ADVANCED SEPARATION TECHNOLOGY FOR FLUE GAS CLEANUP

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Prepared for:

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DOE Contract No. DE-AC22-92PC91344

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INTRODUCTION

The objective of this work is to develop a novel system for regenerable \( \text{SO}_2 \) and \( \text{NO}_x \) scrubbing of flue gas that focuses on (a) a novel method for regeneration of spent \( \text{SO}_2 \) scrubbing liquor and (b) novel chemistry for reversible absorption of \( \text{NO}_x \). In addition, high efficiency hollow fiber contactors (HFC) are proposed as the devices for scrubbing the \( \text{SO}_2 \) and \( \text{NO}_x \) from the flue gas. The system will be designed to remove more than 95% of the \( \text{SO}_x \) and more than 75% of the \( \text{NO}_x \) from flue gases typical of pulverized coal-fired power plants at a cost that is at least 20% less than combined wet limestone scrubbing of \( \text{SO}_x \) and selective catalytic reduction of \( \text{NO}_x \). In addition, the process will make only marketable byproducts, if any (no waste streams).

The major cost item in existing technology is capital investment. Therefore, our approach is to reduce the capital cost by using high efficiency hollow fiber devices for absorbing and desorbing the \( \text{SO}_2 \) and \( \text{NO}_x \). We will also introduce new process chemistry to minimize traditionally well-known problems with \( \text{SO}_2 \) and \( \text{NO}_x \) absorption and desorption. For example, we will extract the \( \text{SO}_2 \) from the aqueous scrubbing liquor into an oligomer of dimethylaniline to avoid the problem of organic liquid losses in the regeneration of the organic liquid. Our novel chemistry for scrubbing \( \text{NO}_x \) will consist of water soluble phthalocyanine compounds invented by SRI and also of polymeric forms of \( \text{Fe}^{++} \) complexes similar to traditional \( \text{NO}_x \) scrubbing media described in the open literature. Our past work with the phthalocyanine compounds, used as sensors for NO and \( \text{NO}_2 \) in flue gases, shows that these compounds bind NO and \( \text{NO}_2 \) reversibly and with no interference from \( \text{O}_2 \), \( \text{CO}_2 \), \( \text{SO}_2 \), or other components of flue gas.

The final novelty of our approach is the arrangement of the absorbers in cassette (stackable) form so that the \( \text{NO}_x \) absorber can be on top of the \( \text{SO}_x \) absorber. This arrangement is possible only because of the high efficiency of the hollow fiber scrubbing devices, as indicated by our preliminary laboratory data. This cassette (stacked) arrangement makes it possible for the \( \text{SO}_2 \) and \( \text{NO}_x \) scrubbing chambers to be separate without incurring the large ducting and gas pressure drop costs necessary if a second conventional absorber vessel were used. Because we have separate scrubbers, we will have separate liquor loops and deconvolute the chemical complexity of simultaneous \( \text{SO}_2/\text{NO}_x \) scrubbing.

We will conduct our work in a 60-month period (5/92 to 4/97), encompassing 16 tasks (Table 1), beginning with studies of the fundamental chemistry and of the mass transfer characteristics of small HFC modules in the laboratory. We will then examine the most favorable method of \( \text{SO}_2 \) liquor regeneration, determine the ability of the HFC devices to withstand particulate matter,
and examine the behavior of scalable modules. In the final 15 months of the program, we will determine the fundamental mass transfer behavior of a subscale prototype system. Based on these data, a computational design model will be devised to guide further scaleup efforts that may follow.

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Table 1
PROJECT TASKS AND SCHEDULE

<table>
<thead>
<tr>
<th>Task Number</th>
<th>Title</th>
<th>Duration</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Project Definition</td>
<td>5/92 – 8/92</td>
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<td>2</td>
<td>Capacity, Reversibility and Lifetime</td>
<td>7/92 – 6/94</td>
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<tr>
<td>3</td>
<td>Chemical Synthesis</td>
<td>7/92 – 6/94</td>
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<td>4</td>
<td>SO$_2$ Scrubbing with HFCs</td>
<td>7/92 – 9/93</td>
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<td>5</td>
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<td>6</td>
<td>SO$_2$ Liquor Regeneration</td>
<td>7/93 – 9/94</td>
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<td>7</td>
<td>Particle Deposition</td>
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<td>8</td>
<td>Integrated NO$_x$ Life Tests</td>
<td>8/94 – 4/95</td>
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<td>9</td>
<td>Scalable Modules</td>
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<tr>
<td>10</td>
<td>Computational Model</td>
<td>11/94 – 7/95</td>
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<td>11</td>
<td>Construction of Subscale Prototype</td>
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<td>Operation of Subscale Prototype</td>
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<tr>
<td>16</td>
<td>Chemical Synthesis for Process Scale-up</td>
<td>5/94-1/96</td>
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SUMMARY OF QUARTERLY PROGRESS

During the first quarter of 1995, we continued work on Task 8. We also began working on Task 9.

In Task 8, we have presented the modified experimental arrangement for testing the efficacy of Co(II)-phthalocyanine solution for NO\textsubscript{X} absorption as well as desorption over extended periods of time. The key feature of this new experimental setup is to continuously circulate the warm Co(II)-phthalocyanine solution (using a computer) through the HFC in order to avoid precipitation within the fibers. Also, this arrangement allows us to automatically acquire process data.

In Task 9, we carried out preliminary design calculations to determine the performance of a rectangular module that will be supplied by Setec. Also, we designed and constructed the apparatus for testing these modules.
TASK 8: INTEGRATED NO\textsubscript{x} LIFE TESTS

Liquid scrubbing systems for NO\textsubscript{x} have traditionally been plagued by degradation of performance over time with subsequent need for convoluted liquor regeneration schemes. Therefore, it is essential to determine whether or to what extent there is any loss with time in the performance of the NO\textsubscript{x} absorption/desorption system. In Task 2, we have showed Co(II)-phthalocyanine as a promising candidate for NO\textsubscript{x} absorption in the presence of O\textsubscript{2}. In Task 5, we also demonstrated the superior mass transfer characteristics of Co(II)-phthalocyanine scrubbing system in a 300 fiber HFC. Consequently, the objective here is to devise a continuously operating system for determining if the NO\textsubscript{x} absorption/desorption chemistry has the potential to be commercially robust.

In Quarterly Technical Report #11, we indicated that over a short period of time (40 hr. cumulative) no deactivation Co(II)-phthalocyanine occurred. We plan to continue these life tests over extended periods of time. In order to carry out these long term experiments with greater efficiency, the apparatus is being set up for automatic data acquisition and control. Specifically, the absorption/desorption output from the NO\textsubscript{x} analyzer, and the temperature and pressure of all streams will be continuously monitored. A safety feature will also be incorporated to shut the system down when any abnormal behavior is detected. It is anticipated that with this automatic data acquisition and control system, individual ('single-stretch') runs of 24 to 48 hours (current individual run time is limited to 8-10 hours because the apparatus must be operated manually) or more can be continuously monitored, thus improving the efficiency and quality of data collection.

Figure 1 shows the data acquisition and control setup using a computer. One of the important features of this automated system is to circulate the warm fluid (Co(11)-phthalocyanine solution) continuously through the absorber (300 fiber HFC). This circulation operation prevents precipitation inside the fibers leading to decreased efficiency of HFC. As shown in the figure, the peristaltic pump is connected to the computer, and will be automatically shut off if any system anomalies are detected (i.e. a sudden pressure drop or increase in the system pressures or temperatures). The computer will also save the data to file that can be opened and analyzed in a spreadsheet or other computer program.

In the meantime, we have received the repaired NO\textsubscript{x} analyzer from the manufacturer and are in the process of testing the equipment for its operation (see Quarterly Technical Report #11). Therefore, we expect to continue the life tests using the automated experimental systems in the upcoming months.
Figure 2. Apparatus for scalable module testing.
TASK 9: PERFORMANCE OF SCALABLE MODULES

Because of the need for billions of (approximately 30-cm long) fibers to treat the flue gas from a 500 MW(e) plant, it is critical to establish the mass transfer characteristics of a module that can be scaled up to a prototypical size. To appreciate this point, one must recognize that approximately 250,000 modules of 2" diameter would be required to provide one billion fibers. Such an arrangement would provide a ducting, plumbing, and maintenance nightmare in a full-scale plant and clearly would not be economical or workable. A new design concept, such as rectangular modules, is needed for a full-scale plant. Therefore, the objective of Task 9 is to develop the mass transfer fundamentals of rectangular modules.

The term "scalable module" is an important concept because it influences our ability to think about an eventual application of HFC devices to a 500 MW(e) power plant. We use the term to mean a module that exhibits the important phenomena that would appear in modules of the 500 MW(e) plant. For example, mass transfer in the rectangular (square) module will be different than that in the cylindrical modules because the flow pattern in a large-scale rectangular module absorber or liquid-liquid extractor will be crossflow, not countercurrent. Probably more importantly, flow distribution and liquid pressure drop behavior will be much different in a large "scalable" module than in our laboratory modules. Therefore, Task 9 is designed to obtain the fundamental mass transfer behavior, including issues of flow distribution and pressure drop, on modules that reflect these basic features of large-scale modules with gas and liquid flow rates in the range of 5-10 cfm and 1-5 l/min respectively.

In our previous report (Quarterly Technical Report #11), we indicated that the rectangular HFCs with dimensions of 0.8' x 1' x 1" will take out 99% SO2 from flue gas streams. These calculations were based on the Hoechst-Celanese fibers. However, we plan to obtain these rectangular HFCs from Separation Equipment Technologies, Inc. (Setec), Livermore, CA, since Hoechst-Celanese has declined to supply the HFCs (see Management Status Report #32). The Setec hollow fiber characteristics substantially vary compared to that of Hoechst-Celanese fibers. Therefore, it is important to design our experimental system based on the Setec fibers.

The specifications and performance characteristics of the module, which we are obtaining from Setec are listed below (refer to Quarterly Technical Report #11 for equations):

1. Rectangular module dimensions = 12" x 4" x 1"
2. Packing density of fibers = 70%
3. Fiber ID = 600 μm
4. Fiber OD = 1000 μm
(5) Maximum pressure drop along length of fiber = 10" water

(6) Number of fibers in module = 2300

(7) Gas flow through module = 200 SLPM

(8) Estimated mass transfer coefficient $K_{og} = 0.52 \text{ cm/sec}$
    (calculated using correlation obtained from previous experimental data)

(9) Estimated SO$_2$ removal > 95%

Therefore, we predict that the above mentioned rectangular HFC will effectively treat gas flow rates up to 200 SLPM containing 3000 ppm SO$_2$ concentration. In order to calculate the scrubbing liquid flow rate, we assumed 99% SO$_2$ removal and a 50% approach to equilibrium SO$_2$ solubility in the liquid.

Rate of SO$_2$ absorption into scrubbing liquid =

$$\frac{(\% \text{ SO}_2 \text{ removal}) \times (\text{concentration SO}_2 \text{ in flue gas})}{\text{(flue gas flow rate)}} = 0.027 \text{ mol/min}$$

Equilibrium SO$_2$ solubility in water at 3000 ppm = 0.0108 mol/L.

Water flow rate = \frac{(\text{Rate of SO}_2 \text{ absorption})}{(\text{Equilibrium SO}_2 \text{ solubility}) \times (\% \text{ approach to equilibrium}/100)} = 5 \text{ L/min}

Equilibrium SO$_2$ solubility in 0.2 M Na$_2$SO$_3$ at 3000 ppm = 0.204 mol/L.

Na$_2$SO$_3$ solution (0.2 M) flow rate = 0.3 L/min.

According to these evaluations, an experimental system is designed to treat a simulated flue gas flow rate of 200 SLPM, an SO$_2$ concentration of 3000 ppm, and a scrubbing liquid flow rate of 5 L/min (Figure 2). Because of the magnitude of these flow rates, the most reasonable way to obtain the gas and liquid supply is to use the house lines. The house water will only be used for those experiments using pure water as the scrubbing liquid. Aqueous sodium sulfite solution flow rates at least an order of magnitude lower compared to that of water will be pumped from a reservoir. Both gas and liquid lines are equipped with filters that will remove particulates down to 0.1 micron from the water and 0.01 micron from the air. The air flow will be controlled by a 0.08" diameter orifice in which the critical flow rate is obtained by maintaining the upstream pressure at least twice compared to the downstream pressure.
Figure 1. Modified NO$_x$ absorption and desorption experimental arrangement.
It is necessary to humidify the air (except in the pure water experiments) prior to passing it through the module because dry air will pick-up water from the sodium sulfite solution and change its effective concentration. The humidification is accomplished by using another cylindrical type HFC. The air flows through the tube side of the HFC and the shell-side is filled with water. This shell-side water is kept at a higher pressure with the help of a pressurized tank in order not to bubble the air into shell-side water. Addition of the SO$_2$ will occur after humidification of the air stream, which will prevent the absorption of SO$_2$ by the humidifier.

We plan to use an SO$_2$ analyzer to measure the concentration of the gas both at the inlet and the outlet of the module. We also periodically monitor the pressure drop across the length of the fibers using a differential pressure gauge to ensure that it does not exceed the maximum value of 10 inches of water. The liquid on the shell side of the fibers will be maintained at a higher pressure than the gas, but not more than the allowable transmembrane pressure of 22 psi, by placing a needle valve on the liquid outlet.

The exiting solution, containing dissolved SO$_2$, will have a pH of approximately 2.5 or 3. In order to comply with environmental regulations, we are required to neutralize this stream before draining the liquid. Therefore, the liquid outlet will flow into a stirred tank, where it will be combined with sodium hydroxide (1.0 M) and monitored with a pH meter.

By the end of this reporting period, we have completed a substantial portion of the construction of the apparatus for testing rectangular HFCs. We expect to receive the rectangular modules in the middle of April. Therefore, the integrated experimental arrangement will be used to conduct SO$_2$ removal tests at gas flow rates up to 200 SLM.