DOE/PC/91344--T16

SRI International

Quarterly Technical Report #15 • February 1996

ADVANCED SEPARATION TECHNOLOGY FOR FLUE GAS CLEANUP

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INTRODUCTION

The objective of this work is to develop a novel system for regenerable SO_2 and NO_x scrubbing of flue gas that focuses on (a) a novel method for regeneration of spent SO_2 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 SO_2 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 SO_2 and NO_x. We will also introduce new process chemistry to minimize traditionally well-known problems with SO_2 and NO_x absorption and desorption. For example, we will extract the 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 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 NO_2 in flue gases, shows that these compounds bind NO and NO_2 reversibly and with no interference from O_2, CO_2, 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 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 SO_2 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 SO_2/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 SO_2 liquor regeneration, determine the ability of the HFC devices to withstand particulate matter,

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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.

Table 1

PROJECT TASKS AND SCHEDULE

Task Number	Title	Duration
1	Project Definition	5/92 – 8/92
2	Capacity, Reversibility and Lifetime	7/92 – 6/94
3	Chemical Synthesis	7/92 – 6/94
4	SO$_2$ Scrubbing with HFCs	7/92 – 9/93
5	NO$_x$ Scrubbing with HFCs	2/93 – 3/94
6	SO$_2$ Liquor Regeneration	7/93 – 9/94
7	Particle Deposition	8/93 – 9/94
8	Integrated NO$_x$ Life Tests	8/94 – 1/96
9	Scalable Modules	9/94 – 1/96
10	Computational Model	3/95 – 1/96
11	Construction of Subscale Prototype	2/96 – 4/96
12	Operation of Subscale Prototype	5/96 – 4/97
13	Refinement of Computational Model	1/97 – 4/97
14	Economic Evaluation	Various
15	Reporting	5/92 – 4/97
16	Chemical Synthesis for Process Scale-up	5/94 – 4/96

SUMMARY OF QUARTERLY PROGRESS

During the fourth quarter of 1995, we continued work on Task 9.

In Task 9, we gathered mass transfer data using single-unit welded rectangular HFC. We experimentally showed that the sulfite oxidation to sulfate (a less desirable compound for SO_2 absorption) to be negligible in the pressence of O_2. We compared mass transfer data between single-unit and four-unit welded module. The four-unit module had displayed poor mass transfer behavior relative to single-unit module. The construction of experimental facility for combined SO_2 absorption/desorption was also completed during this reporting period.

TASK 8: INTEGRATED NO$_X$ LIFE TESTS

Liquid scrubbing systems for NO$_X$ 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$_X$ absorption/ desorption system. We have previously shown that Co(II)-phthalocyanine is a promising candidate for NO$_X$ absorption in the presence of O$_2$. We have also demonstrated the superior mass transfer characteristics of the 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 NOx absorption/desorption chemistry has the potential to be commercially robust.

In the last quarter (Quarterly Technical Report #14), we reported that the observed NO$_X$ removal has been limited by inefficient desorption of the Co(II)-phthalocyanine solution. As pointed out by DOE, this presents a problem during the characterization of the sub-scale prototype modules. The most reasonable solution would be to use another hollow fiber contactor in place of a conventional stripper. However, the maximum operating temperature for polypropylene fibers is about 70°C. Therefore, use of another HFC as a stripper is not possible by a polypropylene fiber contactor because of the higher temperatures (~100°C) involved in the stripping system.

Since the desorption operation is carried out at about 100°C, a large packed tower toner (e.g., packed with glass beads) seem to be a viable alternative. The glass beads would provide higher gas-liquid interfacial areas leading to sufficient description rates. Notice that in our previous Co(II)-phthalocyanine regeneration tests, we have employed the gas sparging arrangement.

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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.

In the beginning of this quarter, we completed testing of the single welded submodule. We conducted additional experiments using 0.2M Na_2SO_3 as the scrubbing liquid, and investigated the possibility of sulfite oxidation by oxygen in the house air.

Table 2 shows all the results using 0.2M Na_2SO_3 solution. The Run Numbers given by S2G (constant gas flow) and S2L (constant liquid flow) represent runs using house air blended with SO_2. Experiments using nitrogen blended with SO_2 are designated by S2NL.

A comparative plot (Sherwood Number vs. Reynolds Number) of the house air and nitrogen experiments is shown in Figure 1. Although the removal rates were slightly higher with nitrogen, there is not a significant difference between the two. Therefore, the figure indicates that oxidation of sulfites to sulfates (less desirable species for SO_2 absorption) by the house air is not a serious concern.

We have received a new contractor from Setec which contains four submodules welded together in the same way as the single submodule. We conducted experiments using water and 0.2M Na_2SO_3 as the scrubbing media and the results are compared with that of the single welded module.

The results obtained for these experiments are shown in Figures 2 and 3. The observed mass transfer coefficients with the four-unit module were significantly lower than that obtained using single sub-unit modules for both scrubbing liquids. The values were about 50% lower using water (Figure 2) and 70-80% lower using 0.2M Na_2SO_3 solution (Figure 3).

Table 2
RESULTS OF SO$_2$ ABSORPTION IN 0.2M Na$_2$SO$_3$

| Run No.	Temp. (C°)	Liquid Flow (mL/min)	Gas Flow SLPM	Inlet SO$_2$ Composition (ppm)	Outlet SO$_2$ Composition (ppm)	Percent SO$_2$ Removed	Kog (cm/s)	Re (gas)	Re (liq)	Sh
S2G1	23.3	77	20.3	3024	1.7	99.9	-	71.4	5.8	-
S2G2	23.3	77	20.3	3024	1.5	99.9	-	71.4	5.8	-
S2G3	23.2	358	20.3	3029	1.4	99.9	-	71.4	27.0	-
S2G4	23.1	77	20.3	3033	1.1	99.9	-	71.4	5.8	-
S2G5	26.1	110	20.2	2994	1.4	99.9	-	71.3	8.3	-
S2G6	25.9	20	20.2	3004	1097	63	0.0555	71.3	1.5	326
S2G7	25.7	43	20.2	3024	79	97	0.200	71.3	3.2	1176
S2G8	25.8	20	20.3	2914	1023	65	0.0577	71.4	1.5	339
S2G9	25.7	43	20.3	2914	68	98	0.206	71.4	3.2	1214
S2G10	25.5	43	20.2	3003	198	93	0.149	71.3	3.2	877
S2G11	25.1	20	20.2	3003	1251	58	0.0481	71.3	1.5	283
S2G12	25.4	54	20.2	3003	36	99	0.241	71.3	4.1	1418
S2G13	25.3	65	20.2	3003	2.8	99.9	-	71.3	4.9	-
S2G14	23.9	43	20.2	3063	140	95	0.168	71.3	3.2	990
S2G15	24.2	43	20.2	3013	136	96	0.169	71.3	3.2	995
S2G16	24.2	110	20.2	3013	1.1	99.9	-	71.3	8.3	-
S2G17	24.1	20	20.2	3018	1246	59	0.0484	71.3	1.5	285
S2L1	23.2	20	20.3	3043	1073	65	0.0570	71.4	1.5	335
S2L2	23.4	20	26.8	3014	760	75	0.0624	59.0	1.5	368
S2L3	23.8	20	23.7	3033	442	85	0.0718	48.4	1.5	422
S2L4	23.9	20	11.9	3033	260	91	0.0798	42.1	1.5	470
S2L5	24.2	20	9.7	3024	58	98	0.104	34.0	1.5	612
S2L6	25.0	20	9.8	2974	164	94	0.0773	34.3	1.5	455
S2L7	25.0	20	14.7	3024	760	75	0.0553	51.8	1.5	325
S2L8	24.7	20	19.8	3004	1188	60	0.0499	69.9	1.5	294
S2L9	23.2	20	20.0	3014	1367	55	0.0427	70.5	1.5	251
S2L10	23.5	20	14.8	3004	952	68	0.0461	52.0	1.5	271
S2L11	23.3	20	20.0	3004	1118	63	0.0534	70.6	1.5	314
S2L12	23.5	20	14.8	3033	680	78	0.0599	52.0	1.5	352
S2L13	23.8	20	9.6	3024	148	95	0.0792	33.9	1.5	466
S2L14	24.7	20	20.0	3019	1153	62	0.0523	70.6	1.5	308
S2L15	25.5	20	9.6	2984	101	97	0.0893	33.9	1.5	526
S2L16	22.7	20	35.2	3033	1791	41	0.0494	124	1.5	291
S2L17	22.7	20	20.1	3033	1171	61	0.0516	70.8	1.5	303
S2L18	22.9	20	9.6	3004	141	95	0.0799	33.9	1.5	470
S2L19	22.8	20	20.1	3004	1171	61	0.051	70.8	1.5	300
S2L20	22.4	20	35.2	3029	1786	41	0.0495	124	1.5	291
S2NL1	24.6	20	9.7	3014	9	99.7	-	34.2	1.5	-
S2NL2	24.0	20	9.8	3014	51	98	0.109	34.5	1.5	641
S2NL3	24.1	20	19.9	3014	1123	63	0.0532	70.2	1.5	313
S2NL4	23.9	20	14.7	3024	655	78	0.0611	51.8	1.5	359
S2NL5	23.8	20	9.9	3014	97	97	0.0926	34.9	1.5	545
S2NL6	23.3	20	20.0	3004	1118	63	0.0534	70.6	1.5	314
S2NL7	24.0	20	14.8	3043	493	84	0.0730	52.0	1.5	429
S2NL8	24.2	20	9.6	3014	23	99.2	-	33.9	1.5	-
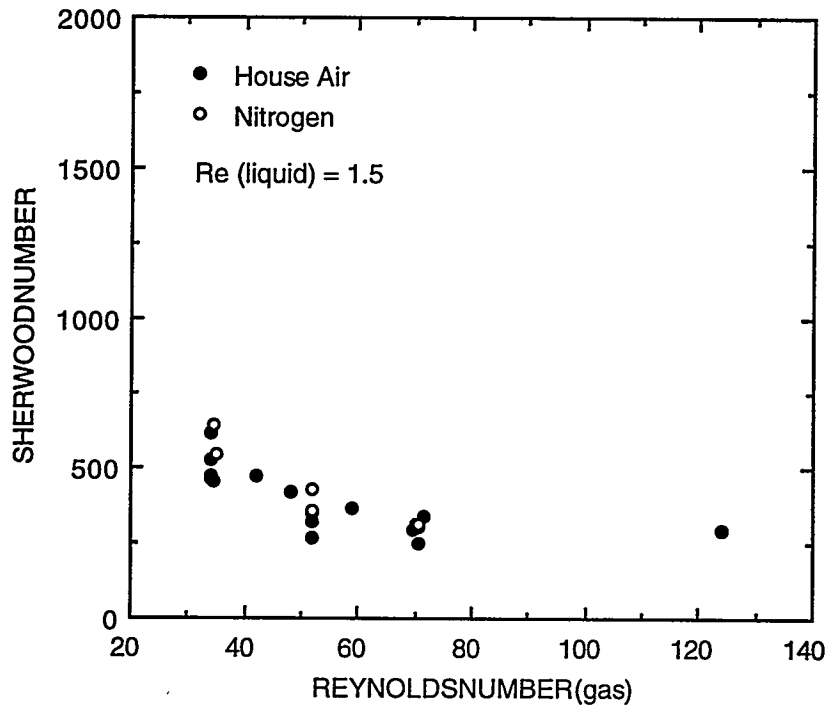
Figure 1. Sherwood Number vs. Reynolds Number.

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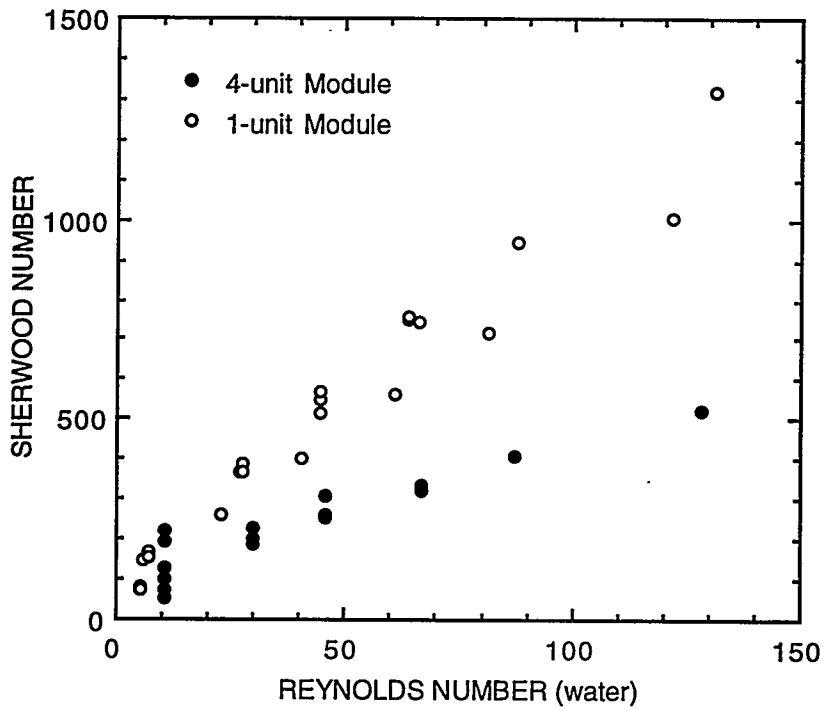
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Figure 2. Sherwood Number vs. Reynolds Number (water).
Re (gas) = 70.

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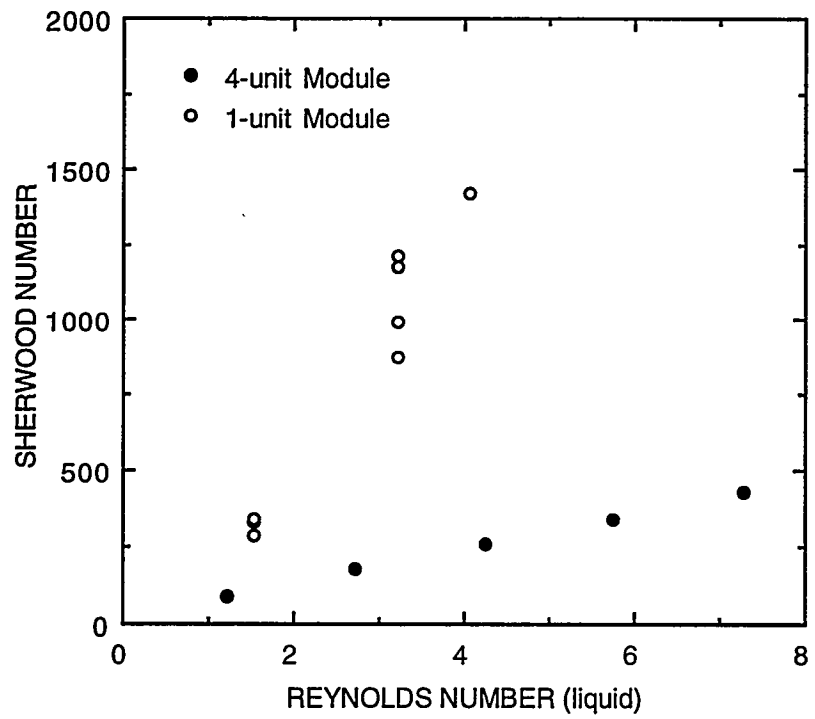
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Figure 3. Sherwood Number vs. Reynolds Number (0.2M Na_2SO_3).
Re (gas) = 70.

We believe this discrepancy may be partly due to poor flow distribution of the gas amongst sub-units in the module. To investigate this, we measured the flow through each of the individual modules using a mass flowmeter. The total gas flow rate was 80 SLPM, the same rate that was used for the SO_2 scrubbing experiments. The flow through each module is shown in Table 3, with the submodule numbers indicating the direction of flow (i.e. the scrubbing liquid contacts No. 1 first and No. 4 last). The table shows that the flow distribution is not even among the four submodules. We are investigating possible ways to correct this problem.

Table 3
Gas Flow Distribution in Four-Unit Welded Module

Submodule No.	Flow (SLPM)
1	17.1
2	13.1
3	21.0
4	28.1

As we approach the portion of Task 9 which involves combined SO_2 absorption/scrubbing liquor regeneration, there are some issues which must be addressed. The first of these involves the design of the experimental apparatus (see Management Status Report #40). Although we are using hollow fiber contactors for both the SO_2 absorption and the scrubbing liquid regeneration, the organic (d-DMA) regeneration will be performed by bubbling sweep gas through a sparger. Because the sparger is not as efficient as the hollow fibers in providing mass transfer areas, we expect the regeneration of the organic liquid to be the factor which limits SO_2 removal. Possible solutions to this problem include the use of a distillation column rather than the sparger or operation of the experiment in a batch process as an alternative to regenerating the organic. Due to the time and expense that would be involved in implementing either of these options, we will perform the experiments as planned and evaluate the results with regard to the limitation occurred by the sparger.

The second issue stems from the results of the d-DMA synthesis. The final product exhibits some different properties than the material that was synthesized and tested in Task 3. This new material is solid at room temperature, but melts at about 30-40°C. The previously tested material was a low-viscosity liquid at room temperature. It seems that the amount of impurities in the d-DMA may determine the final form of d-DMA we obtain. The larger scale product is about 90% pure. We don't have any information on the earlier product, but we suspect it has a lower purity, causing a lower melting temperature. We plan on using the scaled-up synthesis product for the combined SO_2 absorption/scrubbing liquor regeneration step, but we will need to operate at

slightly elevated temperatures. Another option may be to dissolve this material in a high-boiling point solvent, such as sulfolane.

Lastly, it is important to address the safety issues regarding the d-DMA. Little is known about the toxicity of the compound, however, several of the reagents used are toxic and it is likely that the synthesized product is toxic and/or contains residual amounts of toxic compounds. In addition, some possibly carcinogenic solvents were used in the synthesis, so there may be a residue of suspect carcinogens. Therefore, care should be taken to ensure that the d-DMA is not ingested, inhaled or contacted with skin. Safety glasses, gloves and adequate ventilation should be used at all times when handling the material. It should be stored and disposed as a hazardous organic substance.

We encountered some difficulties with the four-unit, welded module, in addition to the observed poor gas flow distribution as mentioned above. There was a liquid leak in one of the four submodules into the fiber lumens (gas-side), and we also observed some deposits on the porex; the module has been sent back to Setec for repairs. We have requested that they check the leaky submodule (and replace if necessary), replace the soiled porex and implement a more efficient flow distribution mechanism.

We completed the construction of the apparatus for combined SO_2 absorption/ scrubbing liquor regeneration in December (see Figure 10, Quarterly Technical Report #14 for a schematic of the apparatus). In addition, because the d-DMA melts above room temperature, we need to heat it slightly and continually circulate it through the process lines. For this reason, we could not have started up the system in December as the apparatus would have been left unattended for ten days during SRI's holiday closing. We intend to begin testing upon receipt of the repaired module.