

SRI International

DOE/PC/91344--T/17

Revised Quarterly Technical Report #17 • October 1996

ADVANCED SEPARATION TECHNOLOGY FOR FLUE GAS CLEANUP

Abhoyjit S. Bhowm
Tracy Riggs
Arash Bahman

Kamalesh K. Sirkar
Sudipto Majumdar
Debabrata Bhaumick

SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

New Jersey Institute of Technology
University Heights
Newark, NJ 07102

SRI Project No. PYU-3501

Prepared for:

U.S. DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
P.O. Box 10940
MS 921-118
Pittsburgh, PA 15236-0940

Attn: Document Control Center

DOE Contract No. DE-AC22-92PC91344

MASTER

RECEIVED
USDOE/PETC
36 OCT 28 AM 11:09
ACQUISITION & ASSISTANCE DIV.

UN

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

CONTENTS

INTRODUCTION 2
TASK 9: PERFORMANCE OF SCALABLE MODULES..... 4

TABLES

1. Project Tasks and Schedule..... 3

INTRODUCTION

The objective of this work is to develop a novel system for regenerable SO₂ and NO_x scrubbing of flue gas that focuses on (a) a novel method for regeneration of spent SO₂ scrubbing liquor and (b) novel chemistry for reversible absorption of NO_x. In addition, high efficiency hollow fiber contactors (HFC) are proposed as the devices for scrubbing the SO₂ and NO_x from the flue gas. The system will be designed to remove more than 95% of the SO_x and more than 75% of the 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 SO_x and selective catalytic reduction of 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 SO₂ and NO_x. We will also introduce new process chemistry to minimize traditionally well-known problems with SO₂ and NO_x absorption and desorption. For example, we will extract the SO₂ 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 NO_x will consist of water soluble phthalocyanine compounds invented by SRI and also of polymeric forms of Fe⁺⁺ complexes similar to traditional NO_x scrubbing media described in the open literature. Our past work with the phthalocyanine compounds, used as sensors for NO and NO₂ in flue gases, shows that these compounds bind NO and NO₂ reversibly and with no interference from O₂, CO₂, SO₂, 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 NO_x absorber can be on top of the 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 SO₂ and 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 SO₂/NO_x scrubbing.

Work was planned to be conducted over a 60-month period (May 1992 through April 1997), encompassing 16 tasks, as shown in Table S-1, beginning with studies of the fundamental chemistry and the mass transfer characteristics of small HFC modules in the laboratory. We would then examine the most favorable method of SO₂ liquor regeneration, determine the ability of the HFC devices to withstand

particulate matter, and examine the behavior of scalable modules. The project was terminated by DOE without completion of Tasks 9 and 10 and without executing Tasks 11,12, and 13.

**Table S-1
PROJECT TASKS AND SCHEDULE**

<u>Task Number</u>	<u>Title</u>	<u>Status</u>
1	Project Definition	Complete
2	Capacity, Reversibility and Lifetime	Complete
3	Chemical Synthesis	Complete
4	SO ₂ Scrubbing with HFCs	Complete
5	NO _x Scrubbing with HFCs	Complete
6	SO ₂ Liquor Regeneration	Complete
7	Particle Deposition	Complete
8	Integrated NO _x Life Tests	Complete
9	Scalable Modules	Incomplete
10	Computational Model	Incomplete
11	Construction of Subscale Prototype	Not executed
12	Operation of Subscale Prototype	Not executed
13	Refinement of Computational Model	Not executed
14	Economic Evaluation	Complete for work done to date
15	Reporting	Complete for work done to date
16	Chemical Synthesis for Process Scaleup	Complete for work done to date

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.

During this quarter, we continued the combined SO₂ absorption/scrubbing liquor regeneration experiments. As we stated in the previous quarter (Quarterly Technical Report #16), we have been attempting to bring the system to continuous operation.

During our second attempt at running the experiment, we observed a significant leak in the absorber module, causing the sodium sulfite solution to pass through the pores into the gas side. This was probably because the absorber module may not have been completely dry (we cleaned both modules with TCE and methanol after the first run). The next problem we encountered was a pressure buildup on the d-DMA inlet to the regenerator module. This seemed to be caused by d-DMA solidifying in the module before reaching its steady-state temperature. We prevented this from happening by preheating the cooling liquid to ensure that the d-DMA leaves the cooler at around 40°C, instead of slowly increasing from room temperature to the steady-state temperature.

The final concern we needed to address before running the experiment continuously was an emergency shutdown system. Initially, we tried to use a thermal dispersion flow switch to detect a d-DMA leak, but this was not effective at detecting flow of the organic liquid. We then set up a system to detect a catastrophic leak based on temperature readings; if the temperature begins to drop in the d-DMA lines, this indicates that flow has ceased due to a leak and the pump will be shut off.

We analyzed (by NMR) the orange material that was extracted into the aqueous phase out of the organic phase. This indicated that some of the d-DMA has degraded; the ether bond was broken and an alcohol was formed. We do not have any quantitative information on what fraction of the d-DMA has reacted, but we found that after several water extractions on a small sample, we were able to completely remove the new compound. This extraction procedure would be quite

lengthy and complicated if we performed it on the entire volume of d-DMA, so we intend to use the d-DMA we have "as is". We do not expect the alcohol to have much effect on SO₂ absorption, but it has probably increased the vapor pressure of the organic material. Still, the overall effect of degradation on the process is expected to be very minor.

In the next experiment, we planned to leave the system running for at least twenty-four consecutive hours, as we believe that it might take a few days to reach steady-state conditions. We were able to circulate d-DMA through the tube side of the regenerator module for several days without problems. The sodium sulfite solution was not flowing through the shell side, because we were still experiencing difficulty keeping the aqueous material from leaking into the tube side of the fibers, so we were unable to flow the solution for long periods of time. Previous to this experiment, we had observed that the d-DMA was not flowing through the fiber pores, perhaps because of its high surface tension. This observation led us to believe that we could circulate d-DMA inside the fibers without the pressurized aqueous solution on the outside. In case of a leak, however, we closed the valves on the shell inlet and outlet.

After a few days of d-DMA circulation, we began flow of the sodium sulfite solution. We opened the valves on the shell inlet and outlet of the liquid-liquid extractor module and attempted to pump the aqueous solution through the shell side. However, we were unable to get any liquid through the shell side of the module. We noticed that d-DMA had traveled through the pores and collected in the inlet and outlet ports of the shell side of the module, where it solidified. We are not sure why the d-DMA came through the pores; possibly the fibers were weakened due to the pressure buildup we experienced in April (see Management Status Report #48) or the higher temperature of d-DMA decreased the surface tension low enough to flow through the pores. In any case, we needed to get the solidified d-DMA out of the ports, so we used heating tape on a low setting. Once the d-DMA melted, we planned to attempt to flow sodium sulfite solution again. However, we were unable to prevent the organic liquid from coming into the aqueous lines after it melted; even the flue gas scrubbing module was contaminated with d-DMA. At this point, we decided that the high melting point of the d-DMA was causing too many problems and we investigated other options. We chose to switch to dimethylaniline (DMA) as the organic extractant. We should be able to use the DMA data to make predictions for system performance using d-DMA.

While waiting for our DMA order to arrive, we thoroughly cleaned the d-DMA out of both the absorber and extractor modules. We then performed one experiment using 0.05M sodium sulfite as the scrubbing solution and DMA as the SO₂ extractant. We were unable to run the experiment long enough to collect any valid data due to several problems we experienced. First, the sodium sulfite solution was leaking through the pores of both the absorber and the extractor module. This caused loss of sodium sulfite through the gas line and into the DMA reservoir, and

also caused inaccurate analyzer readings from sodium sulfite in the sample lines. We have been experiencing this problem for the past year and have been unable to find a way to prevent leaking. In addition, we noticed that the air bubblers in the DMA flask were causing foaming of DMA, leading to overflow and foam in the process lines. Because of these problems, it was necessary to shut down the experiment.

The remainder of the quarter, upon receipt of the Stop Work order, was spent dismantling the apparatus, disposing waste materials and cleaning the laboratory.