

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.

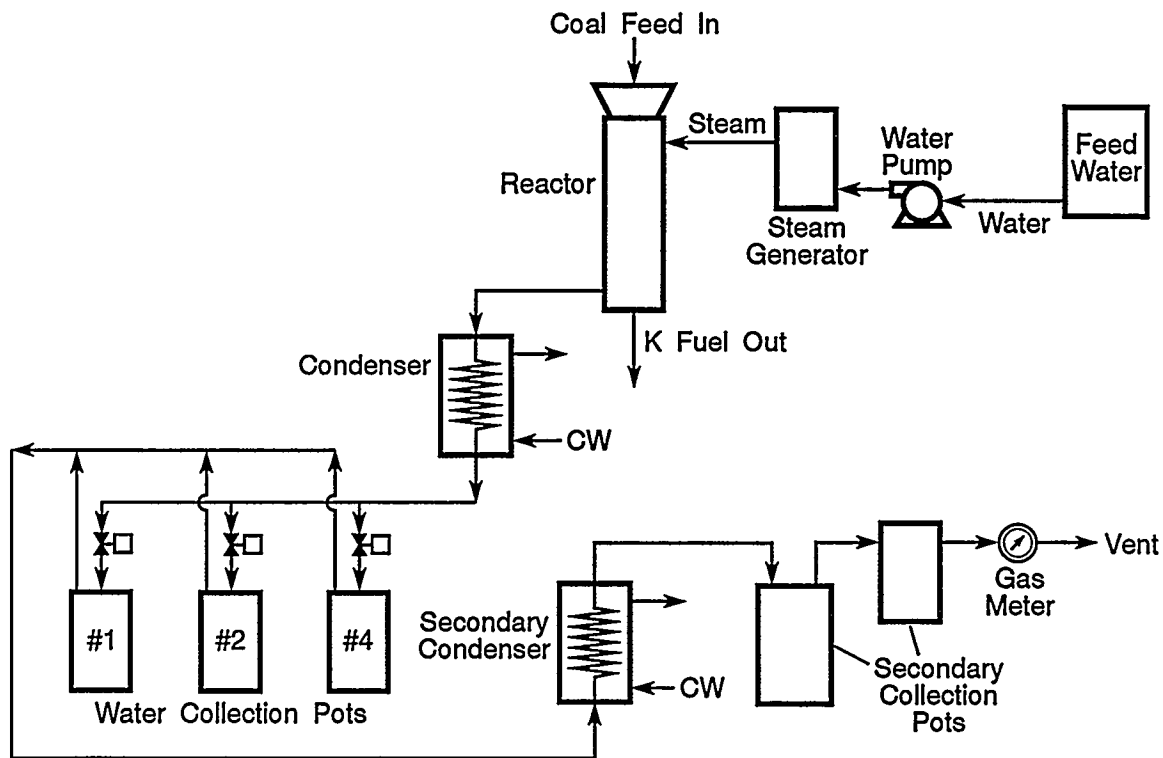


Figure 1. Schematic Diagram of Series B Process

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

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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 (O₂, CO₂, CO, NO_x, and SO₂) 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 SO₂ 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 ₂ O	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

<u>Element</u>	<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.

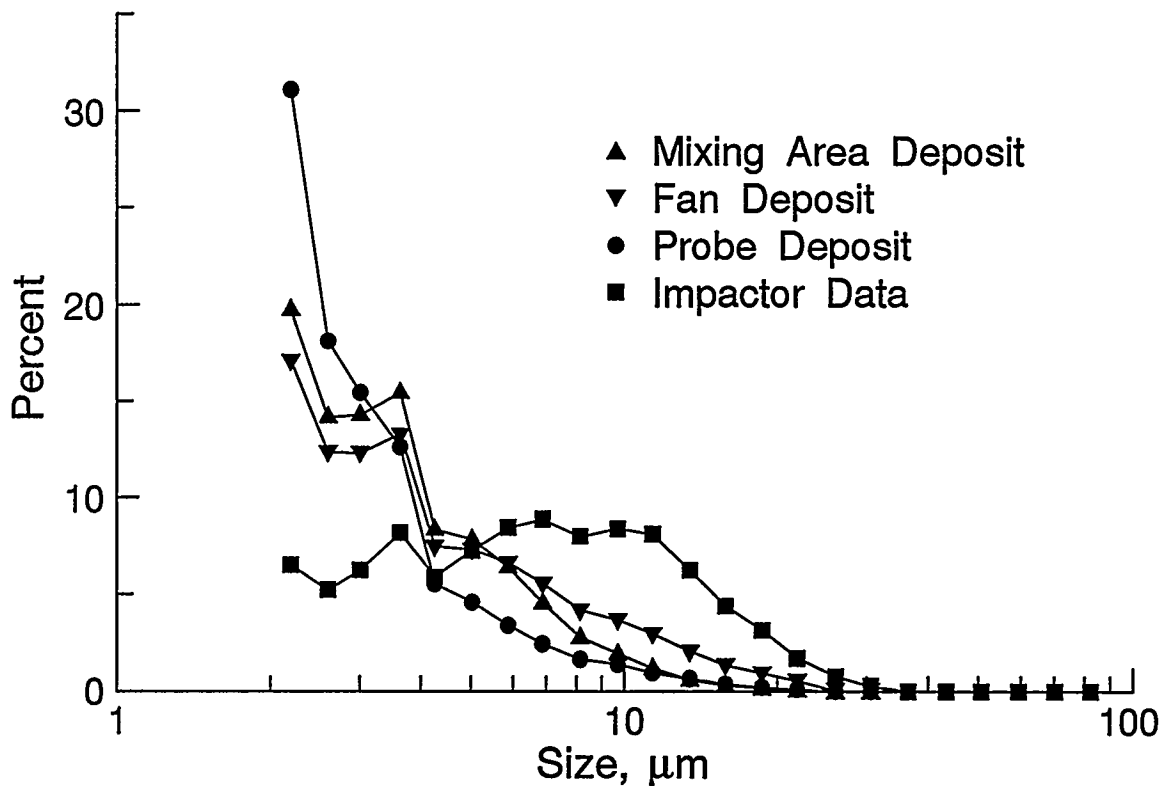


Figure 1. Particle Size Distribution of Deposits from the Air-Cooled Probe and Downstream Components

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 469°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 ROPE™ PROCESS PERFORMANCE ON SUNNYSIDE TAR SAND

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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 (ROPE™) 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 benefited 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: 33-000004-56 and report to DOE, WRI-92-R058.

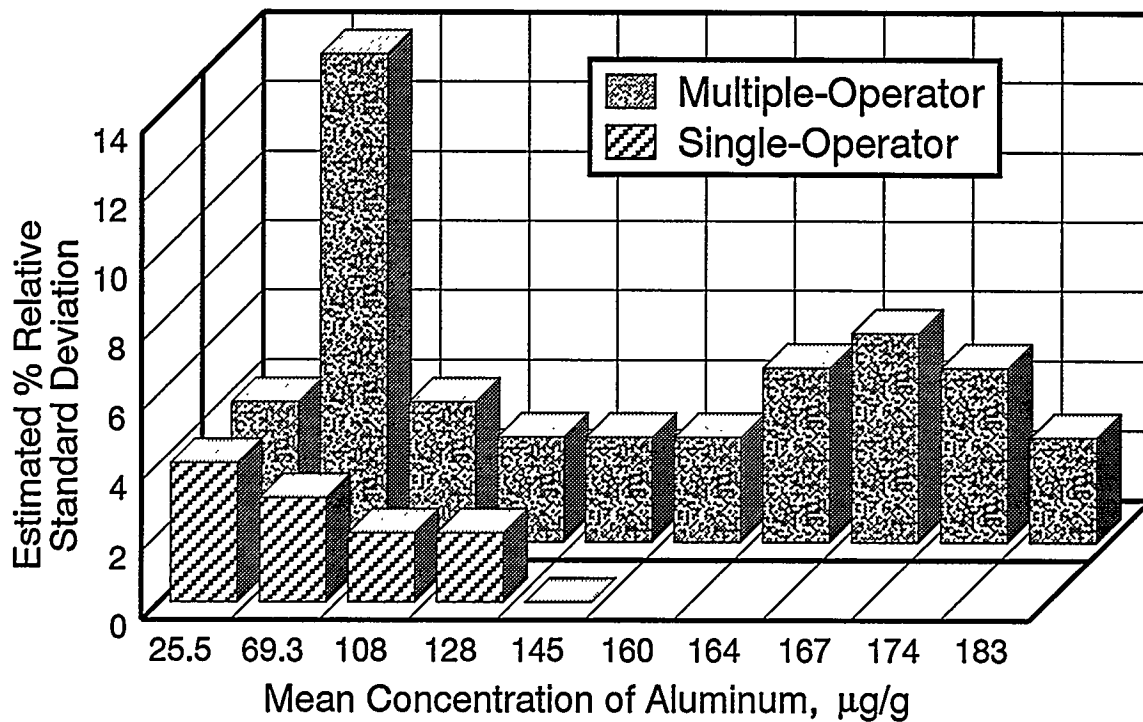


Figure 1. Estimated Precision of the Sequential Batch Extraction Method for Aluminum in the Spray Dryer Waste

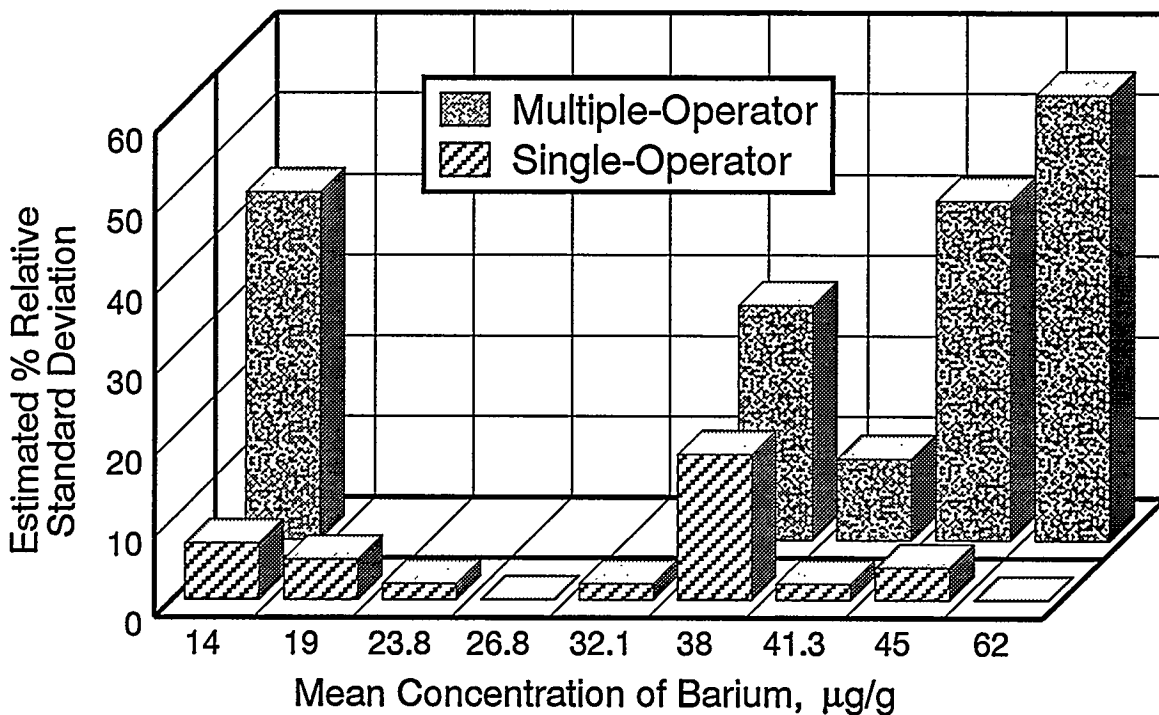


Figure 2. Estimated Precision of the Sequential Batch Extraction Method for Barium in the Spray Dryer Waste

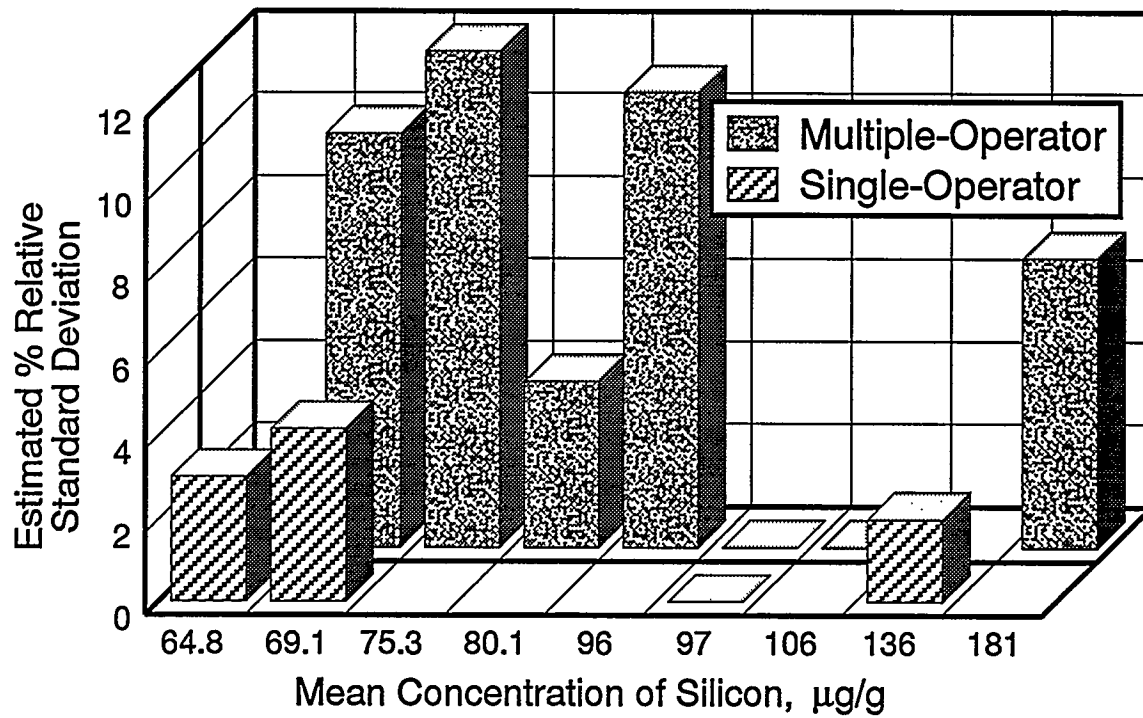


Figure 3. Estimated Precision of the Sequential Batch Extraction Method for Silicon in the Spray Dryer Waste

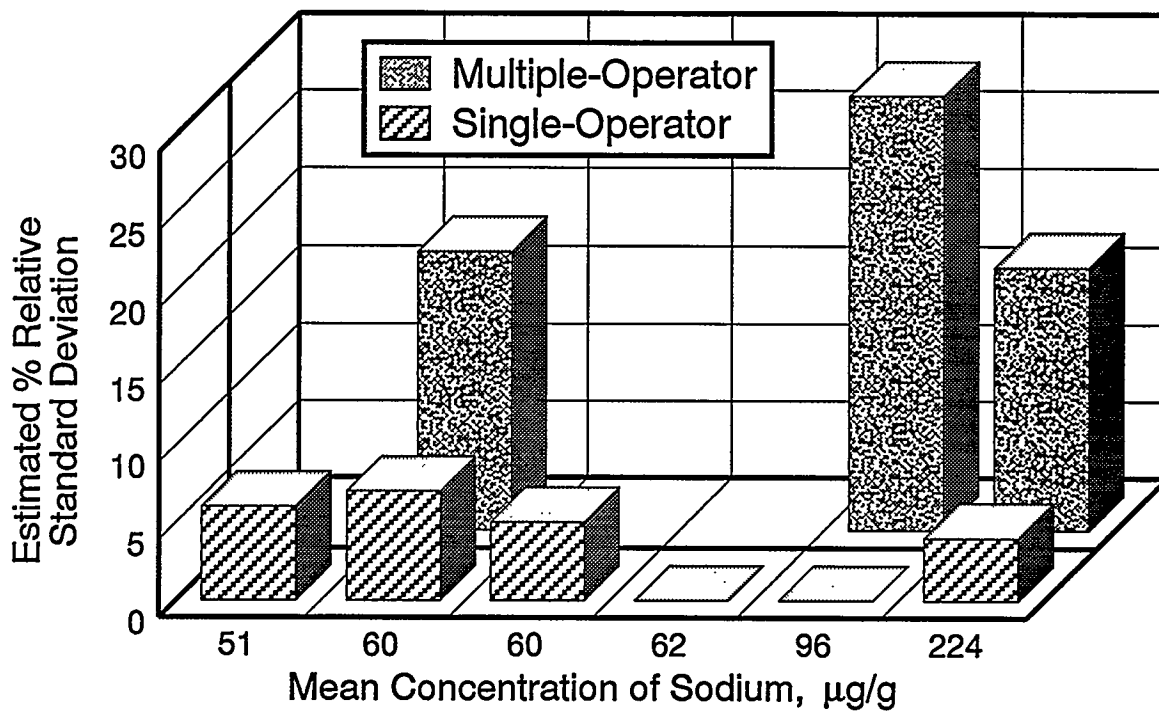


Figure 4. Estimated Precision of the Sequential Batch Extraction Method for Sodium in the Spray Dryer Waste

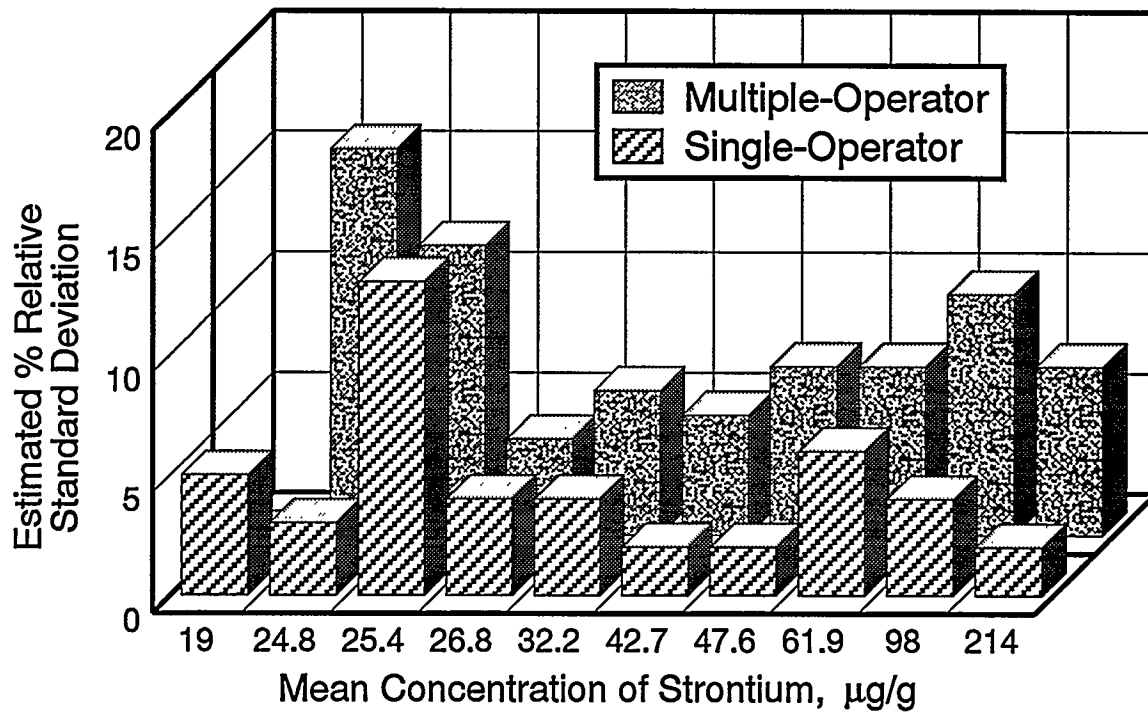


Figure 5. Estimated Precision of the Sequential Batch Extraction Method for Strontium in the Spray Dryer Waste

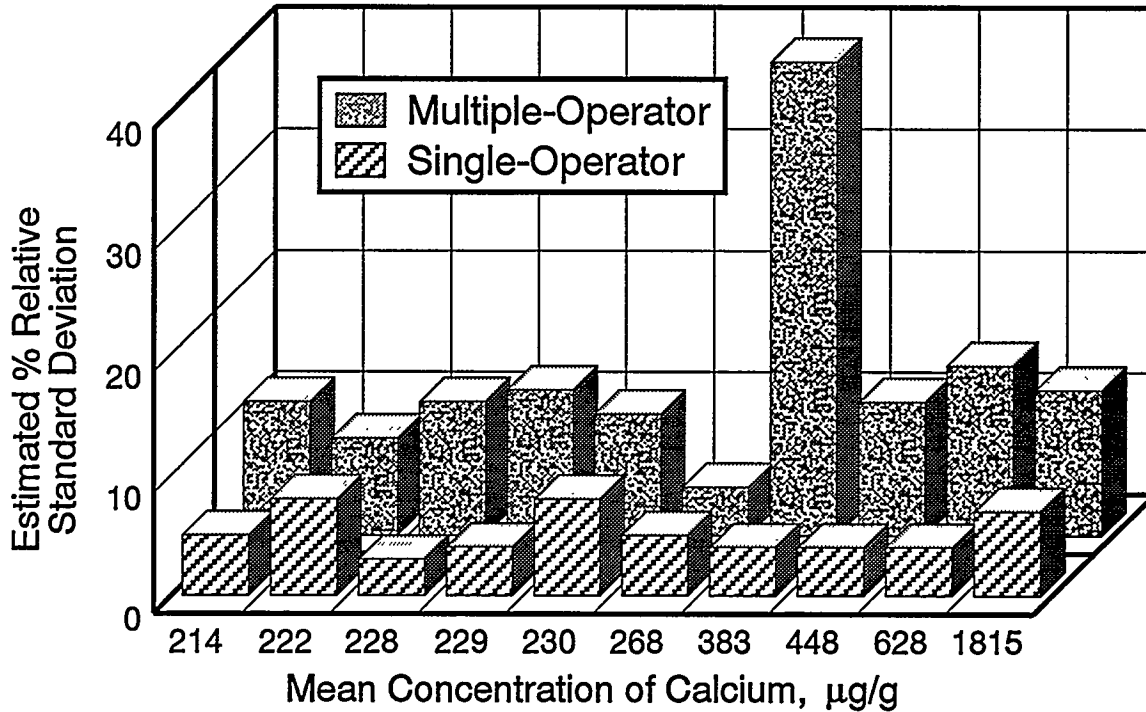


Figure 6. Estimated Precision of the Sequential Batch Extraction Method for Calcium in the Composite Mining Waste

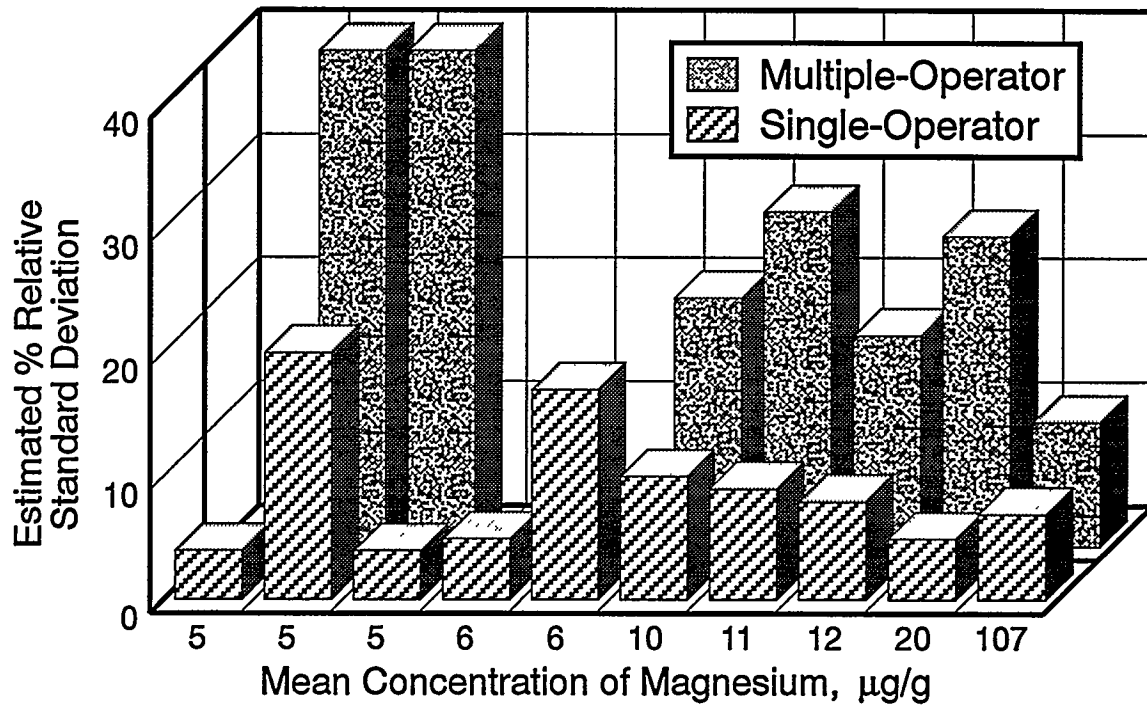


Figure 7. Estimated Precision of the Sequential Batch Extraction Method for Magnesium in the Composite Mining Waste

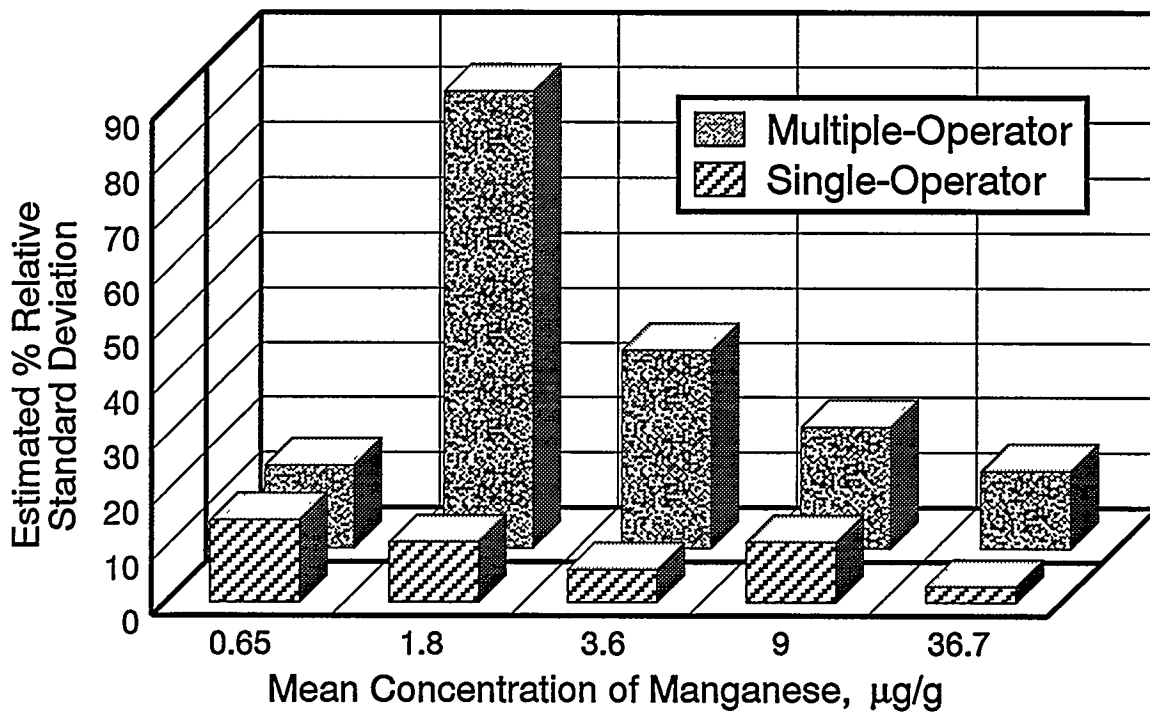


Figure 8. Estimated Precision of the Sequential Batch Extraction Method for Manganese in the Composite Mining Waste

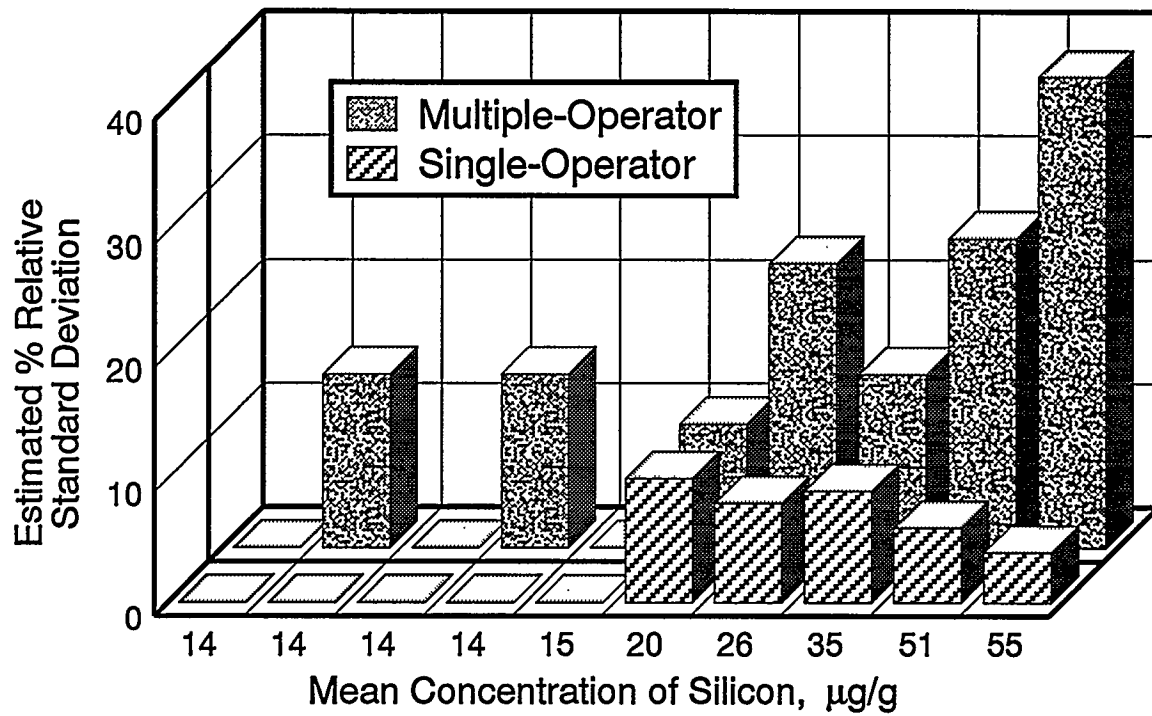


Figure 9. Estimated Precision of the Sequential Batch Extraction Method for Silicon in the Composite Mining Waste

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

Publications

MacGowan, D.B., D.R. Britton, F.P. Miknis, and R.C. Surdam, 1992, Organic Geochemistry and Maturation Trends of Shales and Coals, Almond Formation, Mesaverde Group, Greater Green River Basin, Wyoming: A Comparison With Laboratory Maturation of Almond Coals by Hydrous Pyrolysis. Wyoming Geological Association Guidebook, 43rd Field Conference, C.E. Mullen, ed., Pioneer Printing Cheyenne, WY.

MacGowan, D.B., Z.-S. Jiao, R.C. Surdam, and F.P. Miknis, 1993, Normally-Pressured vs. Abnormally Pressured Sandstones in the Powder River Basin Wyoming: A Comparative Study of the Muddy Sandstone and the Minnelusa Formation. Wyoming Geologic Association Guidebook,

50th Anniversary Field Conference, B. Stroock and S. Andrew, eds., 281-295. Also in GRI Final Report, GRI Contract GRI-5089-1894, GRI-92/0483, p. 89-104.

MacGowan, D.B., Z.-S. Jiao, R.C. Surdam, and F.P. Miknis, 1994, Formation Water Chemistry of the Muddy Sandstone and Organic Geochemistry of the Mowry Shale, Powder River Basin, Wyoming: Evidence for Mechanism of Pressure Compartment Formation. AAPG Memoir, P.J. Ortoleva and Z. Al-Shaeib, eds., in press.

Miknis F.P. 1992, Solid-State NMR Characterization of Mowry Shales. Laramie, WY, WRI-92-R025

Miknis F.P., 1993, Solid-State ^{13}C NMR Analyses of Samples from Leg 139 of the Ocean Drilling Program. Laramie, WY, WRI-93-R011.

Miknis, F.P., 1993, Solid-State NMR Analysis of Mowry Formation Shale from Different Sedimentary Basins. Laramie, WY, WRI-93-R040.

Miknis F.P., and D.B. MacGowan, 1993, Solid-State NMR Analysis of Coals and Oil Shales from the Mesaverde Group, Greater Green River Basin, Wyoming. Laramie, WY, DOE/MC/11076-3554.

Miknis F.P., D.B. MacGowan, and R.C. Surdam, 1993, Solid-State NMR Analysis of Coal Hydrous Pyrolysis Residues. Proceedings 7th International Conference on Coal Science, K.H. Michaelin, ed., Vol II, 289-292.

Miknis F.P., Z.-S. Jiao, D.B. MacGowan, and R.C. Surdam, 1993, Solid-State NMR Characterization of Mowry Shale From the Powder River Basin. J. Org. Geochem., 20: 339-347.

Whelan J.K., J. Seewald, L. Eglinton, and F.P. Miknis, 1994, Time-Temperature Histories of Kerogen and Mineral Ammonia from ODP Leg 139 (Middle Valley) Sediments. Proceedings of the Ocean Drilling Project Results, M.J. Mottl, E.E. Davis, A.J. Fisher, J.P. Slack eds., vol 139, in press.

Yin, P. R.C. Surdam, S.W. Boese, D.B. MacGowan, and F.P. Miknis, 1993, Simulation of Hydrocarbon Source Rock Maturation by Hydrous Pyrolysis. Wyoming Geologic Association Guidebook, 50th Anniversary Field Conference, B. Stroock and S. Andrew, eds., 359-373.

Presentations

F.P. Miknis, 1992, Solid-State NMR Characterization of Mowry Shales. Confab 92, Winter Park, CO.

F.P. Miknis, D.B. MacGowan, and R.C. Surdam, 1993, Solid-State NMR Analysis of Coal Hydrous Pyrolysis Residues. 7th International Conference on Coal Science, Banff, Alberta.

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	56.30	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>					
Fineness,					
% retained 325 mesh	28.48	29.23	18.47	34 max	34 max
Pozzolan Activity Index					
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
Soundness					
Autoclave Expansion, %	-0.009	-0.045	-0.031	0.8 max	0.8 max
Reactivity with Alkalis					
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

Fly Ash Source	Unconfined Compressive Strength – Moisture Relationship				Moisture – Density Relationship			
	7-day Curing		28-day Curing		7-day Testing		28-day Testing	
	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 (A-1b)	Naughton	32.3	27.7	513,088
	Laramie River	18.0	24.9	310,640
RS-2	Naughton	32.8	32.3	494,003
	Laramie River	16.4	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 armoring 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

Bland, A.E., Brown, T.H., and Sheesley, D.C., 1991, Fly Ash use for Unpaved Road Stabilization: Phase I Interim Technical Report. Laramie, WY, WRI-92-R017.

Conklin, T.L. and Ksaibati, K., 1992, Laboratory Evaluation of Cement Treated Bases with Fly Ash. Final Report to WRI.

Conklin, T.L. and Ksaibati, K., Laboratory Evaluation of Cement Treated Bases with Fly Ash. Submitted to ASCE Journal of Transportation Engineering, December, 1992.

Turner, J.P., 1993, Soil Stabilization Using Wyoming Fly Ash: Laboratory Evaluation of Engineering Properties. Final Report to WRI.

HAZARDOUS WASTE STABILIZATION UTILIZING CLEAN COAL COMBUSTION WASTE MATERIALS

Daniel A. Netzel

Background

The implementation of innovative clean coal technologies (ICCT) to reduce SO₂/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 ¹³C 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 624. 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 HNO₃ 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 HNO₃ 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 ¹³C 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.

REFERENCES

- American Society for Testing and Materials, 1991, D 2777-86, Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water. Annual Book of ASTM Standards, 11.01: 31-44.
- American Society for Testing and Materials, 1992, D 3987-85, Standard Test Method for Shake Extraction of Solid Waste with Water. Annual Book of ASTM Standards, 11.04: 139-147.
- American Society for Testing and Materials, 1993, D 5284-93, Standard Test Method for Sequential Batch Extraction of Waste with Acidic Extraction Fluid. Annual Book of ASTM Standards, 11.04.
- Bleakley, W.B., 1964, Here Are Case Histories of Two Thermal Projects. Oil and Gas J., October 26, 123-130.
- Caruccio, F.T., 1968, An Evaluation of Factors Affecting Acid Mine Drainage Production and the Groundwater Interactions in Selected Areas of Western Pennsylvania. Pap. Symp. Coal Mine Drain. Res., 2: 107-152.
- Cha, C.Y., F.D. Guffey, and L.J. Romanowski, 1987, Tar Sand Pyrolysis with Product Oil Recycling--Progress Report. Laramie, WY, DOE/MC/11076-2642.
- Chu, C., 1977, A Study of Fireflood Field Projects. J. of Pet. Tech., February.
- Chu, C., 1982, State-of-the-Art Review of Fireflood Field Projects. J. of Pet. Tech., January.
- Chu, C., 1985, State-of-the-Art Review of Steamflood Field Projects. J. of Pet. Tech., October.
- Cooper, J.L. and L.L. Moresco, 1981, Alkali Control in Fluid Bed Combustion Systems at CPC. Proceedings, High Temperature, High Pressure Particulate and Alkali Control in Coal Combustion Process Streams, DOE/MC/08333-167.
- Durrant, A.J., and Thambynayagam, R.G.M., 1986, Wellbore Heat Transmission and Pressure Drop for Steam/Water Injection and Geothermal Production, A Simple Solution Technique. SPE Res. Eng., 1(2): 148-162.
- Fahy, L.J., L.A. Johnson Jr., D.V.Sola, S.G. Horn, and J.L. Christofferson, 1992, Bell Pole CROW Pilot Test Results and Evaluation. Proceedings of Colorado Hazardous Waste Management Society Annual Conference, 15 p.
- Farouq Ali, S.M., 1981, A Comprehensive Wellbore Steam/Water Flow Model for Steam Injection and Geothermal Application. J. of Pet. Tech., 33(10): 527-534.
- Geffen, T.M., 1973, Oil Production To Expect From Known Technology. J. of Pet. Tech., May.
- Gordon, G.E., 1987, A Decade of Acid Rain Research. The Chemistry of Acid Rain, ACS Symposium Series 349, American Chemical Society, Washington, DC, 2-9.
- Hamrick, J.T., 1991, Development of Biomass as an Alternative Fuel for Gas Turbines. PNL-7673, April.
- Iyoho, A.W., 1978, Selecting Enhanced Oil Recovery Processes. World Oil, November.
- Johnson, C.T.L., 1973, Environment of Deposition of the Pennsylvanian Bartlesville Sandstone, Labette County, Kansas. Geology Masters Thesis, Texas A&M University.
- Johnson, L.A., Jr., and F.D. Guffey, 1990, Contained Recovery of Oily Wastes (CROW) - Final Report. U.S. Environmental Protection Agency Assistance Agreement CR-815333, RREL, Cincinnati, OH.

Johnson, L.A., Jr., and A.P. Leuschner, 1992, The CROW Process and Bioremediation for In Situ Treatment of Hazardous Waste Sites, In Hydrocarbon Contaminated Soils and Groundwater. Vol.2, E.J. Calabrese and P.T. Kosteki eds., Lewis Publishers, Ann Arbor, MI, 343-356.

Lewin and Associates, Inc., 1976, The Potential and Economics of Enhanced Oil Recovery. Federal Energy Administration, Report B76/221.

Nelson, T.W. and McNeil, J.S., Jr., 1959, Thermal Methods Provide Three Ways to Improve Oil Recovery. Oil and Gas J., January.

Poettmann, F.H., 1964, In Situ Combustion: A Current Appraisal. World Oil, Part 1, April, Part 2, May.

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

Sullivan, P.J., J.L. Yelton, and K.J. Reddy, 1988, Iron Sulfide Oxidation and the Chemistry of Acid Generation. Environ. Geol. Water Sci., 11: 289-295.

Taber, J.J., and F. D. Martin, 1983, Technical Screening Guides for the Enhanced Recovery of Oil. Presented at the 58th Annual Technical Conference and Exhibition of the SPE, San Francisco, SPE Paper No. 12069.

Thomas, G.W., 1963, A Study of Forward Combustion in a Radial System Bounded by Permeable Media. J. of Pet. Tech., October.

U.S. EPA, 1980, Extraction Procedure Toxicity Characteristic. Federal Register, May 19, 45: 33063-33285.

U.S. EPA, 1990, Toxicity Characteristic Leaching Procedure. Federal Register, March 29, 55: 11798-11877.