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**Final Report
on
Design and Development
of a
Self-Regenerative
Contained-Liquid Membrane Process
for
Combined SO_x & NO_x Removal**

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**Design and Development
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Self-Regenerative
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Combined SO_x & NO_x Removal**

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Final Report

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Executive Summary

The lack of an efficient, cost effective process for the removal of sulfur compounds from gas streams (either gasified coal or flue gases resulting from coal combustion) is a major obstacle to the economic utilization of high sulfur Ohio coal. The most economically favorable processes for the desulfurization of flue gases are the regenerable processes as opposed to the 'throwaway' processes. In addition, recovery of sulfur from these gases in the form of elemental sulfur or H_2SO_4 does seem to be an essential step in the economic utilization of high sulfur coal. In light of these observations, a recently proposed FGD process which regenerates the scrubbing liquor "in-situ" as well as recovering a concentrated SO_2 stream for use in sulfuric acid production, is quite promising. Conventional processes, presently in operation, employ large packed tower scrubbers for SO_2 absorption which results in very high capital expenditures and operating costs. Recent developments in membrane technology can now provide us with an alternative to these large packed towers for stack gas cleanup. In this research we have investigated the use of novel membrane contactors for replacing more conventional packed absorbers. Contained-liquid membranes, exploiting carrier mediated transport, enable the scrubbing liquid to be regenerated "in-situ", in a single process unit.

Microporous single-ply polymeric membranes have recently been used in gas-liquid and liquid-liquid contactors. These membranes are fashioned into a tubular shape (i.e. long, thin fibers) for use in mass transfer contactors. The design of these units is similar to that of a countercurrent heat exchanger, with the necessary mass transfer taking place across pores in the walls of the membranes. Hollow fiber membrane contactors offer excellent mass transfer characteristics and dramatically higher contact areas per unit volume (several orders of magnitude) than conventional tower packings thus allowing significant downsizing of the separation equipment and capital cost savings. Another

advantage of hollow fiber absorbers (HFA) is their flexibility in the range of operating flow rates. In packed tower designs, the liquid and gas flow rates are interrelated and are limited by the flooding and channeling characteristics of the packing. In HFAs, on the other hand, the liquid and gas flow rates are independent and flow rates at least 10 times higher than comparably sized packed towers can be achieved. The higher surface areas per unit equipment volume and the increased processing rates possible, together lead to much smaller equipment to achieve the same separation as conventional units. Additionally, operating difficulties which seriously limit the operation of packed beds, such as channeling, are not as severe with HFAs, and can be minimized by proper design of the HFAs. Contained liquid membranes can be constructed using HFAs with two sets of fibers (one to carry the flue gas and the other to carry the sweep gas, with the liquid flowing on the shell side of the contactor). These are called dual hollow fiber contained liquid membranes (HFCLMs). Using the HFCLM geometry for the contained liquid membrane affords us all the advantages discussed above, while allowing us to avoid the construction and operational difficulties inherent in other packaging techniques (a dual spiral, for example).

The objective of this proposed research was to carry out a study of SO_2 and NO_x absorption in contained-liquid membranes under conditions representative of industrial flue gas desulfurization to identify appropriate process chemistries for carrier mediated transport of these pollutants. HFCLMs were studied using the identified chemistries to demonstrate their effectiveness to remove SO_2 and NO_x .

Project Objectives

The precise objectives of this research were as follows:

- Explore the use of carrier mediated transport of SO_2 and NO_x through liquid membranes
- Evaluate and identify appropriate liquid membrane chemistries for SO_2 and NO_x

removal.

- Construct a benchscale flat plate membrane module apparatus for experimental testing of membrane chemistries.
- Examine the capability of regenerating the process reagents "*in-situ*"
- Construct and test an appropriate liquid membrane geometry (dual hollow fiber modules) to demonstrate the separation capacity of the process.

Each of the project objectives were met. The experimental results of the project confirmed our original hypothesis that contained liquid membranes can provide effective SO₂ removal, with "*in-situ*" regeneration of the process reagent. The removal of NO_x was hindered by the fact that oxygen in the flue gas oxidizes (and renders inactive) the only effective NO_x carrier we were able to identify. NO_x can be removed using carrier facilitated transport, however, the carrier quickly degrades due to the presence of oxygen, and the removal rate falls. Some of the findings of major interest in this research are :

- Carrier facilitated transport of SO₂ from flue gases resulting from the burning of high sulfur Ohio coal (@ 3500-4500 ppm SO₂ in the flue gases) is possible. The process also performs well for lower sulfur coals producing flue gases in the neighborhood of 1500 ppm SO₂.
- The SO₂ reagents can be regenerated "*in-situ*", which allows absorption (removal) and stripping (regeneration) to take place in the same process unit.
- New water soluble carrier-reagents have been identified that are superior to sulfite for SO₂ removal.
- Dual hollow fiber contactors provide an effective geometry for the construction of contained liquid membrane modules. They offer all the advantages of the originally proposed dual spiral modules, while being much simpler to design, construct and operate. They are also less expensive than the spiral modules.

- Dual fiber contactors can operate over a much wider flow rate range of liquids and gases than can a packed tower. It operates well in the range of liquid to gas flows commonly used in utility packed scrubbers.
- Hydrophobic polypropylene hollow fibers have the necessary chemical resistance requirements and make effective liquid membrane barriers. .
- The presence of nitrogen oxides in the flue gas stream has no deleterious effect on the removal of the SO₂ by contained liquid membranes.
- A detailed mathematical model that describes the carrier facilitated transport of SO₂ through contained liquid membranes was developed and experimentally validated. It can also be used to help predict the required area of the contactor for a given separation.
- The presence of oxygen in the flue gas or sweep gas interferes with the performance of the carriers for NO removal. The carriers are oxidized and rendered inactive over a period of time. This is a significant drawback and the use of CLMs for carrier mediated transport of NO_x is unlikely unless other effective carriers can be identified in the future.
- Dimethyl-aniline (DMA) in cyclohexyl pyrrolidone (CHP) was shown to be a possible organic based carrier system for SO₂ removal. If a carrier for NO_x soluble in CHP can be identified in the future, this may provide a viable alternative to aqueous chemistries.

The technical highlights of the work are noted above, and they are discussed in greater detail in the body of the full report. We have demonstrated that dual hollow fiber absorbers are effective contactors for the carrier-mediated removal of SO₂ from flue gases. Our calculations *estimate* that the cost of incorporating HFCLMs on a 500 MW power plant operating on 3.5% coal to be approximately \$7/ton of coal, and \$108/ton

SO₂ removed. We have not addressed the issue of costs associated with NO_x removal for the contained liquid membrane process as the process chemistry was not perfected to an extent to allow us to do this. Near-term commercialization of this process is unlikely until additional technical problems can be resolved. In the near-term, i.e. the next 12-24 months, the possibility of this project making any significant impact on the use of high sulfur coal is very small. If a pilot plant study could be worked out in that time period, the chances of making an impact in the next 5-10 years could improve markedly. It has to be remembered that this was a research project, whose objective was to generate new knowledge and ideas, where none existed previously. We believe we have done that. We have examined a new process alternative that has some definite possibilities for pollution control. With the new government initiatives and acid rain regulations looming in the near future, we need all the technical innovation that we can find to combat emissions while still allowing the use of high sulfur Ohio coal.

Technical Report
on
Design and Development of a Self-Regenerative
Contained-Liquid Membrane Process
for
Combined SO_x & NO_x Removal

Introduction

Vast research efforts have been expended over the last decade in this country for developing economically viable technologies to promote successful utilization of the abundantly available high-sulfur coal reserves of U.S.. Pre- and post-combustion treatment technologies for pollutant removal have been proposed, with post-combustion treatment offering the most promise as a simple and convenient technology for dealing with a variety of high sulfur coals[1,2].

Recently, we have demonstrated that hollow fiber membrane absorbers (HFA) could replace the conventional packed tower absorbers presently used in regenerative sodium sulfite (Wellman-Lord-Allied) wet-scrubbing processes [3]. HFAs provide superior mass transfer characteristics and dramatically higher gas-liquid contact areas per unit volume than conventional tower packings thus allowing significant downsizing of the separation equipment and higher flexibility in the range of operating flows. Thus HFAs hold promise for retrofitting existing regenerative FGD processes to make them more cost effective with high sulfur coal.

Current regulatory [1,4] and research [5-8] trends in this area of flue gas treatment (FGT) technology leads us to believe that, to surpass the existing technologies and to offer significant cost reductions with high sulfur coals, any new innovation in FGT technology has to meet the following general criteria:

- (1) The process, preferably, shall be capable of removing SO_x and NO_x from flue gases in a *single* step rather than requiring separate treatment procedures

for each of these pollutants.

- (2) The process shall also incorporate a *regeneration* scheme for any liquid phase additives - used to increase the rate of absorption of SO_x and NO_x - if it employs a wet-scrubbing technique, or the spent sorbent if it uses a dry adsorption technique. (Non-regenerative limestone/lime scrubbing type processes, however, are quite unlikely to be economically successful.)
- (3) The recovery of SO_x and NO_x in the form of concentrated streams and their subsequent conversion to sulfuric and nitric acids, or elemental sulfur and nitrogen, also appears to be essential for healthy process economics.

It is obvious, then, that among the several possible technologies that incorporate these three general criteria, those which can perform these tasks in the most efficient manner are the ones that will ultimately be commercialized.

Our experience with membrane separations in general [9,10], and HFA research in particular, leads us to believe that membrane-based techniques possess some unique advantages over other separation techniques. They can perform separations at relatively mild operating conditions with unparalleled selectivities [11] and offer the possibility of packaging extremely large surface areas in a given volume [12]. We, therefore, tried to identify a process which could incorporate the above three criteria in a very efficient manner, while still retaining all the inherent advantages of general membrane-based separations. The purpose of this project was to explore the possibility of exploiting the recently discovered phenomenon of 'carrier-facilitated transport of gases through liquid membranes' [13] to accomplish the combined removal of SO_x and NO_x from flue gases while simultaneously regenerating the carrier substances in an *in-situ* fashion. The liquid membrane process also allows at the same time, recovery of SO_2 and NO_x in the form of a concentrated dry mixture suitable for conversion to sulfuric and nitric acids. Furthermore, this process is of such a nature that it is capable of achieving all these

objectives within a single process unit.

Carrier-Facilitated Transport (CFT) of a Gas Across a Liquid Membrane (LM) Thin

liquid films can form membranes that are potentially superior to conventional polymer membranes for gas separations due to two reasons: First, the permeant (SO_2 or NO , for example) diffusivity is several orders of magnitude higher in liquids implying a much higher membrane permeability. Second, "carriers" can be incorporated into liquid films to *selectively* enhance (by orders of magnitude) the transport rate of any *given* permeant. The flux enhancement of the permeating gas results from a *specific* and *reversible* chemical reaction of the gaseous component with the carrier molecule. The carrier molecule, while mobile within the liquid film, is not capable of leaving it. Therefore, when a partial pressure difference of the pollutant gas is maintained across the liquid film (by flowing the feed gas parallel to one face of the film while sweeping the opposite face with an inert gas), the carrier molecule binds gas molecules at the high pressure side of the membrane, releases the bound molecules at the low pressure side, and diffuses back to the high pressure side to pick up more gas molecules. (This is shown schematically in Figure 1.) Thus the gaseous species is transported across the film not only by diffusion caused by its partial pressure gradient (Fickian diffusion) but also in the carrier-bound complex form. The transport of the gas is thus said to be "facilitated" and this phenomenon is referred to as "carrier-facilitated" transport [13,14]. In this process, although the permeant participates in a reversible chemical reaction with the carrier at every location within the film, there is no overall consumption of the permeant or carrier species within the liquid film under steady-state conditions, i.e. the liquid membrane is globally nonreactive. The so called 'facilitation factor', F , defined by:

FIGURE 1 Schematic diagram for carrier-facilitated transport in a membrane. A reversible reaction $A + B = AB$ takes place in the membrane. Both carrier (B) and carrier - permeant complex (AB) are confined to the membrane.

$$F = \frac{N - N_0}{N_0} \quad (1)$$

where:

N = steady-state flux of the permeant across the film in the presence of the carrier,

and

N_0 = steady - state flux due to Fickian diffusion alone,

F is often employed to denote quantitatively the augmentation in permeant flux caused by the carrier. Values of F ranging from 10 to 1000 are not uncommon implying that, with gas mixtures, the flux of the component undergoing facilitated transport can be orders of magnitude larger than that of the components permeating the liquid film only by Fickian diffusion. Since the concentration ratio of different species in the permeant stream is simply equal to their flux ratio across the liquid film, one recovers a product stream which contains essentially the component whose transport is 'facilitated'. Therefore, if carriers can be identified so that the transport of the two species, SO_2 and NO_x , *only* is facilitated from among the different gases in a feed flue gas mixture, the process forms the basis for the combined removal of SO_2 and NO_x from flue gases.

Advantages of Liquid Membrane Process over Wet-Scrubbing:

One might recognize at once from the foregoing description that carriers play a role analogous to the chemical additives used in conventional wet-scrubbing (i.e., they enhance mass transfer rates). There are, however, some very important fundamental differences between wet-scrubbing and CFT through LMs:

- (i) While the used-up chemical additives of wet-scrubbing must be regenerated *externally*, the carrier undergoes *self-regeneration* within the membrane as it shuttles back and forth inside the liquid film (as explained above). This difference represents a very significant economic advantage in favor of liquid membranes

because sorbent regeneration costs are totally eliminated here.

- (ii) If one employs low-pressure steam as the sweep gas in the LM process, then the sweep-stream from the membrane permeator (carrying SO₂ and NO) can be routed to a steam condenser, thus providing a dry mixture of SO₂ and NO at a pressure sufficient for processing in sulfur and nitrogen recovery plants. Thus, the LM permeator simultaneously accomplishes the two tasks of combined removal of SO₂/NO from flue gases, and recovery of these two absorbed gases into low-pressure steam. It is obvious that with conventional wet-scrubbing, one needs an external steam-stripping column if it is desired to recover the absorbed gases.

Are carriers available to exploit this potentially superior LM process?

Indeed, Roberts and Friedlander had fairly recently shown that the two alkaline salts, Na₂SO₃ and NaOH (used in conventional Wellman-Lord wet-scrubbing process), when added to an aqueous film of about 1 mm thickness at about the same concentration levels used in wet scrubbing, can enhance the transport rates of SO₂ across the film by as much as 370 times via a carrier-facilitated mechanism [18]. The principal mechanism by which facilitated-transport of SO₂ takes place in the film is shown in the upper-half of Figure 2. As can be seen from the figure, the reversible reaction:

is mainly responsible for the observed flux augmentation of SO₂ [18]. Dissolved sulfur dioxide reacts with SO₃⁼ and H₂O on the high pressure side of the film to form two HSO₃⁻ ions which diffuse across the film to the low pressure side where these ions get reconverted to H₂O, SO₃⁼ and SO₂. H₂O and SO₃⁼ diffuse back in the film to the high pressure side to react with more SO₂ from flue gases while SO₂ formed escapes into the steam sweeping the low pressure side of the film. Of course, as shown in the figure,

Figure 2 Aqueous Film Containing Dissolved Na_2SO_3 / NaOH and Fe(II)-EDTA Chelate

dissolved SO_2 undergoes simultaneously Fickian diffusion also through the film. However, as is evident from the large facilitation factor observed by Roberts and Friedlander, carrier-mediated transport of SO_2 forms the dominant mode of its transport through the film.

More interestingly, Harkness et al. (of Argonne National Laboratory) [5,15] and a group of Japanese researchers [16,17] have most recently observed that the addition of the metal chelate Fe(II)EDTA to the scrub-liquid of a Wellman-Lord process can absorb 90% of the NO present in the flue gases without adversely affecting the SO_2 absorption rates. In addition, the Japanese group has also established that NO undergoes *reversible* binding with Fe(II)EDTA [16], according to the following scheme:

The lower half of Figure 2 indicates how the above reaction scheme can lead to facilitation of NO transport across the film.

The considerations of the above two paragraphs indicate that it certainly is feasible to develop a carrier-facilitated liquid membrane process for combined SO_2/NO removal using the schemes outlined in Figure 2.

Two aspects pertaining to the chemistry of the system that need to be paid special attention are:

1. The possible irreversible conversion of small quantities of sulfites in the aqueous film to sulfates by the oxygen present in the flue gases, and
2. Any possible chemical interactions between Fe(II)-EDTA (NO) complex and HSO_3^- (see Figure 2).

To be prepared to handle possible difficulties that might occur with the above chemistries,

we intend to investigate other aqueous as well as nonaqueous chemistries (see Technical Discussion Section for details on the other chemistries actually investigated).

Project Objectives

The specific objectives of this research were as follows:

- Explore the use of carrier mediated transport of SO_2 and NO_x through liquid membranes
- Evaluate and identify appropriate liquid membrane chemistries for SO_2 and NO_x removal.
- Construct a benchscale flat plate membrane module apparatus for experimental testing of membrane chemistries.
- Examine the capability of regenerating the process reagents "in-situ"
- Construct and test an appropriate liquid membrane geometry (dual hollow fiber modules) to demonstrate the separation capacity of the process.

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Technical Discussion

In the material that follows, we shall discuss the technical aspects of the project. The essence of the technical discussion including all the experimental details is embodied in the material which follows. We will discuss in detail:

- ▣ background information
- ▣ the description of the process
- ▣ the experimental and theoretical approach taken to meet the project objectives
- ▣ the detailed results, and
- ▣ the analysis and discussion of those results

Background Information: Operation and Packaging of Liquid Membranes

Immobilized Liquid Membranes (ILMs) versus Contained Liquid Membranes (CLMs): To date the traditional procedure of preparing LM's is to immobilize a thin film of liquid by impregnating it in a microporous hydrophilic polymer membrane [Kimura, 1979] (see Figure 3a). Here, surface tension forces hold the liquid in the pores of the support, and enable the LM to withstand transmembrane pressure drops as large as several hundred psi. Such membranes, however, suffer from some serious operational problems which are mainly responsible for the limited industrial applications enjoyed by LM's despite their superior separation characteristics. Fortunately, Sirkar et al., have recently advanced the concept of "Contained Liquid Membranes (CLM)", and have experimentally demonstrated that CLMs could overcome all the operational problems of traditional ILMs [Sirkar, 1986]. Conceptually, in CLMs the liquid is *contained* in the thin gap (~1mm) formed between two hydrophobic microporous polymeric membranes of high porosity while the other two faces of these membranes are exposed to the flowing

FIGURE 3B

FIGURE 3A

flue gas and the sweep-gas (steam), respectively, as shown in Figure 3b. Here the flue gas/liquid and the sweep gas/liquid interfaces lie inside the pores in the walls of the two membranes sandwiching the liquid film. It should be pointed out that the presence of these membranes at the two faces of the liquid film adds no appreciable extra resistance to mass transfer due to their high porosity [Kiani, 1984; Zhang, 1985]. Even the minor mass transfer resistance offered by the gas-filled membrane-pores can be more than offset by providing for a continuous circulation of the liquid contained in the gap. The advantages of this arrangement over ILM include [Sirkar, 1986]:

- (i) No danger of mixing of the feed and permeant streams even under large transmembrane pressure differentials. (In ILMs, if the immobilized liquid is blown out from the membrane's pores due to the pressure drop, the feed and permeant streams get mixed, and separation is lost.)
- (ii) It is possible to replenish for any lost liquid due to evaporation of the membrane fluid to adjoining gas phases in the CLM. (In actual practice, the two gas streams can be pre-saturated with the vapor of the membrane phase to minimize such losses.)

It is obvious that any membrane-based separation, to be efficient on an industrial scale, should allow for packaging a very large membrane area per unit volume. For example, in industrial scale hyperfiltration and ultrafiltration applications some configurations used to package huge polymer membrane surfaces in a small volume include plate-and-frame, Spiral-Wound, and Hollow-fiber membrane modules [Lonsdale, 1982]. While the concept of CLMs is extremely promising, packaging a large membrane area into a compact device in the framework of this concept required some ingenuity. *(Editorial Note: In the original proposal we suggested a Dual Spiral-Wound Membrane (DSWM) arrangement, as the most suitable configuration to accomplish this task effectively. During the course of research, we determined that an alternate contactor design, namely a Dual Hollow Fiber Membrane Module, would provide*

the same benefits as the DSWM while being simpler to construct and operate. The dual hollow fiber membrane module was approved for study in Milestone Plan 4 of the research. A DSWM was constructed prior to deciding upon the dual fiber design. The details of that effort will be discussed later.). A dual hollow fiber module arrangement was decided upon as the contactor geometry of choice. For treating huge quantities of flue gases on a commercial scale, it is preferable to employ a large number of suitably interconnected membrane modules. The interconnections between the individual modules would be arranged so as to facilitate periodic shut-down of individual purification units, if necessary, thereby permitting rapid replacement of individual membrane modules. Plant maintenance costs are anticipated to be minimized when such modular design is utilized since only single purification unit is affected in case of membrane failure and a complete plant shutdown is not necessary for membrane module replacement. Because of these advantages, modular construction procedure is at present widely practiced in industrial scale membrane-based water desalination plants in the United States and abroad.

Detailed Description of the Research Program

The main tasks of this research project are

- (i) to perform a comparative experimental evaluation of SO_2 transport across flat aqueous films containing suitable reagents to identify the best carrier for SO_2 removal
(Editorial Note: As indicated in the experimental results to be discussed below, sodium citrate was found to be the best "performer" for SO_2 transport across aqueous films. Also, the performance of various chemistries will be compared to sulfite films, which we are using as a benchmark reagent. This choice was made since sulfite is one of the most common regenerable FGD reagents.)
- (ii) to perform an experimental study of NO transport across flat aqueous films containing

- sodium citrate, the best reagent for SO_2 removal, and ferrous chelates
- (iii) to model the facilitated transport of SO_2 across flat citrate films, and compare the predictions of the model against experimental data obtained in a well-characterized CLM device
 - (iv) to determine whether there are any suitable organic chemistries capable of outperforming aqueous citrate films
 - (v) to study the potential of a suitably packaged liquid membrane (Hollow Fiber Contained Liquid Membrane [HFCLM]) as viable alternatives to existing FGD processes

Experimental System and Measurements

In our experiments, we used two kinds of CLM devices. Firstly, we have measured pollutant transport across a "model CLM device" which we refer to as a flat-plate contained liquid membrane (FPCLM) contactor. In this device, a liquid film of the reagent solution, the thickness of which can be controlled precisely, was sandwiched between two hydrophobic microporous polymer sheets. This contactor, while it does not provide appreciable membrane area, allows a rigorous comparison of the model predictions with the experimental data due to its simple geometry. In view of the fact that HFCLMs are more practical devices, we also carried out an experimental comparison of the performance of citrate versus sulfite films in an HFCLM module.

The steady-state flux of SO_2 across aqueous films of known compositions was measured with the experimental apparatus shown in Figure 4. The test cell in the figure was either a FPCLM or HFCLM. All gas flow rates, including SO_2 , were controlled by FMA-700 series mass flow controllers (OMEGA® Engineering, Inc., Stamford, CT). The simulated flue gas feed was prepared by mixing the appropriate amount of SO_2 with air using mass flow controllers. Compressed air was used as the sweep stream.

Figure 4: Experimental apparatus for flue gas studies.

(MFC: mass flow controller; SV: shut off valve; PG: pressure gauge; H: hollow-fiber gas humidifier.)

Both the feed and sweep gas streams were prehumidified, prior to entering the cell, by contacting them with a counter-currently flowing stream of water in microporous hollow fiber modules. A portion of the gas outlet streams was sent to an SO₂ analyzer (Model 40, Pulsed Fluorescent SO₂ analyzer, Thermo Environmental Instruments Inc., Franklin, MA) for continuous monitoring of the SO₂ concentration. The analyzer was calibrated after each experiment using a certified gas mixture (SO₂ and air). The calibration gas cylinders were supplied by LINDE Speciality Gases, Toledo, OH. The sodium citrate and sodium sulfite chemicals used for the preparation of reagent solution were purchased from Fisher Scientific. The details regarding the test cells used in this study and their operating parameters are presented below.

FPCLM operating parameters

An outline drawing of the FPCLM contactor is shown in Figure 5. The cell consists of three stainless steel parts: a casing and two halves. Two microporous polypropylene (Celgard® 2500, Hoechst Celanese, Charlotte, NC) sheets, one for each half cell, are mounted by means of a sliding ring (not shown in figure) and six screws. These halves are mounted in the casing as shown in the figure. Properties of the polymer sheet are given in Table 1.

Table 1. Microporous Polymer Film Properties

Material	Hydrophobic polypropylene film, Celgard® 2500
Film thickness	25.0 µm
Porosity	0.45
Pore size	0.075 µm

The exposed surface area of each polymeric sheet is 18.7 cm², and the volume of each of the gas chambers formed is about 5.4 cm³.

Figure 5 : A sketch of flat-plate contained liquid membrane contactor. (1): microporous polymeric sheets; (2): gas chambers for feed and sweep streams; (3): flexible gaskets that ensure a snug fit of the casing with the two halves (stainless steel blocks) forming the cell.

The thickness of the liquid membrane can be adjusted by using brass O-rings of different thicknesses. Likewise the thickness of the liquid membrane can be varied from 100 to 1700 μm . The thickness employed in the present study was 200 μm . The cell has the provision to flow the reagent solution between the two polymeric sheets. However, in all our experiments, the reagent solution was held stagnant. As already noted, evaporative losses of liquid film were minimized by prehumidifying the gas streams entering the device.

HFCLM operating parameters

The HFCLM module (commercially known as LIQUI-CEL™) was manufactured by Hoechst Celanese, Charlotte, NC. An outline sketch of the module and flow paths of the gas and liquid streams involved are shown in Figure 6a. As shown in the cross-sectional view (Figure 6b), the fiber bundle comprises of *two sets* of microporous hollow fibers enclosed in a casing (shell): feed gas flows through the set fibers marked dark, and the sweep gas flows through the set of fibers shown in gray. The two sets of fibers are well-mingled through out the length of the bundle (so that, on the average, any feed-carrying fiber has one or more sweep-carrying fibers in its immediate vicinity), and are taken apart at the ends of the casing (as shown in Figure 6a) to form inlet and outlet ports for the sweep and feed gas streams. The membrane liquid fills the shell-side of the device and occupies the interstitial region between the two kinds of fibers. SO_2 permeates from feed-fibers into sweep-fibers across this liquid film present in the intervening space. As noted above, a very large membrane area can be packed per unit device volume in an HFCLM module. In addition, it is also possible to flow the liquid film in this device by providing for recirculation of the shell-side liquid; this, in turn, could improve the mass transfer characteristics of the device. A back-pressure valve included in the recirculation loop (Figure 6a), allows one to maintain the shell-side liquid at a slightly higher pressure than the tube side gases, thus preventing the mixing of

Figure 6a: Hollow Fiber Contained Liquid Membrane Apparatus

Figure 6b: Cross-Sectional View of the Fiber Bundle

feed and sweep streams. The specifications of the LIQUI-CEL™ module used in this study and the characteristics of the hollow fibers employed in its construction are given in Table 2.

Table 2. HFCLM Module Properties*

Specifications		Membrane Characteristics	
<u>Materials of Construction</u>			
Fibers: polypropylene		Fiber Type:	celgard® X-10
Case: polypropylene, Teflon®			microporous
Potting: epoxy			polypropylene
		Fiber Wall Thickness:	30 µm
		Fiber Diameter:	240 µm
		Effective Pore Size:	0.05 µm
<u>Dimensions</u>			
Number of Fibers:	700 (350/bundle)	Porosity:	0.3
Length:	34.9 cm	Maximum Operating	
Diameter:	1.59 cm	Pressure	20 PSI
Effective Fiber Length:	25.4 cm	Temperature Operating	
Effective Surface area:	0.14 m ²	Range	0 – 75° C

* As per the supplier (Hoechst Celanese, Charlotte, NC)

In our experiments, the reagent solution was recirculated at a nominal flow rate of 2.5 cc/min using a computer-driven peristaltic pump. Both feed and sweep gas flow rates were 2000 cc/min. Both the gas streams were introduced into the module at pressure of about 1.1 atm. The exit gas streams were at about atmospheric pressure. The feed flue gas SO₂ concentration was 3500 ppm. In all FPCLM experiments, the SO₂ concentration in the feed flue gas was 3500 ppm, and the incoming sweep-gas was air free of SO₂. The feed and sweep gases were fed to the device at a rate of 4000 cc/min.

The operating pressure was atmospheric on both sides of the cell, and the process was carried out at room temperature (25° C). The high gas flow rates used ensured good mixing in the gas chambers. Hence it was assumed that, at any instant, the SO₂ concentration was uniform through out the gas chambers, and the SO₂ concentration in the gas stream leaving the chamber was the same as that in the chamber. Experiments were conducted using aqueous films of both sodium sulfite and citrate. The reagent concentrations studied varied from 0 to 0.66 M in case of sodium citrate, and from 0 to 1 M in case of sodium sulfite.

In a typical experiment, the SO₂ concentration in the two gas streams leaving the device were monitored continuously at specified values of the feed and sweep gas flow rates, feed SO₂ concentration, liquid film thickness, and reagent concentration in the liquid. Steady-state operating conditions are indicated when these concentrations reached values that no longer changed with time. The time needed for the system to attain steady-state conditions increased from about 1 to 4 hours as the reagent concentration in the liquid is raised from 0 to 1 M. Overall SO₂ mass balances were routinely carried out using the measured steady-state SO₂ concentrations in the two exit streams to confirm leak-proof operation of the FPCLM. The measured steady-state partial pressure of SO₂ in the sweep-stream ($p_{SO_2}^S$) was related to the SO₂ flux across the film ($N_{SO_2, exp}$) by the relation:

$$N_{SO_2, exp} = \frac{Q^S (p_{SO_2}^S / RT)}{S \epsilon}$$

In the above relation, Q^S is the flow rate of the sweep-stream (cm³/sec), and S and ϵ are, respectively, the exposed area (cm²) and the porosity of the microporous polymer membranes. This flux was compared to the SO₂ flux predicted by the model (N_{SO_2}) when the two faces of the membrane are exposed to SO₂ partial pressures equal to those in the two streams leaving the FPCLM device. Before discussing the experimental results, we now proceed to develop a theoretical model for facilitated transport that will give us some insight into the processes occurring in the membrane films.

Model Development

Amongst the many existing models of the facilitated transport process, the non-equilibrium boundary layer analysis (NEBLA) of Roberts and Friedlander (1980a) proves particularly convenient for handling systems involving multiple chemical reactions with rates significantly faster than the intrinsic diffusion rate of the permeant across the film. This approach was shown to predict the experimental data very well in the case of SO_2 transport across sodium sulfite/bisulfite films. Accordingly, in this work we adapted this framework to model the transport of SO_2 across sodium citrate films as well.

Consider the schematic diagram of the contained liquid membrane shown in Figure 7. Liquid, containing dissolved sodium citrate, is sandwiched between two microporous polymeric sheets. The liquid film is exposed to the flue gas mixture ($\text{SO}_2 \sim 3500$ ppm) on one side ($x=0$), and to a sweep stream, free of SO_2 on the opposite side ($x=L$). Since the concentration of SO_2 is higher on the feed-side, we expect the transport of SO_2 from $x=0$ to $x=L$. Our goal is to estimate the steady-state SO_2 flux (N_{SO_2}) across the liquid film, given the citrate concentration in the film and SO_2 concentration in the gas streams on both sides of the film.

Modeling the liquid membrane transport requires the knowledge of the different species present in the liquid system and their interconversions when the film is exposed to SO_2 . The possible reactions and their equilibrium coefficients for SO_2 -sodium citrate system are given in Table 3. All the equilibrium coefficients were taken from literature except for K_3 , K_4 , and K_5 which were estimated using the method of Fuoss (1958). Reactions 3-5 represent the sequential dissociation of sodium citrate into citrate ion $\text{R}^{\equiv}$. Similarly, sequential dissociation of citric acid to form citrate ion is given in reactions 6-8. For SO_2 /water/sulfite system, the usual practice is to consider reactions 1 and 2, and the dissociation of bisulfite ion to form sulfite ion ($\text{SO}_3^{\equiv}$). However, the equilibrium

Hydrophobic Microporous Polymeric Sheets
with Gas Filled Pores

Figure 7: Schematic diagram of the contained liquid membrane

Table 3. Possible Reactions in SO₂ - Sodium Citrate system*

Equilibrium Coefficient (25° C)			
<u>Reaction</u>	<u>Symbol</u>	<u>Value</u>	<u>Reference</u>
$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	K_1	0.014 mole/l	Roberts (1979)
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	K_2	$1.008 \cdot 10^{-14}$ mole ² /l ²	Dean (1985)
$\text{Na}_3\text{R} \rightleftharpoons \text{Na}_2\text{R}^- + \text{Na}^+$	K_3	1.194 mole/l	Estimated (see text)
$\text{Na}_2\text{R}^- \rightleftharpoons \text{NaR}^= + \text{Na}^+$	K_4	0.958 mole/l	Estimated (see text)
$\text{NaR}^= \rightleftharpoons \text{R}^{\equiv} + \text{Na}^+$	K_5	0.886 mole/l	Estimated (see text)
$\text{RH}_3 \rightleftharpoons \text{RH}_2^- + \text{H}^+$	K_6	$7.447 \cdot 10^{-4}$ mole/l	Dean (1985)
$\text{RH}_2^- \rightleftharpoons \text{RH}^= + \text{H}^+$	K_7	$1.734 \cdot 10^{-5}$ mole/l	Dean (1985)
$\text{RH}^= \rightleftharpoons \text{R}^{\equiv} + \text{H}^+$	K_8	$4.018 \cdot 10^{-7}$ mole/l	Dean (1985)

constant of the latter reaction is large enough to make the concentration of sulfite ions insignificant for pH values less than 6. As shown later in the Results and Discussion section, for the SO_2 -sodium citrate system, the maximum pH within the membrane liquid was always less than 6. Therefore, the sulfite formation reaction was omitted.

Governing Equations

In the flat-plate CLM, mass transport takes place only in the direction perpendicular to the membrane (i.e., "x" direction), and hence the equation of continuity for any of the species, i , in Table 4 can be written as:

$$\frac{dN_i}{dx} = r_i, \quad (1)$$

where N_i and r_i denote the flux and the rate of formation of species i at any location in the film, respectively. The kinetic mechanisms of the various reactions in which species i participates determine the functional dependence of r_i on the local concentrations of the different species. N_i can be related to its local concentration gradient by the following form of Fick's law of diffusion in the absence of convection transport:

$$N_i = -D_i \frac{dC_i}{dx}, \quad (2)$$

where D_i is the diffusion coefficient of species i . In view of the fact that many of the species involved are ionic, an electrical potential gradient, known as "diffusional potential", develops during their diffusion through the film. In presence of this potential, it is more appropriate to use Nernst-Planck equation to describe ion transport across the film instead of Fick's law. However, it was shown by Roberts and Friedlander (1980a) that the contribution of the diffusional potential to ion flux becomes negligible at high total sodium atom concentrations ($\text{Na}_{\text{tot}} \geq 0.03 \text{ M}$). This is actually the case in all our experimental runs with sodium citrate and hence we have neglected the electrical potential term in Eq. (2).

**Table 4. Diffusion Coefficients and the Values of Parameters α and β
Used in Eq. (14)**

Species	D_i (cm ² /sec) X 10 ⁵ at Infinite Dilution (25° C)	$\alpha_i^{(b)}$	$\beta_i^{(d)}$
SO ₂	1.6(a)	see Eq. (16)	see Eq. (16)
H ⁺	9.3(a)	9.0	0.4
HSO ₃ ⁻	1.47(a)	4.25	0.3
OH ⁻	5.26(b)	3.5	0.3
Na ⁺	1.33(b)	3.05	0.3
Na ₃ R	1.01(c)	—	—
Na ₂ R ⁻	1.03(c)	4.5	0.3
NaR ⁼	0.802(c)	3.05	0.3
R ⁼	0.935(c)	5.0	0.3
RH ⁼	0.832(c)	4.5	0.3
RH ₂ ⁻	1.105(c)	3.5	0.3
RH ₃	1.11(c)	—	—

a) Roberts (1979); b) Newman (1973); c) calculated using Stokes-Einstein equation; d) see text for explanation on these values

Since all other species except SO₂ in Table 4 are non-volatile, they remain confined to the liquid film, and thus satisfy the following boundary conditions:

$$\begin{cases} N_{NV}(x=0) = 0 \\ \text{and} \\ N_{NV}(x=L) = 0 \end{cases}, \quad (3a)$$

where the subscript NV denotes any non-volatile species in the liquid film. The following boundary conditions can be written for SO₂

$$\begin{cases} C_{SO_2}^O = \left[\frac{p_{SO_2}^F}{H_{SO_2} \gamma_{SO_2}} \right] \\ \text{and} \\ C_{SO_2}^L = \left[\frac{p_{SO_2}^S}{H_{SO_2} \gamma_{SO_2}} \right] \end{cases} \quad (3b)$$

In Eq. (3b), p , H and γ are the partial pressure, the Henry solubility constant and the activity coefficient of SO_2 respectively. Also the superscripts O and L refer to the two faces of the film and F and S indicate feed and sweep streams respectively..

If there are 'N' species in solution, it can be shown, following the approach suggested by Schultz et al. (1974), that not *all* of the $2(N-1)$ boundary conditions represented by Eq. (3a) are physically independent. Therefore, in order to define the system uniquely, one must also specify the following integral constraints which represent the fact that the total amounts of (i) sodium atoms, (ii) $R^\bullet$ radicals, and (iii) charge contained in the reagents initially added to the film remain undestroyed during the reaction-diffusion processes taking place in the film:

$$\int_0^L \left(\sum_k n_k C_k \right) dx = L(3C_0), \quad (4)$$

$$\int_0^L \left(\sum_m C_m \right) dx = (LC_0), \quad (5)$$

and

$$\int_0^L \left(\sum_i z_i C_i \right) dx = 0 \quad (6)$$

In Eqs. (4), (5) and (6) summation indices k , m and i refer, respectively, to all the sodium-containing species, $R^{\pm}$ -containing species, and charged species in Table 4. Similarly, n_k and z_i in Eqs. (4) and (6) denote the number of sodium atoms in the k th species, and the valency of the i th ionic species, respectively. C_0 and L , in Eq. (4) are the molarity of sodium citrate added to the liquid membrane and the thickness of the membrane, respectively.

Expression for SO_2 facilitation factor

From the stoichiometry of reaction 1 in Table 3 – the only reaction in which dissolved SO_2 participates – one may note that at any location in the film:

$$r_{SO_2} = -r_{HSO_3^-} \quad (7)$$

From Eqs. (1), (2), (3), and (7), one can derive the net flux of SO_2 across the liquid film as:

$$N_{SO_2} = \frac{D_{SO_2}}{L} [C_{SO_2}^0 - C_{SO_2}^L] + \frac{D_{HSO_3^-}}{L} [C_{HSO_3^-}^0 - C_{HSO_3^-}^L] \quad (8)$$

The flux enhancement factor or facilitation factor (F) is defined as:

$$F = \frac{N - N_0}{N_0} = \left(\frac{N_{SO_2}}{\frac{D_{SO_2}}{L} (C_{SO_2}^0 - C_{SO_2}^L)} \right) - 1, \quad (9)$$

where N_0 represents the flux of SO_2 in the absence of chemical reactions.

In order to find N_{SO_2} and F from Eqs. (8) and (9), we need to know the concentrations of dissolved SO_2 and HSO_3^- ions at both the boundaries of the film.

To determine these concentrations, in principle, one has to solve numerically the system of differential equations described by Eqs (1) and (2) subject to the boundary and integral constraints provided by Eqs. (3) – (6). However, it has been well-established in the vast

body of existing literature on carrier-mediated transport systems that, when the forward as well as the backward rates of all the governing reactions are "fast" compared to the rates of diffusion of the species involved, the reactions would approach equilibrium through most portion of the film, except in two boundary layers adjoining each of the faces of the film. The thickness of these boundary layers is governed by the magnitude of a Damkohler number, ϕ , defined as the ratio of the characteristic time of diffusion of the permeant through the film to that of its reaction with the carrier. Within the non-equilibrium boundary layers, the diffusion and reaction rates will be comparable in magnitude. The boundary layers become progressively thinner as ϕ becomes larger, and in the limit of $\phi \rightarrow \infty$, they become vanishingly thin, and one may assume that all the reactions are at equilibrium *everywhere* in the film. This limit is known as the "equilibrium approximation", and in this case concentrations of the species of interest at the two faces of the film can be computed in a fairly straight forward manner as explained in a later section. When the equilibrium approximation is not valid, one has to account for the presence of the boundary layers in computing the permeant flux (near-equilibrium regime). The singular perturbation analysis developed by Kreuzer and Hoofd (1972) and generalized by Schultz et al. (1974) assumes that, within the thin boundary layers, the reaction rate terms in Eqs. (1) can be linearized about the point where the equilibrium core contacts the boundary layer edge. This approach, although has been successful in predicting the permeant flux in a number diffusion-limited facilitated transport systems, was shown to overpredict the flux in the case of SO_2 transport through sulfite films by Roberts and Friedlander. These authors, therefore, developed an alternate non-equilibrium boundary layer analysis (NEBLA) in which it was assumed that the interconversion between the permeant and the carrier is effectively frozen within the boundary layers, i.e., the permeant transport within the boundary layers takes place by passive diffusion only. The authors showed that this latter approach, which is computationally much simpler than the perturbation analysis, leads to better agreement with experiment in case of SO_2 transport through sulfite films. In what follows, we shall predict the SO_2 flux across citrate films first in the equilibrium limit and then using the NEBLA approximation proposed by Roberts and Friedlander.

Equilibrium Approximation

Here it is assumed that the reaction rates are so fast that the chemical equilibria defined by Eqs. (10) are instantaneously established at any point in the film for all the reactions ($j = 1, 2, \dots, 8$) listed in Table 3.

$$K_j = \prod_i a_i^{v_{ij}} \quad (10)$$

In Eq. (10), a_i is the activity of species i , v_{ij} is the stoichiometric coefficient of species i in the j th reaction, and K_j is the equilibrium constant of the j th reaction. Also, in writing Eq. (10), following the standard convention, the stoichiometric coefficients of the reactants are taken as negative and those of products as positive. Further, activities are used instead of species concentrations, because in ionic solutions, due to long range electrostatic interactions, the activity coefficients could attain values much different from unity.

The equilibrium approximation simplifies the effort involved in predicting the permeant flux immensely because one has to solve now a system of non-linear algebraic equations represented by Eqs. (10) subject to the integral constraints and the boundary conditions on the permeant listed before, instead of the system of differential equations given in Eqs. (1) and (2). The model can be further simplified, if one assumes that the diffusion coefficients of all the ionic species present in appreciable concentrations are approximately the same. Based on the data given in Table 4, with the exception of H^+ and OH^- ions, the diffusion coefficients of the remaining ions are well within a factor of two from one another. However, the diffusional fluxes of H^+ and OH^- ions are negligibly small because of their low concentration in the film. Therefore, we assume in the following development that the diffusion coefficients of the remaining ionic species can be replaced with that of the bisulfite ion, as was done by Roberts (1979). This allows one to replace the three *global* constraints given in Eqs. (4), (5) and (6) by the following three equations which represent, respectively, the conservation of sodium atoms, $R^\bullet$ radical, and electrical charge *locally* in the film.

$$\sum_k n_k C_k = 3C_0, \quad (11)$$

$$\sum_m C_m = C_0, \quad (12)$$

and

$$\sum_i (z_i C_i) = 0 \quad (13)$$

Equations (11) and (12) imply that the total molarities of sodium and $R^{\equiv}$ -containing species at the boundaries are equal to their respective original molarities in the liquid film preparation. Therefore, to obtain the concentrations of the various species at each boundary of film, it is enough to determine separately the liquid phase composition that results when the corresponding gas phase is equilibrated with a sodium citrate solution of molarity C_0 .

SO₂ equilibrium with a bulk solution of sodium citrate

The activity of the species appearing in the equilibrium relations (Eq. (10)) can be related to their concentrations by:

$$a_i = \gamma_i C_i \quad (14)$$

The activity coefficients of all the species other than SO₂ are computed using the extended Davis model (Davis 1962) following Roberts and Friedlander:

$$\log_{10} \gamma_i = A z_i^2 \left[\alpha_i I - \frac{I^{1/2}}{1 + B \beta_i I^{1/2}} \right]. \quad (15)$$

In Eq. (15), A and B are the Debye-Huckel constants which depend on temperature only. The values of these constants at room temperature (25° C) are 0.5085 and 0.3281 Å⁻¹,

respectively (Roberts, 1979). The parameter α_i is the ionic radius of the species ($\text{\AA}$) and β_i is a dimensionless adjustable parameter for which a value of 0.3 was proposed by Davis (Davis, 1962). However, Roberts and Friedlander observed that setting β equal to 0.4 for H^+ ions usually leads to better agreement with experimental data. (Values of α_i and β_i used in this study are listed in Table 4.) I , in Eq. (15), is the ionic strength of the solution and given as:

$$I = \frac{1}{2} \sum_i (z_i^2 C_i) \quad (16)$$

The activity coefficient of SO_2 (Harned and Owen, 1958), and the activity of water (Johnstone and Blankmeyer, 1938) are computed using the relations:

$$\log_{10} \gamma_{SO_2} = 0.076 I, \quad (17)$$

and

$$a_{H_2O} = 1 - 0.018 \left(\sum_i C_i \right) \quad (18)$$

The set of Eqs. (10)–(18) and (3b) constitute a system of 38 simultaneous algebraic equations. This system of equations can be solved numerically for the 38 unknowns (twelve C_i 's, twelve a_i 's, twelve γ_i 's, a_{H_2O} , and I). This was accomplished using the IMSL subroutine DNEQNF on the VAX/VMS system. The input parameters for this equilibrium computations are: p_{SO_2} in the gas phase, and the amount of reagent added to the bulk liquid.

Knowing p_{SO_2} on both sides of the film and sodium citrate concentration, C_0 , in the film, the concentrations of species at the boundaries can be computed. The $C_{SO_2}^0$, $C_{SO_2}^L$, $C_{HSO_3^-}^0$, and $C_{HSO_3^-}^L$ values thus obtained can be substituted into Eqs. (8) and (9) to determine N_{SO_2} and F respectively.

Non-Equilibrium Boundary Layer Analysis (NEBLA)

Since the forward step of hydrolysis reaction of the dissolved SO_2 (reaction 1, Table 3) requires a finite amount of time to take place, the SO_2 molecule, after its dissolution, diffuses through a certain distance before undergoing any reaction. This distance corresponds to the width of the boundary layer on the feed-side of the film in the NEBLA of Roberts and Friedlander. Clearly, within the boundary layer, the permeant transport occurs only by physical diffusion. A similar phenomenon occurs (in the reverse direction) at the other boundary of the film, i.e, SO_2 transport takes place only by physical diffusion over a distance that is determined by setting the diffusion time of the HSO_3^- equal to time needed for the reverse step of the hydrolysis to take place. Accordingly, the boundary layer thicknesses on the feed- and the sweep-sides (δ^0 and δ^L) can be determined based on the characteristic reaction times for the forward and reverse reactions of reaction 1:

$$\delta^0 = \left[\frac{D_{\text{SO}_2}}{k_1} \right]^{1/2}, \quad (19)$$

and

$$\delta^L = \left[\frac{D_{\text{HSO}_3^-}}{k_{-1} C^*} \right]^{1/2}, \quad (20)$$

where C^* is a characteristic value of H^+ ion concentration in the boundary layer, and k_1 and k_{-1} are the forward and reverse rate constants of reaction 1. (Roberts (1979) reported a value of $5 \cdot 10^6 \text{ sec}^{-1}$ for k_1 at 25°C .)

Of course, as is the case with all other boundary layer analyses, it is assumed that at the boundary layer/ core interfaces ($x = \delta^0$ and $(L - \delta^L)$) all chemical reactions are at local equilibrium. Since all chemical reactions are frozen within the boundary layers, the concentrations of all the non-volatile species remain uniform within each boundary layer at their values at the corresponding boundary layer/core interface. Therefore, the H^+ ion concentration (C^*) appearing in the definition of δ^L will be its value at the sweep-side boundary layer/core interface.

From the physical parameters of the system under consideration, it was found that the

ratio (δ^L/δ^0) is about 10^2 to 10^3 , and hence δ^0 was neglected in the following analysis. This implies that the equilibrium core extends right up to the gas-liquid interface on the feed-side of the film. The flux across the boundary layer on the sweep-side is the Fickian diffusion of SO_2 (aq). Therefore,

$$N_{\text{SO}_2} = \frac{D_{\text{SO}_2}}{\delta^L} \left(C_{\text{SO}_2}^{(L-\delta^L)} - C_{\text{SO}_2}^L \right) \quad (21)$$

In the core region of the film, the expression for steady-state flux of SO_2 is the same as that given by Eq. (8), but the concentrations of both the SO_2 (aq) and HSO_3^- on the low pressure-side must be evaluated at $x = L - \delta^L$. Thus, Eq. (8) becomes

$$N_{\text{SO}_2} = \frac{D_{\text{SO}_2}}{(L - \delta^L)} \left[C_{\text{SO}_2}^0 - C_{\text{SO}_2}^{(L - \delta^L)} \right] + \frac{D_{\text{HSO}_3^-}}{(L - \delta^L)} \left[C_{\text{HSO}_3^-}^0 - C_{\text{HSO}_3^-}^{(L - \delta^L)} \right] \quad (22)$$

Under steady-state conditions, the flux of SO_2 across the boundary layer and that across the core region must be the same, and hence Eqs.(21) and (22) should yield the same N_{SO_2} values. Since the feed-side boundary layer thickness is negligible, at $x=0$, the liquid phase C_i 's are in equilibrium with feed flue gas SO_2 concentration. Thus, the feed-side C_i values are computed as described in equilibrium calculations. However, the sweep-side calculations have to be performed iteratively because of the existence of the boundary layer. One way of doing these calculations is shown in the following algorithm.

- i) Assume a value for $C_{\text{SO}_2}^{(L - \delta^L)}$.
- ii) Compute $C_i^{(L - \delta^L)}$ using the equilibrium model.
- iii) Use Eq. (20) to calculate δ^L , and Eqs. (21) and (22) to obtain two values of N_{SO_2} .
- iv) If the difference between the two N_{SO_2} values obtained in step (iii) is within a specified tolerance limit, stop the computations. Otherwise, guess a different value for $C_{\text{SO}_2}^{(L - \delta^L)}$ and repeat steps (ii), (iii) and (iv).

The above completes the model development for SO_2 transport across aqueous sodium

citrate films. The results obtained from these computations can be compared with experiments and are presented below. This model, as already pointed out, is an extension of the original NEBLA of Roberts and Friedlander for SO_2 transport across aqueous sodium sulfite films. Accordingly, for comparing our experimental data on sulfite films with theory, we have used the computer code provided by Roberts (1979).

Results and Discussion of Results

SO_2 Transport across reagent-free aqueous films

The first entry (S1) in Table 5 gives the measured partial pressures of SO_2 on the feed and sweep-sides of the FPCLM device at steady-state and the corresponding $N_{\text{SO}_2, \text{exp}}$ for a reagent-free aqueous film (pure water).

Table 5. Experimental Results with Sulfite Films in FPCLM Contactor *

Run #	sulfite concentration (mole/l)	exit stream SO_2 partial pressure (ppm)		$N_{\text{SO}_2, \text{exp}}$ (mole/cm ² /sec) X 10 ⁸
		feed	sweep	
S1	0	3467	33	1.07
S2	0.015	3459	41	1.17
S3	0.0375	3473	27	0.87
S4	0.075	3476	24	0.78
S5	0.15	3466	34	1.10
S6	0.75	3432	64	2.20
S7	1.0	3408	92	2.98

- * feed flue gas SO_2 concentration= 3500 ppm
- feed gas flow rate= 4000 cc/min
- sweep gas flow rate= 4000 cc/min

It is important to note that even in pure water, transport of SO_2 does not take place by physical diffusion alone, but is facilitated by the HSO_3^- ion formed by the hydrolysis reaction (reaction 1, Table 3). SO_2 flux that results if the transport of SO_2 were to occur

by physical diffusion only (N_0) is computed as $5.34 \cdot 10^{-9}$ mole/cm²/sec for the conditions corresponding to the first entry in Table 5. Clearly, the extent of facilitation in water is small (~ 1). The reason for this low facilitation is as follows: In order to release SO₂, HSO₃⁻ has to recombine with a H⁺ ion on the sweep-side of the film. The rate of this recombination, under steady-state conditions, is determined by the fluxes of HSO₃⁻ and H⁺ ions across the film. By stoichiometry of reaction 1, the fluxes of these two species should be equal under steady transport conditions. However, the driving force that determines the physical diffusion of H⁺ in pure water films is the pH difference across the film. Therefore, H⁺ ion flux in water films tends to be very small, and so will be the flux of HSO₃⁻ ions. This leads to the observed low facilitation factors in pure water films. Obviously, reagents that can facilitate the transport of H⁺ ions across the film should lead to a concomitant increase in the flux of HSO₃⁻ ions, and hence to larger SO₂ facilitation factors. Indeed, commonly used weak-acid pH buffers were shown to be effective in accomplishing proton transport facilitation in immobilized enzyme systems (Engasser and Horvath, 1974) and the facilitated transport of CO₂ across aqueous films (Gros et al., 1976; Meldon et al., 1977). In these studies it was identified that both the binding constant (pK) of the weak acid and its concentration determine its ability to function as an effective proton facilitation agent. Engasser and Horvath also observed that there exists a weak acid with an optimum pK that leads to maximum proton facilitation.

In the following subsections, we shall evaluate the efficacy of sodium sulfite and several other sodium salts of mono- and poly-protic weak acids as proton carriers.

SO₂ transport across sodium sulfite films

The measured partial pressures of SO₂ on the feed and sweep-sides of the FPCLM device at steady-state and the corresponding $N_{SO_2, exp}$ are listed in Table 5 for various concentrations of sodium sulfite in the liquid film. For all the runs of Table 5, the liquid film thickness and the SO₂ partial pressure in the incoming flue gas were held fixed at 200 μ m and 3500 ppm, respectively. The steady-state fluxes predicted by the model both with the equilibrium approximation and with the NEBLA, for each of the reagent concentrations and the corresponding pair of the partial pressures in Table 5, are plotted in Figure 8 as flux

Figure 8: Variation of sulfur dioxide flux with sodium sulfite concentration in the FPLCLM contactor.
 The liquid film thickness is 200μm.

vs. reagent concentration. Figure 8 also shows the experimentally observed flux, $N_{SO_2, exp}$. Clearly, the NEBLA predictions are in much better agreement with the experimental data than those employing the equilibrium approximation. This observation corroborates the previous conclusions of Roberts and Friedlander (1980) and Sengupta et al. (1990).

It may also be noted from Table 5 that the addition of sulfite to the aqueous film, while leading to SO_2 fluxes larger than in pure water as expected at concentrations higher than 0.1 M, actually lowers the flux slightly at smaller concentrations. This anomaly results from the important role played by the diffusional potential on SO_2 flux at low ionic strengths, as noted earlier by Roberts and Friedlander.

As already mentioned, the observed increase in SO_2 flux at high sulfite concentrations, can be attributed to the proton transport facilitation by the sulfite (SO_3^{2-}) ions, which bind H^+ ions at the feed-side of the film and release them on the sweep-side according to the following reversible reaction

Based on the above role of the sulfite ion, one can visualize the transport mechanism schematically displayed in Figure 9 to be operative in sodium sulfite films. As observed by Roberts and Friedlander, in addition to SO_2 hydrolysis, the formation of other sulfur containing species may become important at very high reagent concentrations. (The formation of these compounds is accounted for while comparing of our experiments with NEBLA as well as the equilibrium approximation.) Nevertheless, the HSO_3^- remains the dominant carrier of SO_2 , and thus the schematic shown in Figure 9 makes it easier to envision the physicochemical phenomena involved in SO_2 transport across sulfite films.

One may also note from Table 5 that, while the addition of sulfite improves the SO_2 flux across the film, the increase is only three fold (compared to the pure water case) even at the highest sulfite concentration studied (1 M). In the Wellman-Lord process, the sulfite concentrations used are typically ~ 0.6 M. Higher concentrations are known to lead to

Figure 9: A simple model of SO_2 permeation across sodium sulfite films. HSO_3^- is mainly responsible for the facilitated transport of SO_2 . $\text{HSO}_3^-/\text{SO}_3^{2-}$ conjugate acid-base reaction forms the "shuttle" that facilitates the transport of H^+ ions.

operational problems such as high viscosity of the solution and decreased SO_2 solubility due to the "salting-out" phenomenon. Also, the trend of the flux vs. sulfite concentration behavior predicted by NEBLA (Figure 8) indicates that increasing sulfite concentration beyond 1 M may not lead to any appreciable increase in SO_2 flux. An explanation for this marginal performance of sulfite films can be sought in light of the mechanism shown in Figure 9. The performance of the reagent is directly related to the ability of SO_3^{2-} to serve as a proton carrier. As noted before, this effectiveness of SO_3^{2-} , is determined by its pK. From Schultz et al. 's analysis of carrier-mediated transport systems (1974, p. 438), one can expect that a conjugate acid-base pair with a pK which is the arithmetic mean of the pH values of the proton "source" (feed-side interface in our case) and "sink" (sweep-side boundary layer / core interface) to provide maximum proton facilitation. The pH values at the proton source and the sink, along with their arithmetic mean, are shown in Table 6 for the six sulfite runs.

Table 6. Boundary pH Values and their Arithmetic Averages Calculated using NEBLA for Sulfite Films*

sulfite concentration (mole/l)	pH^0	pH^L	$\frac{(\text{pH}^0 + \text{pH}^L)}{2}$
0.015	2.61	4.43	3.52
0.0375	2.94	4.87	3.91
0.75	3.21	5.07	4.14
0.15	3.48	5.14	4.31
0.75	4.03	5.22	4.63
1.0	4.10	5.23	4.67

* Experimental gas phase SO_2 partial pressures simulated (see Table 5).

The experimentally observed feed and sweep-side SO_2 partial pressures (from Table 5) are used along with NEBLA to compute these pH values. Comparison of the average pH values with the pK of sulfite (~ 7.21 , see Eq. (23)) indicates that SO_3^{2-} is not a very effective proton carrier in this partial pressure range. Indeed, it is incapable of releasing the bound protons on the sweep-side due to its high pK. This implies an inadequate supply of "free-carriers" which can shuttle back to the feed-side to combine with more protons. From the equilibrium solubility data of SO_2 in sulfite solutions, one can verify that at extremely low feed- and sweep-side SO_2 partial pressures (< 100 ppm, and ~ 0.1 ppm, respectively) and high reagent concentrations (> 1.0 M) only, the pH values at the proton-source and sink would give an average anywhere near the pK of sulfite. However, these partial pressures and reagent concentrations, are outside the range of operating conditions of most flue gas desulfurization processes. Therefore, sodium sulfite films seem to be of limited use.

SO_2 transport across monoprotic acid films

Clearly, one can expect (from Table 6) weak-acids which have pK values in the range of 3-5 to give a higher SO_2 flux than sulfite solutions at the same reagent concentration. A number of monoprotic acids such as acetic acid (pK ~ 4.76) and formic acid (pK ~ 3.75) fall in this latter category. Tables 7 and 8 provide the experimental results for acetate and formate films similar to the data given in Table 5 for sulfite films. Figure 10 graphically compares the SO_2 flux results for these films. The formate and acetate films exhibit superior performance to sulfite films. This behavior can most likely be attributed to the fact that the pK of these acids is closer to the arithmetic mean of the pH's of the film boundaries.

SO_2 transport across polyprotic acid films

Polyprotic acids with multiple pKs in the appropriate pH range (3-5) can provide multiple pathways for the transport of protons. Therefore, depending on the efficiency of these paths, the polyprotic acid may lead to a higher net flux than is possible with a monoprotic acid. (Hence we note in passing, that if one of the pKs of a polyprotic acid coincides with the pK of a monoprotic acid, and additionally at least one of the other pKs is in the appropriate pH range, we would expect an enhancement of the SO_2 flux across the polyprotic film.) Citric acid, adipic acid and 1,2,3,4 butane tetra-carboxylic acid are a few examples which have multiple pKs in the above range. Tables 9-11 and Figure 11 show the results obtained with these reagent films.

Table 7. Experimental Results with Acetate Films in FPCLM Contactor *

Run #	acetate concentration (mole/l)	exit stream SO ₂ partial pressure (ppm)		$N_{SO_2, exp}$ (mole/cm ² /sec) X 10 ⁸
		feed	sweep	
AC1	0.015	3471	29	0.95
AC2	0.0375	3467	33	1.08
AC3	0.075	3457	43	1.40
AC4	0.15	3444	56	1.83
AC5	0.375	3375	125	4.08
AC6	0.75	3295	205	6.69
AC7	1.0	3265	235	7.67
AC8	1.5	3230	270	8.84

* feed flue gas SO₂ concentration= 3500 ppm
sweep gas flow rate= 4000 cc/min

feed gas flow rate= 4000 cc/min
membrane thickness= 200 μm

Table 8. Experimental Results with Formate Films in FPCLM Contactor *

Run #	formate concentration (mole/l)	exit stream SO ₂ partial pressure (ppm)		$N_{SO_2, exp}$ (mole/cm ² /sec) X 10 ⁸
		feed	sweep	
F1	0.015	3469	31	1.01
F2	0.0375	3457	43	1.41
F3	0.15	3403	97	3.18
F4	0.375	3345	155	5.06
F5	0.75	3265	235	7.67
F6	1.5	3210	290	9.49

* feed flue gas SO₂ concentration= 3500 ppm
sweep gas flow rate= 4000 cc/min

feed gas flow rate= 4000 cc/min
membrane thickness= 200 μm

Figure 10: Comparison of the performance of the salts of monoprotic acids with sulfite solutions

Certainly these polyprotic acids lead to SO₂ fluxes that are about 5 times higher than those possible with sulfite films at high reagent concentrations. Amongst the polyprotic acids studied, citrate exhibits the best performance. Hence in the discussion that follows, we have selected citrate as the reagent of choice for further investigation.

Table 9. Experimental Results with Citrate Films in FPCLM Contactor *

Run #	citrate concentration (mole/l)	exit stream SO ₂ partial pressure (ppm)		$N_{SO_2, exp}$ (mole/cm ² /sec) X 10 ⁸
		feed	sweep	
C1	0	3467	33	1.07
C2	0.01	3457	43	1.40
C3	0.025	3445	55	1.78
C4	0.05	3426	74	2.40
C5	0.1	3385	115	3.73
C6	0.5	3270	230	7.45
C7	0.667	3225	275	8.91

Table 10. Experimental Results with Adipate Films in FPCLM Contactor *

Run #	adipate concentration (mole/l)	exit stream SO ₂ partial pressure (ppm)		$N_{SO_2, exp}$ (mole/cm ² /sec) X 10 ⁸
		feed	sweep	
AD1	0.01	3470	30	1.00
AD2	0.0375	3456	44	1.44
AD3	0.06	3442	58	1.89
AD4	0.1	3436	64	2.09
AD5	0.2	3380	120	3.91

* feed flue gas SO₂ concentration= 3500 ppm
sweep gas flow rate= 4000 cc/min

feed gas flow rate= 4000 cc/min
membrane thickness= 200 μm

Table 11. Experimental Results with tetra Carboxylate Films in FPCLM Contactor *

Run #	tetra carboxylate concentration (mole/l)	exit stream SO ₂ partial pressure (ppm)		$N_{SO_2, exp}$ (mole/cm ² /sec) X 10 ⁸
		feed	sweep	
T1	0.015	3463	37	1.21
T2	0.0375	3446	54	1.76
T3	0.075	3419	81	2.64
T4	0.15	3380	120	3.91
T5	0.375	3339	161	5.24
T6	0.75	3310	190	6.22

* feed flue gas SO₂ concentration= 3500 ppm
sweep gas flow rate= 4000 cc/min

feed gas flow rate= 4000 cc/min
membrane thickness= 200 μ m

Comparison of SO₂ transport across sodium citrate and sulfite films

Figure 12 shows results for citrate films similar to those given for sulfite films in Figure 8. It is evident that the SO₂ flux increases by almost *an order of magnitude* as the citrate concentration increases from 0.0 to 0.667 M. This increase in flux is much higher than for sulfite films where it increases only by a factor of *two* over the same concentration range. Indeed, at all reagent concentrations levels, citrate leads to an SO₂ flux that is at least a factor of four higher than that obtained with a sulfite film at the corresponding reagent concentration. This can be seen in Figure 13 where the experimental fluxes across citrate and sulfite films are plotted against reagent concentration. We would like to mention here that the higher fluxes across citrate films lead to a larger build up of SO₂ on the sweep-side of the FPCLM device under steady-state conditions, which in turn reduce the driving force. (Compare the steady-state partial pressure data in Tables 5 and 9.) If one were to control the sweep flow rate in each of these runs such that the same sweep-side SO₂ build-up is obtained in all the runs, even higher SO₂ flux enhancement factors will be observed with citrate films.

Figure 11: Comparison of the performance of the salts of polyprotic acids with sulfite solutions

Figure 12: Variation of sulfur dioxide flux with sodium citrate concentration in the FPCLM contactor.

Figure 13: Comparison of the performance of sodium sulfite and citrate solutions in the FPCLM contactor.

To corroborate the observed higher SO_2 fluxes across citrate films with the reagent's superior ability as a proton carrier, in Table 12 we present the pH values at the proton source and the sink, along with their arithmetic mean, for all the citrate runs.

Table 12. Boundary pH Values and their Arithmetic Averages Calculated using NEBLA for Citrate Films*

citrate concentration (mole/l)	pH^0	pH^L	$\frac{(pH^0 + pH^L)}{2}$
0.01	2.58	4.14	3.36
0.025	2.89	4.29	3.59
0.05	3.14	4.38	3.76
0.1	3.42	4.47	3.94
0.5	4.44	5.00	4.72
0.667	4.71	5.10	4.91

* Experimental gas phase SO_2 partial pressures simulated (see Table 11).

From these data, which are similar to the data given for sulfite films in Table 6, it is evident that at all reagent concentrations, the arithmetic average of the two end-pHs, is very close to one of the three pKs of citric acid. The particular conjugate acid-base pair of citric acid the deprotonation-protonation equilibrium of which corresponds to this pK will form the main "shuttle" responsible for the major portion of proton transport. However, since the pKs of citric acid are spaced close (about one pH unit apart), we expect the conjugate acid-base pair with the next higher pK also to contribute to the H^+ ion transport to a certain degree. This multiple shuttle mechanism can lead to a net transport rate of H^+ ions larger than that

possible with a monoprotic weak-acid, and hence to higher SO_2 fluxes. A schematic of the possible H^+ ion transport paths in citrate films is shown in Figure 14. Indeed, the ability of citrate to enhance SO_2 fluxes right from very low reagent concentration levels results from its effectiveness in facilitating proton transport at all concentrations as described above.

As may also be noted from Figure 12, equilibrium theory overpredicts the citrate data by a factor more than 2.5 for reagent concentrations > 0.1 M. NEBLA estimates the fluxes with a maximum deviation of 16% over the range of sodium citrate concentrations studied in the present investigation. Therefore, these experimental results indicate that NEBLA is also applicable for SO_2 transport through aqueous citrate solutions. In light of this success of NEBLA in predicting SO_2 fluxes across sulfite as well as citrate films, we used the model to perform a comparative evaluation of the the two systems, under identical driving force conditions, over a parametric domain of interest to FGD processes. The effect of variation of the feed-side SO_2 partial pressure on the the facilitation factor for sulfite and citrate films at a constant sweep-side SO_2 concentration of 10 ppm is given in Table 13.

Table 13. Comparison of Facilitation Factors Calculated from NEBLA for Citrate and Sulfite Films*

	feed flue gas SO_2 partial pressure (ppm)							
	4000		2000		1000		500	
concentration (mole/l)	citrate	sulfite	citrate	sulfite	citrate	sulfite	citrate	sulfite
0.025	5.5	0.5	9.4	0.7	15.9	1.1	26.5	2.0
0.05	9.7	0.6	16.6	1.3	27.8	2.6	45.2	5.1
0.1	17.0	1.5	28.5	3.1	46.6	6.3	72.7	12.5
0.333	42.4	6.1	68.3	12.3	103.0	24.1	140.7	45.1
0.5	62.1	9.1	98.6	18.1	140.2	34.8	172.2	63.3
0.667	88.6	11.9	130.2	23.3	168.1	44.2	189.0	78.7
1.0	126.7	16.9	166.0	32.8	197.0	61.1	212.2	105.2

* Sweep stream SO_2 partial pressure = 10 ppm

Liquid film thickness = 200 μm

Figure 14: A schematic of the mechanism of SO_2 transport across citrate films. The close spacing of the three pKs of citric acid, permits proton transport by more than one form of the conjugate-base species, at any given reagent concentration. Of the three paths shown (RH_2^- , RH_3^- and RH^-), the fraction of protons carried in each form (f_1 , f_2 and f_3) is determined by the pH values at the ends of the film. The double headed arrows on the two paths RH_2^- and RH^- imply that these forms of the reagent can either be conveying H^+ ions to the sink, or be serving as unbound-carriers moving towards the source. Their actual direction of motion is determined by the pH values at the ends of the film. When these species are moving towards proton source the corresponding f 's will become zero.

The reagent concentration is varied from 0.025 M to 1 M. For all computations the membrane thickness was held constant at 200 μm . For both citrate and sulfite films, it is apparent from the results that for an increase in reagent concentration or a decrease in feed gas SO_2 concentration, F increases. Also, an increase in the feed-side SO_2 partial pressure, affects the facilitation factor of sulfite systems more adversely than that of citrate systems. Consequently, at high SO_2 partial pressures on the feed-side (~ 4000 ppm), the ratio of F for citrate to sulfite is higher than that at low SO_2 partial pressures. These SO_2 partial pressures are typical of waste gases produced from burning high sulfur coal. In view of the increasing emphasis on the utilization of high sulfur coal, this is a promising result.

From a practical stand point, the thickness of the film is a very important parameter in the implementation of facilitated transport systems. While at the laboratory level liquid films of thickness of only a few microns can, perhaps, be prepared by impregnating the pores of very thin polymer membranes with the liquid, these immobilized liquid membranes, as noted in the Introduction, do not hold great promise for commercialization. Nevertheless, as mentioned earlier, hollow fiber contained liquid membranes (HFCLM) seem to offer a viable design. However, in this latter design, since the liquid occupies the shell-side of the device, one has limited control on the effective film thickness, which can be as large as several hundred microns. Therefore, only the reagents which provide high facilitation factors will lead to acceptable SO_2 transport rates in these devices. Figure 15 shows the facilitation factor, predicted by NEBLA, as a function of film thickness for citrate and sulfite films for two different reagent concentrations. For all the computations shown in Figure 15, the feed- and sweep-side SO_2 partial pressures were held fixed at 3500 ppm and 10 ppm, respectively. As can be verified from the figure, over the entire range of membrane thicknesses studied (10 μm – 1000 μm), the ratio of F for citrate to sulfite remains approximately constant; this ratio is as large as ten when the reagent concentration is 0.025 M, while it is about six at the higher reagent concentration of 0.5 M. Also, the high facilitation factors (~ 100) obtained with citrate films with thick membranes ($> 100 \mu\text{m}$) at the high reagent concentration, offer hope that citrate-based HFCLM

The arrows on the right ordinate indicate the facilitation values obtained from the equilibrium approximation.

Figure 15: Effect of liquid film thickness on facilitation factors calculated from NEBLA. Feed and sweep partial pressures are 3500 and 10 ppm respectively.

modules can lead to acceptable SO₂ removal rates from flue gases resulting from high sulfur coal.

Next we investigated the NO removal capabilities of aqueous solutions of sodium citrate and Fe(II)EDTA, the former being the most promising aqueous liquid membrane chemistry for SO₂ removal. It may be recalled that ferrous chelates have previously been discussed as possible carriers for NO_x removal.

Nitrogen Oxide Removal in Aqueous Films

Procedure for Preparing Fe II (EDTA) chelate reagent solution

The ferrous chelate solutions necessary for this task were prepared using the procedure of Harkness *et al.* (U.S. Patent 4,612,175 Sept. 16, 1986): About 0.0125 M equimolar amounts of FeSO₄ and Na₂H₂EDTA were taken in 200 ml of deoxygenated and deionized water. This mixture was stirred constantly under nitrogen blanket for about 2-3 hours. This procedure resulted in the formation of Fe(II)EDTA complex. However, the solubility of this complex in water was low at room temperatures. Higher concentrations of reactants could not be used during the preparation, lest the complex precipitate out.

An absorption spectrum of a sample of the above solution was taken (in the wavelength range 300-800 nanometers) with a DU-70 UV Spectrophotometer to confirm the formation of Fe(II)EDTA complex (Figure 16). The spectrogram is in good agreement with the absorption spectra published by Jones and Long (Jones and Long 1952) for the ferrous EDTA complex.

Chelate Solutions Containing Sodium Citrate

Sodium citrate was next added to the ferrous complex solution. We noticed that the addition of citrate leads to the formation of a clear colorless solution even when the initial chelate solution has an Fe(II)EDTA concentration above the solubility level of this complex. We concluded that citrate promotes the dissolution of the complex. Thus, it appears that citrate is accomplishing two useful results: First, its presence makes the reagent solution capable of absorbing SO₂ from the flue gases. Second, the fact that it promotes the dissolution of Fe(II)EDTA complex increases the potential capacity of the solution towards NO removal as well.

Figure 16: UV/VIS absorption spectrum of 0.0125 M solution of FeSO_4 and $\text{Na}_2\text{H}_2\text{EDTA}$. Solid line is the spectrum obtained in the present study and the dotted line is the spectrum published by Jones and Long (1952) for ferrous EDTA complex. The agreement between the two spectra confirms the formation of the complex in our reaction mixture.

An absorption spectrum of a chelate solution containing sodium citrate is shown in Figure 17. The trends observed in this spectrum are *the same* as those seen in Figure 16, except that the range of wavelengths has been shifted to the right slightly. This unchanged absorption spectrum, perhaps, implies that citrate does not react with the Fe(II)EDTA complex.

FPCLM Runs

We have conducted some SO₂/NO_x combined removal experiments with the citrate/ferrous EDTA membrane using the flat plate cell described previously.

Initially, about 4000 cc/min of air was used on both the sweep- and feed-sides of the liquid film. The feed-side air also contained 4000 and 1080 ppm of SO₂ and NO, respectively. No facilitated transport of NO across the films was observed! The reason was found to be the oxidation of ferrous complex by the oxygen, which is coming in contact with the solution from both the sweep and feed gases. This was confirmed by comparing the absorption spectra of the reagent solution before and after the solution was used as a liquid membrane. Figure 18 shows the absorption spectrum of used solution. Comparison of this figure with Figure 17 demonstrates that the curve is shifted to the right to an extent that will be expected if all the Fe (II)EDTA were oxidized to Fe(III)EDTA. Therefore, we concluded that total removal of oxygen from the flue gases is an absolute requirement for the process to work. Since flue gases invariably contain about 4% oxygen, we must somehow find a way to regenerate the Fe (II)EDTA. Perhaps, one way to deal with this problem is to combine the facilitated transport process with a simultaneous electrolytic reduction procedure. In this procedure the chelates oxidized by oxygen are continuously reduced back into their ferrous form by some means, thus enabling these chelates to complex with NO in the flue gases. While such a scheme is not yet available, a necessary first step before attempting it is to understand thoroughly the NO and SO₂ transport characteristics of ferrous chelate solutions in an oxygen-free environment.

Accordingly, several experiments were carried out with simulated flue gases that *did not* contain O₂. In all the experimental runs, reagent grade N₂ was used as the feed as

Figure 17: UV/VIS absorption spectrum of the ferrous chelate solution containing sodium citrate.

0.03 M Fe(II) EDTA
 0.25 M sodium citrate
 initial pH = 6.12
 Smoothing Pa(B) EDTA

2400 nm/min

Smoothing [no] pts.

Wavelength (nm): 300 400.0 500.0 600.0 700.0 800

%T: 0.00 20.00 40.00 60.00 80.00 100.00

2400 nm/min

Smoothing [no] pts.

Wavelength (nm): 300 400.0 500.0 600.0 700.0 800

%T: 0.00 20.00 40.00 60.00 80.00 100.00

Figure 18: UV/VIS absorption spectrum of the ferrous chelate solution after the solution is exposed to the flue gases containing oxygen for a sufficiently long time.

well as the sweep gas. The inlet feed gas also contained SO₂ (4000 ppm) and NO (800 ppm). The inlet sweep gas was pure N₂, and the outlet from the sweep-side of the liquid film was constantly monitored for the pollutant (SO₂ and NO) concentrations using their respective analyzers. The concentration of sodium citrate in the film was held constant at 0.1 M for all the experiments.

Figure 19 shows the variation of SO₂ and NO fluxes across the liquid film with the Fe(II)EDTA concentration in the film. The liquid membrane thickness was 0.204 mm. The invariance of the SO₂ flux was expected because the concentration of sodium citrate was held constant in all the runs. The presence of the EDTA does not hinder the transport of SO₂. The flux of NO gas has increased steadily by an order of magnitude as the Fe(II)EDTA concentration is increased from 0.01 to 0.06 M. Similar results are shown in Figure 20 for a thicker (0.304 mm) liquid film.

Figure 21 shows the variation in NO flux across the liquid film with the Fe(II)EDTA concentration, for two different liquid membrane thicknesses. It is evident that the NO flux across the thin film is higher than that across the thick film, and the difference becomes larger at higher Fe(II)EDTA concentrations.

While citrate proved to be an excellent reagent for SO₂ removal, the fact that NO_x removal in aqueous membranes was hindered by the presence of oxygen in the flue gases caused us to seek an organic membrane that might function for the combined removal of SO₂ and NO_x. To date, there are no studies in literature in which *simultaneous* absorption of both SO₂ and NO_x into an organic liquid system has been attempted. There are, however, a few studies in which the *independent* absorption of either of these gases in an organic liquid medium has been studied. Specifically, transport of nitric oxide in the solvent N-cyclohexyl-2-pyrrolidone in the presence one of the two carrier ions [Fe(II) and Zn(II)] has been studied (G.G. Godbole, et. al., 1988). Similarly, transport of nitric oxide through formamide films containing ferrous ions was also studied (W.J. Ward III, 1970). As far as SO₂ is concerned, Scott Lynn and his coworkers at University of California,

Figure 19: SO_2 & NO Fluxes through Aqueous Fe(II)EDTA , Citrate Solution

FIGURE 20: SO₂ & NO Fluxes through Aqueous Fe(II)EDTA, Citrate Solution

FIGURE 21: Variation in NO Flux with the Fe(II)EDTA Concentration for Different Film Thicknesses

Berkeley, have used a variety of organic solvents for SO_2 absorption (Demyanovich, R. J. and Lynn, S., 1987):

- Diglime (diethylene glycol dimethyl ether)
- Triglime (triethylene glycol dimethyl ether)
- Tetraglime (tetraethylene glycol dimethyl ether)
- Dowanol DM (diethylene glycol methyl ether)
- Dowanol TBH (triethylene glycol butyl ether)

In addition, dimethylaniline (Basu and Dutta, 1987) and xylidine (Kohl and Riesenfeld, Gas Purification, 4th edition, p.379, Gulf Publishing 1985) were also proposed as promising solvents for SO_2 absorption. We prepared liquid films using *solutions* of some of the above organic liquids to study their ability for simultaneous removal of both SO_2 and NO_x .

FPCLM Studies using Organic Liquids for SO_2 removal

We tried all the organic chemistries suggested by Demyanovich and Lynn (1987). While these solvents were good organic sorbents of SO_2 , they were found to be ineffective in a carrier-mediated transport mode (They bound, but would not release the SO_2). Dimethyl aniline(DMA), Quinoline, xylidine, and o- toluidine were however found to display acceptable affinity for SO_2 – a fact confirmed by us by bubbling SO_2 through these reagents. However, before considering these latter reagents for the preparation of liquid membranes, we decided to ascertain that they would be soluble in the solvent N-cyclohexyl-2-pyrrolidone (CHP) for the following reasons:

- First, the high volatility of some of these reagents makes it impractical to use the pure reagents in the preparation of liquid membranes. Dissolving them in the non-volatile solvent CHP leads to solutions that are less volatile.
- Second, since Fe(II) and Zn(II) dissolved in CHP serve as carriers of NO, we propose to use ternary solutions of one of the above reagents, Fe(II), and CHP as liquid films for combined SO_x/NO_x removal.

We observed that all the above reagents are completely miscible in CHP. However, in preparing liquid films with solutions of these reagents in CHP, we could not use

polypropylene sheets, as was done for aqueous films, because all these organic solutions wet polypropylene. Based on a detailed analysis of the interfacial behavior of these organic liquids with various polymeric materials, we concluded that Teflon™ is the appropriate material. Accordingly, we obtained microporous Teflon™ membranes – of comparable structural characteristics to the polypropylene sheets – from Gore Associates Inc., and prepared liquid membranes of these organic liquids. We carried out permeation studies of SO₂ through these liquid films, the results of which are shown in Table 14.

Table 14. Flux of SO₂ Across Organic Films

Organic Reagent*	SO ₂ Conc. in Sweep Outlet (ppm)	Transmembrane Flux of SO ₂ (moles/cm ² /min)	% SO ₂ Removal	Ratio of SO ₂ flux across film to DMA film
N-N DMA	120	1.060e-6	1.5	1.00
Quinoline	50	4.418e-7	0.625	0.42
2,4 Xylidine	40	3.534e-7	0.50	0.33
o-Toluidine	60	5.301e-7	0.75	0.5

*All reagents are dissolved in the solvent N-cyclohexyl 2-pyrrolidone in the proportion of 1:5 (volume of the reagent : volume of the solvent)

The last column of the table shows the fluxes (obtained with the various organic reagents) normalized relative to that with DMA. This column clearly indicates that of all the organic reagents studied, DMA is the best in its ability to mediate the transport of SO₂ across the film. Additionally, the flux across DMA films is comparable to that observed across citrate films. The measurements were very difficult to obtain, because the organic vapors from the films adversely affected the performance of the SO₂ analyzer.

FPCLM Studies using Organic Liquids for NO_x removal

As was the case with the SO₂ analyzer, the NO analyzer was even more seriously affected by the presence of the vapors from the organic liquids. We tried to resolve this problem by using a gas chromatograph to monitor NO and SO₂, the results of these efforts are described below.

Gas chromatography

The system used for the analyses of gas samples was a *Hewlett Packard* model HP5890A gas chromatograph (GC). It was suggested in the literature that the "Haysep A" polymer packed column in conjunction with a thermal conductivity detector (TCD) is suitable for the separation of both NO and SO₂. Also, the following temperature program was recommended for an effective separation: After injection of the gas sample, the column has to be kept at ambient temperature for about 9 minutes, then the temperature should be increased at the rate of 20°C/ min., until it reaches 110°C and it should be kept at this temperature for about 8 minutes. The idea here is to separate NO at the ambient conditions and to elute SO₂ at a faster rate by increasing the temperature. Accordingly, "Haysep A" column (25' X 1/8", 100/120 mesh) packed with Divinylbenzene and Ethyleneglycolmethacrylate was obtained from *Supelco*. The column was connected to the GC with the TCD. To record the areas of the peaks of different gases, an integrator (model HP3392) was also connected to the GC. The carrier gas was ultra high purity grade (99.999%) helium, supplied by Linde Gases, Toledo. The reference and column flow rates were about 30 cc/min. The same flow rates were maintained through the column and reference channel to achieve maximum sensitivity of TCD. The maximum operating temperature for the column prescribed was 165 °C.

Gas Chromatography - Experimental Protocol

The column was conditioned for about 12 hours at 140 °C and sufficient time was allowed for the signal from the TCD to stabilize. Then, without injecting the sample, a blank run was made to store the base line signal from the TCD for the above mentioned temperature program. Typical chromatogram of the blank run is shown in Figure 22.

Figure 22: A typical temperature-programmed chromatogram when only the carrier gas (helium) is flowing through the "Haysep A" column (blank run). For the first nine minutes the column is at ambient temp., and then the temp. is increased at the rate of $20^{\circ}\text{C}/\text{min}$.

It can be noticed that when the temperature is above 70°C, disturbance appears in the signal. This is due to the bleed of the polymer material. This noise in signal can only be smoothened at the cost of the loss of detection of the component gases present at very low concentrations. Since the concentration of NO from the regular flat plate experimental runs is of the order of 5 ppm, the signal from the TCD was not attenuated.

In any event, various chromatographic runs were made at different NO concentrations to ascertain the reproducibility of the data and the lowest detection limits of the apparatus. Figures 23 and 24 show the chromatograms for the same NO concentration of 1000 ppm. Computation of the area of integration of the NO peaks in these chromatograms revealed that the reproducibility in the measurement of NO concentration was only within 20-30%. SO₂ peak appears at higher temperatures, and it is difficult to even identify the peak because of disturbances. It was also observed that the lowest detection limit for NO was about 200 ppm.

Considering the difficulties associated with the operation of GC for the present system, it was determined that this technique was not a viable analytical procedure for monitoring NO and SO₂ at concentration levels typical of the flue gases. The GC was clearly inadequate and the organic vapors interfered with both the dedicated SO₂ and NO gas analyzers. (However, as noted previously in Table 14, we were able to obtain *some* flux data for SO₂ in organic films using our gas analyzer before the vapors caused it to become inoperable. We were never able to obtain any reliable NO flux data using organic films.)

Thus, in summary, due to the lack of a suitable analytical procedure to monitor NO and SO₂, we were forced to terminate any further investigation of organic liquid membrane chemistries. We then focused our efforts on the design, construction and testing of a Dual-Spiral-Wound Liquid Membrane Module (DSWLM). and a Dual-Hollow-Fiber Contained-Liquid Membrane Module (DHFCLM).

Design & Construction of a Dual-Spiral-Wound Liquid Membrane Module (DSWLM)

The design of the spiral contactor evolved during the actual construction of the device. The original design of the contactor is shown in Figure 25. We modified the original design to overcome some construction difficulties. As shown in Figure 26, the modified spiral design contained several more tubes to obtain the desired flow patterns, but it was easier to construct. We faced considerable difficulty in getting the necessary spacer material

Figure 23: A temperature-programmed chromatogram obtained after injecting a simulated flue gas mixture containing 1000 ppm of NO. The temperature programming rate is the same as that used in Figure 22. (The peaks corresponding to NO and N₂ are identified.)

RUN # 9
 WORKFILE NAME:
 AREA RT AREA TYPE AR/HT ARB
 10.87 1166300 BV 0.963
 12.36 3133500 VP 1.176
 13.90 446970 PV 0.342
 14.54 3622000 VV 0.429
 15.44 1564900 VP 0.450
 16.58 529100 PV 0.170
 17.19 6536400 I VP 1.000
 MUL FACTOR= 1.8140E+04
 MUL FACTOR= 1.0000E+00

Figure 24: A temperature-programmed chromatogram obtained after injecting a simulated flue gas mixture containing 1000 ppm of NO. The temperature programming rate is the same as that used in Figure 22. (The peaks corresponding to NO and N_2 are identified.)

Figure 25: A design drawing of the Dual-Spiral Module

FLOW CONFIGURATION IN DUAL SPIRAL MEMBRANE

Key	
F -	Feed Stream
S -	Sweep Stream
M -	Membrane Liquid
i -	Inlet
o -	Outlet

Figure 26: Modified Spiral Membrane Design

required for the device fabrication. Many companies refused to disclose technical information or provide material for proprietary reasons. Finally, *Decenso Textile Inc.* of Annapolis, MD agreed to provide us with the spacer material. The spacer material is called *TRICOT* and is made of epoxy resin. The spacer provides minute flow channels for the liquid and gas flow paths. A photograph of a spiral module fabricated using the modified design is shown in Figure 27. While the spiral design is a novel and efficient packaging method, its construction proved to be quite involved. Additionally, operation of the device would prove to be quite complicated, with precise pressure control required throughout the spiral to prevent loss of the liquid membrane. We, therefore, explored alternative geometries which share many of the advantages of the spiral design and yet are more easily designed, constructed and operated.

Dual Hollow Fiber Contained Liquid Membrane

After considerable amount of investigating, we concluded that a dual hollow fiber device will be a viable alternative to the spiral design. This design was not available at the time of the original proposal submission. The operation of this device was discussed previously, and was shown in Figure 6.

A dual hollow fiber contained liquid membrane permeator has the following advantages:

- Fiber wall defects lead only to a loss of membrane liquid through the fiber lumen. However, flue gas does not leak into the sweep gas.
- The membrane is stable. Membrane liquid replenishment is easy.
- Gas humidification is unnecessary.
- The flow rates of the gas streams are independent of each other and from the liquid flow rate. This is a significant advantage over packed towers where flooding and channeling are significant problems.
- The use of hollow fibers leads to a high membrane surface area per unit permeator volume and a low effective liquid membrane resistance.

Figure 27: A Photograph of the Dual-Spiral Module fabricated using the modified design shown in Figure 26

Experiments with the Dual-Hollow-Fiber Modules (DHFCLM)

We conducted a number of experiments with the dual-hollow-fiber modules. In these experiments, the aqueous solution containing carriers was introduced into shell side of the module. The shell side liquid pressure was maintained higher than that on the lumen side by means of a back pressure regulator. This back pressure was necessary to prevent bulk mixing of the feed and sweep gases. The liquid flow was recirculated at a nominal rate of 2.5 cc/min which reduces the liquid phase resistance and maintains the integrity of the membrane by compensating for any evaporative losses. The feed gas inlet SO₂ concentration was 3500 ppm. The sweep gas outlet was continuously monitored for SO₂ concentration.

The objective here was to achieve substantial levels of SO₂ removal (% removal) by taking advantage of the large surface area per unit device volume provided by HFCLMs. Accordingly, experiments, similar to those performed with an FPCLM, were conducted in an HFCLM device. The module used is supplied by Hoechst Celanese, Charlotte, NC, the specifications of which are shown in Table 2. The flow rates of both the feed and the sweep gas streams were maintained at 2000 cc/min, and the feed gas contained 3500 ppm of SO₂ while the incoming sweep stream was free of SO₂. Again, steady-state SO₂ fluxes were obtained with the HFCLM containing either citrate or sulfite solution on the shell-side. The results obtained for various reagent compositions are presented in Figure 28. The figure shows the variation of both the percent SO₂ removal from the feed gas and the overall SO₂ flux across the liquid membrane with the reagent concentration. A percentage SO₂ removal of about 32 was realized with citrate at the highest concentration employed (0.5 M) as compared to 15.5 with sulfite. In case of sulfite, percent SO₂ removal displays an asymptotic behavior with increasing reagent concentration (beyond 0.5 M), whereas this does not appear to be the case with citrate. Concentrations larger than 0.5 M would, perhaps, lead to a percent removal higher than 32% with citrate. Also, in the module supplied by Hoechst-Celanese, the sweep-and feed-fibers are not well-mingled along the device length, as is required in a properly fabricated HFCLM. The improper mixing of the two kinds of fibers tends to make the effective film thickness much larger and the membrane surface area smaller, which, in turn, lead to a reduction in percent SO₂ removal.

Since in a regular FGD process SO_2 removal of 90% or higher is required, one could operate HFCLM modules in series wherein the exit flue gas from the first module is fed to the second and so on until the required percent removal is achieved.

From Figure 28 it can also be observed that the ratio of overall fluxes of citrate to sulfite is about 2 at the highest citrate concentration studied (0.5 M). This ratio is somewhat smaller than those observed in FPCLM studies. Obviously, the accumulation of SO_2 in the sweep-side lowers the driving force along the device length in the HFCLM. This reduction in the driving force will be larger for citrate than sulfite due to the higher initial fluxes with the former reagent. This results in a smaller overall flux ratio in an HFCLM compared to FPCLM.

Effect of reagent solution recirculation rate on permeant flux in HFCLM

In a recent study by Guha et al., (1991) on biogas purification using HFCLMs, the liquid membrane solution was kept stagnant and was maintained at a slightly higher pressure than that in the lumen side using high pressure gas. However, it was suggested in this the paper that, during the industrial operation of an HFCLM, the liquid membrane can be circulated at a slow rate either continuously or periodically. This method would eliminate the need for the prehumidification of gas streams, and replenishes the liquid lost due to the evaporation of the membrane into the gas stream. In addition to these advantages, we believe that the recirculation of liquid membrane solution actually aids the flux of the permeant species due to flow.

In our HFCLM experiments described above, the liquid membrane solution was recirculated at a low flow rate of 2.5 cc/min. To substantiate the effect of flow on permeant flux, we have performed one experimental run at high recirculation rate (8 cc/min) using a 0.1 M aqueous citrate solution. The SO_2 flux rate was increased by about 25% compared to the previous experiment with a liquid recirculation rate of 2.5 cc/min. Since the liquid flow rate can be increased without affecting the tube side gas flows, one can adjust the liquid flow rates to obtain higher SO_2 removal rates. However, the upper limit for this process would be at the critical pressure where the liquid intrudes through the membrane pores into the gas streams. Detailed experimentation in well-designed HFCLMs is,

Figure 28: Comparison of the performance of sodium sulfite and citrate solutions in a HFCLM module

however, necessary to identify optimal recirculation rates of the reagent solution that would yield maximum permeant flux.

Conclusions

- ☛ Carrier-mediated facilitated transport of SO_2 was shown to be a promising FGD technique, that allows in-situ regeneration of the reagent.
- ☛ New water soluble carrier-reagents (superior to sulfite) have been identified.
- ☛ We have shown, both by theory and experiment, that rates of SO_2 transport through sodium citrate films are always much higher than those across sulfite films.
- ☛ The observed enhancement in SO_2 flux across sulfite or citrate films relative to reagent-free films is due to the "dynamic role" played by these weak-acid reagents as "carriers" for H^+ ion transport across the film. It is concluded that a weak acid the pK of which is the arithmetic average of the pH values at the two faces of the film would lead to maximum SO_2 flux. It is argued that the low SO_2 transport rates across sulfite films are because of the fact that the pK of $\text{HSO}_3^-/\text{SO}_3^{2-}$ equilibrium falls well outside the pH values prevailing in the liquid film at all SO_2 partial pressures of relevance to flue gas desulfurization. In this regard, any monoprotic weak acid with a pK value in the range of 3.5 to 4.5 is expected to yield much higher fluxes than sodium sulfite at the same reagent concentration level. Citric acid, a *polyfunctional* weak-acid with two of its three pKs in the above pH range, yields even higher SO_2 fluxes than monoprotic acids. This is due to its ability to transport protons in more than one conjugate acid/base form.
- ☛ With citrate systems facilitation factors which are almost an order of magnitude higher than with sulfite systems are obtainable at feed-side SO_2 partial pressures of 4000 ppm at all reagent concentration levels. This is an important result in that the stack gas emissions from high sulfur coals have SO_2 partial pressures in the range of 3500-4000 ppm
- ☛ Dual hollow fiber contained liquid membrane module was shown to be a promising contactor for FGD. This geometry offers the advantages of the spiral design, while being simpler to construct and design.

- ✶ The presence of oxygen in the flue gas or the sweep gas interferes with the performance of the EDTA carriers for NO removal.
- ✶ Efficient carrier facilitated transport of NO from flue gases does not appear feasible at this time.
- ✶ Dimethylaniline (DMA) in cyclohexyl-pyrrolidone is shown to be a possible organic carrier for SO₂ removal. If a suitable carrier for NO_x soluble in CHP can be identified, this may provide a viable alternative to aqueous chemistries.
- ✶ Our attempts to use steam as the sweep gas were unsuccessful due to some unresolved material and operational problems. However, as materials capable of withstanding higher temperatures become available, steam sweeping should become possible.
- ✶ A detailed mathematical model that describes carrier facilitated transport of SO₂ through contained liquid membranes was developed and validated. The non-equilibrium boundary layer analysis (NEBLA) developed by Roberts and Friedlander (1980) was revalidated for sulfite films and it was also shown to be applicable to citrate based systems when properly modified.

Marketing/Commercialization Discussion

We believe that among the existing regenerable cleanup technologies, the bipolar membrane approach of Allied has the most promising economics. In view of this, all our economic calculations are based on a modified Allied process wherein the conventional scrubbers are replaced with comparable HFCLMs. Our calculations, based on updating the economic data of the Allied process presented in the Appendix, *estimate* the cost to be \$7/ton of coal, and \$108/ton SO₂ removed. We have not addressed the issue of costs associated with NO_x removal for the contained liquid membrane process as the process chemistry was not perfected to an extent to allow us to do this.

As discussed earlier, this was a bench scale study of the feasibility of the concept of HFCLMs. The very near term impact (1-2 yrs) on Ohio coal is likely to be very small. The next step necessary to bring this process to commercialization is a pilot scale study.

Waste Disposal Discussion

The commercial implementation of this process will produce a concentrated gaseous SO₂ stream, and condensate containing a small amount of dissolved SO₂. The flue gases exiting the process will be sufficiently cleaned of SO₂ that direct discharge to the atmosphere will be possible. It is recommended that the concentrated SO₂ stream be used to produce sulfuric acid, a valuable byproduct, which will improve the process economics. The condensate can be reused to produce steam and recycled, or neutralized with caustic and discharged. The liquid membrane materials will be continually recirculated and will not add to the waste of the process.

Final Budget Summary

The overall project budget is shown on the in Table 15, on the next page. The expenditures of OCDO funds by line item are shown in Table 16.

Table 15. Overall Project Budget

	OCDO	UT	Total	OCDO%
Total Salaries, Wages and Benefits	\$87,410	\$54,267	\$141,677	62%
Travel	\$648	\$0	\$648	100%
Equipment	\$13,724	\$0	\$13,724	100%
Supplies	\$9,136	\$0	\$9,136	100%
Computer		\$2,850	\$2,850	0%
Total Direct Costs	\$110,918	\$57,117	\$168,035	66%
Total Indirect Costs	\$36,529	\$25,152	\$61,681	59%
Total Project Costs	\$147,447	\$82,269	\$229,716	64%

Table 16. Expenditure of OCDO Funds

	Original Allocation	Amendment #1	Amount Expended
Total Salaries, Wages and Benefits	\$89,477	\$79,143	\$87,410
Travel	\$0	\$0	\$648
Equipment	\$17,350	\$25,237	\$13,724
Supplies	\$5,000	\$11,000	\$9,136
Total Direct Costs	\$111,827	\$115,380	\$110,918
Total Indirect Costs	\$38,051	\$34,498	\$36,529
Total Project Costs	\$149,878	\$149,877	\$147,447

Nomenclature

a_i	= activity of species i, mole/l
A	= coefficient in Eq. (15)
B	= coefficient in Eq. 15, $\text{\AA}^{-1}$
C0	= initial sodium citrate concentration, mole/l
C_i	= concentration of species i (mole/l)
C^*	= H^+ ion concentration in sweep-side boundary layer, mole/l
D_i	= diffusion coefficient of species i, cm^2/sec
F	= facilitation factor $(N-N_0)/N_0$
H	= Henry solubility constant, atm/mole/l
I	= ionic strength of the reagent solution, mole/l
k_1, k_{-1}	= forward and reverse rate constants for the reaction 1, in Table 3
K_j	= equilibrium coefficient of jth reaction
L	= thickness of the liquid film, cm
n_k	= number of sodium atoms in species k
N_i	= flux of species i, mole/ cm^2/sec
N_0	= flux of sulfur dioxide in the absence of chemical reactions
Na_{tot}	= total alkaline sodium concentration, mole/l
p	= partial pressure, atm
Q	= gas flow rate, cc/sec
r_i	= rate of formation of species i by a chemical reaction, mole/ cm^3/sec
R	= gas constant
S	= Exposed surface area of the membrane, cm^2
T	= temperature, $^{\circ}\text{K}$
x	= x - coordinate in the liquid film, runs from feed-side towards sweep-side, cm
z_i	= valency of species i

Greek Letters

- α_i = ionic radius of species i, Å
 β_i = adjustable parameter in Eq. 15
 δ = boundary layer thickness, cm
 γ_i = activity coefficient of species i
 ν_{ij} = stoichiometric coefficient of species i in jth reaction
 ϕ = Damkohler number

Subscripts

- eq = equilibrium approximation
 HSO_3^- = bisulfite ion
 H_2O = water
i = any species
ij = species i in jth reaction
j = any reaction
k = sodium containing species
m = radical $\text{R}^\bullet$ -containing species
NV = non-volatile species
 $\text{SO}_3^{=}$ = sulfite ion
x=0 = gas-liquid interface, near the feed-side
x=L = gas-liquid interface, near the sweep-side

Superscripts

- 0 = feed-side gas-liquid interface
F = feed stream
L = sweep-side gas-liquid interface
 $L-\delta^l$ = contact point where sweep-side boundary layer and core region meets
S = sweep stream

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Appendix

Demonstration of Economic Calculations:

We will be using the as the process design basis the Allied Process, described in the paper by K. Nagasubramanian, et. al. (1980). The design basis is a 500 MW_e power plant burning 3.5% sulfur coal. This design basis would produce a flue gas in the range of 1500 - 4500 ppm SO₂, where all our experiments were run.

The approach we took was to update the numbers in the article to 1991 dollars using cost indices. We chose a 15 year project lifetime, with 10% nominal annual interest rate, with no inflation for levelizing the costs in order to put them on a yearly basis, so that we could determine the cost per ton of coal. The pertinent figures are as follows:

Process	Capital Cost (millions of \$\$, 1978 \$\$)	Annual Operating Cost
Allied Regenerable Process	26.2	7.28
Limestone Throwaway	28.8	11.22

The CE cost indices are 1978=198 , and 1991 = 362 . The multiplier for scaling the costs to 1991 dollars is thus $(362 / 198) = 1.83$. The process is designed to recover 90% of the SO₂, which according to the design basis, amounts to 70,000 tons/yr. The coal rate corresponding to this is 1.11 million tons/year @ 3.5% sulfur content. The cost per ton of coal for the Allied Process is as follows:

$$\text{Present Worth (1991) of Capital \& Operating Expenses} = 1.83 [\text{Capital Cost} + 7.61 * \text{Annual Operating Cost}]$$

where 7.61 is the series present worth factor (10%, 15yrs) for the annual operating costs. The present worth calculated in this manner is then divided by the total coal use for the 15 years of operation. The results are shown below.

Allied Regenerable Process	\$8.96/ton
Limestone Throwaway	\$15.70/ton

We now need to modify the Allied Process numbers to account for the use of HFCLMs. As instead of packed towers and their regeneration process. We now estimate the cost of comparably designed HFCLM from a packed tower.

The area per unit volume for a larger benchscale HFCLM, such as those single fiber devices supplied commercially by CD Medical would be about $54 \text{ cm}^2/\text{cm}^3$. A randomly packed tower with 1.5 inch packing will typically have $1\text{-}2 \text{ cm}^2/\text{cm}^3$ specific area. If we use 1.5 as a representative figure, the ratio of the areas is:

$$\frac{a_{HFA}}{a_{packed}} = \frac{54}{1.5} = 36$$

The costs of packing for the two contactors is also different. The cost for random packings is approximately \$18.35 per ft^3 , 1991 dollars, (Peters and Timmerhaus, 1980.). This is equivalent to \$3.94 per m^2 . The cost for hollow fibers is uncertain on a larger scale. The lowest figure that we have seen is approximately \$0.02/ ft^2 in a reference from Gelman Scientific (Chemical Engineering, p.20, July 7, 1986), but the costs could be considerably higher, up to \$0.20/ ft^2 . To be conservative, we'll use the higher cost figure. This is equivalent to \$2.15/ m^2 . The ratio of the costs of the packing on a per square meter basis is thus:

$$\frac{\$_{HFA \text{ fibers}}}{\$_{packed \text{ packing}}} = \frac{\$ 2.15}{\$ 3.94} = 0.55$$

These numbers are close enough and the numbers uncertain enough that we will take the costs of the packing and fibers to be equivalent on an area basis.

The other advantage that the HFAs have is their superior mass transfer characteristics.

From LeBlanc and Varanasi, the mass transfer coefficient for HFAs (hollow fiber absorbers) is an order of magnitude higher than that of packed towers. This result should hold reasonably well for HFCLMs also.

$$\frac{K_{HFCLM}}{K_{packed}} = 10$$

The important parameter is $(K \cdot a)$ which is related to the required volume of the absorber. The ratio for this parameter is:

$$\frac{K_{HFCLM} a_{HFCLM}}{K_{packed} a_{packed}} = 360$$

This means that the mass transfer possible in an HFCLM is considerably greater than a comparably sized packed tower, or conversely, a much smaller HFCLM can do the same job as a packed tower. Random packed towers are seldom larger than 4 feet in diameter (Peters and Timmerhaus). Therefore, if we base our size comparison on a 4 foot diameter packed tower, we could significantly downsize the HFCLM, however, what one would practically do would be to downsize the tower diameter a bit and use less surface area inside, in order to obtain the required volumetric throughput. We could propose using a 3 foot diameter tower for the HFCLM and less area. The cost of the tower per foot of height for the HFCLM and the packed design can be estimated from Peters & Timmerhaus(1980) using packed tower data, (the towers themselves should be pretty comparable):

$$\log \left[\frac{cost_{HFCLM}}{cost_{packed}} \right] = 1.2 \log \left[\frac{D_{HFCLM}}{D_{packed}} \right]$$

using this set of data we get:

$$\left[\frac{cost_{HFCLM}}{cost_{packed}} \right] = 0.71$$

This is a very rough estimate of the ratios of the capital costs of the towers.

We also estimate a comparable savings in operating expenses due to the decreased liquid flow rates required for the HFCLM absorbers to get comparable performance. For example, a typical installation of packed towers might be 5 towers total, with 4 on-line and 1 off-line. With HFCLMs we could probably reduce this to 4 towers total, 3 on-line and 1 off-line. Therefore we could estimate the savings of an HFCLM unit to be approximately 30% of the packed tower unit. If we modify the Allied Process numbers to reflect this savings we obtain (see table 5 in the Allied article):

Capital Expense for the Towers (SO₂ absorption) = (0.7)(9.58MM) = (6.71MM)

or..... a savings of \$2.87MM. We can now calculate the present worth of this process using the HFCLMs (where 9.58MM is the absorption cost of the Allied Process):

$$\text{Present Worth (1991) of Capital \& Operating Expenses} = 1.83 [(26.2-2.87) + 7.61*(.7)(7.28)] = \$113.7MM$$

or, on a per ton of coal basis, we obtain:

$$\text{Cost of Allied Process using HFCLMs} = \frac{\$113.7MM}{(1.11MM \text{ tons/yr}) (15\text{yrs})} = \frac{\$6.83}{\text{ton}}$$

and finally the cost per ton of SO₂ removed (for 90% removal):

$$\text{Cost of Allied Process using HFCLMs} = \frac{\$6.83}{\text{ton coal}} \frac{(1 \text{ ton coal})}{(0.035 \text{ tons sulfur burned})} \left(\frac{0.9 \text{ tons sulfur removed}}{\text{ton sulfur burned}} \right) \left[\frac{(32 \text{ tons sulfur})}{(64 \text{ tons SO}_2)} \right] = \frac{\$108.42}{\text{ton}}$$

The above calculations should be conservative estimates. They do not account for any savings that could result from the more efficient in-situ regeneration

capabilities of the HFCLM process. However, this savings should not alter the above number a great deal (less than 10%). Since the accuracy of preliminary cost estimates are only "ballpark" figures, this should provide us with an approximation of the cost of an HFCLM process.

We have not addressed the issue of costs associated with NO removal for the HFCLM process as the process chemistry was not perfected to an extent to allow us to do this.

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