WET SCRUBBING FOR CONTROL OF PARTICULATE EMISSIONS FROM OIL SHALE RETORTING

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ABSTRACT

During a week-long field experiment in September 1980, a mobile pilot-scale venturi scrubber was tested for control of particulate emissions from the Laramie Energy Technology Center's 136-Mg(150-ton)-capacity oil shale retort. The entire retort off-gas flow of 15.4 m^3/min (545 ft^3/min), discharged from a heat exchanger at a temperature of 58°C and saturated with water, was scrubbed at liquid-to-gas ratios of 1.5 to 2.4 L/m^3. Sampling and analysis of the scrubber inlet and outlet gases were conducted to determine particulate removal. Outlet particulate concentrations were consistently reduced to 35 mg/m^3, even through inlet loadings varied from 125 to 387 mg/m^3 and 50 weight percent of the particles were less than four micrometers in diameter. Particulate control efficiencies up to 94 percent were achieved, although no correlation to liquid-to-gas ratio was observed. Simultaneous control of ammonia emissions, at efficiencies up to 75 percent, was also observed.

INTRODUCTION

Increasing dependence on foreign oil supplies and rapidly escalating oil prices have recently provided new incentive for oil recovery from shale deposits in Colorado, Utah, and Wyoming. At least four domestic firms (Colony Development Operation, Paraho Development Corporation, Superior Oil Company, and Union Oil Company) have developed surface retorting processes, in which oil shale is mined and crushed prior to thermal processing in aboveground facilities. *In-situ* or modified *in-situ* processes, where the shale bed is hydraulically or explosively fractured and retorting is carried out underground, are now being developed by Geokinetics, Inc., Cathedral Bluffs Shale Oil Company, and Rio Blanco Oil Shale Company.

Oil production by shale retorting has a number of benefits as an alternative energy source. However, byproduct gases containing a complex mixture of pollutants, if released uncontrolled, could have an adverse impact on the pristine air quality of the Rocky Mountain region. Therefore, pollution control methods capable of adequately reducing environmentally harmful discharges must be available to assure the emerging oil shale industry's compliance with future standards. The U.S. Environmental Protection Agency (EPA) has contracted with Monsanto Research Corporation (MRC) to characterize point-source air pollution due to surface and *in-situ* oil shale retorting, focusing on particulate emissions, and to evaluate available particulate control methods. Under a cooperative agreement between EPA and the U.S. Department of Energy (DOE)'s Laramie Energy Technology Center (LETC), a mobile venturi scrubber was tested for control of particulate emissions from a pilot-scale oil shale retort at a site in southeastern Wyoming.

LETC PILOT-SCALE RETORT

In 1969, a batch-type retort with the capacity to process 136 Mg (150 tons) of shale was constructed by the U.S. Bureau of Mines at a site near Laramie, Wyoming [1]. Figure 1 is a flow diagram of LETC's pilot-scale retort and auxiliary equipment [1]. Combustion of oil shale is initiated via a natural gas burner mounted on the retort lid. Air is forced downward through the shale bed, simulating vertical modified *in-situ* processes such as those being demonstrated by Cathedral Bluffs Shale Oil Company and Rio Blanco Oil Shale Company. Shale oil and byproduct water drain to a collection tank located near the retort. The retort off-gas, containing residual oil mist and water, is passed through a series of packed towers and then through a water-cooled heat exchanger in an attempt to remove the entrained material. After line pressure is increased by a positive-displacement blower, the gas stream can be split to allow for recycle. The excess is vented to a waste-gas stack equipped with a natural gas burner to oxidize combustible components before release to the atmosphere. Retorting continues until the bottom grate temperature increases to approximately 260°F, by which time shale oil production has already stopped and the oxygen content of the off-gases has begun to rise.

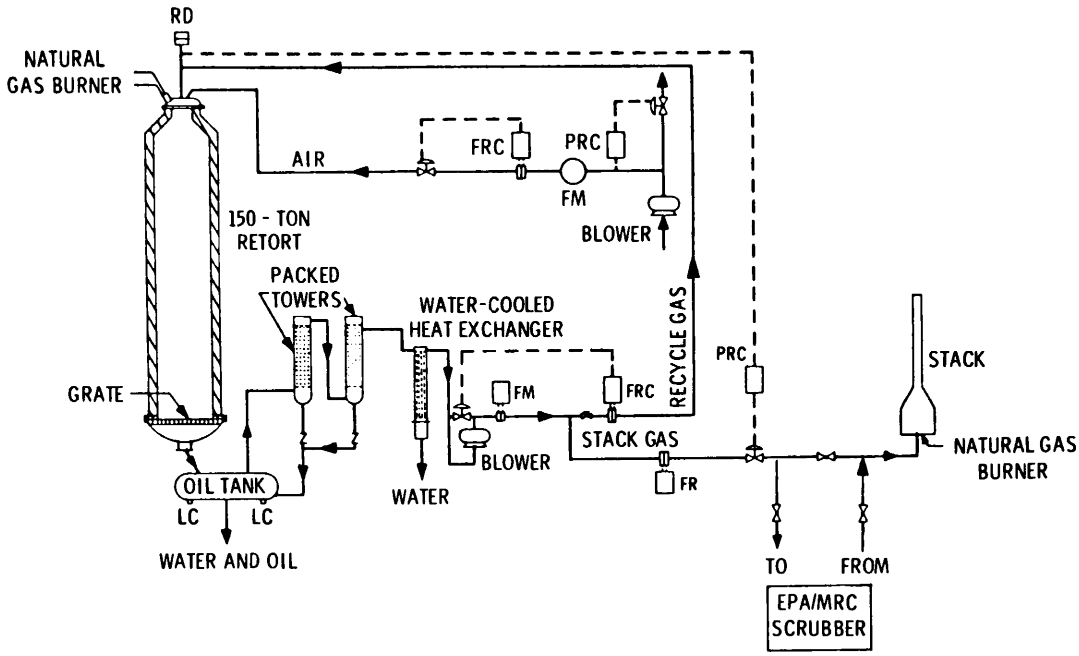

Figure 1. Gas and liquid flows in LETC's retort and auxiliary equipment [1].

Details of retort operation during Run 19, when the pilot scrubber test was conducted, are as follows. The shale retorted was medium-grade material, containing about 0.12 L/kg (28 gal/ton), taken from the DOE mine at Anvil Points, Colorado. A mixture of air and steam was injected to the retort at feed rates of 6.25 dry normal cubic meters per minute (dncm/min) and 0.92 kilograms per minute, respectively. Ignition and air input began at approximately 10:45 AM MDT, 8 September 1980; retorting continued until 12:30 AM MDT, 15 September 1980. Total oil recovery for the 5.5-day burn was 7.5 m^3 (47 barrels), equivalent to a production rate of 1.4 m^3 (8.6 barrels) per day. For comparison, commercial oil shale processing facilities may produce as much as 7,950 m^3 (50,000 barrels) per day, continuously, for 20 years or longer [2].

USE OF WET SCRUBBING

Technology Selection

During the first phase of EPA Contract 68-03-2784, MRC evaluated electrostatic precipitation, fabric filtration, and wet scrubbing relative to their potential ability to control particulate emissions from *in-situ* and surface retorting [2]. The utility of electrostatic precipitation in this application is questionable because of the lack of information on particle resistivity and because of the presence of flammable or explosive gases that represent a potential safety hazard. The formation of a porous dust cake necessary for high particulate removal efficiencies in fabric filtration equipment may be precluded by shale oil mist and possibly by condensed moisture in retorting off-gases. Unlike electrostatic precipitation, there is much less fire or explosion hazard associated with wet scrubbing of retort off-gases containing combustible species. Scrubbers also are preferable to baghouses because the former not only are effective for control of liquid or solid particles in high-temperature, moisture-laden gas streams, but also suitable for treatment of gas streams with fluctuating flow rate, temperature, or composition. Wet scrubbing also has the advantage that simultaneous particulate removal and absorption of gaseous pollutants can be accomplished using an appropriate liquid medium. Primarily based on these considerations, MRC recommended wet scrubbers for pilot-scale testing to study the control of particulate emissions from *in-situ* and surface oil shale retorting [2]. In an independent evaluation, DOE similarly decided that wet scrubbing would be the most effective technology for particulate emission control in the specific case of the LETC retort.

Design of EPA's Mobile Unit

For the pilot-scale particulate control test at Laramie, MRC used a venturi-cyclone scrubber housed in a standard freight trailer and developed by EPA as a mobile research unit. A schematic diagram of the mobile scrubber is given in Figure 2. Of the three interchangeable venturi throats provided with the mobile scrubber, the "medium" throat was used at Laramie. This throat has a diameter of 6.0 cm, a length of 30.5 cm, and two radially opposed liquid feed nozzles 5 cm below the throat entrance. Piping throughout the scrubber trailer, and that used for external hookup to the retort off-gas line, was 15-cm-diameter stainless steel. Because the gas stream treated at Laramie was saturated with moisture and its temperature relatively low, neither the presaturator shown in Figure 2 nor four banks of band heaters along the scrubber inlet line were needed.

Operation at Laramie

Existing retort ductwork was breached just upstream of the inlet to the thermal incinerator (see Figure 1), venting the entire gas flow to the mobile scrubber. In order to reduce any environmental contamination or worker exposure hazards associated with emissions of hydrocarbons and other gaseous pollutants, the scrubber outlet gases were piped to the incinerator. The retort off-gases treated had an average temperature of 58°C, an average moisture content of 21 percent by volume, and an average actual flow rate of 15.4 m^3/min (545 acfm), or 8.9 dncm/min (314 dscfm).

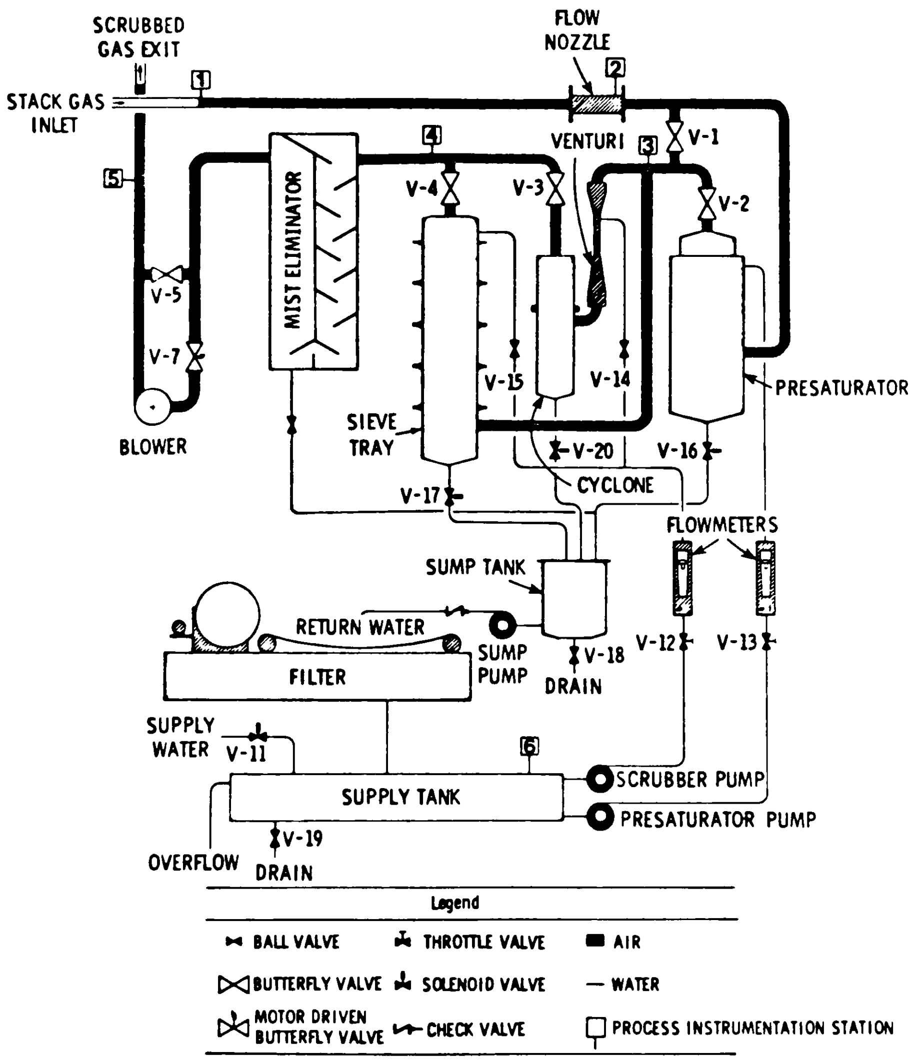

Figure 2. Schematic diagram of EPA mobile scrubber.

During the field testing, MRC varied the scrubbing liquid feed flow, and thus the liquid-to-gas (L/G) ratio, over a range typical of commercial installations. Table 1 describes the various operating conditions employed, in chronological order, specifying the volumetric feed rates and origin of scrubbing liquid, L/G ratios, and the pressure drops across the venturi scrubber and cyclone. Up to 19 L/min of well water was supplied by LETC, and the recycle consisted of scrubber discharge treated in a mobile stream stripping unit operated by the Denver Research Institute. Steam stripping was chosen to experiment with removal of organic compounds and dissolved gases, such as ammonia, carbon dioxide, and hydrogen sulfide, from the scrubber discharge water. Suspended solids were removed by a traveling-grate deep-bed filter mounted in the scrubber trailer. The temperature of the combined scrubber feed varied from 13°C to 43°C, due to heating during steam stripping, and the pH from 6 to 9, due to the uptake of basic dissolved gases.

SAMPLING AND ANALYSIS METHODS

The principal objective of gas and liquid sampling and analysis during the field test at LETC was to determine the particulate control efficiencies achievable when venturi scrubbing is applied to off-gases from oil shale retorting. Points sampled included the scrubber inlet and outlet for the gas phase and the scrubber feed and discharge water for the liquid phase. Equipment and procedures used to determine particulate loading were essentially those described in EPA Method 5 as outlined in the Federal Register [3]. The back half of the Method 5 sampling train was modified by including an XAD-2 resin trap between the filter and the impingers to collect organic vapors.

Because of the small duct diameter (15 cm), single-point sampling was used to determine the particulate loading in the retort off-gases, with the probe tip placed at the point of average velocity as determined by a detailed preliminary velocity traverse (EPA Method 1). Particulate mass, as specified by EPA Method 5, is reported as the sum of that collected on the filter and that rinsed from the probe and connecting glassware upstream of the filter. In addition, MRC measured the amount of "back half" residue rinsed from the downstream half of the filter holder and the glassware down to the XAD-2 resin trap.

Particle sizing data were collected using Andersen Mark III cascade impactors, including a preimpactor for separation of coarse particles [4]. Glass fiber collection substrates were used because the oily nature of the particulate might otherwise have caused problems of carryover from stage to stage. The isokinetic impactor sampling rate with a 3.2-mm-diameter nozzle was approximately 5.7 L/min (0.2 ft^3/min), and sampling durations were 10 and 20 minutes for the scrubber inlet and outlet, respectively.

A secondary objective of MRC's field effort in Laramie was to conduct a comprehensive characterization of air pollutants in retort off-gases from oil shale

Table 1. Scrubber Operating Conditions

Operation code[a]	Scrubbing liquid feed rates, L/min: Well water	Recycle	Total	L/G ratio, L/m^3 [b]	Pressure drop, kPa (in. H_2O)[c]
8A	11	19	30	2.0	8.0 (32)
10A	19	19	38	2.4	9.5 (38)
10B	0	38	38	2.4	9.5 (38)
6A	0	23	23	1.5	6.5 (26)
6A	0	23	23	1.5	6.5 (26)
10C	19	19	38	2.4	9.5 (38)
8B	15	15	30	2.0	8.0 (32)

[a] Numerals in codes indicate total scrubbing liquid feed rates (in gal/min).
[b] Calculated using average actual gas flow rate of 15.4 m^3/min (545 ft^3 min).
[c] Measured between inlet to venturi throat and outlet from cyclone mist eliminator.

processing. In addition to particulate loading and size distribution, scrubber inlet and outlet gases were sampled to measure concentrations of total hydrocarbons, low-molecular-weight hydrocarbon fractions, polycyclic organic matter (POM), carbon monoxide (CO), nitrogen oxides (NO_x), carbonyl sulfide (COS) and hydrogen sulfide (H_2S), ammonia (NH_3), and hydrogen cyanide (HCN). A variety of EPA-approved technniques, including absorption in reactive solutions and gas chromatography with flame ionization, flame photometric, and thermal conductivity detection, were used to make the above determinations.

This program also included an assessment of the particulate control technology's impact on water quality as part of the EPA-DOE interagency agreement. Measurements of the scrubber feed and discharge water composition aid in explanation of the stack sampling data. Because the primary objective of the Laramie test was to control particulate emissions, the water pollutant analysis matrix focused on solids loadings and oil and grease. A number of nitrogen- and sulfur-containing water pollutants were also measured in order to quantify absorption of gaseous compounds during scrubbing.

RESULTS AND DISCUSSION

Particle Size Distribution

MRC's measurements of the size distribution of particles emitted by LETC's retort represent the first such determination for that specific facility and one of only very few for the oil shale industry in general. An average distribution based on three measurements of particle size in the retort off-gases, that is, the scrubber inlet, is listed in Table 2. More than half the particulates, by weight, have a diameter less than four micrometers, with approximately 10 percent less than one micrometer in diameter. Also, the size distribution appears to be bi-modal, with the fractions larger than 20 micrometers (∿35 percent) and between one and two micrometers (∿30 percent) predominating. It is for this reason that a curved line as well as two dashed lines, indicating the two principal size ranges, appear in Figure 3, instead of the single straight line usually resulting on such log-probability plots. Visual inspection of the impactor collection substrates indicated the presence of both straw-colored oily material and a black, possibly inorganic dust, perhaps due to attrition of the shale in the retort.

Table 2. Composite Size Distribution of Particles in Retort Off-Gases

Stage	Size range, micrometers	Weight percent: In size range	Weight percent: Cumulative less than size range
Preimpactor + Stage 0	>19.5	36.8	63.2
1	13.6 - 19.5	0.6	62.6
2	9.1 - 13.6	4.4	58.2
3	6.3 - 9.1	1.3	56.9
4	4.0 - 6.3	7.0	49.9
5	2.0 - 4.0	11.0	38.9
6	1.3 - 2.0	28.4	10.5
7	0.9 - 1.3	5.0	5.5
Backup filter	<0.9	5.5	0

[a] Averages calculated from results of three separate samples.

Particulate Emissions and Control

Table 3 presents the results of seven Method 5 measurements of particulate loading in retort off-gases and in the venturi scrubber outlet for three different scrubber operating conditions. These calculated values are based only on the mass collected from the filter and washes of the front-half glassware in the sampling train, thus making this data equivalent to others taken according to EPA Method 5. By comparison, the mass of condensible organic "particulate" matter rinsed from the glassware between the filter and the resin trap (back half) ranged from 2.7 to 5.5 times the amounts in Table 3 for the scrubber inlet and 4.8 to 21 times as much for the scrubber outlet. Therefore, retort off-gases contained a very substantial quantity of potential "particulate" emissions that condense between 120°C, the approximate temperature of the Method 5 filter holder, and about 20°C, that of the resin trap. The larger ratios of back-half to front-half "particulate" in the scrubber outlet merely indicate, as expected, that venturi scrubbing is less effective for removal of condensible organic compounds than for filterable solids or aerosols.

Several qualitative conclusions can be derived from the particulate emissions data in Table 3. The overall average off-gas concentration of 214 mg/dncm falls within the rather broad range of 20 to 2,200 established from available estimates and data MRC gathered during Phase I of this EPA contract [2]. The scrubber

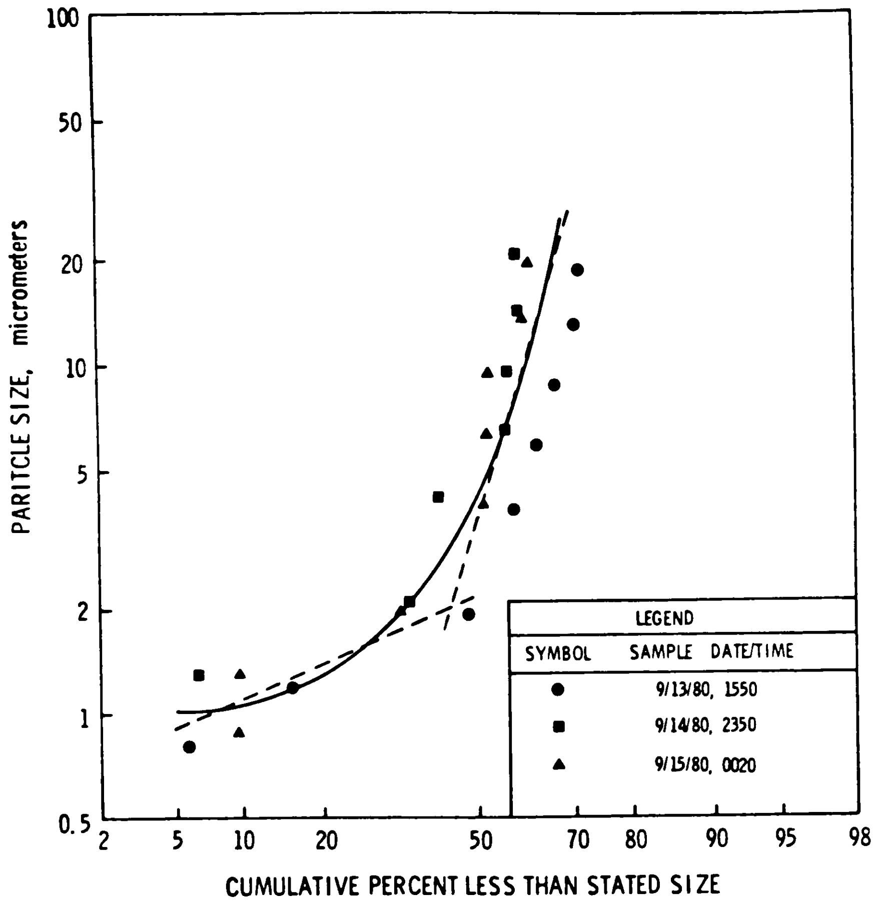

Figure 3. Particle size distribution in scrubber inlet gas samples.

Table 3. Control of Particulate Emissions from Oil Shale Retorting[a]

Operation code[b]	Concentration, mg/dncm[c]		Mass flow rate, g/hr		Percent control[d]
	Inlet	Outlet	Inlet	Outlet	
	245	37	128	17	87
6A	275	32	145	14	90
	152	32	80	14	82
-Averages-	224	34	118	15	87
8B	144	38	78	20	74
	125	46	69	23	67
10C	173	35	96	18	82
	387	24	198	11	94
-Averages-	228	35	121	17	86

[a]Based on masss collected from front-half train wash and filter.

[b]See Table 1 for explanation.

[c]Milligrams per dry normal cubic meter (20°C, 101 kPa).

[d]100 x (inlet flow rate - outlet flow rate) ÷ inlet flow rate.

inlet particulate concentration was, however, highly variable, ranging from 125 to 387 mg/dncm, with no apparent correlation to the progress of the retort burn. By extrapolating the overall average particulate emission rate of 113 grams per hour for LETC's facility, the predicted uncontrolled emissions from a 7,950-m^3(50,000-barrel)-per-day commercial oil shale plant are approximately 5.2 x 10^6 kilograms per year, assuming a 90 percent stream factor.

Regarding the efficiency of venturi scrubbing for control of particulate emissions from oil shale retorting, the most significant conclusion to be drawn from Table 3 is the ability to consistently achieve an average outlet concentration of 35 mg/dncm despite the three-fold variation of inlet concentrations. An unexpected result is that increasing the liquid-to-gas ratio from 1.5 to 2.4 L/m^3 did not improve the particulate removal efficiency, as would be predicted by theory, despite the increased pressure drop. Future experiments should consider determining the minimum liquid-to-gas ratio that yields similar particulate control in order to reduce water consumption. Alternatively, determination of the extent to which the liquid-to-gas ratio must be increased beyond 2.4 L/m^3 in order to achieve control efficiencies greater than 90 percent would also be of interest.

Hesketh [5] has developed an empirical relationship, based on data from a variety of venturi scrubbers, to predict control efficiency for particles less than five micrometers in diameter. Using this model under the conditions of the mobile scrubber test, the liquid-to-gas ratios used - 1.5, 2.0, and 2.4 L/m^3 - should have given control efficiencies of 93.8, 95.5, and 96.5 percent, respectively. The corresponding actual removals achieved were only 87, 74, and 86 percent, considerably less than predicted. One possible explanation for this performance as applied to particulate emissions from oil shale retorting may be the inability to control the relatively large fraction of sub-micrometer-sized particles.

Other Air Pollutants

Additional emissions characterization indicated the effect that venturi scrubbing had on air pollutants other than particulate matter. Table 4 presents a brief summary of these measurements. As appears typical of this source type, retort off-gas concentrations of ammonia, carbon monoxide, hydrocarbons, and hydrogen sulfide were all substantial, that is, greater than that for particulate matter. Hydrogen sulfide data in Table 4 are reported as upper limits because gas chromatograph response was linearly extrapolated into the range of detector saturation. In future sampling efforts at oil shale facilities, regardless of whether H_2S is measured by gas chromatography or a wet chemical technique, the use of a dilution system is recommended to reduce concentrations to levels below about 500 ppm prior to measurement. Other than particulate emissions, ammonia was the only air pollutant consistently controlled by the mobile venturi scrubber. On a mass flow basis, 50 to 75 percent control of ammonia emissions was achieved. This was perhaps a surprising result considering no special measures were intentionally taken to achieve such performance.

Scrubber Water Characterization

Comparisons of the pollutant loadings in the feed and discharge water during the Laramie scrubber test are of interest for several reasons. First, the specific interrelationships between the plumbing and operations of EPA's pilot particulate control device and Denver Research Institute's mobile steam stripping unit make a list of concentrations in the combined well water/recycle feed incongruous in and of itself. More importantly, such comparisons can serve to qualitatively confirm the results of stack sampling measurements of the effect of wet scrubbing on air pollutant emissions. Furthermore, such information on the uptake of air pollutants into the scrubbing liquid may prove useful in any attempt to design a logical system for treatment of the discharge stream.

Table 5 presents the water quality impact of wet scrubbing as the increase in the total amount of each pollutant leaving the scrubber in the liquid phase compared to that entering. This calculation was performed assuming the inlet and outlet liquid flow rates were equal, which is indeed the case to within a very small error. For the most part, the pollutants present in the largest concentrations in the scrubber discharge also happen to be those with the largest mass flow increase, namely alkalinity, carbonate, chemical oxygen demand (COD), ammonia and Kjeldahl nitrogen, and oil and grease. In addition, substantial uptake of sulfite ($SO_3^{=}$) was noted in all cases, the amount increasing roughly linearly with liquid flow rate, indicating solubility-limited absorption of hydrogen sulfide and/or sulfur dioxide from the retort off-gases.

Table 4. Other Air Pollutants Emitted by the LETC Retort[a]

Pollutant	Concentration Units	Concentration Inlet	Concentration Outlet	Mass flow rate, g/hr Inlet	Mass flow rate, g/hr Outlet
Total hydrocarbons (as CH_4)	ppm[b]	25,000	23,000	6,600	5,400
Carbon monoxide	ppm	20,000	21,000	9,100	8,600
Nitrogen oxides (as NO_2)	mg/dncm[c]	42	40	23	19
Carbonyl sulfide	ppm	97	98	94	83
Hydrogen sulfide	ppm	<85,000	<85,000	<47,000	<43,000
Ammonia	mg/dncm	3,000	1,000	1,600	600
Hydrogen cyanide	mg/dncm	0.5	0.6	0.2	0.3

[a]Average values, representing, in some cases, measurements taken at all three scrubber operating conditions.

[b]ppm = parts per million by volume, dry basis.

[c]mg/dncm = milligrams per dry normal cubic meter (20°C, 101 kPa).

Table 5. Uptake of Water Pollutants by Scrubbing Liquid

Pollutants	Mass flow increase,[a] g/hr S.O.C.[b] 6A	S.O.C.[b] 8B	S.O.C.[b] 10C
Water Quality Parameters			
Alkalinity (as $CaCO_3$)	260	690	2,310
Biological oxygen demand	230	<480	560
Carbon - inorganic	30	85	25
- organic	90	520	570
Chemical oxygen demand	780	1,910	1,520
Oil and grease	460	>800	730
pH	-[c]	-[c]	-[c]
Solids - total	64	74	61
- total dissolved	44	74	(93)[d]
- volatile dissolved	25	49	(73)[d]
- total suspended	-[e]	-[e]	-[e]
- volatile suspended	-[e]	-[e]	-[e]
- total volatile	45	5	210
Chemical Species			
Bicarbonate (HCO_3^-)	16	(190)[d]	1,530
Carbonate ($CO_3^=$)	240	880	790
Cyanide (CN^-)	-[e]	<1	<1
Nitrogen - ammonia (NH_3)	560	810	690
- Kjeldahl	580	690	770
- nitrate (NO_3^-)	4	4	(2)[d]
Sulfur - sulfate ($SO_4^=$)	11	42	60
- sulfite ($SO_3^=$)	270	500	830
- thiocyanate (SCN^-)	19	29	41

[a]0.06 x (feed rate, L/min) x (discharge concentration - feed concentration, mg/L).

[b]S.O.C. = scrubber operating condition; see Table 1 for explanation.

[c]Not calculated.

[d]Negative values, i.e., apparent decrease in mass flow rate of pollutant.

[e]Indeterminate due to form of concentration data.

The mass flow increases of total solids in the scrubbing water reflect control of particulate emissions. As for the particulate control efficiencies, the extent of this phenomenon seemed relatively insensitive to total liquid flow rate. Oil and grease and chemical oxygen demand follow similar patterns to that for total solids, reflecting collection of entrained oil droplets, obviously organic in nature, from the retort off-gases. Carbonate uptake implies dissolution of carbon dioxide, a likely possibility. The consistent uptake of ammonia in the discharge water confirms that scrubbing did achieve some control of emissions of that pollutant from the retort off-gases, even though not originally intended.

ACKNOWLEDGMENTS

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