripper producers (i.e., near the end of their productive lives). All of the candidate wells except one were producing at high water cuts. Thus, they were close to waterflood residual oil saturation near the wellbore, where the CO₂ treatments would be applied. The radius of investigations for the SWCT tests ranged from 6.4 to 16.4 ft. The mass balance tracers used for these tests were isopropyl alcohol, n-propyl alcohol, and/or methyl alcohol. The reactive tracer was either ethyl acetate or ethyl formate, with the resultant product being ethyl alcohol.

Eleven wells comprised the stimulation testing program. Two other wells were evaluated with a SWCT test, but the test results eliminated them from the program. The 11 program wells represented 10 fields and four basins in Wyoming. Also included in the program were the collection of data and/or production samples from 45 other CO₂ cyclic stimulations conducted independently by operators. All operators contacted were very cooperative in providing test results and/or samples.

For each well tested, initial samples of the produced oil and gas were collected to

provide baseline data. After production was reestablished following the shut-in period, samples of the produced gas and fluids were collected on a routine basis. Sampling time was generally daily at the beginning of the production period, with the sampling interval increasing as the production period increased. Samples were collected on a weekly basis by WRI from both program wells and from any well tests conducted independently by operators participating in the program.

During the study, 1867 gas and 1623 liquid samples were collected from 34 of the 56 CO₂ cyclic stimulations conducted in Wyoming. The 34 wells represent 25 fields in five major producing basins. Of these samples, 1675 of the gas samples and 203 of the liquid samples were analyzed.

The produced liquids (water and oil) were obtained either from the wellhead or a separator or treater that had been placed on-line to monitor the production. If the liquid sample was obtained from a separator or treater, it was assured that only the stimulated well was flowing to the treater at the time of sample collection. Samples (water and oil) obtained from a separator-treater were entirely single phase (water or oil). However, samples obtained from the production wellhead were a mixture of water and oil.

Routine analysis of the oil samples was conducted usually on a 1- to 2-week basis and included the determination of specific gravity and viscosity. In addition, the distillate range and the percentage of pentane asphaltenes and wax were determined usually on a 2- to 3-month basis. The recovery of a sufficient amount of oil dictated the number and type of analyses that could be conducted on each sample. Also the elemental composition (carbon, hydrogen, nitrogen, and sulfur) of the produced oil was determined at least once during each individual test.

The analysis of the water samples involved primarily the determination of pH. This measurement was conducted routinely about every fourth day and only on water

samples from some of the field tests. In addition, specific metals and the mineral carbon content of selected water samples were determined to determine if specific ions were being mobilized during the process.

Chemical and physical properties of the crude oils and their distillate and residue fractions were measured (1) so they could be incorporated into the development of a mathematical model of the CO₂ cyclic stimulation process and (2) to initiate the development of a capillary gas chromatographic, simulated distillation method that would extend the measured boiling range of high-boiling materials beyond 538°C (1000°F). This model uses continuous thermodynamics for the mathematical treatment of the data. This has several advantages over the more conventional approach that utilizes the data in a pseudocomponent format.

Chemical and physical properties were determined for two crude oils (the Beaver Creek and Little Buffalo Basin - North Dome fields). Their distillate and residue fractions included: distillate range, elemental composition (carbon, hydrogen, nitrogen, and sulfur), molecular weight, specific gravity, viscosity, the percentage of aromatic carbons and hydrogens, and the percentage of carbon types present in selected distillates and the residue from the crude oil from the Beaver Creek field.

A numerical simulator was to be developed for the prediction of the CO₂ cyclic stimulation process through the integration of the simulation with geologic and laboratory data. The first step was the selection of an established compositional simulator to which the modification necessary to predict the cyclic stimulation process could be made. The computer models considered were the TSRS, a thermal-compositional simulator developed by WRI, the MORE simulator developed by Reservoir Simulation Research Corporation (not a public domain simulator), and the UTCOMP simulator developed by the University of Texas with industry and

federal support. After a lengthy evaluation, the UTCOMP simulator was selected.

Results

A summary of the results for the 12 SWCT tests performed are given in Table 1. For all but three of the individual projects (both those part of the WRI/UW Program and those that are not) the physical properties (distillate range, specific gravity, and viscosity) of the oil produced by the CO₂ cyclic stimulation process did not vary with time. This indicates that either the mechanisms responsible for oil production were the same throughout the enhanced production period or the properties monitored were not affected by the production mechanisms. In addition, the percentage of asphaltenes and wax did not vary significantly during the production period. This implies that plugging of the formation by these components was not a problem during the production period. The elemental composition data, although limited, also do not appear to vary during production.

Conclusions

Criteria were developed for accepting or rejecting candidate wells for the CO₂ cyclic stimulation process. These criteria include reservoir flow characteristics and residual oil saturations.

For the selected study wells, the SWCT tests were capable of determining residual oil saturations as well as reservoir flow characteristics such as crossflow, drift, and flow irreversibilities. The residual oil saturations for the fields tested ranged between 13 and 40 pore volume %. The results showed that the field data could be predicted reasonably well with the appropriate simulator.

Eight of the 11 wells that were part of the WRI/UW program could be considered technically successful in that they did produce incremental oil. However, only the Crooks Gap (both cycles) and the Osage wells, P-3 and P-4, would be considered to be highly successful, with Crooks Gap being economically successful and Osage

marginally successful because of increased production from offset wells. Program wells in Beaver Creek, North Grieve, Bonanza Buck Creek, and West Fiddler Creek fields were the marginal technical successes. Reasons that WRI/UW program wells were considered marginally or not technically successful include: Cole Creek and Bonanza (production equipment problems), Beaver Creek and Grass Creek (reservoir flow problems), and West Fiddler Creek and North Whitetail (lack of CO₂ containment caused by lack of reservoir pressure).

Regarding wells that were not part of the WRI/UW program, insufficient data are available to determine technical and economic successes. However, three companies did provide analysis as to the success of their individual wells. Conoco Inc. stated that three of the six stimulations they conducted could be classified as technically or marginally technically successful, with one of those, the South Glenrock test, being a technical success.

Amoco Productions projected that they had at least nine marginally to completely successful technical demonstrations, six in the Wertz-Lost Soldier area and three in the Salt Creek field. Of these nine wells, only four in the Wertz-Lost Soldier area were considered to be economically successful. Petrospec, the operator of the LAK field, indicated that their test was a complete success.

Although not part of this study, it is of interest that Amoco Production has demonstrated the technical feasibility of field-wide carbon dioxide flooding in the Wertz and Lost Soldier fields near Bairoil Wyoming. Results from the Osage and West Fiddler Creek wells in the WRI/UW study also support this observation.

Related Publication

Johnson, L.A., Jr., R.M. Satchwell, H.A. Deans, and K.P. Thomas, Operation and Technical Evaluation of the CO₂ Huff-N-Puff Process. Laramie, WY, WRI-94-R030.

Table 1. SWCT Test Summary

Test No.	Field	Model ^a	Drift ft/day	Crossflow bbl/day	Irreversibility Ratio	(S _{or}) _{avg} %
1	Beaver Creek	SS	0	4.0	2.87	23
2	Bonanza	SS	0	0	1.28	23
3	Buck Creek	SS	0	0	1.21	20
4	Crooks Gap	SS	0	0	1.12	26
5	Fiddler Creek	SS	0	0	1.54	20
6	Garland	C	0	0	na	39
7	Grass Creek	SS	0	31.6	6.52	23
8	Osage	SS	0	10.7	1.24	28
9	Salt Creek	D	3.3	0	na	13
10	Steamboat Butte	SS	0	7.6	3.47	20
11	Wertz	SS	0	0	1.50	15
12	N. Whitetail	SS	0	0	1.18	40

^a SS - Sandstone Model; C - Carbonate Model; and D - Drift Model

OIL FIELD WASTE CLEANUP USING THE TANK BOTTOM RECOVERY AND REMEDIATION PROCESS

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Lyle A. Johnson, Jr.

Background

During oil production, wastes are generated that are stored either in open pits or in storage tanks. These wastes, known as tank bottoms, typically contain substantial quantities of oil mixed with solids, free water, and emulsified oil and water. Several processes are being tried to recover oil from these wastes. So far, mechanical separation techniques have not been successful in removing solids or water from the oil. WRI has developed a thermal recovery process that, in bench-scale testing, has shown that salable products can be recovered from tank bottoms. The process, termed TaBoRR™ (Tank Bottom Recovery and Remediation), has been patented and is being readied for demonstration with support from Envir-Oil Inc. of Kaycee, Wyoming.

Objectives

The objectives of this study were to design, construct, and test a TaBoRR plant capable of producing 200 bbl/day of salable product from tank bottoms.

Procedures

The TaBoRR process involves a two-step scheme for separating water and solids out of the tank bottoms. A conceptual schematic of the process is shown in Figure 1. As depicted, the tank bottom wastes are heated under pressure followed by a flash operation. This flash operation provides a means of vaporizing and removing the water from the tank bottom waste. Water-free waste is then treated in a stripping operation, whereby a large amount of the hydrocarbons are distilled away from the solids.

Figure 1. Conceptual Schematic of the TaBoRR™ Process

To improve the economics of the process, the vaporized hydrocarbons produced in the stripping operation are used to preheat the feed stream entering the flash operation, and then sent to a condenser where a salable product is recovered. All noncondensable materials are sent to a flare, and the stripper waste stream, consisting of solids and heavy hydrocarbon liquids, is returned to the pit.

For this study, a candidate pit-site was selected and samples of stored waste were analyzed. These analyses served as a guide for devising a reference feed material composition. The model feed material composition was then used for process modeling.

Process modeling was undertaken to develop design criteria for various components and streams. HYSIM, an interactive process model designed for gas processing, oil refining, petrochemical, chemical, and synthetic fuels processing, from Hyprotech Ltd. was used to establish optimum processing parameters for the flash and stripper operations. Results were also used to size the process components, transfer lines, and pumps, and also to establish thermal loads. The effect of varying feed material composition on the process was also investigated.

Based on the results from numerical simulations, design specification and duty requirements for various components were established. Major components were fabricated and assembled as a skid-mounted plant at the Envir-Oil facilities in Kaycee, Wyoming.

Results

Table 1 lists the analysis of the tank bottom waste from the candidate pit. The table also displays the values and ranges used for the reference feed material in the numerical simulation of the process.

Process modeling confirmed that the optimum process conditions for the flash and stripper operations are sensitive to the feed material composition, and other properties. For a given feed material, process yield can be maximized by increasing the stripping temperature. However, increasing temperature increases the likelihood of hydrocarbon losses to coking. Similarly, overall thermal requirements for the process can be minimized by the proper selection of pressure and temperature of the fluids being flashed. Process modeling showed that the stripper overheads contain enough heat to sustain optimum flash operation, however, an alternate heat source is required during startup.

Table 1. Numerical Simulation Initial and Input Conditions

Description	Source Material	Data Investigated
Temperature, °F	~70 ^a	40
Pressure, psia	12.4 ^a	14.5
Mass Flow, lb/hr	na	4000
Standard Density, lb/ft ³	56.2	60.0 - 64.5 ^b
Solids, wt %	1.38	0 - 10
Water, wt %	3.50	10 - 16
Hydrocarbon, wt %	95.12	74 - 90

na - not applicable

^a - at time of sampling

^b - dependent on composition

Based on the results from the process modeling, mass flows and energy requirements for various components were compiled assuming the reference feed material. These are compiled in Table 2. Based on the data, specifications for major components were prepared. All vessels were specified to be constructed from 316 stainless steel with external insulation to minimize thermal losses. Weld quality and finish were specified to be in accordance with ASME code section VIII, Division 1 and TEMA Standards. For heat exchangers, 20% excess surface area of the tubes was included as a safety factor. All vessels were specified for construction with adequate expansion joints to reduce stresses under elevated temperature conditions.

The plant is divided into five major systems. These systems are: (1) the feed system, (2) the flash process, (3) the stripper, (4) product recovery system, and (5) support systems. The finalized plant schematic is shown in Figure 2. The feed system consists of a positive displacement pump, and two heat exchangers for heating the feed material to the desired temperature for flash, namely feed preheater and flue gas preheater. The flash system includes the flash valve, flash tank, and the flash tank pump. The stripper system consists of the stripper, a tube-and-shell heat exchanger, with provisions for quiescent boiling of hydrocarbons in four stages by installing weirs, and a sparger arrangement whereby

sweep gas also serves as a mild agitator to prevent solids accumulation. The product recovery system consists of a condenser, separator, and blower. The support system includes a heat source capable of delivering all the process heat requirement (a dual-fuel burner) and a flare.

The skid-mounted layout for the plant is shown in Figure 3. The plant is being readied for a shakedown at the Envir-Oil facilities. After a brief shakedown, the plant will be shipped to the candidate pit-site for extended operations and testing.

Conclusions

WRI's patented process for thermal recovery and remediation of tank bottom wastes is being developed for field demonstration. Based on numerical simulations of the process, a 200 bbl/day plant has been designed and fabricated. The plant is to be operated at a candidate pit-site for extended periods.

Related Publication

Satchwell, R.M., V.K. Sethi, and L.A. Johnson, 1994. Oil Field Waste Cleanup Using the Tank Bottom Recovery and Remediation (TaBoRRTM) Process. Laramie, WY, WRI-94-R029.

Patent

Patent Number 5,259,945. Process for Recovery of Tank Bottom Wastes

Table 2. Component Design Data

Design Data	Feed Pump	Feed Preheater	Flue Gas Preheater	Flash Valve	Stripper	Condenser
Feed Rate, lb/hr	4000	4000	4000	4000	2858 ^a	2858 ^a
Solids, wt %	7 - 10	7 - 10	7 - 10	7 - 13	6 - 20	0
Water, wt %	13 - 18	13 - 18	13 - 18	13 - 18	0	0
Temperature Range, °F	40	40 - 600	40 - 600	425 - 600	300 - 850	400 - 150
Pressure Range, psia	12 - 1000	600	600	337 - 19	25 - 8	25 - 8
Heat Required ^b , MMBtu/hr	na	1.0	0 - 1.0	na	1.7	-0.4

na - not applicable

^a - dependent on feed composition

^b - input or removal

Figure 2. Finalized Plant Schematic

Figure 3. Skid-Mounted Plant Layout

ENHANCED GRAVITY DRAINAGE OF OIL IN THE NORTH TISDALE RESERVOIR

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Alan L. Merrill

Background

A commercial oil mining project exists at the North Tisdale field located on the western flank of the Powder River Basin in Johnson County, Wyoming. The project consists of a horizontal tunnel conventionally mined into a hillside to gain access to the low-pressure, medium gravity oil (28.5°API), located at an approximate depth of 250 ft in the Cretaceous Lakota Sandstone reservoir. From the tunnel, drill rooms were constructed from which horizontal holes were drilled. The reservoir is currently producing at low rates through the dominant gravity drainage mechanism.

Objective

The objective of this study was to evaluate the feasibility of applying secondary and tertiary techniques to accelerate recovery from the Lakota reservoir.

Procedures

Miscible, immiscible, chemical, and thermal processes were screened for applicability to the horizontal well system in the Lakota reservoir. The screening criteria developed by Taber and Martin (1983) were used to evaluate the processes. Economic and safety factors were also used in the selection of the oil recovery processes to be investigated in detail. From the review, waterflooding and steamflooding were determined to have the greatest potential for enhancing production.

A numerical simulation study of the two processes was conducted using the simulation program TETRAD marketed by Dyad 88 Corporation, Calgary, Alberta, Canada. The TETRAD simulator was used in the thermal mode to run both simulations. The estimate of oil and water production rates in horizontal wells with waterflood and steamflood processes under

varied reservoir and operating conditions and well configurations were the evaluation criteria used in the numerical simulations. The study consisted of a wellbore pattern study and a reservoir parameter sensitivity study. A different model configuration was used for each part of the study.

The reservoir model configuration used in the wellbore pattern study was a half-symmetry pattern representing two horizontal wells which were 1000-ft long. One well in the pattern was a steam or water injector, while the other well simulated a producer. The reservoir simulation configuration was blocks, with 10 cells of 100 ft in the x-direction, 7 cells of 30 ft in the y-direction, and 5 cells of 6 ft in the z-direction. The wells were located in the center of the grid blocks. Injection rates and the productivity and injectivity indexes of the wells were halved to simulate the half-symmetry pattern. Five well configurations of various vertical, horizontal, and diagonal offset configurations were used to determine which was the most efficient pattern (Figure 1). The edges of the model consisted of no-flow boundaries.

The reservoir parameter sensitivity study was conducted to determine the effect of varying the permeability, oil saturation, and gas saturation. The model configuration used was the same as that in the pattern study, except the lengths of the wells and reservoir were shortened from 1000 ft to 500 ft. During the parameter study, distillation effects of the oil were not taken into account because of a lack of detailed distillation data. However, distillation appears to be an important factor in the case of Lakota oil. Preliminary distillation data indicated that 18% of the oil can be distilled at 200°C (392°F) and 760 mm mercury.

Figure 1. Pattern Study-Wellbore Configuration

Water/oil and gas/liquid relative permeabilities were estimated for the reservoir because laboratory data were unavailable. Water/oil relative permeability was estimated from resistivity logs and oil and water production ratios. Oil and water saturations were calculated from the resistivity logs and matched with water/oil ratios to obtain an estimated relative permeability curve. The gas/liquid relative permeability curve was modified from published data for similar reservoirs.

The samples used in the physical simulations were consolidated blocks, weighing approximately 800 lb each, of Lakota Sandstone removed from the North

Tisdale oil mine. The reservoir material was analyzed and found to have an average porosity of 23% and an average horizontal permeability to air of 1100 md.

The blocks were shaped into 2 x 2 x 1.5-ft rectangular blocks and horizontal production and injection wells were drilled into them. The shaped blocks were grouted into steel reactor boxes. The well pattern was designed to simulate the spacing and configuration of horizontal wells in the North Tisdale oil mine. Temperature monitoring wells with four thermocouples per well were installed in the steamflood block on an evenly spaced grid to monitor vertical and horizontal temperature fronts.

To resaturate a block to near reservoir conditions, oil and water were slowly pumped from the bottom of the block through special ports, towards the top, until the oil and water saturations were restored to approximately the original reservoir saturation conditions.

For the waterflood simulation, injection was initially established at 7 cc/min and held at that level for 7.5 hours. It was then raised to 10 cc/min. At 29.5 hours, the rate was raised to the final rate of 15 cc/min. The injection rates were increased in this manner to maintain a near constant flux rate at the flood front and to indicate any possible rate-dependent behavior. The oil and water production rates were measured by weighing the quantities of the produced fluids at 1-hour intervals.

For steamflood simulation, cold-water-equivalent (CWEQ) steam injection rates were the same as the water-injection rates in the waterflood simulations. Steam injection was initially established at 7 cc/min CWEQ for 7.5 hours, raised to 10 cc/min until 29.5 hours when the rate was increased to 15 cc/min. Total injection time was 72 hours. Injection temperature and pressure increased with increased injection rate. Oil and water production were measured on an hourly basis. Samples were taken and centrifuged when the produced fluid consisted of an emulsion.

After completion of the simulations, core samples were taken from each block to determine the distribution of residual oil and water saturations.

Results

In the screening study, miscible processes were eliminated from consideration because of the low reservoir pressure and shallow depth. Immiscible processes consisting of using water or a gas such as air, nitrogen, or flue gas were all technically feasible processes. Air injection is currently being used to enhance recovery from the Lakota reservoir. However, damage to the reservoir due to oxidation of oil may be occurring.

One of the immiscible processes, water injection, was selected for further investigation. Water injection was selected over gas injection because of improved mobility ratios and less severe channeling problems. Polymer and surfactant additives may be feasible, but they were not investigated in detail because of economic limitations for field applications. Alkaline processes were ruled out because the Tiedale crude oil is not acidic, with a pH of 7.5. Thermal processes were screened, with both steam and combustion meeting most of the selection criteria. Steamflooding was selected for detailed investigation. However, steamflooding did not meet the minimum depth criteria of the high permeability (1100 md) and the use of horizontal injection wells would permit high steam injection rates without fracturing the reservoir. Combustion processes were not considered because of the hazards they would create for personnel in the oil mine.

In the wellbore pattern numerical simulations, the pattern study was conducted to investigate the consequences of locating the injection wells either high or low in the reservoir. All simulations for the pattern study were run for 1,000 days. Steam and water injection rates were held constant at 150 CWEQ bbl/day. The pore volume (PV) injection rate was 0.000566 PV/day with a total of 0.566 PV injected.

Comparison of the well patterns under steamflood conditions showed that all patterns with the producer and the injector vertically offset had essentially the same oil recoveries, 46.1 to 48.0%. The oil and water production rates were also similar for the patterns. However, rapid steam breakthrough occurred in the pattern with the injector and producer vertically in line, lowering oil recovery to 17.7%.

Comparison of steamflood and waterflood in the same pattern showed that waterflooding provided better sweep of the reservoir than steamflooding, based on a lower water/oil ratio for the waterflood. But the recovery predicted for waterflooding was slightly lower than that predicted for steamflooding, 45.0% versus 47.7%.

For the numerical simulations study of reservoir parameter sensitivity, the factors investigated included (1) permeability variation, (2) oil saturation, and (3) presence of a gas saturation. The steam and water injection rate was held constant at 250 CWEQ bbl/day over the entire simulation period. The pore volume injection rate was 0.0001888 PV/day for 500 days for a total of 0.944 PV injected. A simulation run of both waterflooding and steamflooding was completed with each of the four cases investigated. Case 1 consisted of a homogenous reservoir with $S_O = 0.55$, $S_W = 0.45$, a horizontal permeability (K_H) of 300 md, and a vertical permeability (K_V) of 150 md. Case 2 had the same saturations as Case 1, but three 10-ft layers were used. The top layer had a K_H of 333 md and K_V of 67 md, the middle layer had a K_H of 333 md and a K_V of 167 md with the bottom layer having a K_H of 667 md and K_V of 500 md. It was believed that the permeabilities used in Case 2 were the closest match to the actual reservoir and were also used in Case 3 and Case 4. In Case 3, the saturations were changed to $S_O = 0.50$, $S_W = 0.50$. In Case 4, a gas saturation was added for a saturation distribution of $S_O = 0.475$, $S_W = 0.475$, and $S_G = 0.05$. Case 4 was run because a large amount of air has been injected into the reservoir in an effort to maintain oil production levels.

Both the steamflood and waterflood simulations showed slightly decreasing oil recovery with increased heterogeneity, decreased oil saturation, or the presence of a gas saturation. The steam-to-oil ratios for the steamflood were about the same for Cases 1, 2, and 3, but in Case 4 the steam-to-oil ratio rose dramatically after about 200 days. The rise in the steam-to-oil ratio for Case 4 is attributed to the gas saturation allowing the steam to move rapidly through the reservoir, thus a quicker breakthrough of steam at the production well. A comparison of steamflood and waterflood recoveries for all cases showed higher oil recoveries for the steamflood.

For the first 7 hours of the steamflood physical simulation, only oil was produced due to the relatively high initial oil saturation of 73.6%. For the next 30 hours, the water production rate increased and the oil rate decreased. For the remainder of the test, the oil production only slightly decreased. The steam-to-oil ratio gradually increased from 1 to 10 cc CWEQ/cc during the test.

Temperature profiles for the steamflood block were used to determine the sweep efficiency. The temperature distribution was mapped at 10, 25, 40, and 60 hours into the test. Heat, spreading out from the injection well, heated the top of the block first, then progressed downward in the block. The bottom of the block never became fully heated. This suggests that placing the steam injector nearer the bottom would be more efficient than placing it at the top.

In the steamflood block, the post-test oil saturation was reduced below 10% near the injection well in the middle of the block. The top of the block was swept with steam, although the residual oil saturation appeared to be slightly higher at the top than in the middle section of the block where the injection well was located. The bottom of the block was not well swept by the steam with the exception of the area below the injection well. The relatively high oil saturation in the bottom of the block was caused by a gravity override effect of the steam.

The initial oil production rate for the waterflood block was quite high, with a low water cut for the first 10 hours of the test. Initial oil saturation was 69.4%. After 10 hours, the oil production rate began a steep decline and the water production rate increased rapidly until the water cut reached levels above 95% at 30 hours. From 30 hours until the end of the test very small amounts of oil were produced.

The waterflood block had a high average uniform residual waterflood oil saturation of 43%. The uniform residual oil indicates that, while the sweep efficiency was quite good, the displacement efficiency was poor in this test.

The steamflood process recovered a significantly greater amount of oil when compared against waterflooding in the physical simulations, 63.5 versus 37.9% original oil in place. Both processes recovered oil at approximately the same rate for the first 30 hours of the tests. After 30 hours, the water cut from the waterflood block increased rapidly to levels above 95%, and the oil production fell sharply. In the steamflood block, the water cut increased to approximately 80% and remained steady for the duration of the test. At approximately 30 hours, an oil-in-water emulsion appeared in the produced fluids from the steamflood. This emulsion consisted of approximately 80% by volume water.

Conclusions

Conclusions of the numerical simulation studies were:

- Numerical simulations indicated that locating horizontal producers or injectors either high or low within the formation had an insignificant effect on oil recovery for well spacings of approximately 200 ft.
- Oil recovery decreased for steamflooding and waterflooding processes with increased heterogeneity and decreased oil saturation.

- Steamflooding showed only small increases in oil recovery when compared with waterflooding using numerical simulation. This small increase was inconsistent with the physical simulation data, where a considerable increase in oil recovery by steamflooding was noted.

Conclusions of the physical simulation studies were:

- Steamflooding yielded 80% more oil than waterflooding.
- A residual oil saturation of 27% was left after steamflooding, compared to 43% for waterflooding.
- An oil-in-water emulsion may be formed when steamflooding the North Tisdale Lakota reservoir

The physical simulations showed that steamflooding produced significantly more oil than waterflooding. Therefore, steamflooding may be an economical alternative to waterflooding, depending on the unit cost of fuel to generate steam and the increased capital costs of a steam generator and water treating facilities. Economic evaluation of the two processes should be used to determine which process is best for the North Tisdale field.

Related Publication

Merrill, A.L., L.A. Johnson, Jr, and R.M. Satchwell, 1992. Three-Dimensional Physical and Numerical Simulation of Steamflooding and Waterflooding of the North Tisdale Reservoir. Laramie, WY, WRI-92-R023.

ASSESSMENT, DESIGN, AND TESTING OF OIL RECOVERY AND PROCESSING TECHNOLOGIES FOR NEAR-SURFACE RESERVES

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Vijay K. Sethi

Background

Recovery and production of oil is an integral part of Wyoming's and the national economy. Geological studies have shown that Wyoming has many minable rock formations which contain substantial concentrations of oil. Some of the highest concentrations of oil in such occurrences exist in Big Horn, Natrona, Fremont, and Crook Counties in Wyoming. The formations typically consist of unconsolidated or friable sandstone that is unsuited for development by conventional oil recovery techniques. Nevertheless, the rock material acts as a trap for oil, containing millions of barrels per occurrence. At the present time, such resources are undeveloped and do not provide any economic benefits to Wyoming, nor do they enter into the national energy independence equation.

WRI has developed a broad base of technologies for processing and recovering oil and other hydrocarbons from organically-rich materials such as tar sand, oil shale, tank bottoms, and coal. Realizing that some of these technologies can be applied to the surface recovery of oil from the oil-bearing, minable, surface and near-surface rock formations, WRI obtained support from the State of Wyoming, Economic and Community Development Division for this two-phase study.

Objectives

The main objectives of this study were to develop and demonstrate an economic surface processing scheme for recovering oil from surface and near-surface oil bearing outcrops. Specific objectives in phase 1 were: (1) to select and characterize a target

oil reservoir; (2) to perform bench-scale tests to determine the suitability of various thermal processes using reservoir material; (3) to perform linear gravity drainage tests to determine if conventional recovery techniques, such as horizontal wells, are feasible; and (4) to evaluate processes and their products. The objectives of phase 2 were: (1) based on the bench-scale test results, to design and build a scale-up of the most promising configuration of the process to a field-pilot scale and (2) to perform a field demonstration of the process.

Procedures

Phase 1 of the study consisted of bench- and laboratory-scale work to evaluate the viability of the existing technologies for surface thermal processing of oil-bearing rock. This phase also included gravity drainage tests to determine if recovery techniques such as horizontal drilling could be applied. Work was also conducted to identify the optimum processing conditions for these materials, and based on the economics and other factors such as complexity and scale-up considerations, to identify the best candidate for field demonstration.

The reservoir selected for the testing and development of the technology was the Sherard Dome reservoir located in the Big Horn Basin. This reservoir has been previously characterized by the U.S. Geological Survey (USGS) and several developers. Previous estimates have shown that approximately 6 million barrels of oil are present in the readily accessible Sherard Dome.

Two one-dimensional gravity drainage simulation tests were performed in laboratory reactors. Gas permeabilities were also determined. Sand was packed in the tubular reactors and saturated with water and oil at levels far in excess of those typical of the reservoir. Gravity drainage and other pertinent data were monitored over a 7-month period.

Three different surface recovery options were investigated. These included water extraction, solvent extraction, and thermal processing using either a variation of the WRI's ROPE™ technology in an externally heated screw reactor, or thermal processing in a fluidized-bed reactor. Water extraction was rejected because of two major drawbacks: (1) relatively small recovery achieved by others in previous recovery attempts and (2) the fact that large volumes of process waters are required, that in turn lead to large amounts of alkaline effluent.

The option of using solvent extraction employing a light hydrocarbon as the solvent also suffers from two major drawbacks: (1) the excessive cost of the solvent and (2) complete recovery of the solvent requires subsequent thermal processing of the spent sand, increasing the cost of the process.

Phase 2 of the study was planned to evaluate the best candidate process in detail, leading to the design and evaluation of an economically and technically viable process, including a field site demonstration.

A schematic flow diagram of the pilot facility designed for the field demonstration is given in Figure 1. The facility was designed to process approximately 100 tons per day of oil sand. Equipment sizing was based on mass-flow rate, and energy balances.

Figure 1. Schematic Representation of the Pilot Facility Layout

The pilot facility consisted of three major systems: (1) a feed system consisting of a crusher, conveyor, surge hopper, and a twin feed screw, (2) a fluidized-bed reactor and associated subsystems, such as particulate cleanup and burner assembly, and (3) a cooling, condensing, and product recovery system. The design considerations for sizing the reactor are given in Table 1.

Table 1. Reactor Design Criteria

Fluidizing Velocity	up to 4 fps
Feed Rate	10,000 lb/hr
Bed Height	18 - 36 inches
Temperature	750 - 850°F
Bed Area	15 ft ²

The distributor design was of the bubble cap type. An uncooled, type 310 stainless steel plate was used. Type 304 stainless steel bubble caps were made from 1-inch schedule 80 tube nipples and attached to the 310 stainless steel plate by welding.

The reactor was a refractory-lined box, 5.5-ft long by 3.5-ft wide. The height of the reactor was about 7 ft. Provisions for temperature and pressure measurements were incorporated in the reactor design. The primary particulate cleanup device was a set of four cyclones that were installed in parallel inside the reactor. The cyclones were suspended in the freeboard area. Collected solids were removed through an inclined tube exiting the reactor. A secondary, high efficiency cyclone was used external to the reactor. The secondary cyclone was constructed from type 304 stainless steel. The cyclone was externally insulated to minimize thermal losses without adversely impacting performance.

Particulate-free gases passed through an air-cooled condenser. Cooled gases and mist then passed through a series of knock-out pots to remove the liquids. Gases exiting the knock-out pots entered a recycle blower train. A portion of the stream was recycled to the main reactor bed and mixed with the fluidizing gas, while the rest was sent to a flare.

The pilot facility was assembled at the field site and operated for a period of approximately 1 month.

Results

The geologic interpretation of the Sherard Dome Formation was consistent with that determined earlier by the USGS. Sherard Dome is a small faulted anticline. Based on the records and logs of previous cores and wells available at the Wyoming Oil and Gas Conservation Commission, it is postulated that some of the earlier estimates of oil-in-place were exaggerated because they failed to include some of the known surface geology. Geological evaluation also showed that conventional oil recovery from the outcrop will be difficult because there is not enough reservoir energy, and because there are some sandstone laminations that flow water while others flow oil. Large diameter holes might be used for recovery if only the oil saturated portions are penetrated. However, a very small portion of the oil-in-place will be recovered. The Third Frontier sand, because of its higher oil content over a 9-acre area at the crest of Sherard Dome, was selected for the demonstration site.

The revised estimate of the oil-in-place in the minable area of the Sherard Dome outcrop (approximately 34.3 acres) is about 1.13 MMbbl. It is estimated that the oil from this area can be recovered at a ratio of 1 bbl/1.6 cubic yd of overburden. The ratio for the area selected for the field demonstration is estimated to be about 1 bbl/0.7 cubic yd.

Core samples, taken for laboratory testing and characterization were analyzed for water and oil content. On the average, the samples contained about 5 wt % oil and 10 wt % water. The range of values observed was 1.4 to 10.8 wt % for oil, and 6.0 to 13.7 wt % for water. No discernible trends were detected in the oil content as a function of the depth. Lack of any discernible trends in the data suggested the presence of barriers at various depths and a large degree of heterogeneity in the reservoir. It should be pointed out that the laboratory samples for analyses and bench-scale

processing were collected after the sand was allowed to drain. Actual oil content of the sand is believed to be considerably higher than that indicated by the data.

The recoveries achieved in the one-dimensional gravity drainage tests were in the 20 to 35% range. However, the residual oil concentrations were about two times those measured in the reservoir samples. These results demonstrated the futility of using gravity drainage as a means of oil production from the resource.

Both of the thermal recovery options were tested at the bench scale. ROPE tests conducted with a two-inch screw reactor showed promising recovery rates. Carbon recovery in the tests was in the 85 to 90% range for processing temperatures in the 454 to 524°C (850 to 975°F) range. Limited data obtained during short-term, steady-state tests showed that oil recovery may be related to the residence time in the hot zone of the reactor. At short residence times and higher feed rates, the oil recovery was much higher than at longer residence times. Similar data were also obtained in a fluidized-bed reactor at comparable temperatures. However, because of some equipment constraints, the entire gas stream could not be condensed. Gas data, in conjunction with the spent solids chemistry, indicated that the oil recovery was comparable to that achieved in the screw reactor.

The process selected for field demonstration was the fluidized-bed technology. The main advantages of this technology over the screw reactor were the process scale-up considerations and the need to achieve high heating rates and shorter residence times than those possible in the screw reactor system. Fluidized-bed technology also offered an additional advantage in that higher throughput is possible in a relatively small-scale reactor.

In the field testing in phase 2, several problems were experienced related to the feed system, burner operations as affected by changes in the ambient temperature,

product collection system, and the variations in the feedstock. Nevertheless, the operations showed that fluidized-bed technology can be adopted for the recovery of oil from minable oil reserves.

Conclusions

An investigation was made into developing an oil recovery process for near-surface petroleum deposits that are impractical to develop by conventional technologies. The Sherard Dome reservoir was selected as a suitable resource for study. A review of the geological characterization of the reservoir indicated that the oil-in-place in the minable area is about 1.13 MMbbl, with an oil to overburden ratio of 1 bbl/0.7 cubic yd for the field demonstration site. Data from analyses of core samples did not show any discernible trends, indicating likely barriers at different depths and a large variability in the reservoir. Laboratory tests demonstrated that gravity drainage is not a suitable means for resource production.

Three surface recovery options were evaluated. Hot-water extraction and solvent extraction were rejected in favor of thermal processing. Two thermal recovery options were tested at bench scale, from which it was concluded that the fluidized-bed process was the best candidate for field testing.

Several problems were encountered in the field demonstration, but it was shown that fluidized-bed technology can be applied to minable oil reserves. Additional testing is required to develop this technology to its potential capability.

Related Publications

Satchwell, R.M., L.A. Johnson, Jr., and V.K. Sethi. 1993. Assessment, Design and Testing of Oil Recovery and Processing Technologies for Near-surface Reserves. Laramie, WY, WRI-93-R029.

Sethi, V.K., R.M. Satchwell, and L.A. Johnson, Jr., 1994. Surface Process Study for Oil Recovery Using a Thermal Extraction Process. Laramie, WY, WRI-94-R020.

SHALLOW OIL PRODUCTION USING HORIZONTAL WELLS WITH ENHANCED OIL RECOVERY TECHNIQUES

Robert M. Satchwell
Lyle A. Johnson, Jr.

Background

An early steamflood project in the Chetopa field was performed by Tenneco between 1965 and 1967 that produced approximately 68,000 barrels of oil. Approximately 70% was used as fuel, resulting in a net production of 21,000 barrels. Efforts by Kaycee Oil Company and Shallow Oil Limited in 1987 used horizontal wells and a steam huff-n-puff process. Failure of the project was attributed to insufficient heat input and an inadequate drive mechanism.

Objectives

This study was undertaken with support from Kaycee Oil Company to determine the causes of failure of previous attempts and to devise appropriate enhanced oil recovery (EOR) strategies for the Chetopa field. The initial part of the study included reservoir characterization and EOR process screening using laboratory tests. Based on the screening results, a pilot demonstration test was performed using the most technically feasible EOR technique.

Procedures

After assessing the site geology, EOR techniques were screened to find the most technically feasible process for the Chetopa field. The techniques included thermal, chemical, miscible, and non-miscible processes. The initial review used criteria established by Taber and Martin (1983). The review revealed that miscible gas and chemical processes were not suitable for this field. The initial screening favored thermal stimulation. Heating the oil to 121°C (250°F) would make the oil more mobile. This heating could be accomplished by either steam injection or in situ combustion. Therefore, advanced screening was performed for both steam injection and in situ combustion.

Steamflood was further reviewed by using criteria and correlations compiled by Chu (1985). Results of this evaluation showed that steam injection was not an attractive alternative, since the shallow depth and thinness of the reservoir would limit heat injection and increase heat losses, respectively. Advanced screening of the in situ combustion process used guides provided by Poettmann (1964), Geffen (1973), Lewin and Associates Inc. (1976), Chu (1977, 1982), and Iyoho (1978). The major items of concern that were identified were the high crude oil viscosity and the shallow depth of the reservoir. These could result in low recoveries and fracturing to the surface.

Results

The Chetopa field is located in southeastern Kansas. The production horizon consists of Bartlesville sandstone within the Krebs Subgroup of the Cherokee Group. According to Johnson (1973), the Bartlesville sandstone of the Chetopa field was deposited primarily as a point bar with associated channel fill surrounding the sand body.

Log analyses indicate that the porosity ranges from 26 to 30% from the top to the base of the point bar. In the region of interest, the water saturation ranges from 29 to 38%. Oil-in-place was approximately 1.61 MMbbl (9.1 Mbbl/acre). The pay zone (12 ft) has been limited to only the continuous and permeable portion of the point bar and omits any of the adjacent channel fill sands. Figure 1 illustrates the highly permeable point bar and presents the highest oil saturated sands which are up-dip of the water-oil contact.

Figure 1. Schematic of Permeable Point Bar

The results of the EOR screening suggested that in situ combustion is the most technically feasible process for the site. From the advanced screening study it was determined that injection rate limitations caused by the shallow depth of the reservoir and the large oil viscosity could be detrimental to the in situ combustion process. To determine if these concerns were justified, combustion tube tests were performed.

The two vertical combustion tube tests were performed with reservoir material to access fuel deposition and associated air requirements. These tests also defined the effects of oil saturation and reduced air injection rate. Both tests produced upgraded oils and indicated that sufficient oil volumes and fuel contents are present in the Chetopa field. Lower oil saturations, higher water saturations, and lower air injection rates resulted in lower peak temperatures, higher fuel contents, and higher produced volumes of carbon dioxide. These results were consistent with data reported in the literature.

Based on the existing horizontal well pattern and vertical wells located between the horizontal wells, and assuming a burning rate of 0.125 ft per day and a volumetric sweep efficiency of 100%, the maximum oil production rate was projected

to be approximately 21.3 bbl/day, with the total oil recovered to be approximately 819 bbl/acre-ft. Since the oil-in-place is approximately 1086 bbl/acre-ft, then the potential recovery would be approximately 74.8%. The data also indicate that lower injection rates and pressures could be employed while still sustaining combustion.

From the work of Thomas (1963), it was estimated that the maximum radial distance that would sustain combustion was less than 150 ft. To obtain a vertical coverage of 70% for the combustion front, over a distance of 100 ft, a gas injection rate of 377 scf per ft-hr was required. However, a maximum injection rate of only 300 scf per ft-hr could be achieved, since larger injection rates would result in higher injection pressures that could cause fracturing in the formation.

Thomas (1963) indicated that higher combustion front temperatures occur above the horizontal plane of the ignited interval. Thus, in order to minimize gas production and maximize oil production, the location of the horizontal production wells in the lower portion of the target zone seemed adequate. Furthermore, since the horizontal wells were located approximately 50 ft on either side of the vertical wells, the production wells would act as containment of the combustion front, as shown in Figure 2.

Figure 2. Vertical and Horizontal Well Orientations

Following ignition with a propane and air burner, air injection was continued for 80 days. A total of 40 barrels of oil were produced. Gases were sampled and analyzed from both horizontal production wells. The two production wells did not produce similar gas analyses. Carbon dioxide concentrations as high as 20% were observed. Other interesting observations included the failure to detect increased temperatures in the production wells and the lack of any upgrading of the crude oil.

High oxygen and low carbon dioxide concentrations observed in horizontal production well #1 indicate that the combustion front moved mainly toward horizontal production well #2. If the combustion front moved preferentially toward horizontal well #2 in a radial shape, then the combustion front should have reached the well after approximately 29 days. The high carbon dioxide concentration and absence of oxygen in horizontal well #2 during the 31-40 day period tend to support this hypothesis. The preferential burning direction could have been caused by failure to sustain complete ignition around the wellbore, directional

permeability, or a combination of both factors.

Since there was no upgraded oil production nor any increase in temperature, it appears that the combustion front was located in the upper portion of the formation. Assuming a 6-inch thick combustion front would produce a 4.2% volumetric sweep efficiency, then the sweep efficiency for the reservoir stimulated by the process but not burned and the overall recovery efficiency can be determined using the method prescribed by Nelson and McNeil (1959). The sweep efficiency of the unburned zone was determined to be approximately 13.2% with an overall recovery efficiency of 16.0%.

The poor overall recovery efficiency can be attributed to two major factors. First, production was created exclusively by reservoir pressure. This prevented the creation of a pressure sink that would permit the hotter oil to enter the wellbore and hence improve the overall sweep efficiency. Second, the transfer of heat from the burned zone was minimal, which reduced the volumetric sweep efficiency because a reduction in viscosity was not achieved.

Conclusions

This study evaluated the use of horizontal wells with in situ combustion in a heavy oil reservoir. The causes of failure of previously attempted oil production techniques were determined and an EOR strategy was tested in the Chetopa field.

Screening identified in situ combustion as the most viable EOR process for the study site. The process was tested in the forward mode in laboratory tests and then used in the field pilot demonstration. The field test showed that in situ combustion could be sustained at shallow depths. Gas analyses identified the movement of the combustion front to and past one of the production wells.

The overall recovery efficiency was determined to be approximately 16%. This poor oil production was a result of the inability to remove the heavy oil from the production wellbores and the frontal advancement characteristics of forward in situ combustion. Improvements in recovery could be obtained by implementing a closed loop pump system that would preheat the production wellbore. By changing the frontal advancement characteristics of the combustion front, such as by using a water-alternating-gas injection process, improved sweep efficiencies and higher recovery would result.

Related Publication

Satchwell, R.M. and L.A. Johnson, Jr., 1994, Shallow Oil Production Using Horizontal Wells with Enhanced Oil Recovery Techniques. Laramie, WY, WRI-94-R009.

MODEL DEVELOPMENT AND TESTING OF STEAM INJECTION TUBULARS

Robert M. Satchwell
Lyle A. Johnson, Jr.

Background

Efficient methods of transferring the energy of steam from the surface to the oil reservoir can reduce the cost of enhanced oil recovery. Furthermore, increased production rates and oil recoveries can be attributed to higher sandface steam qualities. Thus, the use of insulated tubulars can reduce the thermal losses and make the economics of steam injection projects even more favorable.

To evaluate the feasibility of a steam injection project, an accurate estimate of the heat carried by the injection fluid is extremely important. Knowing the temperature, pressure, and quality of the fluid at the formation sandface is necessary to calculate heat content. However, at the present time, a physical method for measuring these bottom hole parameters is not available. An accurate computer model must be used to estimate these parameters.

A double-walled tubular product has been privately developed that has the potential for use as a steam injection string. However, laboratory verification of the performance of the system was needed. To that end, this study was undertaken with support from Inter-Mountain Pipe Company.

Objectives

The objectives of this study were to evaluate a double-walled tubular product using steam injection and to develop a computer model to simulate the transient effect of steam injection under field conditions.

Procedures

Laboratory testing was accomplished by constructing a flow loop system to determine heat losses from the double-walled tubing. The major components of

the flow loop system were a steam boiler, a vertical test section, a horizontal test section, a water recovery system, and a data acquisition system. Each test section was composed of an entrance subsection, a test subsection, and an exit subsection. The subsection lengths were selected based on boundary layer theory for establishing stabilized flow conditions in each test section.

Four different experimental configurations of the double-walled tubular were tested. These were: (1) no annular insulation, no vacuum; (2) no annular insulation, with vacuum; (3) annular insulation, no vacuum; and (4) annular insulation, with vacuum. Each of the configurations were tested at steady-state flow conditions for a duration of approximately 4 hours.

The heat injection rate through the flow loop during each test ranged from 227 to 257 MBtu/hour. The steam quality varied from 93.9 to 97.3%. The total cold-water-equivalent flow rate varied from 725 to 819 gallons per day.

To evaluate tubulars over extended periods a computer model was developed to simulate single- and double-walled tubing performance under a variety of conditions. A review of the literature found that wellbore heat loss models have become more accurate and sophisticated, using more advanced numerical solutions with a reduction in the many assumptions. However, discrepancies still exist between observed data and predicted results; therefore, an accurate model for comparative purposes was required. For the model developed in this study, improved accuracy was accomplished with the use of several theoretical, semi-theoretical, and mathematical correlations (Satchwell and Johnson 1992).

The model's technique uses a finite difference simulation in length, at a specific time level. It has been specifically designed to simulate the flow of a hot-injection fluid from its source to the sandface. To simulate transient effects, simulation runs are required for successive time steps. The model is capable of simulating surface piping configurations that include buried, unburied, insulated or uninsulated conditions. The wellbore modeling can simulate single- or double-walled tubing with or without insulation, multiple casing strings, different gases in the casing or tubing annulus with or without a vacuum, and multiple downhole formations.

To evaluate model variation with parameter changes, several different cases were investigated. Parameters investigated were: (1) single tubing versus dual tubing string configurations, (2) insulation thickness, (3) injection rate, and (4) injection temperature and pressure. Other parameters that were not investigated, but entered as input parameters included the heat transfer properties of steel, other insulating material, and the surrounding formations, and surface pipe heat loss configurations.

To determine the effects of time and provide a comparison of the single tubing string to the double-walled tubing string, numerical simulations were performed with constant input parameters for various completion cases to a depth of 4,000 ft. The completion cases were:

Case A - Single tubing string (2.992 x 3.500 inches) with casing (8.017 x 8.625 inches) cemented in a 11.0-inch hole;

Case B - Single tubing string (2.992 x 3.500 inches) with 2.0 inches of external insulation, with casing (8.017 x 8.625 inches) cemented in a 11.0-inch hole;

Case C - Double-walled tubing string (inner pipe - 2.992 x 3.500 inches, outer pipe - 4.950 x 5.500 inches) with casing (8.017 x 8.625 inches) cemented in a 11.0-inch hole;

Case D - Double-walled tubing string (inner pipe - 2.992 x 3.500 inches, outer pipe -

4.950 x 5.500 inches) with 1.45 inches of annular insulation, with casing (8.017 x 8.625 inches) cemented in a 11.0-inch hole;

Case E - Double-walled tubing string (inner pipe - 2.992 x 3.500 inches, outer pipe - 4.950 x 5.500 inches) with 1.45 inches of annular insulation and 2.0-inch external insulation, with casing (8.017 x 8.625 inches) cemented in a 11.0-inch hole.

Results

The physical test results for heat losses were determined for several combinations of independent variables that included: the test section orientation (either horizontal or vertical), the pipe body or coupling, insulation installed or not installed, and vacuum in the annulus (with or without). Statistical analysis was performed with respect to heat loss and the independent variables. The analysis showed that insulation and location terms were the only significant variables. The insignificance of the vacuum variable can be attributed to the fact that a reasonable vacuum could never be maintained in the annular space.

Results of the tests on the 3-ft test sections indicated that the insulated pipe body had an average heat loss rate of about 105 Btu/hour, whereas the uninsulated pipe body had an average heat loss rate of 4,703 Btu/hour. The application of insulation to the annular portion of the tubular resulted in a 98% reduction in the overall heat loss. The 6-inch long insulated pipe coupling had a heat loss rate of 3,384 Btu/hour, whereas the uninsulated coupling averaged a heat loss rate of 3,575 Btu/hour. Insulation in the annular portion of the coupling achieved only a 6% reduction in the heat loss rate. This relatively minor reduction in the heat loss rate in the insulated coupling is a direct consequence of the major heat loss path through the metal to metal contact of the inner tube support steel ring located in the coupling.

Published field data for steam temperature (Bleakley 1964) were used for validation of the developed model and also as a comparison to previously published models.

The new model more accurately predicted steam temperature than either the Farouq Ali (1981) or the Durrant and Thambynayagam (1986) model. A comparison of these models to the new model shows that the steam qualities differ by more than 30% at steam qualities lower than 0.35%.

Results of tests of the model sensitivity to parameter changes indicate that for constant heat input conditions, heat loss was reduced as insulation thickness increased. As the injection rate increased, the temperature and steam quality at the bottom hole depth increased, resulting in a reduction in the net heat loss. Another phenomena predicted by the model is the existence of a critical flow rate below which adverse conditions persist, an interesting aspect of wellbore heat transfer not normally found in the literature. This phenomena showed that saturation pressures and temperatures could be larger at the stated depth than under wellhead injection conditions.

Results of the tubing string simulations are given in Figures 1 and 2 for heat losses and steam quality, respectively, as a function of time. In Figure 2, an average increase of steam quality of 44% was obtained when comparing double-walled tubing with insulated annulus to an uninsulated tubing string (Case D to Case A). Also, there was little net change in heat loss and steam quality by using external insulation on the double-walled tubing (Case E to Case D). Another interesting result was the small difference in steam quality and heat loss between the uninsulated double-walled tubing string and the insulated single tubing string (Case C to Case B).

Conclusions

A flow loop was designed and constructed to test a double-walled tubular product. Insulation applied to the annular portion of the double-walled tubing pipe body resulted in a 98% reduction in heat losses. Only a minor reduction of 6% was obtained by applying insulation to the double-walled tubing coupling.

Coupling heat losses could be reduced by using a thermal resistant support, instead of the presently used carbon steel support ring, and/or by using a smaller cross-section area in the new or existing ring. The change in cross-section area may be accomplished with the use of knife-edges. An alternate solution would require a new design that would eliminate the metal-to-metal contact between the two pipes.

A modification to the seals used in the coupling design is recommended. This seal modification is required to ensure that steam does not leak into the annular portion of the pipe. In addition, a positive (pressure-vacuum) seal would allow a vacuum to be maintained in the annular portion of the pipe. By lowering and maintaining an annular vacuum less than 0.1 torr, further reductions in heat loss should be attainable.

A new model for simulating the thermal hydraulics of saturated steam was developed. The model is capable of simulating a variety of surface and wellbore configurations. The model was shown to be more accurate in predicting bottom hole steam temperatures over a wider range of operating ranges than any of the previously published models.

Sensitivity studies showed that the heat loss experienced by the injection fluid decreased with an increase in either injection rate, insulation thickness, or injection time. The model showed that a minimum injection rate exists below which severe heat loss occurs. The depth at which these adverse effects occur can be determined using the new model. Results of the completion simulations indicate that an average increase of 44% in steam quality can be achieved over a year when a double-walled, annular insulated string is used instead of a single uninsulated string.

Related Publication

Satchwell, R.M. and Johnson Jr., L.A., 1992, Testing of and Model Development for Double-Walled Thermal Tubular. Laramie, WY, WRI-92-R044.

Figure 1. Heat Losses for the Numerical Simulation Cases

Figure 2. Steam Qualities of Numerical Simulation Cases

EVALUATION OF A MOLECULAR SIEVE CARBON AS A PRESSURE SWING ADSORBENT FOR THE SEPARATION OF NITROGEN FROM NATURAL GAS

R. William Grimes

Background

About one-half of the natural gas produced in the United States is low-quality natural gas, contaminated by other gases or water to the extent that it cannot be used without processing. Technologies for dehydration of low quality gas are used extensively, but application of available technologies for the separation of other contaminants, particularly nitrogen, from natural gas has been limited because of economic considerations.

In the past decade, an increasing number of gas separation problems have been solved economically by the use of pressure swing adsorption (PSA) systems. These systems make use of various microporous solids that preferentially adsorb certain components from a gas mixture, thereby separating it into adsorbed and non-adsorbed fractions. The solid adsorbent has an increased capacity for the sorbate at elevated pressure; therefore, a cycle based upon adsorption at higher pressure followed by desorption as the pressure is reduced can be used to separate a gas mixture into its component streams. The characteristics of the adsorbent, particularly with respect to the ease with which desorption takes place, dictate the economics of a pressure swing separation process.

Objective

As part of an effort to develop an economically viable PSA system to remove nitrogen from a natural gas stream, WRI undertook a series of laboratory experiments, jointly sponsored by DOE and Williams Technologies Inc. The experimental work was to determine the effect caused by varying adsorption cycle parameters on the performance of a molecular sieve carbon (MSC) used as a pressure swing adsorbent for the separation

of methane/nitrogen mixtures. The principal steps to do this were: (1) to assemble and calibrate a PSA test apparatus and (2) to test an MSC in a simulated PSA cycle at various pressures, flow rates, and temperatures.

Procedures

A PSA test apparatus, consisting of a feed gas supply and measurement system, adsorption column, and effluent gas collection and measurement system, was supplied by Williams Technologies Inc. During assembly three-way valves were added at each end of the adsorption column to allow for easy reversal of column flow at selected points in the pressure cycle. Pressure transducers and gauges were calibrated using a dead weight gauge calibrator. Inlet gas volume measurements were checked by water displacement using the effluent gas collection cylinders.

Adsorption testing began with a simple two-step adsorption cycle and progressed to a five-step cycle commonly used in multiple-column bulk separation systems. The experimental work involved systematically changing adsorption cycle parameters and observing the effect upon performance in the separation of a mixture of 70% methane and 30% nitrogen. Separation performance for all tests was evaluated in terms of product purity, product recovery, and sorbent productivity. Successive tests used the best conditions established in previous tests as a starting point; therefore, a steady increase in purity, recovery, and sorbent productivity was noted during the test program.

Tests with the two-step cycle used a constant pressurization flow rate and adsorption pressures of 20, 30, and 50 psig. Cocurrent and countercurrent depressurization were tried as well as

several rates of flow from the outlet end of the column during pressurization.

Most of the testing was conducted using four-step and five-step pressure swing cycles. The five-step cycle consisted of pressurization, feed-at-pressure, depressurization, blow-down, and purge. For the four-step cycle the feed-at-pressure step was eliminated.

The first tests using the four-step cycle were conducted to determine the effect of changing purge rate and volume and to establish values for these parameters to be used in subsequent tests. The four-step cycle was used to investigate the effect of changing pressurization and depressurization rates, increasing adsorption pressure, and holding the column at pressure between the pressurization and depressurization steps. Countercurrent blow-down and purge steps were also tested using the four-step cycle.

In tests using the five-step cycle, separation performance was evaluated for three feed rates and four adsorption pressures. A final test series was conducted to determine the effect of increasing purge volume using the five-step cycle.

Results

The best separation performance for the two-step cycle was attained in a test where the adsorption pressure was 20 psig and 62% of the pressurization gas stream was allowed to escape from the column outlet as the column was pressurized. For this test, product purity was 79.96%, product recovery was 18.30%, and sorbent productivity was 3.79 cm³/g/cycle.

Initial testing with the four-step cycle was conducted to establish the purge volume to be used in subsequent tests. Purge gas to pressurization gas volume ratios ranging from 1:1 to 38% were tried. For these tests the column was purged with the feed gas mixture (70% CH₄, 30% N₂) after a two-stage depressurization step. The methane purity of the effluent from the purge step began to decline at a purge/pressurization

ratio of about 0.25. The purge volume corresponding to this ratio was used for most of the subsequent tests.

Purge gas flow rates ranging from 59 to 326 mL/min were tried with no significant effect on separation performance. Product purity, product recovery, and sorbent productivity were all increased with countercurrent flow in the blow-down and purge steps.

Purging the column with 100% methane instead of the feed gas mixture resulted in a slight increase in product purity (86.60 versus 85.69%). This increase was more than offset by decreased recovery (39.30 versus 49.26%) and decreased sorbent productivity (7.42 versus 8.72 cm³/g/cycle).

Pressurization gas flow rates of 132.3, 13.92, 4.89, and 1.86 L/min were tried using the four-step cycle and an adsorption pressure of 50 psig. Separation performance was not affected by the pressurization flow rate except at the highest rate, where purity, recovery, and productivity all declined. Separation performance was not affected by delays of 0, 20, 30, and 60 seconds between the pressurization and depressurization steps.

In tests using the four-step cycle with adsorption pressures of 30, 38, 50, and 59 psig, product purity increased with increasing adsorption pressure. Methane purities of 80.7, 82.4, 85.4, and 85.7% were obtained as the adsorption pressure was increased. In all four tests the column was purged with 590.8 cm³ of the feed gas mixture. For the four-step cycle using an adsorption pressure of 50 psig product purity was 85.4%, product recovery was 49.3%, and sorbent productivity was 8.72 cm³/g/cycle.

The first test series using the five-step adsorption cycle compared separation performance for feed rates of 1.74, 1.16, and 0.58 L/min with 50 psig adsorption pressure. These feed rate changes had no significant effect on separation performance. The five-step cycle with 50 psig adsorption pressure gave a purity of

85.9%, recovery of 56.7%, and sorbent productivity of 14.5 cm³/g/cycle. With the five-step cycle product recovery and sorbent productivity were increased significantly when compared to the four-step cycle.

A series of tests was conducted using the five-step cycle, adsorption pressures of 20, 30, 50, and 60 psig, 1 minute of feed at 1.16 L/min, and purge with the feed gas mixture. In this series product purity increased from 82.5% at 20 psig to 88.4% at 60 psig. Product recovery was 52.6% at 20 psig and 51.3% at 60 psig. Sorbent productivity increased from 10.1 to 14.7 cm³/g/cycle as the adsorption pressure was increased from 20 to 60 psig.

For the final test series the blow-down step was begun at lower pressure (6 versus 10 psig) and the purge volume was increased. The blow-down effluent and the first 63.6% of the effluent from the purge step were collected as product, with the remainder of the effluent gas going to the waste stream. With an adsorption pressure of 60 psig this cycle gave a product purity of 91.6%, a recovery of 37.1%, and a sorbent productivity of 11.1 cm³/g/cycle.

Conclusions

A pressure swing adsorption system using a molecular sieve carbon adsorbent can successfully separate a mixture of nitrogen and methane without the use of a vacuum regeneration step. The tests showed that the saturated adsorbent can be regenerated by purging with the feed gas mixture. Flow rate in the feed and pressure changing steps was not an important factor in separation performance. Separation performance seemed to improve with increasing adsorption pressure through the range tested, but because of the limited nature of this study and the interrelation of process variables, further study will be required before a positive conclusion can be reached.

The results indicate that a multiple-bed PSA system using a molecular sieve carbon adsorbent for the separation of nitrogen from low quality natural gas is technically feasible. The fact that flow rates have little effect on separation performance indicates that the various cycle steps can be coordinated in a multi-bed system. More work is needed to determine the economic viability of such a system.

Related Publication

Grimes, R.W., 1993, Natural Gas Cleanup, Evaluation of a Molecular Sieve Carbon as a Pressure Swing Adsorbent for the Separation of Methane/Nitrogen Mixtures. Laramie, WY, WRI-93-R035.

CHARACTERIZATION OF PETROLEUM RESIDUA

John F. Schabron

Background

The precise chemical and physical constitution of petroleum residua is not well understood because of the overall lack of well-documented and acceptable analytical procedures. Many techniques are applicable to the characterization of residua, but few have been developed to a satisfactory stage of systematic methodology. To investigate the development of such methods, Mobil Research and Development Corporation supported this study for the definition and demonstration of a characterization scheme for petroleum residua.

To study residua in detail, it is necessary to subdivide them into several well-defined fractions. This can best be achieved by removing the asphaltenes prior to fractionation, using solid adsorbents. Trace metals that can have a deleterious effect on catalysts are then concentrated in the asphaltenes.

Objective

The purpose of this study was to develop a better understanding of the chemical composition of crude oil residua through the coordinated application of existing characterization methods. This involved demonstrating a standardized approach for a well-balanced, cost-effective characterization program. Application of the characterization scheme should provide data that can be used to improve the economic viability of processing operations.

Procedures

Since the major complex constituents of crude oils are concentrated in the residua, the characterization scheme was applied to six residua from different heavy crude oils. Each residuum was deasphalted in heptane, and the heptane-soluble materials were separated into saturate, aromatic, and polar fractions on activated silica gel. The asphaltenes were separated into four

fractions according to apparent molecular size by preparative size exclusion chromatography (SEC). The whole residua were evaluated for elemental composition, trace metals content, carbon residue, simulated distillation profile, specific gravity, pour point, and rheological profile. The asphaltenes and silica gel chromatographic fractions were evaluated for elemental composition, trace metals content, molecular weight, carbon residue, analytical SEC profiles, and aromaticity by nuclear magnetic resonance (NMR) spectroscopy. The preparative SEC fractions from the asphaltenes were evaluated for sulfur content, molecular weight, and trace metals content.

Results

All but two of the residua, which were waxy, had specific gravities greater than 1. The pour points of the six residua ranged from 32 to 96°C (90 to 205°F). The rheological profile results for all six residua show reasonable Newtonian flow over three orders of magnitude of shear rate. Heptane asphaltene contents ranged from 4.4 to 32.4 wt % for the six residua. Pentane asphaltene values were uniformly higher, ranging from 7.7 to 35.8 wt %. Saturate fraction content ranged from 6.3 to 45.7 wt % for the six residua, with the two highest values observed for the two waxy residua. Aromatic fraction content ranged from 29.8 to 61.2 wt % for the six residua. Polar fraction content ranged from 11.1 to 37.4 wt %. Total recoveries for the separations for the six residua were good, ranging from 99.5 to 102.8 wt %.

The elemental analyses for the six residua and their fractions showed good closure and material balances. The hydrogen-to-carbon (H/C) values for the individual residua decreased from saturate to aromatic to polar fractions. The asphaltenes from one of the waxy residua had a higher H/C ratio than the

corresponding polar fraction, due to waxes which occurred in the heptane asphaltenes.

The sulfur content for the six residua ranged from 0.4 to 5.6 wt %. For any particular residuum, the sulfur content was less for the saturate fraction than for the aromatic and polar fractions and asphaltenes. There was no clear trend for sulfur distribution for the aromatic and polar fractions and asphaltenes. Nitrogen content ranged from 0.4 to 1.4 wt % for the six residua. In general, the saturate fractions contained no detectable nitrogen. Most of the nitrogen occurs in the polar fractions and asphaltenes, with lesser amounts present in the aromatic fractions. Oxygen content ranged from 0.5 to 1.0 wt % for the six residua. The oxygen content of the polar fraction typically was greater for a particular residuum than the other fractions and asphaltenes. In general, the metals content (Ni,V,Cu,Fe) for the six residua increase in the order: saturate < aromatic < polar < asphaltenes.

The Conradson carbon residue values for the residua correlated well with the corresponding microcarbon residue (MCR) values. For the individual residua studied, the MCR values increased according to the series: aromatic < polar < asphaltenes. This indicates that the greatest residue/coke forming species are in the asphaltene material.

In general, an increase in molecular weights were observed for individual residua in the order: saturate < aromatic < polar < asphaltenes. For the four SEC fractions from the asphaltenes, the apparent molecular weights decreased about an order of magnitude from the highest to lowest molecular weight fraction. The material balances calculated for the SEC molecular weights were good, indicating that the very large apparent molecular weights observed for the high molecular weight fractions for the six residua appear to exist in the total asphaltene material as well as in the isolated fraction. The high molecular weight fractions from residua asphaltenes could provide a useful material for studying the coking process.

NMR aromaticity results showed very little aromatic structures in the saturate fractions for the six residua, with significant aromatic structures in the aromatic and polar fractions and asphaltenes.

The material balances for the various characterization parameters were consistent with proportional contributions from the various fractions for all six residua. This indicates that the contributions from the parts add up to the whole. It should be possible, therefore, to study and modify important properties such as coking tendency and the effect of variables such as metals, elemental, and aromatic content for individual fractions and relate them to properties of the whole material.

Conclusions

Petroleum residua can be effectively characterized using the analytical scheme developed in this study. The material balances show that the data obtained on the fractions and asphaltenes account for the data obtained on the original material. Thus, it is possible to study the contribution of the fractions and asphaltenes to properties observed in the whole residuum. Additional residua can be separated, and the results compared with data obtained on the six residua in the present study. Correlations between the characterization results and the behavior of a whole residuum, its fractions, or asphaltenes in processing or production processes can also be studied.

Related Publication

Schabron, J.F., G.W. Gardner, J.K. Hart, N.D. Niss, G. Miyake, and D.A. Netzel, 1993, The Characterization of Petroleum Residua. Laramie, WY, WRI-93-R023.

MILD GASIFICATION OF USIBELLI COAL

Norman W. Merriam

Background

Western Research Institute, in cooperation with DOE, has been developing the Inclined Fluidized-Bed (IFB) Coal Drying and Stabilizing Process. In this process, coal is dried to near-zero moisture and partially pyrolyzed in the first of two IFB reactors. The partially pyrolyzed coal is then fed into the second IFB, where it is rapidly quenched with cool carbon dioxide liberated from coal to keep the produced tar on the coal particles. This remaining tar, as well as adsorbed carbon dioxide, stabilizes the dried coal. The IFB reactor is also an excellent classifier. Consequently, coal fines are easily separated during drying. The amount of fines separated can be controlled by the fluidizing gas flow rate or gas-to-solid ratio. This study was undertaken with support from Usibelli Coal Mines, Inc. to apply the process to Usibelli coal.

Objectives

The objectives of this task were to determine the quantity of liquid produced by mild gasification of Usibelli coal and to characterize the products from mild gasification of Usibelli coal.

Procedures

A process research unit dryer was used to dry 1163 lb of minus 16-mesh Usibelli coal at a feed rate of 95 lb/hr and a recycle gas flow of 76 scfm at 371°C (700°F) as fluidizing gas. The flow rate of 76 scfm is somewhat higher than what is needed to fluidize the minus 16-mesh coal, but this rate was used to be sure that sufficient flow of heat was carried into the dryer. The high gas flow rate relative to the small particle size contributed to the high production of fines from the dryer. (Typically, 5 to 7 wt % of the raw coal is produced as fines when drying minus 8-mesh Wyodak coal. The fines production is the minus 100-mesh fraction in the feed coal).

A series of mild gasification tests was conducted on the dried coal. The series consisted of six 8-hour tests, one 6-hour test, and one 24-hour test. The tests were run at a dry-coal feed rate of 7.5 lb/hr, which is equivalent to a wet-coal feed rate of 10 lb/hr, and maximum bed temperatures of 566, 593, 621, 649, and 677°C (1050, 1100, 1150, 1200, and 1250°F).

Results

Mild gasification of the dried coal resulted in production of 44 to 56 wt % of the dried coal as char, 10 to 13 wt % as liquids, 17 to 28 wt % as gas, and 8 to 21 wt % as fines (Figure 1). Numbers on the graph in Figure 1 refer to test run numbers. The yield of moisture- and ash-free (MAF) liquids varied from 11.4 to 14.2 wt % of the dried coal feed.

Hardgrove grindability indices were 28 for the raw coal, 49 for the dried coal, and 82 for the char. The char produced contained 16 to 22 wt % volatiles and had gross heating values ranging from 10,500 to 11,600 Btu/lb. The char equilibrium moisture content was measured at 10 wt %, whereas the raw coal contains 22 wt % moisture at equilibrium.

The liquids collected from one test were separated by distillation into a -371°C (-700°F) boiling distillate (40 wt %) and a +371°C (+700°F) boiling residue (60 wt %). The distillate contained 23.5 wt % alkanes, 26.2 wt % alkenes, and 22.7 wt % aromatic hydrocarbons; plus 26.9 wt % of polar heteroatomic-containing compounds, for which group-type analysis could not be done. The distillate also contained 0.4 wt % sulfur, 0.3 wt % nitrogen, and 4.1 wt % oxygen. These are relatively low values for an untreated coal distillate.

Figure 1. Distribution of Char, Gas, and Liquid Produced from Usibelli Coal

Conclusions

Mild gasification of dried Usibelli coal results in production of about 50 wt % char, 20 wt % gas, 11 wt % coal liquids, and 11 wt % fines.

Char produced by mild gasification contains about 20 wt % volatiles, has a hydrogen-to-oxygen mas ratio of 0.24, and has a gross heating value of about 10,800 Btu/lb. The char does not contain as much moisture at equilibrium as the raw coal.

The coal liquid is a heavy, tarry, substance that contains about 5 wt % boiling in the gasoline range, about 35 wt % in the diesel-fuel range, and about 60 wt % in the electrode-binder-pitch range. Extraction, caustic washing, or hydrotreating is recommended to upgrade the distillate to diesel blending stock.

The MAF yields of dry, hydrocarbon liquids of the coal feed to the mild gasification reactor vary from 11.4 to 14.2 wt % under the conditions tested.

Related Publication

Merriam, N.W., K.P. Thomas, and C.Y. Cha, 1991, Mild Gasification of Usibelli Coal in an Inclined Fluidized-Bed Reactor. Laramie, WY, WRI-91-R021.

SERIES B PILOT-PLANT TESTS

Norman W. Merriam

Background

With cosponsorship from Heartland Fuels, WRI conducted a technical evaluation of the K-Fuel® Series B Process. This process is designed to remove substantially all of the moisture from Powder River Basin coal, partially decarboxylate the coal, and remove a portion of the sulfur containing compounds from the coal. In the process, coal is contacted by steam and heated as the pressure of the steam in the reactor increases. The high-temperature treatment causes the coal to undergo changes in structure, whereby the pores in the coal particles are sealed off and the resulting product contains about 2 wt % moisture, has a gross heating value of about 12,000 Btu/lb, and has some of the sulfur-containing compounds removed by processing.

Objectives

The primary objectives were to perform technical due diligence and to verify design conditions for a commercial plant. Other objectives included: having a clean and thorough audit trail, substantiating product quality claims, strengthening the design basis, providing samples for combustion tests, increasing the bulk density of the product, and determining the process and product characteristics when using different feed coals.

Procedures

Batch tests were conducted using a 45-lb capacity Series B pilot plant to produce 39 batches from Fort Union coal, 11 batches from Dry Fork coal, 28 batches from Center lignite, and nine batches from Caballo Rojo coal. The process is shown in Figure 1.

Figure 1. Schematic Diagram of Series B Process

In the tests, a pre-weighed amount of coal was charged into the preheated reactor through the top valve. The electrical strip heaters were turned off and steam was introduced into the reactor, increasing the pressure. Condensate was drained from the reactor and when the desired temperature was reached, the reactor was depressured. The flashed condensate was cooled and collected, and the uncondensed gas vented through a meter. The bottom valve was then opened and the product collected.

Material and energy balances were prepared for each test and the product was analyzed for moisture, sulfur, proximate, and heating value.

Results

Test results agreed well with the results from earlier screening tests conducted by another organization in the spring of 1991. The WRI results showed that the product heating value, moisture content, sulfur content, and proximate composition were essentially the same as claimed for the process. The product yield was slightly higher and the processing cycle time was slightly faster than found in the earlier work. It was possible to increase the bulk density of the product by widening the particle size distribution. Several recommendations were made for features to include in the design for the commercial plant using the process.

Conclusions

It is technically feasible to design, construct, and operate a commercial plant using the K-Fuel® Series B Process. Characteristics of the products from the tests are substantially the same as had been claimed in earlier testing.

Related Publications

Merriam, N.W., and V.K. Sethi, 1992. Technical Evaluation of the K-Fuel® Series B Process. Laramie, WY, WRI-92-R032.

Merriam, N.W., and V.K. Sethi, 1992. Comparison of Powder River Basin Coals as Feed for the K-Fuel® Series B Process. Laramie, WY, WRI-92-R045.

FEASIBILITY OF USING WOOD-DERIVED FUEL FOR COGENERATION

Vijay K. Sethi

Background

Power Generating Incorporated (PGI) is developing a wood-fired gas turbine system for specialized cogeneration applications. The system is based on a patented pressurized combustor designed and tested by PGI in conjunction with McConnell Industries. The other components of the system are (1) the fuel receiving, preparation, storage and feeding system, (2) gas clean-up equipment, and (3) a gas turbine generator.

In previous system development attempts at lower turbine inlet temperatures, a major technical hindrance to long-term operation of a gas turbine power system has been the degradation of the hot section of the turbine (Hamrick 1991; Cooper and Moresco 1981). Deposition, erosion, and corrosion are considered to be the main issues that need to be addressed. In the wood-fired PGI system, erosion is not likely to be of concern because of the low silica and low overall ash content of the fuel and the fact that the wood ash particle size is expected to be in the range where little or no erosion would be expected. However, because of the high alkali content of the fuel, deposition and corrosion can become major issues.

Realizing that some key issues need to be addressed before designing a prototype demonstration facility, PGI and WRI conducted a series of preliminary tests in an atmospheric pressure wood-fired McConnell combustor at a major sawmill complex.

Objectives

The main goal of the work was to obtain some preliminary information on the nature of the entrained ash, and the fate of the alkali and other elements suspected of causing deposition and corrosion in a wood-fired combustor/gas turbine system.

Specific objectives of the work were (1) to isokinetically collect particulate and gas samples from an atmospheric pressure wood-fired McConnell combustor from a location where gas temperature is close to that projected for the PGI turbine inlet temperature and (2) to collect ash/deposit samples by exposing a cooled probe to the combustion gases under conditions where gas temperature is comparable to that anticipated in the PGI system.

Procedures

Gas and particulate sampling were performed in an atmospheric pressure wood-fired combustor. The main combustion chamber of the combustor was a horizontal refractory-lined, 5-ft diameter, 10-ft long cylindrical vessel. Wood waste (dry sawdust and planer shavings) were pulverized to 0.125-inch top size and pneumatically injected and fired in a suspension. Secondary combustion air entered the chamber tangentially. The temperature at the outlet of the combustor was controlled by the fuel flow and by the addition of dilution air. An analysis of the wood waste is given in Table 1.

The start-up fuel was natural gas. Under normal operation, a start-up time of about an hour was required from cold start. Once the refractory in the combustor had reached the system operating temperature, combustion of the wood was sustained by the hot refractory with no auxiliary fuel required.

The particulate sampling followed the EPA protocol for isokinetic sampling (40 CFR Part 60, Appendix A, Method 1 and Method 5). Approximately 120 standard cubic feet of gas were sampled. Using an Inconel nozzle and a stainless steel sampling probe, the particulates were collected on a set of eight stainless steel foil filters contained in a Mark III Impact Sampler.

Table 1. Composition of Wood Fuel

	As-Received	Dry Basis	Dry Ash Basis
Ultimate Analysis, wt %			
Moisture	34.50	-	
C	34.50	52.67	
H	3.76	5.74	
N	0.16	0.24	
Cl	0.02	0.03	
Ash	0.40	0.61	
O (diff.)	26.65	40.69	
Ash Composition, wt %			
Si		0.024	3.9
Fe		0.014	2.3
Al		0.021	3.5
Ca		0.116	19.0
K		0.057	9.3
Mg		0.013	2.1
Na		0.005	0.9
Ti		0.001	0.2
Mn		0.007	1.2
Heating Value, Btu/lb	8670		

Any particles and aerosols that escaped the filters and did not deposit on the probe surfaces were collected in the impinger wash solutions. The materials collected on the filters, deposited on the sampling probe, and those captured in the impinger waste solutions were analyzed for their chemical composition.

An air-cooled probe carrying several thermocouples was installed in the combustor to collect ash deposits at typical turbine inlet conditions expected in the PGI system. The probe was constructed out of 6-inch long, type 304 stainless steel tubular elements of 1-inch diameter, schedule 80 tube stock. Each element carried a thermocouple at the mid-wall. The elements were held together by a threaded rod with restraining fasteners at the both ends, which ran through the entire length of the probe. The air flow through the probe was selected such that the surface temperature along the length of a tubular

probe encompassed a temperature range of 482 to 927°C (900 to 1700°F). The probe was exposed to the combustor environment for periods ranging from a few minutes to several hours. Ash/deposit buildup was removed from the probe and analyzed for ash constituents and water soluble alkali compounds.

Results

During particulate sampling, the combustor was operated at two different firing rates, labeled as high- and low-fire. Mean particle size during high-fire conditions was approximately 1.0 micron, whereas during low-fire condition, the mean particle size was about 4.0 micron. Total dust loading during low-fire condition was about 200 parts per million by weight (ppmw) while during high-fire condition the loading was about 300 ppmw. Particles were also collected on a positive filter during a high-fire run. These were then analyzed using a

Coulter counter. The total dust loading determined from this test was again about 300 ppmw. The mean particle size however was about 6.0 micron.

During the course of the tests, several on-line gas analyses (O_2 , CO_2 , CO, NO_x , and SO_2) were performed. These results are summarized in Table 2. The water content of the gases was calculated from the amount of gas sampled and the amount of condensed water. Other gases were monitored directly using the gas analyzer. Data indicate that CO, NO_x , and SO_2 concentrations in the combustion gases were higher during high-fire conditions than during low-fire. The behavior is expected to be a direct consequence of the excess air condition and flame temperature during the two firing conditions.

Particulates collected at various plates of the Mark III impactor were also analyzed using a scanning electron microscope coupled with an energy dispersive X-ray analyzer. The results are given in Table 3. The data indicate a great deal of variability in the particulate composition as a function of the size.

Table 2. Gas Analyses

Gas	Concentration	
	<u>Low-Fire</u>	<u>High-Fire</u>
O_2	17.3 vol %	12.5 vol %
CO_2	6.4 vol %	6.4 vol %
CO	275 ppmv	380 ppmv
SO_2	4 ppmv	46 ppmv
NO_2	24 ppmv	48 ppmv
H_2O	11.6 vol %	12.9 vol %
N_2	Bal.	Bal.

Table 4 displays the composition of the deposits collected on the air-cooled probe surface from three locations after a 20-hour exposure. The temperature at these locations varied a great deal, and therefore the temperature values in Table 4 give a range. As expected, the chemical makeup of the deposit is a strong function of the surface temperature.

Table 3. Chemical Analysis of Particulates Collected on Mark III Impactor

Plate Number	<u>Low-Fire</u>		<u>High-Fire</u>	
	1	4	8	4
Particle Size, μm	>13.7	4.0 - 5.8	<0.52	4.0 - 5.8
Element	<u>Concentration, wt %</u>			
Mg	7.26	6.07	0.89	9.22
Al	3.23			
Si	11.18	0.69	0.46	0.75
P	2.65	1.71	0.38	2.47
S	23.65	6.04	16.03	2.84
Cl	0.94	1.64	3.67	1.20
K	16.88	29.24	67.35	15.56
Ca	30.02	50.82	5.51	63.29
Mn	4.20	3.79	1.95	4.66

Table 4. Chemical Analysis of Deposits from the Air-Cooled Probe

Temperature, °F	>1400	700 - 900	<700
<u>Element Concentration, wt %</u>			
Mg	5.47	22.16	20.12
Al	0.72		0.35
Si	0.95	4.28	2.52
P	1.89	22.16	11.62
S	6.30	10.75	9.58
Cl	0.18		
K	49.41	16.93	14.52
Ca	30.73	22.16	39.11
Mn	3.77	1.58	2.18

Some of the deposit materials were also analyzed for soluble alkali. Within the error associated with the technique used, all of the alkali present in the deposit could be solubilized in water.

Particle size distribution of the deposit retrieved from the hot section of the probe and the particulates collected from the combustion gases is presented in Figure 1.

Figure 1. Particle Size Distribution of Deposits from the Air-Cooled Probe and Downstream Components

It is clear from the comparison that the deposits contain a larger fraction of smaller particles than that present in the combustion gases.

Conclusions

Based on the data presented, particulate loading in the wood-fired PGI system is expected to be in the 200 to 300 ppmw range. Using a conventional or a high efficiency inertial separator, the dust loading can be decreased. Either conventional or high-efficiency cyclones can efficiently remove the particles in the size range of > 5-10 micron, such that erosion of turbine components should not be a concern. The overall dust loading in the gas stream, however, is likely to remain high enough that the EPA particulate emissions limit cannot be met, and the likelihood of deposition remains. Using the deposits formed on the air-cooled probe as a guide, it is speculated that the deposits formed in the gas path of the turbine in the PGI system would not be very tenacious, and a periodic washing or nut shelling treatment would be required.

The chemical makeup of the ash particles in a wood-fired system is such that small particles arriving at the turbine blades and other gas path components will be enriched in alkali and phosphorus. Data indicate that a large fraction of the alkali are not present as sulfate, and hence it is quite likely that they are present in the form of a hydroxide.

Alkali will be present in the gas stream entering the turbine. Alkali concentration in the gases may increase as larger particles are removed by the particulate removal devices. Positive high temperature filters can reduce the level of alkali entering the turbine by removing smaller particles. However, any vapor phase alkali, if any present, will still enter the turbine system. An alkali gettering bed can alleviate these concerns.

Related Publication

Smith, V.E., B. Selzer, and V.K. Sethi, 1993, Development and Demonstration of a Wood-Fired Gas Turbine System. Proceedings of the Coal-Fired Power Systems 93 -- Advances in IGCC and PFBC Review Meeting, Morgantown, WV. DOE/METC-93/6131.

BENCH-SCALE SIMULATION OF QUENCHING AND STABILIZATION OF MODIFIED IN SITU OIL SHALE RETORTS

F. Alan Barbour

Background

Occidental Oil Shale Inc. (OOSI) successfully demonstrated its modified in situ (MIS) oil shale retorting technology by conducting large-scale field tests at its Logan Wash facility near De Beque, Colorado. OOSI operated the Logan Wash MIS retorting facility from 1972 until 1982. The MIS technology developed by OOSI was proven technically feasible, and commercial projections suggest that the technology can be profitable in the future.

One of the environmental concerns surrounding MIS retorting technology is the impact of the process on local groundwater. Chemical compounds that will solubilize in groundwater are created during MIS retorting. The hot spent retorts must be cooled and then cleaned of these water-soluble chemical compounds to mitigate the process's impact on local groundwater. Spent retorts were cooled and cleaned at Logan Wash by circulating water through the retorts to remove soluble materials. Water produced from the MIS retorts (process water) was used in the cooling and initial stages of the cleaning. Baseline quality groundwater collected in the mine sumps (mine water) was used in the later stages of the cleaning. The groundwater quality from most spent retorts at Logan Wash was restored to near baseline. These experiments demonstrated that impact on groundwater quality from MIS retorting can be mitigated. However, a commercial-scale operation will require careful water management to ensure that MIS retorts do not cause environmental problems. OOSI supported this study to investigate quenching and stabilization options.

Objectives

Western Research Institute constructed a laboratory-scale simulator of the MIS retorting process and conducted simulations to develop a post-retorting operating procedure that optimizes water

management during the cooling and stabilization of spent retorts. After conditions in spent retorts were simulated, procedures to accelerate retort cleanup without using large volumes of water were investigated.

Procedures

A reactor tube (3-5/16-inch i.d. x 32-inch long) was uniformly packed and vertically oriented within a series of insulated shield heaters. The heaters were operated adiabatically to reduce radial heat loss. The retort was charged with approximately 5000 g of crushed shale sized -1/2 inch to +60 mesh. The sample material was well mixed to ensure a uniform shale bed for each of the tests. Ignition of the shale was accomplished by preheating the top 6 inches of the reactor with the first shield heater. This heater was set to 649°C (1200°F), and air was introduced into the top of the reactor at a rate of 0.09 scfm. The oxygen content of the gas exiting the retort was monitored and ignition noted by a drop in oxygen content. The remaining temperature controllers were operated adiabatically for the duration of the experiment. The retorting was halted when the conditions in the simulation retort were similar to those in MIS retorts (about 85% retorted). This provided three zones of interest: combusted, >538°C (1000°F); retorted, 260 to 538°C (500 to 1000°F); and unretorted, <260°C (500°F). The ranges for these zones were estimated by the temperature profiles observed during retort operation.

Once retorting had been halted, several post-retorting operating procedures were tested. The quenching and deluge cleaning techniques used by OOSI were evaluated with respect to usefulness and effect on individual zones of the retort. Reverse combustion was examined as a method of organic source removal after completing the retorting operation. These methods of

remediation were compared with retort simulations in which nothing was done after the retorting.

Simulation of the deluge procedure was performed on cooled retorts. The oil collection system was isolated from the retort, and the bottom of the retort was opened to a clean collection pot. When the deluge simulation was started immediately following the quench procedure, the retort temperature was very near that of steam. When the deluge procedure was performed without quenching, the retort was allowed to cool to ambient temperature prior to starting the deluge.

Immediately after the retorting was completed, the quenching procedure was started. The retort was still very hot, with most temperatures above 489°C (1200°F). The oil collection system was isolated from the retort, and the bottom of the retort was opened to a clean collection pot. The top of the retort was vented through the condensers for collection of the steam generated during the quench procedure.

Reverse combustion was started after the retorting reached a point at which about 85% of the shale had been retorted. At the end of retorting, the air to the top of the retort was shut off, and the top of the retort was vented through the condensers for oil and water collection. The oil collection pot at the bottom of the retort was isolated from the retort production and air lines. Air flow was introduced into the bottom of the retort very slowly. The air flow was increased to the operating flow of 0.15 scfm over 5 minutes. The reverse burn was terminated when the thermocouple at the bottom of the retort indicated the combustion front had been drawn to that point.

Shale samples from the three retort zones were leached with deionized water to determine the amount of water-soluble constituents in the spent shale and rehydration characteristics of the spent shale.

The operation of the simulation retort was duplicated as close as possible for all of the

tests. This was done to simulate post-retorting conditions that resembled the conditions in the MIS retorts. In addition, the duplication also gave approximately the same starting point for remediation tests that followed retorting. Gas analyses and Fischer assay data were used to evaluate the retorting portion of the experiments and provide material balance data.

Material balances were performed for each simulation retort test. The balances were calculated from the feed shale, products, and water used for retort quench and deluge studies. The amount of gas produced was determined by nitrogen balance and calculated from the average gas analysis for each test. The mass closures ranged between 96 and 104% with most of the tests in the 98 to 102% range.

The deluge simulation was monitored by analyzing the water that exited the retort for total organic carbon (TOC). The simulation was terminated when the TOC reached an asymptote. The organic concentration in the deluge water was plotted against pore volume, which is defined as that volume of water that equals one void volume of the reactor. This provided an easy nondimensional method for comparing one test to another.

Results

Deluge tests simulated an in situ retort that had been allowed to cool and then cleaned by a deluge of water. The TOC concentrations in the water exiting the retort indicated that the organic content was relatively high at the start of the deluge with a value near 550 mg/L. Within 1 pore volume, the value had decreased to about one-third of the original value. The TOC concentrations between the first and third pore volume showed quite a bit of variation, but they tended to stabilize near a value of 50 mg/L. The phenol concentration (910 µg/L) accounted for only a small portion of the organic carbon present in the composite water. The total dissolved solids (TDS) concentration of 2410 mg/L resulted from metals, carbonate, bicarbonate, and sulfate ions.

Water quenching was considered as a possible method of accelerating the cooling of the spent MIS retorts. The recovery of residual heat from spent retorts as well as gas generated through steam-char reaction was also investigated. The quenching procedure was started immediately after retorting stopped. The retort was still very hot with most temperatures greater than 649°C (1200°F). There was no reverse combustion applied during these tests. However, the retorts were deluged with well water after the quenching procedure. All of these tests were retorted until about 85% of the oil had been removed.

The combination of quenching followed by deluging the retort was followed by TOC analysis of the water exiting the bottom of the retort. Approximately 1 pore volume of water migrated through the retort before the conclusion of the quench procedure for these tests. The water quench was performed with the adiabatic shields of the tube reactor remaining on. After the retort temperatures dropped below that of steam, the deluge procedure was started.

During quenching, several grams of thick shale oil-water emulsion were observed in the water collection vessel. The TOC analyses of the quench and deluge water from each test were very similar to most of the organic material being removed after about 1 pore volume of water had passed through the retort. The organic loading in the deluge water after quenching the retorts was significantly lower compared with cool deluge only. The TOC concentrations for the deluge after quench were one-fifth or less than TOC values during the cool deluge. A similar reduction was also noted in the phenol concentration, with the quenched retort runs showing one-tenth or less of the amount of the cool-deluged retort run.

The amount of inorganic material present in the deluge waters after quenching varied considerably. The inorganic material, represented by total alkalinity and TDS of the deluge water collected after the hot quench from the top of the retort, was substantially lower compared with cool

deluge and the quenches at the combustion front. Materials from runs quenched at the combustion front contained much higher inorganic loadings than material from the run that received the cool deluge.

Reverse combustion was examined as a method of organic source removal from the simulation retorts. After completing the retorting portion of the test, the air flow direction was reversed, and the combustion front was drawn to the bottom of the retort countercurrent to the air flow.

Different combinations of quench and deluge procedures were performed in conjunction with the reverse-combustion tests. The combination of quenching and/or deluging following the reverse combustion of the retort was monitored by TOC analysis of the water exiting the bottom of the retort. In tests where the quench water was introduced into the top of the retort, most of the water vented out the top of the retort as steam. Approximately 1 pore volume of water migrated through the retort before the quench procedure ended in these tests. The water quench was performed with the adiabatic shields of the tube reactor remaining on. After the retort temperatures were below that of steam, the deluge procedure was started.

All of the tests involving reverse combustion demonstrated that most of the organic material was removed by the combustion prior to the quenching procedure. The organic loading of the quench and deluge water exiting the retort were considerably lower than the exit water in tests without reverse combustion. The very first TOC values measured during the quench and/or deluge for these tests were the same or less than TOC values measured at the end of the deluge procedure for tests using only the quench and/or deluge procedures as the method of retort remediation. Comparison of the analyses of the quench waters shows that very little organic material was left in the retort after reverse combustion. The TOC analyses of the quench waters from tests with no reverse combustion suggest that the amount of

water-soluble organic material removed from the retorts was approximately 1000 mg. The total organic material in the quench water after reverse combustion was an order of magnitude smaller than that without reverse combustion and was very near the detection limit of the analytical method. In addition, no oil was removed from the retort during the quench of the reverse-combustion tests as was the case for the other quench experiments.

A significant difference between the hot quenching and the reverse combustion was apparent. Reverse combustion converted most of the residual oil from retorting into carbon and lighter organic compounds. The carbon can remain in place and act as adsorbent, whereas the lighter organic compounds can be easily removed by a deluge with water. The hot quench removed most of the organic material by thermally reducing its viscosity, allowing it to drain from the retort. This permits a certain portion of the heavier oil to adhere to the unretorted shale as an organic source. These organic materials can undergo slow chemical changes, for example, low-temperature oxidation, and be slowly leached from the retort by groundwater.

The water quench while the retorts are at high temperatures is probably removing part, if not all, of the carbon layer deposited on the spent shale during the reverse combustion. The hot quench promotes steam-char reactions that produce hydrogen and carbon oxides. This carbon layer can prevent the deluge water from contacting the spent shale and dissolving inorganic components. Evidence for the carbon layer isolating the spent shale from the deluge water can be noted by comparison with tests which were not subjected to the water quench, showing much less inorganic material present in the deluge water.

Rehydration of spent shale can greatly affect the amount of water needed in the remediation of MIS retorts. Once the shale

has been thermally altered, a great deal of surface area has been made available for contact with water during the remediation process. For this reason, the rehydration properties of spent shale become significant when trying to minimize water use.

The thermally affected zones of a retort greatly increase their affinity for water. The combusted zones, which make up the majority of the shale in the retort, contain between 25 and 30 wt % water. The retorted zones generally contain between 7 to 12 wt % water. The unretorted shale only contains 2 to 4 wt % water after rehydration. To evaluate the effect of water readsorption by the spent shale in place, the Fischer assay data were compared with the total amount of water adsorbed by the retort with respect to the percent of the retort which had been thermally affected. The amount of shale thermally affected was determined by the amount of oil remaining in the retort after the simulation test. A fair correlation can be made for those retort tests that did not involve any reverse combustion.

Reverse combustion appears to prevent the readsorption of water by the spent shale; however, the effectiveness of this method varied with each test. The conditions for each of these tests was examined to explain some of the differences in the results. A test where only 60% of the shale was retorted before the air flow was reversed and the remaining shale reverse combusted, showed a heavy deposit of carbon. Tests which were reverse burned after approximately 85% of the shale had been retorted readsorbed more water than the 60% retorted test. A test, which had been quenched with water immediately after reverse combustion, readsorbed water in about the same way as retorts without reverse combustion. The average gas analysis for this test showed a large amount of hydrogen, indicating that a steam-char reaction is prevalent. This reaction removes the carbon from the spent shale, increasing the amount of water that could contact the spent shale.

Conclusions

Reverse combustion is the most effective method for removing organic material on the unretorted shale at the bottom of the retort. Hot quench and deluge after the reverse combustion removed very little additional organic material. Visual inspection of the bottom portion of the retort showed no evidence of organic components after reverse combustion.

Hot quench was effective in removing most of the organic material near the bottom of the retort. Although the deluge water analyzed after the hot quench suggested that this method was as effective as the reverse combustion, visual examination of the unretorted zone showed that heavy oil was still present. This heavy oil may act as a source of organic contaminants if it undergoes chemical changes that increase its water solubility.

Cool deluge was not as effective as reverse combustion or quench in removing organic material. Water used as a cool deluge removed the least amount of organic material from the unretorted portion of the reactor. The addition of a biodegradable detergent to the cool deluge water was slightly better than using plain water, but it still left a lot of organic material on the unretorted shale.

Reverse combustion reduced water readsorption by spent shale. A carbon layer deposited on the spent shale as a result of reverse combustion provided a barrier to water and reduced the water uptake by the spent shale substantially. A hot quench after reverse combustion removed part of the carbon deposit. The removal of the carbon layer was the result of the steam-char reaction taking place during the quench.

The amount of inorganic material leached from the shale was slightly less in the reverse-combustion experiments than in other tests. This is probably related to the water barrier provided by the carbon deposit that results from the reverse combustion.

Related Publications

Barbour, F. A. and J. E. Boysen, 1991, Quenching and Stabilization of MIS Retorts: Bench-Scale Experiments. Laramie, WY, WRI Report-91-R041.

Barbour, F. A. and J. E. Boysen, 1992, Bench-Scale Simulation of Quenching and Stabilization of MIS Retorts. Proceedings of the 25th Oil Shale Symposium, Golden, CO, 153-186.

Boysen, J.E., J.R. Covell, K.G. Kofford, J.E. Marshall, and R.G. Vawter, 1990, Management Program for Spent Modified In Situ Retorts. Proceedings of the 23rd Oil Shale Symposium, Golden, CO, 133-141.

INVESTIGATION OF THE ROPETM PROCESS PERFORMANCE ON SUNNYSIDE TAR SAND

Lyle A. Johnson, Jr.
Frank D. Guffey

Background

Major obstacles to the commercialization of tar sand are the high costs associated with mining and processing, the upgrading of the raw tar sand oil, and refining the upgraded tar sand oil to produce salable products. To encourage tar sand commercialization with reduced financial risks, WRI has developed the Recycle Oil Pyrolysis and Extraction (ROPETM) process. The process consists of four major steps: (1) preheating and extracting the hydrocarbonaceous material with product oil, (2) retorting the extracted material at a low temperature with recycle product oil, (3) completing the pyrolysis of the residue at a higher temperature ($>400^{\circ}\text{C}/750^{\circ}\text{F}$) in the absence of product oil recycling, and (4) combusting the solid residue and pyrolysis gas to produce the required process heat.

The results from numerous tests with 2-inch and 6-inch diameter screw pyrolysis reactor (SPR) systems suggest that the ROPE process will assist existing surface and in situ recovery process economics in the following ways: (1) by producing a diluent to decrease the pour point and viscosity of produced bitumen for pipeline transportation, (2) by producing a solvent for solvent extraction processes, and (3) by producing feedstocks for the production of unleaded gasoline and advanced aviation turbine fuel. These encouraging results led to interest and support from AMOCO for further testing of the process.

Objectives

The objectives of this study were to determine the optimum pyrolysis temperature for the ROPE process and to confirm that temperature at steady-state conditions by conducting tests in the 2-inch SPR. In addition, the characteristics of the product oil were determined.

Procedures

The ROPE process has been designed to facilitate both laboratory experimentation and commercial application. The system consists of the following major subsystems:

- Feed system including a preheating screw reactor
- Pyrolysis screw reactor
- Drying (inclined pyrolysis) screw reactor
- Heavy product oil recycle system
- Reflux condensers and knockouts
- Sweep gas injection system
- Spent solids tank

Four 24-hour tests and one 105-hour test were performed in the 2-inch SPR using Sunnyside tar sand. The 24-hour tests were started using SAE-50 weight motor oil as the initial recycle oil. The 105-hour test was initiated with a mixture of product oils collected during the 24-hour tests. Some product oil and heavy oil produced during the initial 33 hours of the 105-hour test were recycled for the final 72 hour steady-state period of the test. The 24-hour test conditions were used to determine the optimum pyrolysis temperature and to produce the initial recycle oil for the 105-hour test.

Based on the optimum pyrolysis temperature from the initial four tests, the 105-hour test was designed to produce oil at steady-state conditions. This long-term test was operated in two phases, an initial phase with a pyrolysis temperature of 316°C (600°F) to produce a larger amount of heavy recycle oil and a second phase at 343°C (650°F) to provide products in a steady-state environment. The heavy oil was not recycled in the initial phase, and the product oil produced from previous tests was continuously injected. The initial 33-hour and final 72-hour phases were conducted without any break in operations.

The tar sand used for these tests was prepared by crushing and screening a large sample obtained from a quarry at Sunnyside, Utah. The bitumen content of the tar sand ranged from 8.9 to 10.9 wt %, with a total organic content of 9.5 to 11.6 wt %. A mass balance Fischer assay of the Sunnyside tar sand was also performed to provide a baseline for comparison of the ROPE process yield data.

For the evaluation of the end use of the product oil, hydrocarbon group-type distributions were determined for three product oils from the two phases of the 105-hour test. Because this test was conducted with tar sand product oil only and for a long period of time, it was believed that the hydrocarbon-type distributions would closely simulate commercial results.

Total saturates and aromatics for three product oils were determined on composite samples from the individual phases. The oils were evaluated to determine their potential market value as a fuel or fuel-blending stock. Two distillate ranges were selected for this evaluation: IBP-177°C (IBP-350°F), which represents a motor gasoline or blending stock, and 177 to 371°C (350 to 700°F), which represents conventional and high-density aviation turbine fuel feedstock and diesel fuel.

Results

For the four 24-hour tests, the overall material balances varied from 96.1 to 105.2% closure and are assumed acceptable for the determination of the optimum pyrolysis temperature. Calculated product yields from the four tests ranged from 65.5 to 82.4 wt %. The determination of the optimum temperature was based on the residual carbon content in the spent sand and the product yields. Based on the higher oil and the relatively low residual carbon content, the selected optimum pyrolysis temperature is 343°C (650°F).

Measured oil yield for the entire 105-hour test of 82.3 wt % is in excellent agreement with the 82.4 wt % oil yield for the 343°C (650°F) 24-hour test. The calculated oil

yield of 81.2 wt % for this test also supports the measured oil yield and is 124% of the Fischer assay oil yield. The measured residual carbon content for the individual phases are also in agreement with the results of the 24-hour test and support the validity of the 105-hour test data. In addition, closures near 100% for the overall and total organic balances indicate a high degree of accuracy for the test data. Excellent carbon and hydrogen balance closures were also obtained.

The test results suggest that the change in the oil yield is very small in the pyrolysis temperature range of 316 to 371°C (600 to 700°F). Also, the pyrolysis temperature is approximately 56°C (100°F) lower than that determined for the Asphalt Ridge tar sand (Cha et al. 1987).

For the evaluation of the end use of the product oil, examination of the hydrocarbon group-type distribution for the IBP-177°C (IBP-350°F) distillate fractions indicates that the distillates do not compare well with similar data for unleaded gasoline. However, the hydrocarbon group-type distribution of the 177-371°C (350-700°F) distillates may have market value as a blending stock for the production of diesel fuel.

Conclusions

The following conclusions can be drawn from the Sunnyside tar sand 2-inch SPR tests:

- Sunnyside tar sand can be processed using the ROPE process without any major operational difficulty.
- Oil yields greater than Fischer assay were obtained when the Sunnyside tar sand was pyrolyzed in the presence of recycled oil at 316 to 371°C (600 to 700°F). An oil yield greater than 80 wt % was obtained from the 105-hour test.
- The pyrolysis temperature of Sunnyside tar sand in the presence of recycled oil was approximately 56°C (100°F) lower than the pyrolysis temperature of

Asphalt Ridge tar sand. Also, the oil yield did not change significantly in the pyrolysis temperature range of 316 to 371 °C (600 to 700 °F), which provides a wide operating window.

- The gas yield was more than two times the gas yield for Asphalt Ridge tar sand, but the residual carbon remaining on the spent sand was less than one-half of that for the Asphalt Ridge tar sand.
- The ratio of heavy oil to light product oil is strongly dependent upon the pyrolysis temperature and increases as the reaction temperature decreases.

- ROPE process product oils from Sunnyside tar sand have market application as blending stocks for the production of diesel fuels, but they are not suited for the production of unleaded gasoline or conventional and high-density aviation turbine fuels.

Related Publication

Cha, C.Y., L.A. Johnson, Jr., and F.D. Guffey, 1990. Investigation of the ROPE® Process Performance on Sunnyside Tar Sand. Laramie, WY, DOE/MC/11076-2912.

EVALUATION OF PRODUCTS RECOVERED FROM SCRAP TIRES

John F. McKay

Background

In January 1991, the Amoco Corporation and the University of Wyoming began the first phase of a project to develop an advanced pyrolysis process that produces oil and solid carbonous residue from scrap tires. The process uses shredded scrap tires together with waste motor oil, asphalt binder, or refinery bottoms to produce upgraded oil, gas, and solid residue at temperatures of about 370 to 427°C (700 to 800°F). WRI began jointly sponsored work on the project in July 1991 and the work continued through May 1992.

Objective

WRI's objective in this study was to evaluate the solid residue recovered from scrap tires as asphalt modifiers. Asphalts modified with solid carbonous residue underwent rheological testing and water sensitivity testing.

Procedures

All scrap tire pyrolysis products tested as asphalt modifiers were prepared by a proprietary process at the University of Wyoming.

The sample preparation procedure consisted of placing a total of 17.5 g of asphalt or asphalt plus appropriate amounts of asphalt modifier(s) into a glass vial. For mixing and sample annealing purposes the glass vial, sealed with a cone-shaped Teflon stopper-cap assembly, was placed inside a large aluminum block (thermal sink) maintained at 150°C (302°F). The vial was removed from the block and allowed to cool to ambient temperatures, without agitation, for 2 hours before commencing rheological measurements. Each sample (control or modified) was prepared individually to ensure rheological measurements were made with the same elapsed time after sample preparation.

The sensitivity of asphalt-aggregate test specimens and asphalt-aggregate mixtures to moisture-induced damage (specimen failures or stripping of asphalt from the aggregate surface) were assessed using the freeze-thaw pedestal test. Various combinations of unmodified and modified AC-10 asphalts with four different (two granites and two siliceous) aggregates were evaluated.

Rheology measurements were made using a Rheometrics instrument, model RMS-605. Complex dynamic rheological properties were measured on project samples to evaluate changes in viscoelastic behavior of AC-10 and AC-20 asphalts modified with different solid carbonous residues. These measurements were made at 25°C (77°F) on a 2-mm asphalt film sandwiched between 25-mm parallel plates. Instrument parameters were 0.1 to 100 radian/second shear rate, 3% strain (amplitude of sine wave) with a 10-second hold between different shear frequencies. All measurements were initiated 2 hours after sample preparation procedures had been completed.

Results

In the moisture sensitivity tests, all test specimens containing calcium oxide from the retorting process or calcium hydroxide additions to the asphalt or aggregate had significant reductions to moisture sensitivity. Moisture sensitivity evaluations were terminated after 50 repeated freeze-thaw cycles with no specimen failures.

Test specimens prepared from AC-10 asphalt with granite or granite modified with commercial carbon black "Microfilm-8"; pyrolyzed tire residue; or residues from batch experiments or residues from the continuous reactor all failed in less than three freeze-thaw cycles.

Moisture sensitivity tests with Simon Pit gravel showed only slight increases in cycles to failure following additions of various solid residue modifiers to the asphalt.

Data show pretreatment of aggregates with residuals recovered from batch or continuous reactor experiments can reduce the sensitivity of test specimens to moisture-induced damage. Some aggregates were beneficiated more than others, especially when either calcium oxide or calcium hydroxide was present. Calcium hydroxide additions to the aggregate were more effective than calcium oxide in the carbonous residue.

For the rheology tests, the effect of adding solid carbonous residues from continuous reactor experiments to AC-10 asphalt was measured. Addition of residue to the asphalt caused a decrease in viscosity which corresponded to the process conditions used to produce the residue. Viscosity decreases ranged from 44 to 72%.

Time dependent molecular structuring properties of AC-10 asphalt and AC-10 asphalt containing pyrolyzed tire or waste motor oil residue was measured. Complex dynamic rheological measurements were made at several time periods between 2 and 6525 hours. The control AC-10 asphalt after 4514 hours cure at 25°C (77°F) in a sealed glass vial had a viscosity increase of 39% compared to 43% for pyrolyzed tire and only 2% for the waste motor oil residue modified AC-10 asphalt. The results from the 427°C (800°F), 2-hour residue represent an important benefit for reducing the embrittlement process of a modified asphalt.

Similar time-dependent molecular structuring measurements were obtained on laboratory-aged AC-10 asphalt and waste motor oil modified AC-10 after 6100 hours cure. The increases in viscosity were 107 and 114%, respectively. These results show addition of the solid residue to the asphalt initially decreased the storage (elastic) modulus G' by only 2% but increased the loss (viscous flow) modulus G'' by 0.3% and the viscosity (η') by 29%. After 6100 hours cure the values of G' and G'' for modified asphalt increased by 3% and the viscosity by nearly 34%. These increases are important to reducing permanent deformation (rutting) of pavement and indicate there is no adverse effect from addition of a solid carbonous material (filler) to the asphalt. Both samples showed similar increases after the prolonged cure.

Calcium hydroxide additions to the batch reactor-modified asphalts raised the viscosity value by 39%. For one sample the increase was 57%.

Conclusions

Rheological and water sensitivity tests were used to evaluate asphalts modified with products from the pyrolysis of scrap tires. Asphalt cements modified with carbonous residue showed increased viscosity values and decreased elasticity values. Moisture sensitivity tests with specimens containing solid carbonous residue and calcium oxide were significantly more tolerant to repeated freeze-thaw cycles than their corresponding controls.

Related Publication

McKay, J., 1992, Evaluation of Products Recovered from Scrap Tires for Use as Asphalt Modifiers. Laramie, WY, WRI-92-R034.

REMOTE CHEMICAL SENSOR DEVELOPMENT

John F. Schabron

Background

The capability to detect and monitor groundwater contaminants using real-time in situ measurements promises to be a valuable tool in the environmental industry. The development of chemical sensors to provide in situ information on groundwater parameters will eliminate many problems and significantly lower costs associated with conventional sampling and analysis techniques. Conventional sampling techniques may affect the integrity of the sample in a variety of ways. Changes in the partial pressure of CO₂ during sampling may affect the sample pH, and pressure changes may make quantification of volatile organic compounds difficult. Differences between in situ and surface oxidation-reduction potentials, exposure to light, and oxidation can also affect sample integrity.

Conventional sampling and analysis techniques may have high costs associated with them. Regulations covering groundwater monitoring for contaminant release and transport are continually being expanded. As monitoring programs expand and regulations become more stringent, associated sampling and analysis costs will escalate considerably unless new technology is developed to monitor water contamination in real time. The development of in situ chemical sensor capabilities will help lower analytical costs in the long term, provide valuable information during remediation activities, and help optimize treatment techniques.

Field test kits are available for a variety of inorganic and organic analytes. Many of these are based on existing laboratory methodologies using the sequential addition of pre-packaged reagents. One field method used for measuring total petroleum hydrocarbons involves extraction with 1,1,2-trichlorotrifluoroethane followed by infrared spectrophotometry.

Chlorofluorocarbon solvents have been implicated with ozone layer depletion and are being phased out. An immunoassay test for hydrocarbon contamination has been developed, and a kit based on the Friedel-Crafts alkylation reaction for detecting aromatic rings has been introduced recently. Improved and simplified test kits, sensor probes, and miniaturized chemical analysis systems are badly needed.

Fiber optic chemical sensors involve various optical techniques including absorbance, reflectance, fluorescence, fluorescence quenching, refractive index, or Raman scattering. The excitation source can be a lamp, light emitting diode, or laser. The light interacts directly with the analyte or indirectly with an indicator compound or the product of a chemical reaction involving the analyte.

Western Research Institute is conducting a 30-month development project with In-Situ Inc. (ISI) to design, test, and construct prototype field instrumentation for qualitative identification and quantitative determination of selected soil and groundwater pollutants. This project began in October 1992. The remainder of the project will continue under a new cooperative agreement. Therefore, the results discussed below are only from the initial phases of work.

Objectives

The overall objective is to develop new products for field screening and site monitoring activities. The technical challenge is to be able to qualitatively identify a substance of interest in a selective, sensitive, quantitative, and reversible manner. Specific areas being investigated include developing a test kit to measure the level of diesel fuel in contaminated soils using a non-freon extraction medium, remote determination

and monitoring of pH, and developing technologies for the measurement of volatile organic compounds recommended as potential indicator parameters for site evaluation and monitoring. Hopefully, new tools will be developed from basic and applied research efforts throughout the country, involving technology transfer efforts, that will result in the availability of new commercial products.

Procedures

There are three general phases of activity for each development effort. The first is technology evaluation and analyte selection. In this phase, target analytes for initial work are selected. The detection levels are based on regulatory requirements. Technologies for measurement are reviewed and selected. This involves interacting with universities, national laboratories, and other research institutions where basic and applied research on novel measurement and chemical sensor technologies is occurring. The initial extraction, pretreatment, and detection approaches are selected. These are tested in the laboratory at WRI, ISI, or under subcontract to the research facility where they were developed, and modified as needed.

In the second phase, prototype instrument and method development, experiments are performed in the laboratory. Experiments are performed to develop and construct prototype field instrumentation. Appropriate features such as stability, calibration, and linearity are evaluated. One or more prototype field instruments is designed, and components for its construction are obtained. The prototype instrument is then constructed and modified as needed.

Instrument construction and evaluation is performed in the third phase. Based on the results of the work with prototypes, field instrumentation is designed and constructed. This includes designing a portable power supply, data logger interface, and packaging for a field instrument. The prototype unit is

converted into a field unit. The capabilities of the new unit must be tested and validated under actual field conditions.

Results

Investigations have been undertaken in three areas. These are the development of a test kit to measure the levels of diesel and other fuels in contaminated soils using a non-freon extraction medium, the development of a downhole probe for measuring volatile organic contaminants in groundwater, and the use of surface enhanced resonance Raman spectroscopy for remote pH monitoring.

The diesel test kit work involves chemical development efforts at WRI and instrument development efforts by ISI. The work includes evaluation of a current ISI field product for soil head space analysis after the addition of water. Head space analysis works well for gasoline, but not for the less volatile diesel fuel components. An extraction/photometric approach for measuring the diesel fuel content of soils was developed at WRI using a non-chlorofluorocarbon solvent of low toxicity. Method validation is in progress at WRI and a prototype laboratory instrument is being built by ISI. After some additional testing, prototype hand-held field photometers will be built by ISI. The method will be evaluated by some of ISI's clients under actual field conditions in late 1993, and commercialization is expected to occur in early 1994. Work is underway to extend the method to other fuel types and to develop lower detection limits.

Volatile organic compounds (VOCs) are the most significant organic contaminants in groundwater associated with disposal sites. Monitoring for key indicator VOCs could be used as an early warning system for excursions, to indicate the need for more extensive analysis for organics. Extensive work leading to the conclusion that key volatile organic indicator monitoring could eventually replace some current indicator monitoring strategies has been led by Dr. Russel Plumb under a Lockheed contract with EPA.

Initial experimental work on VOCs indicators has been started by WRI. A test cell for allowing head space measurements to be made from distilled water spiked with VOCs has been constructed at ISI. Some approaches for creating a head space below the water surface have been tried. Measurement techniques using various electro-optical devices have been evaluated and some have been tested. Results have been compared with gas chromatography analysis at WRI. This effort will require extensive experimental efforts at WRI and is expected to be a major activity in the continuation of this study.

The work using surface enhanced resonance Raman spectroscopy for pH monitoring has been completed. Initially, it was thought that this effort would bring an easy, early success. However, a suitable indicator that could be used with an inexpensive red diode laser was not found, although many indicators were tested and some chemically modified. Earlier work had been successfully performed using a green laser.

Conclusions

Development work is underway on two promising areas of field analysis and remote chemical sensing technology. These are a field test kit for determining diesel and other fuel types in contaminated soil and devices for the determination of key indicator volatile organic compounds in groundwater.

A STANDARD TEST METHOD FOR SEQUENTIAL BATCH EXTRACTION

Susan S. Sorini

Background

Single batch extraction methods, such as the Extraction Procedure (EP) Toxicity Test (EPA 1980), American Society for Testing and Materials (ASTM) Method D 3987, Standard Test Method for Shake Extraction of Solid Waste with Water, (ASTM 1992), and the Toxicity Characteristic Leaching Procedure (TCLP) (EPA 1990), are commonly used to characterize waste materials. A single batch extraction procedure can give useful information concerning the constituents that can be extracted from a material during its initial contact with a leaching medium. However, evaluation of the leaching characteristics of material during repeated exposure to an extraction fluid requires a method involving multiple leaching sequences. For example, sequential batch extractions can indicate whether or not the majority of soluble constituents is leached in the first extraction step, or if the buffering capacity of a matrix decreases with repeated exposure to the leaching fluid. In addition, the increasing occurrence of acid rain throughout the world has resulted in a need for a detailed, multiple-step extraction procedure involving extraction fluids simulating acid rain solutions. For these reasons, a sequential batch extraction method using a dilute acid solution simulating acid rain was developed and validated within ASTM Committee D-34 on Waste Management. The Institute for Standards Research, a subsidiary of ASTM, helped locate private sponsors for this task. The private sponsors were the American Mining Congress, Environment Canada, and AMAX Mining Company.

Objectives

The purposes of this project were to develop a sequential batch extraction method using a dilute acid solution simulating acid rain as the extraction fluid and to conduct a collaborative study using the method to

determine its precision when applied to two different waste materials using two different extraction fluid pH values. The collaborative study was conducted to provide information on the variability that can be expected when the method is used by one or more laboratories. This information will help users to assess the usefulness of the method in their applications. Specifically, the project objectives were to (1) develop an ASTM standard test method for sequential batch extraction using extraction fluids simulating the composition and pH of acid rain and (2) determine the precision of the extraction procedure when applied to specific waste materials by conducting a collaborative study using the method.

Procedures

A method for sequential batch extraction of waste with acidic extraction fluid was developed by ASTM Task Group D-34.02.01 on Waste Leaching Techniques. This method contains great detail and explanation to prevent confusion in performing the extraction steps and to ensure, with each sequence, the correct solid-to-liquid ratio is maintained. The method calls for mixing a known mass of waste with an acidic extraction fluid, prepared using a 60/40 wt % mixture of sulfuric acid/nitric acid solution, and separating the liquid phase for analysis or testing. The acid ratio of 60/40 wt % sulfuric acid/nitric acid was selected because about two-thirds of the acid in rainfall is sulfuric acid and one-third is nitric acid (Gordon 1987). The method requires that the pH of the extraction fluid reflect the pH of acidic precipitation in the geographic region where the material being tested is to be placed. The procedure is conducted 10 times in sequence on the same sample of material and generates 10 solutions. It can be applied to any material containing at least 5% dry solids.

The procedure became an ASTM standard test method on August 15, 1992 that is designated as ASTM Method D 5284-92, Standard Test Method for Sequential Batch Extraction of Waste with Acidic Extraction Fluid (ASTM 1993). The new standard allows flexibility in selection of extraction fluid pH in an attempt to more closely represent site-specific conditions. It can be used to evaluate the buffering capacity of materials repeatedly in contact with acidic media, such as acid rain, and provides a relatively fast and inexpensive procedure for examining the effects of acidic media on the leachability of various waste types and treated waste materials. The method can be used in conjunction with long-term modeling or field studies. Sequential batch extraction data are useful for site assessment, for modeling source term depletion, and for risk assessment.

Ten laboratories participated individually or as teams in the study, using a spray dryer waste from an innovative clean coal technology process and a composite mining waste. These were extracted in duplicate using the test procedure, and the materials were homogenized prior to being sent to the laboratories. The spray dryer waste was extracted using an extraction fluid having a pH of 4.3 ± 0.05 , and the composite mining waste was extracted using an extraction fluid having a pH of 5.0 ± 0.05 . The resulting extracts were then analyzed for specific inorganic analytes. The study participants also analyzed six analytical standards in triplicate to generate data for calculating analytical precision. These standards contained high, medium, and low concentrations of the elements of interest in the extracts. All of the participants in the study analyzed the extracts and analytical standards using inductively coupled plasma spectrometry. Two of the laboratories digested their extracts and analytical standards prior to analysis. The other participants did not digest the extracts and standards.

The collaborative study of the sequential batch extraction method was designed so

an estimated analytical error could be determined and subtracted from the total error due to both performing the extraction method and analyzing the resulting extracts. In this way, the error due to the extraction procedure can be estimated. ASTM Practice D 2777, Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water (ASTM 1991), was used as a guideline for the statistical evaluation of the data.

The data generated in the study can be divided into two categories: (1) data from extraction of the test materials and analysis of the resulting extracts, which were used to determine the mean concentration for each element in each extract and the total standard deviation of the extraction procedure-plus-analysis of the extracts and (2) data from analysis of the analytical standards, which were used to determine the mean concentration for each level of analytical standard and the standard deviation for analysis of the analytical standards. Three types of precision can be determined from the data. These are: the total standard deviation, the analytical standard deviation, and the estimated standard deviation of the extraction procedure, which represents the estimated error due to only the extraction method.

The three types of precision values, total, analytical, and extraction procedure, can also be calculated based on a single operator. Calculations were performed to determine the total single-operator precision, the single-operator analytical standard deviation, and the estimated single-operator precision of the extraction procedure.

Results

Eight data sets were generated by the collaborative study participants. Two of the laboratories did not follow the study specifications. Their data were not used in the statistical evaluation, and as a result, six data sets were used to evaluate the precision of the extraction procedure.

It was not economically practical to determine analytical precision using actual extracts of the wastes because of the extensive number of analyses that would have been required. The analytical standards were, therefore, used to determine analytical precision. Calculation of the standard deviation of the extraction procedure can provide only an approximation because the analytical standards do not contain the specific matrix resulting from the interaction of the extraction fluid and solid waste. In addition, the analytical standards were limited to three concentration levels for each element. To calculate the precision of the extraction procedure for a particular element, the analytical standard deviation for analysis of the analytical standard containing the concentration of the element closest to its concentration in the extract was used. For some of the extracts, the elemental concentration in the extract varied significantly from the element's closest concentration in the analytical standards. Because of the way in which the total precision and analytical precision were determined, in some cases, the analytical standard deviation values were larger than the total standard deviation values. In these cases, the precision of the extraction procedure could not be determined.

The estimated precision of the sequential batch extraction procedure varied somewhat with the concentration of aluminum, barium, silicon, sodium, and strontium in the spray dryer waste extracts as shown in Figures 1 to 5. The estimated precision of the sequential batch extraction procedure varied somewhat with the concentration of calcium, magnesium, manganese, and silicon in the composite mining waste extracts (Figures 6 to 9). The figures are plots of the calculated percent relative standard deviation of the extraction method versus the mean concentration of the constituent in the extract. The three-dimensional bar graphs are helpful in examining trends and interpreting the data. As indicated by these graphs, the relative precision of the single-operator values are

better than those of the multiple-operator values and are encouragingly good.

Conclusions

A general precision statement that covers all wastes, analytical parameters, and extraction fluid pH values can not be written for this method because the data generated in the collaborative study are specific to the test materials, extraction fluid pH values, and elements of interest in this study. However, the data generated in the study provide information on both multiple-laboratory and single-operator precision of the extraction procedure when it is applied to two different waste materials using two different extraction fluid pH values. Based on the information obtained in this study, it can be concluded that (1) 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; (2) for most elements of interest in the study, the estimated precision of the extraction procedure varies with the extraction number in the sequence; (3) for the materials tested in the study, the estimated multiple-laboratory precision of the sequential batch extraction method for extracting many of the elements of interest varies somewhat with the elemental concentration extracted from the test material, and in many of these cases, there is a direct relationship between estimated multiple-laboratory standard deviation and extract concentration; and (4) as expected, the estimated single-operator precision of the extraction method in many cases is much better than the estimated multiple-laboratory precision.

Related Publication

Sorini, S.S., 1993, Development and Validation of a Standard Test Method for Sequential Batch Extraction of Waste with Acidic Extraction Fluid. Institute for Standards Research, Philadelphia, PA, PCN: 93-000004-56 and report to DOE, WRI-92-R058.

Figure 1. Estimated Precision of the Sequential Batch Extraction Method for Aluminum in the Spray Dryer Waste

Figure 2. Estimated Precision of the Sequential Batch Extraction Method for Barium in the Spray Dryer Waste

Figure 3. Estimated Precision of the Sequential Batch Extraction Method for Silicon in the Spray Dryer Waste

Figure 4. Estimated Precision of the Sequential Batch Extraction Method for Sodium in the Spray Dryer Waste

Figure 5. Estimated Precision of the Sequential Batch Extraction Method for Strontium in the Spray Dryer Waste

Figure 6. Estimated Precision of the Sequential Batch Extraction Method for Calcium in the Composite Mining Waste

Figure 7. Estimated Precision of the Sequential Batch Extraction Method for Magnesium in the Composite Mining Waste

Figure 8. Estimated Precision of the Sequential Batch Extraction Method for Manganese in the Composite Mining Waste

Figure 9. Estimated Precision of the Sequential Batch Extraction Method for Silicon in the Composite Mining Waste

NMR ANALYSIS OF ORGANIC MATTER IN SEDIMENTARY ROCKS

Francis P. Miknis

Background

The University of Wyoming (UW), through funding by the Gas Research Institute (GRI), has begun a multidisciplinary research program that is aimed toward development of an innovative exploration and production strategy that will optimize the efficient exploitation of hydrocarbon resources in the various basins of Wyoming and Montana. The development of this strategy will be based on establishing a thorough understanding of the processes affecting the natural gas resources and hydrocarbon reservoirs.

A major task of the UW research program is to construct diagenetic/maturation models for the potential hydrocarbon sources and reservoir rocks in the different basins. This task involves, *inter alia*, modeling of selected source rock intervals using kinetic modeling and time-temperature indices. A key to understanding the diagenetic/maturation behavior is knowledge of the organic carbon structure of the hydrocarbon source rocks. The kinetic model will be developed using geochemical analyses, hydrous pyrolysis measurements, and solid-state ^{13}C NMR measurements on coals and shales. The model will be validated and refined by comparing calculated transformation ratios from the maturation model with observed production indices, vitrinite reflectance values, and kerogen structural determinations using solid-state ^{13}C NMR techniques.

Objectives

The objectives of the NMR studies were to measure the structure of the organic matter in sedimentary rocks and to relate these measurements to changes brought about naturally by maturation in the geologic environment and artificially by laboratory

hydrous pyrolysis experiments. Support for these studies was provided by GRI, the Experimental Program to Stimulate Competitive Research, and the Woods Hole Oceanographic Institution.

Procedures

Drill cuttings and core samples for geochemical and NMR analyses were obtained from the American Stratigraphic Institute in Denver, Colorado. Generally, the samples spanned a present day depth interval between 3,000 and approximately 18,000 ft. Samples of coals and shales from the Mesaverde Group, Greater Green River Basin, and Mowry Formation shales, Powder River Basin, were acquired. Samples from Leg 139 of the Ocean Drilling program were also studied. These were supplied by the Woods Hole Oceanographic Institution.

Solid-state ^{13}C NMR measurements were made using a Chemagnetics 100/200 solids NMR spectrometer. Carbon aromaticity measurements were made at 25 MHz using the technique of cross polarization with magic-angle spinning (CP/MAS) and high-power decoupling. These measurements were made using a large-volume sample spinner (2.1 mL), a spinning rate of ~3.8 kHz, a pulse delay of 1 s, a contact time of 1 ms, and a pulse width of 6.2 μs . Between 3,600 and 7,200 transients were recorded for coals and between 54,000 and 64,800 transients were recorded for shales.

Hydrous pyrolysis experiments were conducted in a stainless steel reactor using 200 g of coal and 400 g of distilled water. The coals were matured to different stages by heating separate samples of the same coal isothermally for 72 hours at temperatures ranging from 290 to 360°C (554 to 680°F).

Results

The coal and shale samples of the Almond Formation of the Mesaverde Group in the Green River Basin examined in this study show a fairly normal maturation-depth relationship, with the oil window lying somewhere between about 4,500 and 14,500 ft present burial. CP/MAS ^{13}C NMR spectra of coals and shales taken from these depths showed the expected trends of loss of aliphatic components and increasing aromatic components during maturation. For the shale samples, little aliphatic component remained below about 12,000 ft suggesting little additional capacity for oil generation at greater depths. Similar trends were noted for the coal samples. However, at the maximum depth sampled (10,837 ft) for the coals, some capacity for hydrocarbon generation still remained.

Solid-state NMR measurements on residues from hydrous pyrolysis of Almond coal clearly showed a preferential loss of aliphatic carbons relative to aromatic carbons. Relative to the original coal, there was about a 60% decrease in the aliphatic carbon for the 360°C (680°F) residue. The remaining aliphatic carbon appeared to be due to methyl groups attached to aromatic rings. In addition, there was definite line narrowing in the aromatic carbon region with increasing temperature due to cleavage of phenolic carbons and alkyl substituents during hydrocarbon generation. Rapid evolution of CO_2 occurred during hydrous pyrolysis, as evidenced by the loss of carboxylate functional groups in the NMR spectra at 300°C (572°F).

Solid-state ^{13}C NMR measurements made on petroleum source rocks from the Mowry Formation showed that beyond a present day depth of ~11,000 ft, the kerogen had little capacity to generate additional oil, but still had some capacity to generate gas. NMR measurements, combined with Rock-Eval measurements, were used to assess the hydrogen budget during maturation. The calculations indicated that about 20% of the original organic matter was converted to hydrocarbons during maturation.

Additional calculations showed that sufficient hydrogen was generated from aromatization and condensation reactions during maturation to form stable hydrocarbon liquids and gases.

NMR measurements of sediments from Leg 139 of the Ocean Drilling Program correlated with the maturity of the sediments. For cases where the sediments had been heated by hydrothermal flow, there was a noticeable loss of aliphatic component in the kerogen, and the remaining organic material was almost exclusively aromatic.

Conclusions

Solid-state ^{13}C NMR measurements on coals and shales from different sedimentary basins provided information about the maturity and generative capacity of the organic matter for production of hydrocarbons. In all cases, the aliphatic carbon component decreased with increasing maturity. With the use of a large-volume sample spinner, NMR measurements were made on samples containing as little as 1% organic carbon.

Related Publications and Presentations

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TESTING AND DEMONSTRATION OF UTILIZATION OF WYOMING FLY ASH

Alan E. Bland

Background

The use of ash byproducts from the combustion of coal is one of the driving environmental forces associated with power production in the United States today. Ash disposal is a significant operational cost to the utility and cogeneration industry. Attempts to find uses for these byproducts has been underway for the last two decades. Unfortunately, only approximately 20 to 25% of the fly ash produced from coal-fired power plants is presently used. The rest is still placed in landfills. Most utilization efforts are in the eastern states due to a series of technical, market, and economic considerations. Perhaps the most obvious of these considerations is the lack of adequate disposal areas and the resultant escalating costs of disposal in the eastern states.

Two options, stabilization of unpaved roads, and enhanced replacement of cement treated bases, may provide a significant market for fly ash. Conventional fly ash stabilization techniques use cement or lime alone, or with fly ash at levels of 20-25%, to stabilize soils. The costs of these techniques when applied to unpaved roads are in the neighborhood of \$30,000 to \$40,000/mile. The development and demonstration of novel construction methods employing low fly ash dosage levels could result in lower construction costs, reduced maintenance costs, and a potentially large new market for Wyoming fly ash. Also, fly ash use in standard cement treated bases (CTB) has been generally 20% of the portland cement content for Wyoming Department of Transportation projects. Higher replacement percentages would result in lower costs of CTB mixes through the reduction of portland cement costs. This could also provide an expanded market for Wyoming fly ashes.

Objectives

The objectives of this study were to test 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 cement treated bases. In addition to DOE, support for this research effort was provided by PacifiCorp, the Wyoming Science and Technology Energy Authority, the Wyoming Department of Transportation, and Converse County, Wyoming.

Procedures

The two principal activities carried out in this study were (1) laboratory testing of fly ash materials for soil stabilization and cement replacement and (2) demonstration of stabilization of an unpaved road using fly ash.

Laboratory testing for soil stabilization using fly ash was conducted on a range of soils and fly ashes from several of plants in Wyoming. The soils ranged from AASHTO soil types A-1b to A-6. Fly ash from three plants (Dave Johnston, Laramie River, and Naughton) were extensively tested. These ashes represent both Class F and Class C fly ashes produced in Wyoming. The fly ash additions to the soils ranged from 5 to 25%.

Laboratory tests included moisture-density relationships (ASTM D 698), unconfined compressive strength (ASTM D 2244), wet-dry cycle durability (ASTM D 559), and freeze-thaw durability (ASTM D 560). Unconfined compressive strengths were determined using a Harvard Miniature preparation method.

The testing also included an evaluation of fly ash replacement of cement in CTB. The aggregate used was a scoria from northern Wyoming and the cement was specially prepared by Mountain Cement of Laramie.

Wyoming. The same fly ash sources were used at replacement levels ranging from 20 to 75%. Approximately 8% portland cement or cement plus fly ash was used in the CTB mixes. Standard ASTM testing procedures were followed in all testing except the modified freeze-thaw cycling where modifications were made to evaluate the durability at 14 days to account for the slower strength development of high fly ash replacement cements. Test samples were prepared according to the method described in ASTM D 558 at the moisture content determined according to the moisture-density relationship of a CTB using 8% portland cement (ASTM D 558). Compressive strength (ASTM D 1633), wet-dry durability (ASTM D 559), freeze-thaw durability (ASTM D 560), and resilient modulus (ASTM D 4123) were determined.

Based on laboratory testing using ash from the PacifiCorp Dave Johnston Power Plant near Glenrock, Wyoming and different soil types from a road adjacent to the plant, a field demonstration of fly ash stabilization of unpaved roads was conducted. The unpaved road selected for the demonstration had a continued history of washboarding and required a high level of maintenance. The construction procedure was to stabilize the upper 9 inches of the road surface mechanically in one case and mechanically with fly ash stabilization in another. The impacted road sections were scarified, fly ash added and blade mixed with the road materials and water using a grader. Compaction with truck tires transformed the mixture into a very dense and stable road surface. It was required that the road be immediately available to traffic and it was assumed that the fly ash-treated section would continue to improve in strength and durability with time.

Two 1,000-ft experimental test sections demonstrating the fly ash stabilized unpaved road process were constructed in July 1991. Fly ash from Unit 3 of the plant was used for the treatment. Water from the Dave Johnston recycle pond was used. The materials consisted of 240 tons of fly ash and 10,000 gallons of water. Based on calculations of the depth of treatment and

the bulk density of the road material, a fly ash treatment of 20% and a water addition of 11% were achieved.

Results

The chemical characteristics and the general geotechnical properties of the fly ashes are presented in Table 1. The testing results of the evaluation of fly ash for soil stabilization applications are presented in Tables 2 and 3. The moisture-density relationship (optimum moisture and maximum dry density) and the unconfined compressive strength data for the different soils-fly ash combinations are shown in Table 2. The durability data from the wet-dry, freeze-thaw, and resilient modulus testing are presented in Table 3.

The unconfined compressive strength development at 7 and 28 days for the range of fly ash-soil mixtures ranging from 5% to 25% fly ash were in the range of 100 to 150 psi. This appears to be marginally adequate for application to unpaved roads.

The results of the durability tests provide the assessment of whether or not sufficient strength and durability can be realized at these low dosages under the climatic conditions of the Rocky Mountain Region. The durability requirements for pavement construction includes the survival of the cement-soil mixture under 12 cycles of freezing and thawing as well as less than 14% weight loss under wet-dry cycling (ASTM D 559) and freeze-thaw cycling (ASTM D 560). The Naughton fly ash treated soils ranged from 26 to 33% weight loss after 12 wet-dry cycles, while the Laramie River fly ash averaged 16 to 21%. Both fly ashes were unable to meet the ASTM requirements for soil cement applications. None of the soil-alone mixtures were able to survive three wet-dry cycles, indicating that the fly ash treatment is improving the durability performance of the soils. All of the mixtures survived the 12 freeze-thaw cycles. Weight losses of 21 to 32% for the Naughton treated soils and 18 to 28% for the Laramie River treated soils were measured. None of the untreated soils passed the freeze-thaw tests.

Table 1. ASTM C 311 Test Data

	Dave Johnston Unit 1	Naughton	Laramie River Unit 1 & 2	<u>ASTM C-618 Specifications</u>	
				Class F	Class C
<u>Chemical Properties</u>					
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃ , wt %	74.18	77.33	56.90	70 min	50 min
Sulfur Trioxide, wt %	0.55	0.75	2.34	5 max	5 max
Calcium Oxide, wt %	17.09	11.17	28.05		
Moisture Content, wt %	0.15	0.04	1.20	3 max	3 max
Loss on Ignition, wt %	1.32	0.50	0.41	6 max	6 max
Available Alkalis, wt %	nd	nd	nd	1.5 max	1.5 max
<u>Physical Properties</u>					
<u>Fineness</u>					
% retained 325 mesh	28.48	29.23	18.47	34 max	34 max
<u>Pozzolanic Activity Index</u>					
With PC, % control-28 days	76.8	90.4	91.1	75 min	75 min
With Lime, psi-7 days	985	1470	820	800 min	No Limit
Water Requirement, % control	94.2	93.4	93.4	105 max	105 max
<u>Soundness</u>					
Autoclave Expansion, %	-0.009	-0.045	-0.031	0.8 max	0.8 max
<u>Reactivity with Alkalis</u>					
Expansion @ 14 days, %	nd	nd	nd	0.02 max	0.02 max
Specific Gravity, g/cc	2.29	2.49	2.75	none	none

nd = not determined

Table 2. Summary of the Moisture-Density and Strength Properties of the Fly Ash Stabilized Soils

<u>Fly Ash Source</u>	<u>Unconfined Compressive Strength -- Moisture Relationship</u>				<u>Moisture - Density Relationship</u>			
	<u>7-day Curing</u>		<u>28-day Curing</u>		<u>7-day Testing</u>		<u>28-day Testing</u>	
	UCS ^a	Moist. ^b	UCS ^a	Moist. ^b	Density ^c	Moist. ^b	Density ^c	Moist. ^b
Dave Johnston	126	19.51	na	na	90.98	19.51	na	na
Naughton	749	11.9	1053	11.9	112.66	13.8	112.37	13.7
Laramie River	1787	13.8	2226	15.9	119.91	13.8	117.96	14.6

^a Unconfined Compressive Strength, psi^b Moisture, wt %^c Density, pcf

na - not available

Table 3. Wet-Dry, Freeze-Thaw Cycle and Resilient Modulus Data for Fly Ash Stabilized Soils

Soil Type (AASHTO)	Fly Ash Source	Wet/Dry, weight loss, %	Freeze/Thaw, weight loss, %	Resilient Modulus (psi)
RS-1	Naughton	32.3	27.7	513,088
(A-1b)	Laramie River	18.0	24.9	310,640
RS-2	Naughton	32.8	32.3	494,003
	Laramie River	18.4	18.1	321,522
RS-3	Naughton	29.8	21.1	600,409
	Laramie River	16.1	28.3	120,977
RS-4	Naughton	25.9	25.1	460,124
	Laramie River	21.5	24.1	904,353

Resilient modulus specimens were prepared in accordance with AASHTO T 190. Resilient modulus of the fly ash treated specimens ranged from 121 to 904 k psi. All of the untreated soils failed during the conditioning phase of the test. According to AASHTO, they would represent a very poor or potentially failed subgrade condition. The data indicate that the relationship of resilient modulus is both fly ash sensitive and soil type sensitive. The behavior of Naughton material compared to Laramie River material varies by up to a factor of 5, with the Naughton material showing higher resilient modulus values for soils RS-1, RS-2, and RS-5. However, for the RS-7 soil (more clay), the response is the reverse, with the Laramie River showing the higher values, by a factor of 2. The chemical reasons for this behavior must be understood before commercial applications can be considered. Clearly, the fly ash treatment is improving the stiffness of the soils.

For the CTB portion of the laboratory testing, the optimum moisture content was determined to be 16.5% at a maximum density of about 108 pcf. The results of the unconfined compressive strength and durability testing of the fly ash replaced CTB are presented in Table 4.

For the compressive strength testing, the control samples 7-day compressive strength was 525 psi and the 28-day compressive strength was 1350 psi. The maximum strength for any set of samples after 7 days of curing was 1525 psi for 20% replacement level with Dave Johnston fly ash. The Laramie River fly ash at the 20% replacement level produced the highest strength (2900 psi) after 28 days of curing. Relative to the CTB control mix (0% fly ash replacement), fly ash containing CTB mix strengths increase as the fly ash replacement percentage of portland cement increases to approximately 40 to 55% fly ash replacement, and then decrease at higher fly ash replacement percentages. Strengths at 28 days were in excess of the control CTB mix for fly ash replacements of 40% for Dave Johnston, 40% for Naughton, and 65% for Laramie River.

In the durability testing, all freeze-thaw and wet-dry samples performed well enough to sustain less than 14% sample loss over the duration of the test cycles (Table 4). The Dave Johnston fly ash performed the poorest with failing results past the 55% replacement level for the standard freeze-thaw test. The Laramie River fly ash performed well in all tests and may be usable for replacement levels beyond 75%.

if the compressive strength is not of concern. Naughton fly ash performed significantly better than Dave Johnston fly ash, but not quite as well as the Laramie River material.

The resilient modulus was determined for all fly ash types at 0, 20, 40, and 55% replacement levels after 7 days of curing. The resilient modulus test results showed several significant features about the effect of fly ash. Table 4 indicates that the resilient modulus for all samples was greater than 1,600,000 psi. Naughton fly ash had the highest average resilient

modulus value of all the fly ashes tested, although it did not demonstrate the highest compressive strength. Dave Johnston fly ash had the lowest average resilient modulus overall. As the percentage cement replacement was increased the resilient modulus decreased, but at a slower rate than the compressive strengths. Although the relationship between compressive strength and resilient modulus is apparent, it also appears that the addition of fly ash to the samples has a positive effect on the overall resistance of CTB to plastic deformation under repeated loads.

Table 4. Summary of the Results of the Cement Treated Base Testing

Fly Ash Source	Unconfined Compressive Strength 7 days, psi	Unconfined Compressive Strength 28 days, psi	Wet/Dry 12 Cycles weight loss, %	Freeze/Thaw 12 Cycles weight loss, %	Resilient Modulus psi x 10 ⁶
<u>Cement Only</u>					
(8% Cement)	532	1373	0.5	3.5	1.87
<u>Dave Johnston</u>					
20% Replacement	1532	2809	1.5	0	1.92
40% Replacement	927	1900	3.5	2.5	1.39
55% Replacement	573	1084	6.0	9.0	1.36
65% Replacement	366	736	9.5	14.0	nd
75% Replacement	271	501	8.0	55.5	nd
<u>Naughton</u>					
20% Replacement	1126	2380	1.0	0	1.97
40% Replacement	780	1956	2.5	4.0	1.85
55% Replacement	577	979	6.5	4.5	1.75
65% Replacement	422	951	7.0	6.5	nd
75% Replacement	287	589	6.5	7.0	nd
<u>Laramie River</u>					
20% Replacement	1329	2944	0	0	1.68
40% Replacement	951	2447	2.0	1.5	1.46
55% Replacement	545	1453	6.5	6.5	1.39
65% Replacement	422	1429	9.0	6.5	nd
75% Replacement	346	1098	7.5	7.0	nd

nd = not determined

In the road stabilization demonstration, samples were taken from the road to examine the effectiveness of the construction procedure and the geotechnical properties of the road. Visual monitoring of the road showed that some areas required remedial attention due to inadequate mixing of the fly ash and soil, and insufficient water addition during construction. Soft spots in the road as a result of high fly ash content, were patched to reduce dusting and to improve the road surface. The test sections were dusting because either insufficient water was added during construction or the fly ash mixtures dried out before sufficient curing could occur. The treated sections were covered with bottom ash to act as a moisture barrier and armor to the surface. The barrier was successful, but the bottom ash developed severe washboarding. As a result, the bottom ash was removed after the fly ash-soil mixture achieved sufficient strength and durability. Additional water applications helped develop a hard, upper 2- to 3-inch surface in the fly ash-treated section of the road.

Performance monitoring and evaluation of the construction techniques show that mixing was inadequate, whereas compaction appeared to be satisfactory. Fly ash distribution via blade mixing did not produce a homogeneous mixture, although improvement may have been possible if additional passes had been performed. Evidence for both lateral variations in the test section from 15 to 50% fly ash and a vertical layering in the treated section have been documented. Inadequate water distribution due to improper mixing was also noted as evidenced by the fact that areas were found that appeared to have received little or no water. Compaction of the fly ash-treated soil mixtures was in the range of 95% of the laboratory results and the estimated maximum dry density.

The performance of the fly ash-treated section was quite good, showing continued strength development and reduced potential for dusting. The poorly mixed areas showed deterioration in the spring of 1992 and were subsequently removed. The

fly ash treatment slowed the formation of washboards; however, washboarding did subsequently occur.

Conclusions

The laboratory testing program and the field demonstration of the fly ash stabilization process appears to be promising. The CTB testing was quite successful and the Wyoming Department of Transportation is prepared to jointly pursue a field demonstration of the high fly ash replacement of cement in CTB. The fly ash stabilization technique appears to hold promise in the stabilization of unpaved roads. However, the performance is very sensitive to the fly ash properties and improved construction techniques need to be developed for such applications.

The strength development of the fly ash-soil mixture does not have to be high to reduce washboarding of the unpaved roads. Lower fly ash treatment percentages may serve to control the development of washboarding. Future test sections need to be constructed to verify lower fly ash treatment percentages. Lower fly ash treatment percentages should also reduce the dust generation and lower the costs of construction.

New methods of testing and predicting the performance of fly ash treatment in the laboratory need to be developed to predict the performance in the field. The current specifications for soil-cement treatment requiring 400 psi unconfined compressive strength at 7 days does not appear to adequately reflect the requirements for the fly ash treatment of unpaved roads. Appropriate design methods and specifications need to be developed and validated.

New methods of applying the fly ash to the scarified road need to be developed and demonstrated. The dust generation associated with pressurized tank-truck discharge techniques is clearly unacceptable. The use of low-pressure spray bars as used with lime spreading and/or accompanied with water for dust

control need to be examined and demonstrated. The reduction in the level of ash treatment will also assist in the reduction of fugitive dust with future demonstrations.

Improved methods of mixing of the fly ash, water, and soil during construction are needed to ensure adequate dispersion of the reactive components. The lack of adequate mixing with the scarifying and blade mixing alone implies the need to examine alternative methods, such as the pulverizer-mixers or rotary tillers commonly used in soil-cement applications. The benefits and costs associated with mobile, central processing facilities need to be evaluated.

Additional fly ash types and soil types need to be tested to determine the range of performance, both in the laboratory and the field. The development of design and construction guidelines needs to be based on this data. Additional laboratory tests and field demonstration test sections are necessary.

The applicability of this technique to other roads, such as mine haul roads, may significantly reduce maintenance costs for these roads. These applications need to be addressed in future field demonstration activities.

Related Publications

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HAZARDOUS WASTE STABILIZATION UTILIZING CLEAN COAL COMBUSTION WASTE MATERIALS

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Background

The implementation of innovative clean coal technologies (ICCT) to reduce SO_2/NO_x emissions from coal-fired power plants has resulted in a new generation of solid waste materials that must be disposed. The use of ICCT wastes for hazardous inorganic and organic waste stabilization may be an effective alternative that could reduce the cost of conventional disposal. The high alkalinity of ICCT wastes may result in a significant reduction in the mobility of many heavy metals. Further, ICCT wastes may contain solids that can sorb organic compounds. In addition to being highly alkaline, some ICCT wastes may also possess environmentally deleterious properties, such as high leachate salinity, sodium, boron, and selenium levels. Combination of ICCT wastes with other types of waste materials may mitigate some of these problems that are associated with ICCT waste disposal. Thus, co-disposal of ICCT wastes with hazardous inorganic and organic waste materials may be an effective means of waste stabilization.

Objective

The objective of this research was to evaluate the ability of solid waste products from clean coal technology combustion processes to stabilize hazardous organic and/or inorganic waste. To perform the evaluation, a laboratory study was conducted with support from EPRI.

Procedures

The ICCT materials used in this study were: (1) Tennessee Valley Authority (TVA) Atmospheric Fluidized Bed Combustor (AFBC) waste, (2) TVA Spray Dryer (SD) waste, (3) Laramie River Station SD waste, and (4) Colorado-Ute AFBC waste. Four types of hazardous waste stream materials were chemically characterized for use in evaluating the ability of the ICCT wastes to

stabilize hazardous organic and inorganic wastes. The wastes were an API separator sludge, mixed metal oxide-hydroxide waste, metal-plating sludge, and creosote-contaminated soil.

The evaluation involved (1) characterizing hazardous waste materials and waste products from clean coal technology combustion processes, (2) evaluating the ability of the ICCT waste to stabilize the hazardous waste material using waste mixing ratio methodology, (3) studying the effects of simulated weathering on mixtures of ICCT wastes and hazardous wastes, (4) characterizing the mineralogical properties of ICCT waste and hazardous waste mixtures, and (5) investigating the use of solid-state ^{13}C NMR to study the bonding interactions between the ICCT waste and hazardous waste materials.

Each of the wastes was blended for 6 hours in a batch mixer equipped with paddle-style blades to homogenize the material. A random sample was then taken for TCLP characterization and total metals characterization by digestion and analysis using inductively coupled plasma (ICP) spectrometry and atomic absorption spectrometry. In addition, the API separator sludge and creosote-contaminated soil were analyzed for their semivolatile and volatile compounds. Volatiles were determined using EPA Method 824. Each of the wastes was also characterized by the TCLP for the RCRA metals, and the API separator sludge and creosote-contaminated soil TCLP extracts were analyzed for semivolatile and volatile compounds.

Mixtures of the four hazardous wastes with the Colorado-Ute AFBC ash and TVA spray dryer waste were prepared using six different ratios for each solid-to-solid mixture. The mixtures that were prepared

were 20% clean coal waste/80% hazardous waste, 50% clean coal waste/50% hazardous waste, 75% clean coal waste/25% hazardous waste, 90% clean coal waste/10% hazardous waste, 100% clean coal waste, and 100% hazardous waste. The mixtures were equilibrated for 7 days. At the end of the equilibration period, deionized, distilled water was added to each mixture and filtered. The resulting filtrates were analyzed for the hazardous chemical constituents of interest.

Simulated nonequilibrium weathering experiments using a humidity cell were conducted to characterize the behavior of organic and inorganic hazardous/ICCT waste mixtures under oxidizing nonequilibrium conditions. The procedure that was followed for the humidity cell experiments and a description of the apparatus are discussed by Caruccio (1968) and Sullivan et al. (1988). The leachate sample was split: one sample was acidified to pH 2 with HNO_3 and subjected to metals analysis by ICP spectrometry and the other sample was subjected to organic analysis.

Modified-batch equilibrations were conducted to characterize the behavior of organic and inorganic hazardous waste/ICCT waste mixtures and ICCT wastes under oxidizing equilibrium conditions. At the end of the equilibration period, the solution phase was separated from the solid by centrifugation and filtration. The solution was split: one sample was acidified to pH 2 with HNO_3 and subjected to metals analysis by ICP and the other sample was subjected to organic analysis.

At the completion of the equilibrium and nonequilibrium weathering studies, the solids from the hazardous/ICCT waste mixtures were subjected to TCLP extraction to assess the regulatory status of the weathered waste mixtures.

Results

Chromium was leached from both the Laramie River Station SD and TVA SD wastes. Thus, these materials cannot be

used to stabilize hazardous materials containing chromium, such as metal plating sludge. However, the four ICCT wastes can be used to stabilize cadmium found in the metal oxide-hydroxide hazardous waste.

In general, it was found that the mixtures of the ICCT wastes with the API separator sludge and creosote-contaminated soil were too complex for initial evaluation of the ability of the ICCT wastes to stabilize hazardous waste.

Simulated weathering experiments were performed using mixtures of TVA AFBC/metal oxide-hydroxide, Colorado-Ute AFBC/metal oxide-hydroxide, and TVA AFBC/API separator sludge. Evidence for stabilization of cadmium over time in the metal oxide-hydroxide mixtures and stabilization of organics in the mixture of the API separator sludge were observed.

X-ray diffraction and scanning electron microscopy/energy dispersive X-ray analyses were performed on a number of ICCT wastes and hazardous wastes mixtures. Quartz and ettringite were the most dominant minerals phase in most of the mixtures. Other minerals identified include gypsum, portlandite, and calcite.

Solid-state ^{13}C NMR was used to investigate the adsorption of pentachlorophenol on TVA AFBC waste. A downfield chemical shift of the phenolic carbon resonance in pentachlorophenol was observed when adsorbed on the TVA AFBC waste relative to the "free" solid-state position.

Conclusions

For all four ICCT wastes mixed with the metal oxide-hydroxide waste, no cadmium was detected in the leachates from any of the ratio mixtures. Thus, mixing the metal oxide-hydroxide waste with the clean coal wastes appears to reduce the leachability of cadmium from the waste.

Semivolatile analyses were performed on the filtrates from ratio mixtures of the four

ICCT wastes, with the API separator sludge. Alkane substituted pyridine compounds were detected in some ratio mixtures but not others. It is postulated that the higher carbon content of the AFBC ash may have some effect on the solubility of the pyridine compounds. But because of the chemical complexity of the API separator sludge, no conclusions concerning stabilization of the sludge by the ICCT wastes can be made.

The results obtained from the ratio mixtures involving the API separator sludge and creosote-contaminated soil indicate that real world organic wastes are too complex. However, it can be concluded that the basic characteristics of the ICCT wastes may be used to stabilize acidic components of hazardous wastes.

For the nonequilibrium weathering experiments, cadmium was not detected. However, an increase in chromium in the leachates was observed after the sixth week.

Modified-batch equilibrium studies of mixtures of the ICCT wastes with the hazardous wastes indicated no organic priority pollutants in any of the leachate samples. The concentration of identified organics (carboxylic acid and/or esters) in the leachates decreased over a sampling period of 6 months.

X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray techniques were used to study the mineralogy of mixtures of ICCT ashes and hazardous wastes. Ettringite was found to be the most abundant phase. Calcium, silicon, and sulfur were the dominant elements identified. Mineralogically, samples of the TVA AFBC waste mixed with the API separator sludge waste were found to be similar to samples of the TVA AFBC/metal oxide-hydroxide mixture.

However, four mineral phases were tentatively identified in the TVA AFBC/API separator sludge samples that were not found in any mixtures of the TVA AFBC ash/metal oxide-hydroxide waste. Elemental analyses show that calcium, silicon, and sulfur are again the major components of the TVA AFBC/API separator sludge samples. It was found that quartz was the dominant phase identified in samples of the Colorado-Ute ICCT waste mixed with the metal oxide-hydroxide hazardous waste. Other major phases identified were calcite and ettringite. Calcium, silicon, sulfur, and aluminum were the elements identified in these samples.

Solid-state ^{13}C NMR spectra were obtained for pentachlorophenol adsorbed on TVA AFBC ICCT waste. These preliminary experiments have shown that hazardous waste material can be directly observed on the ICCT waste and that changes in the chemical shift of the phenolic carbon of pentachlorophenol should be a measure of the bonding strength between the two waste materials. However, additional NMR experiments are needed to properly assess the technique as a means to study adsorption properties of hazardous wastes and ICCT wastes.

Related Publication

Netzel, D.A., D.C. Lane, M.A. Brown, K.A. Raska, J.A. Clark, J.F. Rovani, 1993, Organic and Inorganic Hazardous Waste Stabilization Utilizing Fossil Fuel Combustion Waste Materials. Laramie, WY, WRI-93-R031.

DEVELOPMENT OF A HYDROLOGIC DATA MANAGEMENT SYSTEM

Verne E. Smith

Background

Western Research Institute developed a preliminary hydrologic data management system for the Wyoming Department of Environmental Quality (WDEQ). That system was used by WDEQ to determine the probable and actual impact of individual surface coal mines, assess the cumulative hydrologic impact of surface coal mining within a structural basin, verify the quality of monitoring data submitted by the mining companies, decrease the time required to evaluate surface coal mine permit applications, and improve the quality of permit evaluations.

Objective

The objective of this task was to develop an overlay to the hydrologic data management system that provides menu-driven access to the data and data entry forms. Matching financial support for this study was provided by WDEQ.

Procedures

A menu interface was developed that allows both data entry and retrieval. The original data management system was developed using the data base software package, ORACLE. The menu interfaces were developed using the ORACLE utility, SQL*MENU. User documentation was done using the word processor, MASS11.

Results

A hydrologic data base management system was enhanced for use on an IBM-compatible 386 or higher personal computer. The system provides for fast and easy interface to store and retrieve hydrologic data from surface coal mines in Wyoming. The system stores surface and groundwater quality data, aquifer test data, groundwater elevation data, and surface water flow data. It also contains sampling station location and other descriptive information. Users have the option to view retrieved data on a screen, print it on a printer, send it to a file, or send it to a spreadsheet.

Related Publication

Barteaux, W.L., 1992, Hydrologic Data Management System. Laramie, WY, WRI-92-R043.

CHARFUEL® PROCESS

Western Research Institute's work with Carbon Fuels of Wyoming is complete and an agreement has been reached between WRI and Carbon Fuels of Wyoming with respect to the work performed. Use of the

Glenrock Coal in an electrically heated isothermal system did not produce data applicable to commercialization of the Charfuel® process.

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