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Process for Cleaning and Removal of Sulfur Compounds From Low BTU Fuel Gases

April 1976

Prepared for the Energy Research
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under Contract E(45-1):1830

Battelle

Pacific Northwest Laboratories

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"PROCESS FOR CLEANING AND REMOVAL OF SULFUR
COMPOUNDS FROM LOW BTU FUEL GASES"

Interim Report for the
Period January - March 1976

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QUARTERLY SUMMARY REPORT

January-March 1976

"Process for Cleaning and Removal of
Sulfur Compounds from Low Btu Gases"

I. OBJECTIVE AND SCOPE OF WORK

It is proposed to achieve the following objectives (completion of Phase III):

- o By continued operation of the PDU, determine the effectiveness of new de-entrainer packing for control of salt losses. Also, determine the effectiveness of chemical absorbents for salt loss control.
- o Demonstrate salt recycle and reuse.
- o In a separate laboratory scale research, evaluate parameters which control the effectiveness of COS extraction.

Phase IV Objectives

In this phase of work **i**t is proposed to remodel the PDU by incorporation of appropriate sub-systems to permit operation in continuous process mode. The PDU will be operated for a period of time sufficient to demonstrate process viability.

II. SUMMARY

- (1) Following refunding of this project and during the report period, the PDU has been relocated to an **improved** support facility and repaired to a state of near readiness for operation.
- (2) A theoretical analysis of the COS extraction problem has been completed.

INTRODUCTION

This project was refunded effective October 1, 1975, with funding sufficient to cover demonstration of improved salt de-entrainment in a series of short runs with the Process Demonstration Unit (PDU). The PDU was to be operated in batch mode.

During the interval from December 1974 to October 1975 the PDU had stood idle and a decision had been reached to relocate the unit to a new site if it were to be operated again. This move was to be for Battelle's convenience and at Battelle's expense. The long period of idleness and the move made it necessary to carefully test each component prior to operation. In addition, it was necessary to repair damage which had occurred during earlier operation of the PDU.

The scope of work also included provision for an analytic and laboratory-scale study of the carbonyl sulfide equilibria which control the concentration of COS in the system. In view of the inclement weather to be experienced in December-February in this region and to interfering effects caused by relocation of the PDU, this work was scheduled fairly early in the program. It had not progressed far, however, when (early in December 1975) instructions were received to omit further study of the problem.

Despite inclement weather and delays caused by relocation of the PDU, repair and testing of components of the PDU were approaching completion on March 1, 1976. On that date, Battelle was instructed to suspend further efforts to prepare the PDU for operation in batch mode. Instead, all further work on this program was to be focused on redesign and remodeling of the PDU for operating in continuous mode. This reorientation of the program is a most desirable change and will lead to accomplishment of the program objectives in a much more direct manner.

With this report, work in progress prior to March 1, 1976, is summarized. As a consequence of changing directives, it was not possible to complete the projects which were underway during this period, and this report is, therefore, a progress report.

WORK ACCOMPLISHED DURING THE QUARTER

The PDU had been idle since the last run was made in November 1974 and it was necessary to make a detailed assessment of the condition of the various components and to effect necessary repairs. Both the upper and lower pots were found to contain a small heel of solidified salt. The inner surfaces of all piping and the de-entrainer were also coated with a thin film of salt. Over the months, partial hydration of the salt had occurred giving it a slimy feel.

The de-entrainer top flange assembly was removed to expose the wire screen demister and the underlying ball packing. Severe corrosion and partial dissolution of the demister had occurred (Figure 1) and the material was soot blackened, but very little salt appears to be present.

The ball packing was removed in entirety (a new packing is to replace this one). The balls were also soot blackened and a few showed slight surface etching. Some, near the bottom of the packing, exhibited a thin layer of salt on their surfaces. Soot present on both the balls and on the rolls of wire screen used for a demister is evidence that the reverse Boudouard reaction occurs.

The lower pot furnace was removed from beneath the venturi scrubber. The latter was found to have a broken support brace and the inlet line exhibited a cracked weld where it joins the throat area. This venturi scrubber has been repaired but is not considered safe for prolonged service.

The decision was made to fabricate a new venturi scrubber with a slight design change to eliminate the weak spot that caused the failure. Figure 2 shows the dimensions and configuration. Instead of a tapered junction and support brace, a standard tee configuration is used. This should be much stronger. The inlet hole is tangential to the bottom circumference of the inlet line so the line will drain properly. Two scrubbers were fabricated and have been "alonized."

The lower pot furnace cover was removed to expose the pot liner. The alonized pot appeared to be in excellent condition and was removed and washed free of salt.

The pot liner is welded to a wide flange containing a circle of stud bolts to which the pot cover is secured. A flexitallic gasket under the cover provides a gas tight seal. A small crack was found where this flange was welded to the pot liner. The leak at this cracked weld prevented pressurization of the pot to force salt from the lower to the upper pot via a transfer line.

Warping of the flange was so severe, it was decided to fabricate a new flange. The pot liner was chucked in a lathe and machined away from the flange, which was discarded. The liner was welded to a new flange containing double the number of stud bolts and the pot cover was drilled to match the additional studs.

Inspection prior to all this work disclosed a thin layer of salt on the bottom of the pot liner. This was washed out, a tedious procedure due to the low solubility. When the pot and liner were reassembled, a steel O-ring fabricated from 1/4-inch stainless steel tubing was placed under the pot lip. This left a space which was filled with a grout of high density refractory which had been screened to remove coarse particles. It

is hoped this grout and steel O-ring will prevent salt which splashes over the pot rim from making its way into the liner. Should the latter ever be penetrated by salt, loss of the furnace could result.

During reassembly of the lower pot furnace liner, pot cover, and connecting piping, time was taken to service the slide valves and replace all gaskets. All bolts were torqued down and the unit was valved off and leak tested. A low leak rate, but one insufficient to be a problem, was found.

The large pot furnaces are 40 KVA units wired in three phase 480 volt circuits. The resistance to ground was found to be abnormally low, presumably due to moisture picked up during the long period of idleness. It would be risky to start these furnaces under an applied e.m.f. of 480 volts, so a 110 volt, 20 ampere, variable voltage transformer was hooked up and a modest current passed through the furnace elements. This procedure applied sequentially to the furnace elements has resulted in a marked increase in resistance to ground and the furnaces can now be safely operated.

During the last run in November of 1974 a spool piece in a one-inch line containing a bellows sealed valve was removed and in subsequent efforts to remove solidified salt the valve bellows was damaged. The valve bonnet and bellows assembly has now been replaced and this spool piece and valve is again ready for installation.

Inspection shows a number of cracked or broken trace heaters are in need of replacement. These have been procured, but have not been installed. A supply of 1/2-inch balls for the new de-entrainer packing have also been received and are ready for installation. Last, but not least, the salt flowmeter probe damaged during alonizing has been repaired by the vendor and partially calibrated by the vendor. The probe and control are now ready for installation and use.

The blower and controls, steam generator and controls and the secondary burner and controls have all been test operated in conjunction with another program. Operation of these units has been found to be satisfactory. The only units which remained to be checked prior to the March 1 re-orientation of this program were the gas preheater and controls and sections of trace heating and controls. It is estimated this work was within two weeks of completion and on schedule.

THE COS PROBLEM

During early pilot plant operation relatively high concentrations of COS were often found in the offgas from the scrubber. In some cases, these concentrations exceeded the inlet COS concentration. A theoretical study has been initiated to investigate the equilibrium of various reactions which may contribute to COS formation. The objectives of this study are:

- (1) Identify reactions which produce COS.
- (2) Based on measured concentrations of various species found during PDU runs, eliminate those mechanisms which could not account for the observed COS concentrations.

- (3) Devise laboratory tests to identify the correct mechanisms and provide data useful in (4), e.g., rate data.
- (4) Specify modifications to the design or operation of the PDU which will result in reduced COS formation or improved scrubbing.

Thermodynamic data have been collected for a number of reactions of interest. One such, is the reaction:

All of the species appearing in this reaction were measured during pilot plant tests. The data indicate that the gases coming from the gasifier had a much higher COS/H₂S mole fraction ratio than predicted by the equilibrium of reaction (1). After emerging from the gasifier but prior to the scrubber, supplemental H₂S was added to the gas entering the scrubber. In passing through the scrubber and de-entrainer, the COS concentration was generally found to have increased. In several instances, it has increased 2 to 4 times the equilibrium value based on reaction (1), and on the H₂S concentration from the gasifier. When H₂S extraction was occurring in the scrubber, the outlet COS concentration was generally many times the equilibrium value based on the outlet H₂S concentration (following supplemental H₂S addition).

This behavior suggests that following addition of supplemental H₂S, reaction (1) proceeds to the right producing COS. Upon entering the scrubber, H₂S is rapidly extracted and reaction (1) tends to the left. As the gas exits, the COS concentration is higher than equilibrium with the outlet H₂S, but lower than equilibrium with the inlet H₂S. This requires that the reaction rate be fast but not so fast that the reaction rate can keep up with the rate of H₂S extraction. (It should be noted that the average residence time of the gases in the extraction section is only about 0.1 second.) It is also required that the rate of direct COS extraction be substantially less than the rate of H₂S extraction.

If this is the correct explanation, solution of the COS extraction problem is simple. Merely increase the residence time in the scrubber or conduct the absorption in two stages. The latter could be readily accomplished by irrigating the packed bed de-entrainer with fresh salt (from regeneration). This would result in additional stages of extraction with the packed bed still acting as an effective de-entrainer for the venturi scrubber.

In addition to reaction (1), a number of reactions which can produce COS are listed below. Only reactions involving species known to be present in significant concentration are included in this preliminary analysis:

Reaction (2) appears less favorable than (1) because of the relatively high concentration of H_2O during steam gasification. Reaction (3) and (5) are highly favored provided O_2 is available in sufficient quantity to satisfy the equilibrium. This would require only 0.05 percent by volume, an amount too low to be detected by the gas chromatograph due to the failure of the column in use to separate O_2 and Ar. Reaction (5a) is favorable and reactions (4) and (7) are unfavorable.

PROPOSED WORK DURING THE NEXT QUARTER

Reorientation of the work required has necessitated preparation of a revised work plan. This has been submitted and will be summarized in next quarter's report. A conceptual process has been devised and submitted for ERDA Fossil Energy approval. Detailed design should be completed in time for next quarter's report.

OVERALL PROJECT STATUS AND CONCLUSIONS

Reorientation of this project can have only a favorable effect. Those experimental parameters which were to have been studied through operation of the PDU in batch mode can be studied even better with the plant configured in continuous mode. The time for demonstration of process viability will be appreciably shortened. Not much has been lost. Such repairs as have been made would have been made had the project been reoriented from the start. The project is on schedule.

FIGURE 1. Portions of Wire Screen Demister Showing Soot Deposits and Evidence of Corrosion.

FIGURE 2. Venturi Scrubber

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