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Nitrogen and Carbon Oxides Chemistry in the HRS Retorting Process

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ABSTRACT

Average gas concentrations of selected gas phase species were determined from data measured at several places on the combustion system of the Lawrence Livermore National Laboratory Hot-Recycled-Solids Retort Pilot Plant for representative rich and lean shale runs. The data was measured on-line and in real time by on-line meters (CO_2 , CO , O_2 , and NO), mass spectrometry (CO_2 , O_2 , H_2O , NO , CH_4 , SO_2 , N_2 and Ar), and Fourier transform infrared spectroscopy (CO_2 , CO , H_2O , NO , N_2O , NO_2 , CH_4 , SO_2 , NH_3 , and HCN).

For both the rich and lean shale runs, the Lift-Pipe Combustor (LFT) exhibited gas concentrations (sampled at the exit of the LFT) indicative of incomplete combustion and oxidation; the Delayed-Fall Combustor (DFC) exhibited gas concentrations (sampled at the annulus and the exit of the DFC) indicative of much more complete combustion and oxidation. The Fluidized-Bed Combustor exhibited gas concentrations which were controlled to a large extent by the injection atmosphere of the FBC. High levels of nitrogen oxides and low levels of CO were detected when full air injection was used, while high levels of CO and low levels of nitrogen-oxides were detected with partial N_2 injection.

Sequential sampling limitations and nitrogen balances are also discussed.

INTRODUCTION

The Hot Recycle Solids (HRS) Oil Shale Retort process developed at Lawrence Livermore National Laboratory (LLNL) consists of a pyrolysis section which converts kerogen of the shale to liquid and gaseous products, and a combustion section which burns residual carbon on the shale to heat the process.¹ Figure 1 shows a diagram of the retort in the configuration used for these experiments. The pyrolyzing section is a gravity-fed single stage unit which operates in the range of 500-550°C. The combustion section has been divided into four sequential units, the Lift Pipe (LFT), the Classifier (CLS), the Delayed-Fall Combustor (DFC), and the Fluidized-Bed Combustor (FBC). In the LFT, combustion is initiated, continuing in the CLS and DFC, and completing (if desired) in the FBC (gas block isolates

the FBC). Both the LFT and the FBC have gas-injection ports to control oxygen content and flow. After the FBC, some of the hot combusted shale is collected in the spent hopper, while the rest is mixed with fresh, incoming shale in the Fluidized-Bed Mixer (FBM). There, heat transfer occurs and the fresh shale is heated to pyrolyzing temperatures.

As expected in hydrocarbon-combustion processes, carbon oxides are produced in the combustion gas effluent. In addition, because of high N content in the Green River oil shale² (which is the typical feedstock), nitrogen oxides are also produced in the combustion cycle. Knowledge of the concentrations of these species is important in the design and operation of the retorting process. Carbon oxides are critical in determining mass balances, combustion mechanisms and rates, and are distinctive

in helping study process parameter variations. Nitrogen oxides are important in understanding fuel nitrogen oxidation chemistry and mechanisms. Both are potentially important as environmentally sensitive components of the flue gas. Further knowledge of the nitrogen oxidation chemistry will be important if abatement is necessary³.

Figure 1. Diagram of the Lawrence Livermore National Laboratory Hot-Recycled Solids Retorting Process.

Table 1 shows average flue-gas emission concentrations for the HRS retorting process, as well as Federal standards for flue gas emissions.^{4,5} The HRS retort concentrations were measured by on-line FTIR spectroscopy and are ranges of concentrations determined over several runs. Because there are no U. S. standards set for Oil Shale retorting processes, the maximum allowed concentrations are listed for industrial boilers for SO₂ and NO_x concentrations, and industrial coke burners for SO₂ and CO concentrations. Clearly, SO₂ emissions from the HRS process flue gas are well below any levels needing regulation. The retort can be operated in such a manner that NO_x is close

to compliance with levels set for industrial boilers. CO, however, is considerably higher than standards set for coke burners. Whether the current average emission levels from the HRS retort are sufficient to meet flue-gas emission standards for Oil Shale retorting processes when (and if) they are set, remains to be seen. However, knowledge of these levels will be extremely important. To support this goal, this manuscript reports the concentrations of carbon and nitrogen oxides in various places along the combustion system of the HRS retorting process for typical retort runs at different conditions, and discusses some of the overall chemistry occurring.

Component	Concentration Ranges ^a Measured	Maximum Allowed Based on: Boilers ^b	Coke Burners ^c
SO ₂	10 to 30 ppm	370 ppm	250 ppm
NO _x	250 to 850 ppm	220 ppm	-
CO	1000 to 3000 ppm	-	500 ppm

a) Measured by FTIR.
b) Assuming retorted shale contains 3 wt% char with the composition CH_{0.5}. Applying Code of Federal Regulations, vol 40, parts 53-60. Utility boilers with coal or oil shale derived fuel at 1.2 lbs SO₂/10⁶ B.t.u. and 0.5 lb NO_x/10⁶ B.t.u.
c) Applying Federal Regulations 60.103 and 60.104 for Petroleum Refineries, Catalytic Cracking (July 1, 1991).

Table 1. Concentration ranges of SO₂, NO_x, and CO for the HRS Retort and Federal Emission Standards for Industrial Boilers and Coke Burners

EXPERIMENTAL

The combustion gases were sampled from the HRS retort directly (for flue gas) or through dust filters (all other ports) to inhibit plugging in the sampling lines due to dust. Calibration for all gases species detected except H₂O was accomplished by means of commercial gas standards and air. All instruments were connected to the retort gas sampling line by heated (150 °C) 304 stainless steel lines.

On-line meters (OLM). CO₂ and CO concentrations were measured by Horiba model PIR-2000 gas meters. NO concentrations were measured by a Horiba model CFA - 311A gas meter. O₂ was measured by a Teladyne Analytical Instruments 326 RA gas meter equipped with an A5 microfuel cell.

Mass Spectrometry (MS). CO₂ (m/z 44), NH₃ (m/z 17), NO (m/z 30), N₂ (m/z 28), H₂ (m/z 2), O₂ (m/z 32), H₂O (m/z 18), Ar (m/z 40), SO₂ (m/z 64), and CH₄ (m/z 16) concentrations were measured by an EXTREL

Questor model mass spectrometer. NH_3 was corrected for H_2O ; CH_4 was corrected for H_2O and NH_3 ; N_2 was corrected for CO_2 fragmentations. Data was taken every 10 to 15 sec. Because both N_2O and CO_2 have the same mass to charge ratios (m/z 44), they can not be differentiated in the mass spectrometer. No NO_2 was observed because it fragments entirely into NO in the mass spectrometer.

Whenever NH_3 and O_2 were passed into the mass spectrometer, H_2O and N_2 were observed as products. The ratio of H_2O to N_2 indicated approximately 20% of the NH_3 was combusted in the hot MS source. This side reaction was accounted for by measuring a baseline concentrations of these species before each run.

Fourier Transform Infrared Spectrometer (FTIR). The gas concentrations were measured by a Bio-Rad FTS-40 equipped with a gas cell (6 meter path length) having NaCl windows. With the appropriate baseline and interfering species corrections, the species were measured at the following locations (in cm^{-1}): CO_2 , 2391-2420; CO , 2126-2137; NO , 1900; N_2O , 1240-1285; NO_2 , 1586-1617; H_2O , 3911-3967; SO_2 , 1367-1402, NH_3 ; 866-870; HCN , 3339-3352.

Data Handling. Output from the meters went directly to an HP-1000 data logging system. Output from the MS was reduced to ASCII II format by the Questor system software, and downloaded onto the HP-1000 data tracking system. Output from the FTIR was reduced to ASCII II format by the Unix based software system and downloaded onto the HP-1000 data tracking system.

Average values were calculated based on the data obtained during the time the instruments were sampling a particular port. Only the data was used which appeared to be at or close to a steady state. Because of the configuration of only sequential sampling of ports, the retort was not necessarily at exactly the same conditions for the sampling of each port.

RESULTS

On-Line Gas Sampling. The combustion gas concentrations were measured on-line in real time by three different techniques -- On-line meters, mass spectrometry, and Fourier

transfer infrared spectroscopy. Several species were measured by more than one technique, allowing for internal checks of analytical reliability. CO_2 was measured by all three instruments. Generally, the FTIR gave results which were consistently over 10% higher than the OLM or MS. As a result, absolute CO_2 concentrations were taken from either OLM or MS data (although the same trends were seen in the FTIR data). NO was also measured by all three instruments. Generally, the MS gave results which were consistently 5% higher than the OLM and FTIR (attributed to fragment contributions from other ions). As a result, absolute NO concentrations were determined by either the OLM or FTIR. H_2O was measured by MS and FTIR. The values measured by the FTIR were always several percent higher than the MS. Drying the combustion gas using a water trap still yielded water concentrations of ~ 2%, indicating a baseline problem in the method of determination. CO was determined by both OLM and FTIR. Because the FTIR response is non-linear at higher concentrations of CO (1% and higher), the OLM was used for high concentrations. However, at very low concentrations, the OLM meter was not sensitive enough, so the FTIR was used exclusively for low concentrations. Both instruments agreed well in the intermediate range. CH_4 was determined by MS and FTIR. In some cases, the MS gave significantly higher concentrations than the FTIR (attributed to fragment contributions due from larger hydrocarbons). SO_2 was measured by MS and FTIR. Because the concentrations of SO_2 are so low in most cases, neither method gave data with good standard deviations.

For these studies, the gas streams were sampled at the top of the LFT (Port A), the annulus of the DFC (Port C), the exit of the DFC (Port D), the exit of the FBC (Port E), and the flue gas (Port F). Because of the gas block and separate gas injections, the flue gas is a combination of effluents from the DFC and the FBC.

Figure 2 shows a typical example of CO_2 concentration as a function time for an entire run monitored by OLM. All the instruments sample the flue gas (Port F) during start-up, and remain there until the retort reaches a reasonable steady operation. The port-

sampling sequence shown is usually (but not necessarily) followed with sampling periods being approximately 30 min. Repeats are attempted only after the entire suite of ports has been sampled. As seen in Figure 2, the concentrations of CO₂ can vary from almost 0 (seen only at start-up), to higher than 15% (full combustion), so the instruments need to be able to detect a wide range of concentrations quantitatively.

Figure 2. CO₂ concentration as a function time for an entire run monitored by OLM.

Figure 3. CO₂ concentrations determined by on-line meter, mass spectrometry, and FTIR sampled at the top of the LFT.

Figure 3 is a typical example of on-line determination of CO₂ concentrations utilizing all three instruments while monitoring the top of the LFT. The agreement between OLM and MS concentrations are excellent, even during changes in conditions ("early" is considered one steady state while "late" is considered another, "middle" is a transition period). The

values in the figure are averages over the period limits as delineated by the arrows. These average values for the OLM and MS agree very well, also. The corresponding FTIR concentrations are much higher, even though they parallel the OLM and MS determined concentrations. The average values for the early and late periods also reflect this discrepancy. As mentioned above, this happened consistently in all of our determinations of CO₂.

Carbon-Oxide Chemistry. The following diagrams of the HRS have been simplified to only show the combustion side. Included are average concentrations of species relevant to carbon-oxygen chemistry next to the specific port on the diagram. Some ports were not sampled during particular runs. Also included are the average temperatures of the various combustion units during the run from our Run Summary data compilation. These values are averages over yield periods and can vary considerably over a run.

Rich Shale. Figure 4 shows the average concentrations for CO, O₂, and CO₂ for a rich shale run. Ports A, C, E, and F only were sampled during this run. Clearly, the CO₂ and O₂ concentrations at the top of the LFT (Port A) indicate combustion is not complete. This high level suggests either incomplete mixing or too short of a residence time. The very high level of CO also corroborates this incomplete combustion.

The concentration of the species measured at the annulus of the DFC (Port C) indicate much more complete combustion has occurred in the CLS and the DFC, with higher CO₂ levels and much lower CO and O₂ levels.

The FBC gas inlet was operated with full air injection. The average concentrations in the effluent of the FBC (Port E) indicate that some char remained after the spent shale passed from the CLS to the FBC (depleted oxygen level). The high CO₂ content suggests that some carbonate decomposition is occurring in addition to the combustion. This is consistent with the high average operating temperature.

The flue gas concentrations (Port F) should be an average of the DFC and FBC concentrations weighted by the LFT and FBC flow rates.

Figure 4. Average concentrations of CO, O₂, and CO₂ for a rich shale run.

Figure 5. Average concentrations of CO, O₂, and CO₂ for a lean shale run

This is the case for CO₂ and O₂, but not for CO. This will be discussed in more detail below.

Lean Shale. Figure 5 shows the average carbon-oxide concentrations for a lean shale run. Ports A, B, C, and F only were sampled. The concentrations of gases measured at Port A show, as in the rich shale case, incomplete combustion is occurring in the LFT -- high O₂ and CO levels and relatively low CO₂ levels. The concentrations of the gases at the annulus of the DFC (Port C) show that combustion has progressed. Note, the high O₂ level in the DFC. This is inconsistent with the lower level in the LFT, but could be a result of sequential sampling.

Unlike the rich shale run, the FBC was operated on partial air injection. As a result, CO levels are higher than expected with full air injection, but the high CO₂ levels indicate considerable char combustion still has occurred. The gas concentrations measured in the flue gas are a weight balance of those concentrations measured for Ports D and E.

Nitrogen-Oxide Chemistry. The above diagrams also show average concentrations of species relevant to nitrogen oxidation chemistry.

Rich Shale. Figure 4 shows average concentrations of NO, N₂O, NO₂, NH₃, and HCN for a rich shale run. Ports A, C, E, and F only were sampled. The concentrations of gases measured at the top of the LFT (Port A) show moderate levels of NO, N₂O, and NH₃, low levels of NO₂, and very high levels of HCN. The very low level of NO₂ and high level of HCN indicate that incomplete oxidation is occurring in the LFT. This is in agreement with carbon-oxide behavior shown in Figure 4 which indicates incomplete combustion is also occurring in the LFT.

The gas concentrations measured at the annulus of the DFC (Port C) indicate oxidation chemistry has proceeded -- HCN is no longer present, higher levels of NO and NO₂. This is also in agreement with the combustion chemistry occurring from the LFT to the DFC.

The gas concentrations measured at the exit of the FBC (Port E) indicate highly oxidative

conditions. -- very high levels of NO₂ and NO, low levels of HCN, NH₃, and N₂O. The high concentrations of NO₂ and NO are probably not due all to fuel N being oxidized, because 1) there is probably not enough N in the char to produce such high concentrations of N-containing gas species, and 2) the temperature of the FBC is high enough to cause some decomposition of the ammonia-bearing mineral buddingtonite (NH₄AlSi₃O₈•0.5H₂O).⁶ (As the buddingtonite decomposes, the NH₃ is easily oxidized to nitrogen oxides such as NO₂ and NO.)

The flue gas concentrations measured at Port F are not a very good weight balance of those of the individual gas streams from the FBC (flow - 0.00 mol/sec) and the DFC (flow - 0.00 mol/sec). This could be due to additional chemistry occurring in the cyclone gas-solid separation system which precedes Port F, or (more likely) because all three ports are not sampled simultaneously.

Lean Shale. Figure 5 shows average concentrations of nitrogen oxides and related species for a lean shale run. Ports A, C, E, and F only were sampled. The concentrations of gases measured at Port A show similar behavior to the gas concentrations measured for Port A in the rich shale case -- moderate levels of NO, N₂O, and NH₃, low levels of NO₂, and very high levels of HCN. The very low level of NO₂ and high level of HCN indicate that incomplete oxidation is occurring in the LFT. This is also in agreement with carbon-oxide behavior shown in Figure 5 which indicates incomplete combustion is also occurring in the LFT.

The gas concentrations measured at the annulus of the DFC (Port C) indicate that oxidation has proceeded significantly, having higher levels of N₂O and lower levels of NH₃ and particularly HCN. The poor N balance between Port A and C will be discussed below.

The NO concentration is relatively low measured at the exit of the FBC (Port E), while the NH₃ concentration is relatively high. The reduced availability of O₂ due to partial N₂ injection accounts for the much reduced NO and NO₂ levels compared to the rich shale case which had full air injection. As indicated above, this is also reflected in CO

concentrations from this port. The NH_3 level is also very high. The temperature of the FBC is high enough to cause so buddingtonite decomposition,⁶ but the concentration of oxygen in the exit of the FBC (0.03 %) indicates a non-oxidative environment which would cause little oxidation of the NH_3 to NO_x .

Except for NH_3 , the flue-gas concentrations measured at Port F are roughly weight balanced averages of the gas concentrations measure for the DFC (flow - 0.603 mol/s) and for the FBC (flow - 0.441 mol/s). The NH_3 is much higher than calculated (~ 150%). This could be due to additional chemistry occurring in the cyclone gas-solid separation system which precedes Port F, or because of sequential sampling.

Several other runs were examined for nitrogen oxide chemistry. In a lean shale run with full air injection in the FBC, the behavior for each port was similar, except for the FBC where very high levels of NO and NO_2 and low levels of NH_3 were measured, consistent with the rich shale run.

DISCUSSION

A particular problem with monitoring a large scale apparatus is instantaneous sampling at every point of interest. With on-line capabilities, we can obtain momentary changes in gas chemistry as well as average compositions. However, because of the expense of the equipment utilized for these measurements, we are limited to recording data from each port sequentially. For example, in our normal sampling sequence, the annulus of the DFC is sampled one hour after top of the LFT. Any changes in conditions during that time could cause the overall chemistry to be different for sampling Port A than Port C. This must be accounted for when comparing average values of each port, and is one of the major limitations of our analyses. This could cause comparisons of data (possibly taken under different conditions) which would hide process parameter effects, and complicate mass balances. To examine how much this can be a problem, the flue-gas (Port F) compositions were examined in more detail. Because of the combination of gas streams, Port F must be a weighted average of concentrations in Ports C and E. If the above sequential sampling is not

much of a problem, then the weighted average of Ports C and E should be relatively close to average concentrations of Port F. This assumes, of course, that no additional combustion or oxidation chemistry is occurring in the cyclones on the flue gas system.

Retort Run	Gas	Calculated ^a	Measured ^b
Lean	CO , ppm	697 - 766	650-848
	O_2 , %	5.27 - 5.70	5.37 - 5.43
	CO_2 , %	15.29 - 15.71	15.35 - 15.60
Lean	CO , ppm	2880 - 4244	3560 - 3820
	O_2 , %	0.81 - 0.82	0.29 - 1.34
	CO_2 , %	14.85 - 15.98	15.15 - 16.58
Rich	CO , ppm	1973	1988-2690
	O_2 , %	9.63	6.42 - 6.73
	CO_2 , %	14.86	14.31 - 14.86
Rich	CO , ppm	3056	930
	O_2 , %	5.36	5.60
	CO_2 , %	13.86	14.00

a. Calculated from the weighted average of Ports C and E.
b. Measured directly at Port F.

Table 2. Flue gas compositions for selected retort runs.

Table 2 shows CO , O_2 , and CO_2 concentrations of the flue gas for selected retort runs. The calculated values are from the weighted averages (based on flow rates) calculated from the average concentrations determined from data measured at the exits of the DFC and FBC. The range of values in the table is a result of ports being sampled more than once. The highest and lowest values were selected for the limits of the range.

In general, the calculated values fall within the range of the measured values, indicating that the sequential sampling of the ports is sufficient to accurately record the combustion gas chemistry. CO_2 and O_2 are close in all cases in the table (except for the O_2 value in the first rich shale listing). However, CO shows significant variation in the ranges calculated and measured, as well as a big disagreement between calculated and measured for the second rich shale run in the table. The is probably due to sequential sampling. However, CO determinations were not as consistent as other species monitored.

The oxidation of fuel N-containing compounds is an extremely complicated process.⁷ All the mechanistic steps have not been determined, but the oxidation appears to go through a sequence which involves HCN , N_2O , NO , NO_2 , and others. Reaction pathways are complicated and can interconnect. In addition,

in Green River oil shale combustion, NH_3 oxidation must be accounted for, whether it is from the fuel N oxidation pathway or from decomposition of Buddingtonite: $\text{NH}_3 \rightleftharpoons \text{NO}$.

Run	Unit	NO	N_2O	NO_2	NH_3	HCN	Total N_{eq}
Lean	LFT	211	14	0	281	568	1088
Lean	DFC	386	307	0	29	0	1020
Special	LFT	354	90	2	216	594	1344
Special	DFC	209	187	0	73	0	656
Rich	LFT	280	115	5	378	812	1705
Rich	DFC	343	131	17	404	0	1026

Table 3. Gas-phase nitrogen concentrations (ppm) in Lift Pipe (LFT) and Delayed-Fall Combustor (DFC)

Table 3 shows the gas-phase nitrogen concentrations measured for the LFT and the DFC. These concentrations are related because they are determined by sampling the same gas stream at different places. The top lean shale run shows the HCN concentration is high in the LFT but is zero in the DFC. The levels of NO and NH_3 are moderate in the LFT, but increase and decrease, respectively, in the DFC. N_2O is low in the LFT, but is reasonably high in the DFC. If the N is redefined as nitrogen equivalents (N_{eq}), that is 1 ppm of NO is 1 ppm N_{eq} , while 1 ppm N_2O is 2 ppm N_{eq} , the total N_{eq} balance is excellent. This suggests the nitrogen-oxygen chemistry is related through the above reactions.

The second lean shale run listed in Table 3 shows similar behavior to the first, except the NO concentration decreases and the total N_{eq} at the annulus of the DFC is about one half of that measured at the top of the LFT. The rich shale run behaves similarly, except the NO decreases, the NH_3 increases, and the total N_{eq} measured at the annulus of the DFC is significantly less than that measured at the top of the LFT.

This loss of nitrogen in the latter two listed runs could be a result of sequential sampling as discussed above. However, the carbon-oxygen chemistry shows that sequential sampling may not be a problem (at least in the cases mentioned when comparing Ports C, E, and F). Another possibility is that some type of NO reduction chemistry is occurring in the LFT-CLS-DFC system. These possible types are: Thermal deNO_x , selective catalytic reduction (SCR),

and char reduction. Reaction 1 shows the generally recognized reaction for thermal and catalytic NO reduction and reactions 2 and 3 show the char reduction reactions, with and without O_2 .

We have shown in laboratory studies, combusted oil shale³ as well as residual char on shale^{3,8} are capable of reducing NO. Further testing is necessary to deconvolute the origin of this imbalance.

CONCLUSIONS

Several general conclusions can be made about behavioral trends of the combustion gas system:

- LFT exhibits incomplete combustion and oxidation chemistry -- high level of CO (~ 1.5%), lower levels of CO_2 (~ 9%), residence time or mixing limited (O_2 available), high levels of HCN (500 to 10000 ppm), and low levels of NO_2 .
- DFC exhibits more complete combustion and oxidation -- dramatic decrease in CO, most O_2 consumed (~ 2% residual in some cases), and a dramatic decrease in HCN.
- FBC exhibits CO and NO_x concentrations which depend upon injection atmosphere -- excess air yields low CO and high NO_x , and limited air yields low NO_x and high CO.
- Poor N closure is seen in some runs suggesting the possibility of NO reduction chemistry.

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FIGURE LEGENDS

Figure 1. Diagram of the Lawrence Livermore National Laboratory Hot-Recycled Solids Retorting Process.

Figure 2. CO₂ concentration as a function time for an entire run monitored by OLM.

Figure 3. CO₂ concentrations determined by on-line meter, mass spectrometry, and FTIR sampled at the top of the LFT.

Figure 4. Average concentrations of CO, O₂, and CO₂ for a rich shale run.

Figure 5. Average concentrations of CO, O₂, and CO₂ for a lean shale run