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on

**SIMULTANEOUS SO₂/NO SEPARATION FROM
FLUE GAS USING HFCLM**

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by

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ABSTRACT

Abatement technologies for oxides of sulfur and nitrogen present in flue and stack gases from coal fired boilers are becoming increasingly important. Scrubbing the gases with an aqueous limestone slurry to remove SO_2 is a widely used treatment process. These scrubbing solutions are, however, not very effective in removing NO. In addition, the process is expensive and produces large volumes of sludge.

The liquid membrane from a 0.01 M aqueous solution of Fe^{2+} EDTA has been found to have a very high selectivity for NO over N_2 . Thus, SO_2/NO_x , identified as the source of acid rain, can be removed simultaneously using an aqueous Fe^{3+} EDTA solution in a hollow fiber contained liquid membrane (HFCLM) permeator with hydrophobic fibers (Mujamdar et al., 1992). The HFCLM configuration has addressed previous concerns about liquid membrane stability for an application such as this.

In this project, a flow apparatus was constructed that will allow simultaneous SO_2/NO removal and recovery using two hollow fiber modules in series. Flowing the liquid membrane on the shell-side of the modules it is hypothesized will enhance the performance over that of HFCLMs without loss of stability. From the work completed in this exploratory project, it was concluded that to move the current state-of-the-art for this promising technology toward commercialization will require progress in the following areas: (1) sensitivity of the performance of the system to temperature changes, (2) validation of a mass transfer model to be used in scale-up calculations, (3) data on alternative flow

schemes, and (4) overall process economics calculations. Partial funding to complete these tasks has been secured along with Christopher Haggins, a NACME Lincoln Hawkins Undergraduate Research Fellowship recipient who will be a chemical engineering senior next year.

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PROJECT ACCOMPLISHMENTS

Considerable work has been accomplished through this exploratory grant. Due to the complexity of the experimental setup necessary to safely perform the desired experiments, most of the tasks accomplished have been in the area of experimental setup design and development. Tasks completed in this area include:

- 1) Purchase and testing of a TOX ARRAY 1500 (McNeil International) for measuring NO concentrations in the range of 100 to 1,000 ppm.
- 2) Purchase and testing of CHROMOSIL 310 (Supelco, Inc.) GC packed columns for measuring SO₂ concentrations in the range of 1,000 to 10,000 ppm.
- 3) Purchase of mass flow controllers and dynablender (Matheson) for control of feed composition and flow rate.
- 4) Purchase, construction, and testing of flow setup that includes compressed gases (air, SO₂, NO/N₂, and CO₂), stainless steel pressure vessels, pressure gages, flow controllers, teflon fittings and tubing, and two Celgard hollow fiber membrane modules (Hoechst Celanese) for simultaneous extraction and recovery of SO₂ and NO.

Toward the end of having the capability of theoretically predicting the behavior of the flow system, the FORTRAN code for the mass transfer model of Yun (1993) has been obtained, tested, and is being modified. Previously this code was for the transport of a single chemical species (copper) in a hollow fiber extraction module. The code is being modified to describe both the extraction and recovery of a single chemical species. Future work will extend this code to the multispecies case of simultaneous extraction and recovery of SO₂ and NO.

From the work completed in this exploratory project, it was concluded that to move the current state-of-the-art for this promising technology toward commercialization will require progress in the following areas: (1) sensitivity of the performance of the system to temperature changes, (2) validation of a mass transfer model to be used in scale-up calculations, (3) data on alternative flow schemes, and (4) overall process economics calculations. Partial funding to complete these tasks has been secured along with Christopher Haggins, a NACME Lincoln Hawkins Undergraduate Research Fellowship recipient who will be a chemical engineering senior next year. Additional funding to complete these tasks is currently being sought from EPA and DOE.

INTRODUCTION

Advanced separation technologies are being developed to effect SO_2 -NO removal from flue gas (Walker et al., 1985), improve separation efficiency, and reduce the treatment cost. Membrane gas separation is one of the technologies under development. Membrane processes are simple, often less expensive, and are modular in nature for ease of scale-up or flexibility. Polymeric membranes, however, do not currently exhibit the required combination of high flux and selectivity.

Liquid membranes may be, therefore, better candidates, since diffusivities of gaseous species through liquids are orders of magnitude larger than those through polymeric solids. Furthermore, facilitating agents can be added to liquid membranes to enhance the flux of certain species significantly while generating high selectivity between the permeants of interest (here SO_2 and NO, and the other species (CO_2 , O_2 , and N_2)). In addition, the membrane process not only removes SO_2 and NO from the flue gas, but also can concentrate simultaneously these species in the product side for easier disposal and/or possible further use.

Liquid membranes have been studied in immobilized liquid membrane (ILM) form for gas separations (Ward and Robb, 1967; Otto and Quinn, 1971; Suchdeo and Schultz, 1974; Matson et al., 1977; Kimura and Walmet, 1980; Bhave and Sirkar, 1986; Hughes et

al., 1986; Meldon et al., 1986). The first study on SO₂ separation via an ILM was carried out by Ward and Neulander (1970). ILMs are generally stable, but they have short operating lives and can not be regenerated *in situ* (Kimura and Walmet, 1980; Matson et al., 1983; Sengupta and Sirkar, 1986).. A different liquid membrane structure called the Hollow Fiber Contained Liquid Membrane (HFCLM) has been used recently for liquid separations (Sengupta et al., 1988a, 1988b; Basu and Sirkar, 1991) and for separation of gas mixtures (Majumdar et al., 1988, 1989; Guha et al., 1991, 1992); it eliminates most of the deficiencies of the traditional ILM. The lumen of the hollow fibers carries the feed and strip solutions under proper pressure conditions. Guha et al. (1992) have demonstrated that the HFCLM system can be operated successfully in different modes: sweep gas, sweep liquid, permeate side vacuum, and conventional permeation.

Sengupta et al. (1990) have studied the permeation behavior of SO₂, CO₂, O₂, and N₂ present in a typical flue gas through various liquid membranes. Excellent permeabilities of SO₂ and very high selectivities between SO₂-CO₂ (50-250) and SO₂-N₂ (1500-3500) were obtained using pure water and facilitated transport with aqueous solutions of various inorganic salts, e.g., NaHSO₃, Na₂SO₃, Fe²⁺EDTA, and Fe³⁺EDTA, and with SO₂ concentrations in the range 500 to 5000 ppm. These values are considerably higher than the polymeric membrane selectivities (SO₂-CO₂ selectivity of 10 and SO₂-N₂ selectivity of 250) obtained by Baker et al. (1988).

In facilitated transport permeation-separation of a gas species (permeant) from a gas mixture, the liquid membrane contains a nonvolatile carrier that reacts reversibly with the particular species. Any free species in the liquid membrane diffuse across the membrane; simultaneously the carrier-permeant complex formed at the feed/membrane interface diffuses through the membrane and dissociates into the carrier and the permeant at the sweep/membrane interface. Simultaneous diffusion of the free permeant species and the permeant-carrier complex enhances the total mass flux of the permeant. Such systems, although complex, have been analyzed for ILMs by solving the reaction-diffusion equations in one dimension along the film (Majumdar et al., 1992). For pure water membranes, the following principal ionization reaction occurs with SO_2 (Roberts and Friedlander, 1980):

On the other hand the permeation of NO through an aqueous solution of Fe^{3+} EDTA is facilitated by the complex formed by the reaction:

The liquid membrane from a 0.01 M aqueous solution of Fe^{3+} EDTA has been found to have a very high selectivity for NO over N_2 . Thus SO_2/NO_x , identified as the source of acid rain, can be removed simultaneously using an aqueous Fe^{3+} EDTA solution in a

HFCLM permeator with hydrophobic fibers (Mujamdar et al., 1992). Majumdar et al. (1994) have carried out HFCLM separation studies at 25°C to remove SO₂ from a mixture of SO₂-CO₂-O₂-N₂ using water and 1 N NaHSO₃ liquid membranes operating in the sweep and vacuum modes. They report SO₂ removal of 60-95% from a feed of 5000 ppm SO₂. Majumdar et al. (1994) have also performed HFCLM studies to eliminate SO₂ and NO simultaneously from a mixture of SO₂-NO-CO₂-O₂-N₂ using 0.01 M Fe²⁺EDTA at 24°C and 70°C and 0.01 M Fe³⁺EDTA at 70°C. They report 70-90% removal of SO₂ and 50-70% removal of NO with little performance difference between the high and low temperatures.

In this exploratory research project, the removal and recovery of SO₂ and NO from gas containing O₂, N₂, and CO₂ was explored using 0.01 M Fe³⁺EDTA liquid membrane in two hollow fiber membrane permeators in series using the sweep operating mode. The novel concept of using a mobile liquid membrane to improve the performance is explored.

THEORETICAL WORK

The contained liquid membrane in the shell side of a HFCLM permeator operated in either the sweep or vacuum modes is generally stationary except for any movement caused by membrane liquid replenishment. Unlike ILM, a HFCLM configuration offers the additional possibility of operating a module with the liquid membrane in uniform motion; the liquid exiting from one end of the permeator may be recirculated to the other end of the shell side of the permeator. The movement of the liquid membrane should be beneficial in systems such as the one to be explored in this study in which most of the mass transfer resistance lies in the membrane liquid. Such a liquid membrane may be identified as a mobile liquid membrane (MLM). The behavior of such a hollow-fiber contained mobile liquid membrane has not been previously studied (Majumdar et al., 1992). Because HFCLM modules are no longer commercially available, the desired phenomenon will be studied using two hollow fiber modules in series.

The modeling of transport in hollow fiber membrane modules is complex for a variety of reasons. For example, the analyte concentrations in the feed, strip, and membrane phases vary along the permeator length. The mass transfer patterns are not uniform due to the cylindrical geometry of the fiber surface. Further, there are uncertainties regarding the effect of analyte concentration on its distribution coefficient, the true diffusion inside the tortuous pores, and the two dimensional effects as the

analyte diffuses from the bulk into the pores and vice versa. Majumdar et al. (1993) have provided theoretical first order estimates of the rate of mass transfer in HFCLM permeators by assuming that the overall mass transfer resistance can be expressed as the sum of individual resistances in series. In general, the transfer resistances of the microporous hollow fiber walls are practically negligible. The substrate transfer coefficients are typically an order of magnitude higher than the liquid membrane transfer coefficients. Further, if feed and sweep (or permeate, for vacuum runs) flow rates are known, one can estimate the film transfer coefficients using average correlations and overall mass transfer coefficients may be calculated from the available experimental data (pressures, flow rates, and compositions).

Yun et al. (1993) have presented a model for the extraction of copper from an aqueous stream with a chemical reaction occurring in the liquid membrane. This model is presented below and is being modified to predict both the removal and recovery of copper. This model will then be further modified to describe the removal and recovery of SO_2 and NO in a gas containing oxygen, carbon dioxide, and nitrogen.

A. Mathematical Model

In solvent extraction, a commonly used industrial process, a solute in a solution (aqueous or organic) is extracted into an

immiscible solvent (aqueous or organic) by dispersing one of the immiscible phases as drops in the other phase. Thus, a large interfacial area is created, and the extraction rate is increased. After the extraction is completed, the phases are separated and the dispersed phase is coalesced (Prasad et al., 1992).

Membrane-based solvent extraction devices were recently developed. In such devices, extraction was accomplished without dispersing one phase as drops in another phase, and coalescence is not essential. The flow rates of both phases (aqueous and organic) were varied over wide ranges without flooding as long as appropriate pressure conditions were maintained (Prasad et al., 1992).

Microporous membranes may be in each of the following forms: symmetric, asymmetric, and composite, and their pore sizes may be evenly or unevenly distributed. However, The theoretical aspect of membrane-based solvent extraction was developed primarily for thin, symmetric membranes with no variations in porosity and pore sizes across the membrane (Prasad et al., 1992).

For a hollow fiber microporous membrane configuration, the interfacial areas on the two sides of the hollow fiber are different. The overall mass transfer coefficients may be determined based on the surface area using either the inside or outside diameter of the hollow fiber. In order to calculate an overall mass transfer coefficient, the interfacial area must be based on the diameter where the aqueous-organic phase interface

is located (Prasad et al., 1992).

The steps in the extraction process of copper are as follows (Yun, 1993):

- 1) The copper ion in the aqueous phase (tube-side) diffuses from the bulk to the aqueous-organic interface (inside wall of tube) through the boundary layer.
- 2) At the aqueous-organic interface, one mole of copper ion in the aqueous phase reacts with two moles of free oxime (active component) in the organic phase filled in the membrane pore to form copper-oxime complex by interchanging with two moles of hydrogen ion of free oxime. Next, the hydrogen ion interchanged with copper ion is released into the boundary layer of the aqueous phase. The hydrogen ion diffuses to the bulk of the aqueous phase.
- 3) Copper-oxime complex moves from the aqueous-organic interface to the outside wall of tube through the microporous hydrophobic membrane pore by diffusion and free oxime diffuses in the opposite direction from shell-side into the pore.
- 4) Copper-oxime complex diffuses from outside wall of the tube to the bulk of the organic phase (shell-side) which is flowing countercurrently to the aqueous phase (tube-side).

The reaction occurring in the liquid membrane may be represented as follows:

where M=copper ion in aqueous phase, Cu^{2+} ; H=hydrogen ion in aqueous phase, H^+ ; O=free oxime in organic phase, $RH(org)$; and C=copper-oxime complex in organic phase, $R_2Cu(org)$.

The equilibrium constant of equation (2.1) may be expressed as follows:

$$K_{eq} = \frac{[R_2Cu(org)] [H^+(aq)]^2}{[RH(org)]^2 [Cu^{2+}(aq)]} \quad (2.2)$$

or

$$K_{eq} = \frac{[C(org)] [H(aq)]^2}{[O(org)]^2 [M(aq)]} \quad (2.3)$$

B. Governing Equations

Regions along the radial direction of a hollow fiber are defined as follows:

- t = tube-side,
- tm = the boundary between the tube inside and the membrane substrate at $r=R_i$,
- m = the membrane substrate,
- sm = the boundary between the membrane substrate and the tube outside at $r=R_o$,

and s = the shell-side.

Regions along the axial direction are defined by

- z=0 : the tube-side inlet or the shell-side outlet,
- z=L : the tube-side outlet or the shell-side inlet.

The superscript '-' on the chemical species refers to the axial position at $z=z-\Delta z$.

1. Chemical reaction for copper extraction

The rate of transfer of copper by interfacial chemical reaction in the module segment of length ΔZ consisting of N_f fibers is given by $(-J^R)$:

$$J^R = (2\pi R_f \Delta Z N_f) k_e \left[\frac{C_{tm} H_{tm}}{K_{eq} O_{tm}} - \frac{M_{tm} O_{tm}}{H_{tm}} \right] \quad (2.4)$$

2. Shell-side

free oxime:

$$J_0^s = (2\pi R_o \Delta Z N_f) k_o^s (O_s - O_{sm}) \quad (2.5)$$

$$J_0^s = Q_s (O_s - O_s^-) \quad (2.6)$$

complex:

$$J_c^s = (2\pi R_o \Delta Z N_f) k_c^s (O_s - O_{sm}) \quad (2.7)$$

$$J_c^s = Q_s (C_s - C_s^-) \quad (2.8)$$

3. Membrane substrate

free oxime:

$$J_0^m = (2\pi R_{im} \Delta z N_f) k_o^m (O_{sm} - O_{tm}) \quad (2.9)$$

complex:

$$J_c^m = (2\pi R_{im} \Delta z N_f) k_c^m (C_{sm} - C_{tm}) \quad (2.10)$$

4. Tube-side

copper ion:

$$J_M^t = (2\pi R_{it} \Delta z N_f) k_m^t (M_{tm} - M_t) \quad (2.11)$$

$$J_H^t = Q_t (M_t - M_t^-) \quad (2.12)$$

hydrogen ion:

$$J_H^t = (2\pi R_{it} \Delta z N_f) k_H^t (H_{tm} - H_t) \quad (2.13)$$

$$J_H^t = Q_t (H_t - H_t^-) \quad (2.14)$$

The eleven equations (equation (2.4)-equation (2.14)) contain the following eleven variables: J , M_t , M_{tm} , H_t , H_{tm} , O_s , O_{sm} , O_{tm} , C_s , C_{sm} , and C_{tm} . From equation (2.5)-(2.14), M_{tm} , O_{tm} , H_{tm} , and C_{tm} can be expressed by one variable, J ,

$$2J - 2J^R - 2J_c^s - 2J_c^m - 2J_M^t - J_o^s - J_o^m - J_H^t \quad (2.15)$$

since O_s^- , C_s^- , M_t^- , and H_t^- are known from calculations in the previous cell. Therefore,

$$O_{tm} = O_s^- (1 + K_8 J) \quad (2.16)$$

$$C_{tm} = C_s^- (1 + K_9 J) \quad (2.17)$$

$$M_{tm} = M_t^- (1 + K_{10} J) \quad (2.18)$$

$$H_{tm} = H_t^- (1 + K_{11} J) \quad (2.19)$$

After substituting equations (2.16)-(2.19) into equation (2.4), the following cubic equation in J is obtained:

$$J^3 + a_1 J^2 + a_2 J + a_3 = 0 \quad (2.20)$$

where the coefficients a_1 , a_2 , and a_3 are

$$a_3 = \frac{k_{12} + k_{13}}{k_8 k_{11} + k_9 k_{11}^2 k_{12} + k_8^2 k_{10} k_{13}} \quad (2.21c)$$

$$a_1 = \frac{k_8 + k_{11} + k_{11}^2 k_{12} + k_8^2 k_{13} + 2k_9 k_{11} k_{12} + 2k_9 k_{10} k_{13}}{k_8 k_{11} + k_9 k_{11}^2 k_{12} + k_8^2 k_{10} k_{13}} \quad (2.21a)$$

$$a_2 = \frac{1 + k_9 k_{12} + k_{10} k_{13} + 2k_{11} k_{12} + 2k_8 k_{13}}{k_8 k_{11} + k_9 k_{11}^2 k_{12} + k_8^2 k_{10} k_{13}} \quad (2.21b)$$

and constants k_1 to k_{13} are given by

$$k_1 = (2\pi R_I \Delta z N_f) k_e \quad (2.22a)$$

$$k_2 = (2\pi R_o \Delta z N_f) k_o^s \quad (2.22b)$$

$$k_3 = (2\pi R_o \Delta z N_f) k_c^s \quad (2.22c)$$

$$k_4 = (2\pi R_{lm} \Delta z N_f) k_o^m \quad (2.22d)$$

$$k_5 = (2\pi R_{lm} \Delta z N_f) k_c^m \quad (2.22e)$$

$$k_6 = (2\pi R_I \Delta z N_f) k_H^t \quad (2.22f)$$

$$k_7 = (2\pi R_I \Delta z N_f) k_H^t \quad (2.22g)$$

$$k_8 = \frac{-2}{O_s^-} \left(\frac{1}{Q_s} - \frac{1}{k_2} - \frac{1}{k_4} \right) \quad (2.22h)$$

$$k_9 = \frac{1}{C_s^-} \left(\frac{1}{Q_s} - \frac{1}{k_3} - \frac{1}{k_5} \right) \quad (2.22i)$$

$$k_{10} = \frac{1}{M_t^-} \left(\frac{1}{Q_t} + \frac{1}{k_6} \right) \quad (2.22j)$$

$$k_{11} = \frac{-2}{H_t^-} \left(\frac{1}{Q_t} + \frac{1}{k_7} \right) \quad (2.22k)$$

$$k_{12} = \frac{-k_1 C_s^- H_t^-}{K_{eq} O_s^-} \quad (2.22l)$$

$$k_{13} = \frac{k_1 O_s^- M_t^-}{H_t^-} \quad (2.22m)$$

From equations (2.4), (2.7), (2.10), and (2.11), J can be expressed by

$$-J = (2\pi R_f \Delta z N_f) K_o \left[M_t - \left(\frac{C_s}{K_{eq} \alpha^2} \right) \right] \quad (2.23)$$

where $\alpha = O_{tm}/H_{tm}$, and

Total Resistance = Reaction Resistance + Shell-side
Resistance + Membrane Resistance + Tube-side Resistance

$$\frac{1}{K_o} = \frac{1}{\alpha} \frac{1}{k_e} + \frac{R_f}{R_o} \frac{1}{K_{eq} \alpha^2} \frac{1}{k_c^s} + \frac{R_f}{R_{lm}} \frac{1}{K_{eq} \alpha^2} \frac{1}{k_c^m} + \frac{1}{k_H^t} \quad (2.24)$$

C. Calculation Algorithm

The FORTRAN code for a program to perform the mass transfer calculations is provided in Appendix A. The major steps involved in this calculation are outlined as follows:

- 1) Assume M_t^{out} and set $M_t^{\text{out}}|_{\text{old}} = M_t^{\text{out}}$.
- 2) Calculate C_s^{out} by total mass balance at steady state:
 $Q_t(M_t^{\text{in}} - M_t^{\text{out}}|_{\text{old}}) = Q_t C_s^{\text{out}}$, if there is no complex in the organic inlet stream.
- 3) Calculate O_s^{out} by total oxime molar balance at steady state: $O_s^{\text{out}} + C_s^{\text{out}} = O_s^{\text{in}}$.
- 4) Set $M_t = M_t^{\text{in}}$, $H_t = H_t^{\text{in}}$, $C_s = C_s^{\text{out}}$, and $O_s = O_s^{\text{out}}$ at $z=0$.
- 5) Calculate J at $z=z+\Delta z$ from equation (2.20) and choose the correct J .
- 6) Calculate other variables from equations (2.5)-(2.14).
Repeat steps 5 and 6 up to $z=L$.
- 7) Set $M_t^{\text{out}}|_{\text{new}} = M_t^{\text{out}}$ calculated at $z=L$.
- 8) Compare $M_t^{\text{out}}|_{\text{new}}$ and $M_t^{\text{out}}|_{\text{old}}$. If $|M_t^{\text{out}}|_{\text{old}} - M_t^{\text{out}}|_{\text{new}}| >$ allowable error, set $M_t^{\text{out}}|_{\text{old}} = M_t^{\text{out}}|_{\text{new}}$ and go back to step 2; if not stop the calculation and get the results.

EXPERIMENTAL WORK

The permeator modules to be used in these experiments are prefabricated (Liqui-Cel Hoechst Celanese #5PCM-106) and utilize Celgard X-10 microporous hydrophobic polypropylene hollow fibers (Hoechst-Celanese, Charlotte, NC). The experiments consist of removing SO_2 and NO from a gas stream containing carbon dioxide, oxygen, and nitrogen using two microporous hydrophobic hollow fiber modules in series. The first module allowed the extraction to take place, and the second module allowed the back extraction to take place. The modules were manufactured by Hoechst Celanese Corporation, and their specifications are listed in Table 3.1. Both the feed and strip stream were in a closed loop. The flow rates, temperature, feed concentration, liquid membrane composition, and differential pressures were the major experimental variables. The gas phase was maintained at a pressure lower than the aqueous phase pressure in order to keep the reaction interface at the outside wall of the lumen since the membrane was hydrophobic.

The experimental setup is shown in Figure 3.1. The setup consists of three segments: a waste gas side, a liquid membrane loop, and a permeate gas side. The waste gas side segment is located in the top portion of Figure 3.1 starting at the extractor and above. The liquid membrane loop is located between the extractor and back extractor. The permeate gas side starts at the back extractor and below.

Table 3.1: Characteristics of hollow fiber modules

Fiber Specs.			Module Specs.	
<i>Type</i>	Celgard X-10 microporous polypropylene		<i>Material</i>	Polypropylene
<i>Number of fibers</i>	2100		<i>Diameter</i>	2.5 cm
<i>Internal diameter</i>	240 μm		<i>Length</i>	20 cm
<i>Wall thickness</i>	30 μm		<i>Overall length (incl. endcaps)</i>	30 cm
<i>Effective pore size</i>	0.05 μm		<i>effective surface area</i>	0.23 m^2
<i>porosity</i>	30%		<i>Effective area/volume</i>	40 cm^2/cm^3
<i>Effective fiber length</i>	16 cm		<i>Priming volume (tubeside)</i>	19 cm^3
<i>Potting material</i>	epoxy		<i>Priming volume (shellside)</i>	41 cm^3

The gases that make-up the waste gas stream are stored in three gas cylinders. In addition to these three gas cylinders, the waste gas stream also utilizes an air line. The first cylinder contains a mixture of NO and N₂. The second and third cylinders contain SO₂ and CO₂ respectively. The delivery pressure of the gas

RM: Rotameter	SP: Sample Port
OF: Oil Filter	VP: Vacuum Pump
BV: Ball Valve	LMP: Liquid Membrane Pump
3BV: 3-Way Ball Valve	LMST: Liquid Membrane Storage Tank
PRV: Pressure Relief Valve	BPR: Back Pressure Regulator
PG: Pressure Gauge	LT: Liquid Trap
FH: Feed Humidifier	MT: Moisture Trap
CV: Check Valve	HTP: Humidity & Temperature Probe
FC: Flow Controller	NOA: NO Analyzer

Figure 3. Experimental setup for gas separation using hollow fiber contained liquid membrane.

from the cylinders and the air line are controlled by pressure regulators. The flow rate and blending of the gases in to the desired ratio is controlled by four Matheson flow controllers and a Matheson Multichannel Dyne Blender (Matheson Gas, Montgomeryville, PA). After the waste gas stream is combined into one stream it is humidified in a feed humidifier(FH), a stainless steel pressure vessel. The FH is fitted with a pressure gauge (PG), pressure relief valve (PRV), and ball valve (BV). The humidity and temperature of the waste gas is measured by a humidity and temperature probe (HTP) after leaving the FH. The gas mixture then flows through a rotameter (RM) where the overall flow rate of the gas mixture is measured. The gas mixture then flows through a three-way ball valve (3BV) that allows the gas mixture to by-pass the extractor when needed. Before and after entering the extractor the pressure is measured by two pressure gauges (PG). The gas mixture passes through the tube side of the extractor. After exiting the extractor the purified waste stream passes through a three-way ball valve (connected to the previous 3BV), liquid trap (LT) and moisture trap (MT). Between the LT and MT a fraction of the gas stream is diverted to an in-line NO analyzer (NOA). Then the flow rate is measured by a RM. Finally, the purified waste gas stream passes through a back pressure regulator (BPR), a sample port (SP), and then exits through a fume hood.

The liquid membrane is stored in the liquid membrane storage tank (LMST) that is equipped with the same equipment as the FH. The liquid membrane is forced into the extractor and back extractor

by pressure supplied by a N₂ gas cylinder. During operation the liquid membrane is circulated through the extractor and back extractor by the liquid membrane pump (LMP). The flow rate is measured by a RM. The pressure supplied by the N₂ gas cylinder also forces more liquid membrane into the loop to replenish liquid membrane that is lost during operation.

The concentration of SO₂ will be measured by a gas chromatograph. Samples of the waste gas side will be taken before and after processing by the extractor. Samples of the permeate gas side will be taken after the back extractor. The concentration of NO will be measured by an in-line gas analyzer after the waste gas is processed by the extractor.

A major concern of this experiment was the determination of the feasibility of utilizing the existing gas chromatograph (GC), (Perkin Elmer #8410). Several samples, which modeled the concentration levels of SO₂ that would be present in the purified waste gas stream with 90% SO₂ removal, were injected into the GC. The existing GC accurately measured these samples in a reproducible manner. Furthermore, it was determined from this testing of the GC that it would also accurately measure concentrations of SO₂ at sufficiently lower levels. Therefore, the existing GC was determined to be capable of being utilized in this experiment.

CONCLUSIONS

A flow apparatus for the study of SO_2 and NO removal and recovery from flue gas has been successfully designed and constructed. The apparatus includes compressed gases (air, SO_2 , NO/ N_2 , and CO_2), stainless steel pressure vessels, pressure gages, flow controllers, teflon fittings and tubing, and two Celgard hollow fiber membrane modules (Hoechst Celanese) for simultaneous extraction and recovery of SO_2 and NO.

Toward the end of having the capability of theoretically predicting the behavior of the flow system, the FORTRAN code for the mass transfer model of Yun (1993) has been successfully obtained and tested and is being modified.

FUTURE WORK

The FORTRAN code of Yun (1993) is being modified to describe both the extraction and recovery of a single chemical species. Future work will extend this code to the multispecies case of simultaneous extraction and recovery of SO₂ and NO in a gas containing carbon dioxide, oxygen, and nitrogen.

Experiments are currently being performed to gather data in the following areas: (1) sensitivity of the performance of the system to temperature changes, (2) validation of a mass transfer model to be used in scale-up calculations, (3) data on alternative flow schemes, and (4) overall process economics calculations. Partial funding to complete these tasks has been secured along with Christopher Haggins, a NACME Lincoln Hawkins Undergraduate Research Fellowship recipient who will be a chemical engineering senior next year. Additional funding to complete these tasks is currently being sought from EPA and DOE.

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APPENDIX: Mass Transfer Model Fortran Code

Implicit REAL*8 (A-H, O-Z)

PARAMETER(N=202)

REAL*8 L,NF,KE,KEQ,KMO,KMC,KSO,KSC,KTM(N),KTH(N),
& K1,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11,K12,K13,
& MTIN,MTOU,LIXIN,RJ(4),CHK(N),J1(N),J2(N),J3(N),
& RW(N),ALFA(N),RREX(N),RSHE(N),RMEM(N),RTUB(N),
& MT(N),MTM(N),HT(N),HTM(N),OTM(N),CTM(N),OSM(N),
& CSM(N),OS(N),CS(N),JT(N),QQT(41),QQS(21),REF(N),
& DUMJ1(N),DUMJ2(N),DUMJ3(N),DUMJ4(N),JC(N),NUES,
& MTO,HTO

REAL COEFF(4)

COMPLEX ZERO(3)

REAL*8 COEFF(4)

COMPLEX*8 ZERO(3)

DIMENSION IA(N)

F(P)=P**3 + COEFF(3)*P**2 + COEFF(2)*P + COEFF(1)

OPEN(UNIT=1,FILE= 'IN1.DAT',STATUS='OLD')

OPEN(UNIT=2,FILE= 'IN2.DAT',STATUS='OLD')

OPEN(UNIT=3,FILE= 'IN3.DAT',STATUS='OLD')

OPEN(UNIT=10,FILE= 'OUT.DAT',STATUS='OLD')

OPEN(UNIT=11,FILE= 'SOL.DAT',STATUS='OLD')

OPEN(UNIT=12,FILE= 'RW.DAT',STATUS='OLD')

OPEN(UNIT=13,FILE= 'CHK.DAT',STATUS='OLD')

-----INPUT DATA AND STATEMENT-----

QT=0

DO J=1,8

QT=QT+0.0125

QQT(J)=QT

END DO

DO J=9,12

QT=QT+0.025

QQT(J)=QT

END DO

DO J=13,16

QT=QT+0.05

QQT(J)=QT

END DO

DO J=17,22

QT=QT+0.1

QQT(J)=QT

END DO

WRITE(*,601) (J,QQT(J), J=1,22)

QS=0

DO J=1,8

QS=QS+0.00625

QQS(J)=QS

END DO

DO J=9,12

QS=QS+0.0125

QQS(J)=QS

END DO

DO J=13,20

QS=QS+0.05

QQS(J)=QS

END DO

WRITE(*,601) (J,QQS(J), J=1,20)

FORMAT(20(1X,4(I7,F8.5)/))

C*****PHYSICAL CONSTANTS FOR SOLUTES AND SOLVENTS*****

DTH=2.5984D-5

DTM=8.5773D-6

KE=9.0D-6

```

WRITE(*,*) 'ENTER THE VALUE OF KE'
READ(*,*) KE
KEQ=1.7
WRITE(*,*) 'ENTER INLET COPPER CONCENTRATION, mg/L'
READ(*,*) MTO
MTIN=MTO/63.55/1000./1000.
WRITE(*,*) 'ENTER INLET pH'
READ(*,*) HTO
HTIN=10.**(-HTO)/1000.

```

C*****CHARACTERISTICS OF SYSTEM*****

```

PI=3.141593
NF=2100
TAUM=2.8
L=16.
EM=0.3
RI=0.012
RO=0.015
RSI=0.95
FI=NF*(RO/RSI)**2
RLM=(RO-RI)/DLOG(RO/RI)
DH=2.*(RSI**2.-NF*RO**2.)/(RSI+NF*RO)

```

C

C-----Reading input data-----

```

C WRITE(*,*) 'ENTER NZ'
C READ(*,*) XNZ
C NZ=XNZ
C NZ=100

```

```

NNZ=FLOAT(NZ)/5.+0.1

```

```

WRITE(*,*) NZ, NNZ

```

C WRITE(10,500) NZ,NNZ

500 FORMAT(10X,'NZ =',I4,4X,'NNZ =',I3)

C-----

```

WRITE(*,*) 'IF YOU WANT TO USE OLD DATA OF LIX CONC.

```

& FOR SHELL INLET ENTER 1, OTHERWISE 6'

```

READ(*,520) MC

```

```

FORMAT(I2)

```

```

IF(MC.EQ.1) GO TO 10

```

```

WRITE(*,*) '1) IF 5.0 V/V % LIX -- ENTER 1'

```

```

WRITE(*,*) '2) IF 10.0 V/V % LIX -- ENTER 2'

```

```

WRITE(*,*) '3) IF 20.0 V/V % LIX -- ENTER 3'

```

```

READ(*,520) ILIXV

```

```

IF(ILIXV.EQ.1) THEN

```

```

LIXIN=5

```

```

NUES=0.8993

```

```

DSO=1.0486D-5

```

```

QS=0.0209

```

```

ELSE

```

```

IF(ILIXV.EQ.2) THEN

```

```

LIXIN=10

```

```

NUES=0.9858

```

```

DSO=9.7019D-6

```

```

QS=0.0158

```

```

QT=0.0698

```

```

ELSE

```

```

LIXIN=20

```

```

NUES=1.1968

```

```

DSO=8.2144D-6

```

```

WRITE(*,*) 'ENTER FLOW RATE OF ORGANIC SOLVENT, ml/sec'

```

```

READ(*,*) QS

```

```

END IF

```

```

ENDIF

```

```

GO TO 20

```

```

10 READ(MC,*) LIXIN,NUES,DSO,QT,QS

```

```

20 WRITE(1,*) LIXIN,NUES,DSO,QT,QS

```

```

NUES=NUES*0.01

```

```

LIXIN=1.5596*(LIXIN/100.)/1000.

```

```

DSC=0.66*DSO
WRITE(*,620) LIXIN,NUES,DSO
WRITE(10,620) LIXIN,NUES,DSO
620  FORMAT(1X,'LIXIN =',E11.4,' MOL/ML', 2X,'NUES =',F8.6,
&      ' CM2/S',2X,'DSO =',E11.4,'CM2/S')

```

```

-----
C      write(*,*) 'If you want to use old velocity data of both sides
&      enter 2, otherwise 6'

```

```

C      read(*,560) mv
C560  format(i2)
C      if(mv.EQ.2) GO TO 30
C      write(*,*) 'enter FEED-SIDE and STRIP-SIDE
&      flow rate = $, $ (ml/sec)'
C      read(*,*) Qt, Qs
C      go to 40

```

```

C30  read(2,*) Qt, Qs
C40  write(2,*) Qt, Qs
C      write(*,*) 'Enter fs of the shell-side correlation.'
C      read(*,*) fs

```

```

fs=3.
write(11,240) fs,ke,Qt,Qs
240  Format(13x,'fs=',f4.2,6x,'ke=',e8.2,6x,'Qt=',f7.5,3x,'Qs=',
&      f6.4/13x,'Qt',19x,'kth',11x,'ktM',6x,'Ct'11x,'%R')
C240  Format(13x,'fs=',f4.2,6x,'ke=',e8.2,4x,'Qt=',f7.5,3x,'Qs=',
&      f6.4/13x,'Qs',19x,'kso',11x,'ksC',6x,'Ct'11x,'%R')

```

```

write(12,241) fs, ke, Qt, Qs
241  Format(1x,'fs=',f4.2,'ke=',e8.2,'Qt=',f7.5,'Qs=',f7.5/
&      7x,'Q',10x,'RW',7x,'Rrex',5x,'Rshell',7x,'Rmem',
&      6x,'Rtube',7x,'alfa')

```

```

C      Initial assumption of tube outlet conc.
write(*,*) "Enter assumed value of Ctout, ppm"
read(*,*) Mtout
Mtout=Mtout/1000./63.55/1000.

```

```

C      Do 950 iQt=1,22
C      Qt=QQt(iQt)
C      Do 950 iQs=1,20
C      Qs=QQs(iQs)
aVt=Qt/(Nf*pi*Ri**2.)
aVs=Qs/((Rsi**2.-Nf*Ro**2.)*Pi)
Ret=2.*Ri*aVt*1./0.01
Res=dH*aVs/Nues
Sch=0.01/DtH
ScM=0.01/DtM
ScO=Nues/DSO
ScC=Nues/DSC

```

```

write(10,660) Mtin,Qt,Qs,Ret,Res,ScO,ScC
660  Format(3x,'Mtin=',e11.4,'mol/ml',3x,'Qt=',f7.4,
&      'ml/s',3x,'Qs=',F7.5,'ml/sec'/3x,'Ret=',
&      f9.6,'Res=',f9.6,'ScO=',f10.4,'ScC=',f10.4)

```

```

C      write(10,665) aVt,aVs
665  Format(3x,'<Vt> = ', f6.4,' cm/s',2x,
&      '<Vs> = ', f6.4,' cm/s')

```

```

C      Calculation of concentration profiles

```

```

dz=L/float(nz)

```

```

C      GzH=Pi*Ri*Ret*Sch/(2.*L)
C      GzM=Pi*Ri*Ret*ScM/(2.*L)
C      write(10,664) GzH,GzM
664  format(3x,'GzH=',f8.5,' GzM=',f8.5)

```

```

c*****Tube-side & Shell-side Correlations*****

```

```

c      (Dahuron and Cussler, 1988)

```

```

c      ShtH=1.5*(4.*GzH/Pi)**(1./3.)
c      ShtM=1.5*(4.*GzM/Pi)**(1./3.)

c      ShsO=8.*(Res*dh/L)*ScO**(1./3.)
c      ShsC=8.*(Res*dh/L)*ScC**(1./3.)

c_____ (Prasad and Sirkar, 1988)_____

      Bf=5.8*fs
      ShsO=Bf*(dh*(1.-Fi)/L)*Res**0.6*ScO**0.33
      ShsC=Bf*(dh*(1.-Fi)/L)*Res**0.7*ScC**0.33

c_____

      kmO=DsO*Em/(Ro-Ri)/Taum
      kmC=DsC*Em/(Ro-Ri)/Taum

      ksO=ShsO*Dso/dh
      ksC=ShsC*Dsc/dh

c      write(10,671) ktM,ktH,kmO,kmC,ksO,ksC
671      format(5x,'ktM=',e11.4,'ktH=',e11.4/5x,'kmO=',
&          e11.4,'kmC=',e11.4,'ksO=',e11.4,'ksC=',e11.4)

c_____

      k1=2.*Pi*Ri*dz*Nf*ke
      k2=2.*Pi*Ro*dz*Nf*ksO
      k3=2.*Pi*Ro*dz*Nf*ksC
      k4=2.*Pi*Rlm*dz*Nf*kmO
      k5=2.*Pi*Rlm*dz*Nf*kmC

c_____ Initial condition of both - side _____

      Mt(1)=Mtin
      Ht(1)=Htin
      Osin=LIXin
      Csin=0.
      iter=1

c      write(13,702) Qt,Qs, LIXin
702      format(5x,'Qt =',f8.5,' LIXin =',e12.5/2x,'k',6x,'Ref',10x,
&          'J1',10x,'J2',10x,'J3',10x,'Mt')

90      continue
      Cs(1)=Qt*(Mtin-Mtout)/Qs
      Os(1)=LIXin-2.*Cs(1)

c_____

      iterlo=1
      do 180 k=2, nz+1

      if(iterlo.EQ.1) then
          zk=(k-1)*dz

          sum1H=0.
          sum1M=0.
          sum2H=0.
          sum2M=0.
          do m=1,20
              beta=4.*Float(m-1)+8./3.
              Cn=1.01276*beta**(-1./3.)
              sum1H=sum1H+Cn*dexp(-zk*beta**2/(Ri*Ret*Sch))
              sum1M=sum1M+Cn*dexp(-zk*beta**2/(Ri*Ret*ScM))

```



```

        sum2H=sum2H+(Cn/beta**2)*dexp(-zk*beta**2/(Ri*Ret*ScH))
        sum2M=sum2M+(Cn/beta**2)*dexp(-zk*beta**2/(Ri*Ret*ScM))
    end do

```

```

c      write(*,112) k,Qt,sum1H,sum2H,sum1M,sum2M

```

```

        ShtH=sum1H/(2.*sum2H)
        ShtM=sum1M/(2.*sum2M)

```

```

c      GztH=Pi*Ri*Ret*ScH/(2.*zk)
c      GztM=Pi*Ri*Ret*ScM/(2.*zk)

```

```

c      write(*,112) k,Qt,ShtH,ShtM,GztH,GztM
112    format(1x,i4,f8.5,4e14.5)

```

```

        ktH(k)=ShtH*DtH/(2.*Ri)
        ktM(k)=ShtM*DtM/(2.*Ri)

```

```

        diffH=dabs(ktH(k)-ktH(k-1))
        diffM=dabs(ktM(k)-ktM(k-1))

```

```

        if(diffH.LE.1.0d-10.and.diffM.LE.1.0d-10) iterlo=2
        else
            ktH(k)=ktH(k-1)
            ktM(k)=ktM(k-1)
        end if

```

```

c      write(*,113) k,Qt,ktH(k), ktm(k)
113    format(1x,i4,f8.5,2f15.12)

```

```

        k6=2.*Pi*Ri*dz*Nf*ktM(k)
        k7=2.*Pi*Ri*dz*Nf*ktH(k)

```

```

        k8=-2.*(1./Qs-1./k2-1./k4)/Os(k-1)
        k9= (1./Qs-1./k3-1./k5)/Cs(k-1)
        k10= (1./Qt+1./k6)/Mt(k-1)
        k11=-2.*(1./Qt+1./k7)/Ht(k-1)

```

```

        k12=-k1*Cs(k-1)*Ht(k-1)/(Keq*Os(k-1))
        k13= k1*Mt(k-1)*Os(k-1)/Ht(k-1)

```

```

        a1=(k8+k11+k12*k11**2+k13*k8**2+2.*k9*k11*k12+2.*k8*k10*k13)
&      /(k8*k11 + k9*k12*k11**2 + k10*k13*k8**2)
        a2=(1. + k9*k12 + k10*k13 + 2.*k11*k12 + 2.*k8*k13)
&      /(k8*k11 + k9*k12*k11**2 + k10*k13*k8**2)
        a3=(k12 + k13)/(k8*k11 + k9*k12*k11**2 + k10*k13*k8**2)

```

```

        coeff(1)=a3
        coeff(2)=a2
        coeff(3)=a1
        coeff(4)=1.

```

```

        call ZPLRC (3,COEFF,zero)

```

```

c      write(*,*) zero(1)
c      write(*,*) zero(2)
c      write(*,*) zero(3)

```

```

        dJ1=real(zero(1))
        dJ2=real(zero(2))
        dJ3=real(zero(3))

```

```

        dum1=F(dJ1)
        dum2=F(dJ2)
        dum3=F(dJ3)

```

```

c      write(*,600) dJ1,dJ2,dJ3,dum1,dum2,dum3
c600    format(1x,6d12.4)

      jj=1
      RJ(1)=0.
      RJ(2)=0.
      RJ(3)=0.
      RJ(4)=0.

      if(dabs(dum1).LE.1.d-6) then
        jj=jj+1
        RJ(jj)=dJ1
      end if

      if(dabs(dum2).LE.1.d-6) then
        jj=jj+1
        RJ(jj)=dJ2
      end if

      if(dabs(dum3).LE.1.d-6) then
        jj=jj+1
        RJ(jj)=dJ3
      end if

c      write(*.*) jj

      if(jj.EQ.2) then
        Jt(k)=RJ(2)
      end if

      if(jj.EQ.3) then
        if(RJ(2).GE.0.) then
          Jt(k)=RJ(3)
        else
          if(RJ(3).GE.0.) then
            Jt(k)=RJ(2)
          else
c      write(*,710) k,RJ(2),RJ(3)
710    format(1x,'jj=3 and RJ(2) & RJ(3) are negative at k=',i3,
&      ' RJ(2)=' ,e11.4,' RJ(3)=' ,e11.4)
          if(RJ(2).LT.RJ(3)) then
            Jt(k)=RJ(3)
          else
            Jt(k)=RJ(2)
          end if
        end if
      end if

      if(jj.EQ.4) then
c      write(*,715) k,RJ(2),RJ(3),RJ(4)
715    format(1x,'jj=4 at k=',i3,' J1=' ,e11.4,' J2=' ,e11.4' J3=' ,e11.4)

        if(RJ(2).GT.RJ(3) .and. RJ(2).GT.RJ(4)) then
          high1=RJ(2)
          if(RJ(3).GT.RJ(4)) then
            high2=RJ(3)
            high3=RJ(4)
          else
            high2=RJ(4)
            high3=RJ(3)
          end if
        end if
        if(RJ(3).GT.RJ(2) .and. RJ(3).GT.RJ(4)) then
          high1=RJ(3)
          if(RJ(2).GT.RJ(4)) then

```

```

        high2=RJ(2)
        high3=RJ(4)
    else
        high2=RJ(4)
        high3=RJ(2)
    end if
end if
if(RJ(4).GT.RJ(2) .and. RJ(4).GT.RJ(3)) then
    high1=RJ(4)
    if(RJ(2).GT.RJ(3)) then
        high2=RJ(2)
        high3=RJ(3)
    else
        high2=RJ(3)
        high3=RJ(2)
    end if
end if

c      write(*,*) 'high1,          high2,          high3'
c      write(*,716) high1,high2,high3
716  format(1x,3e13.5)

    Ref(k)=-Qt*Mt(k-1)
    dummy=k11+k8*k10*k13
    b1=(1.+k8*k13+k10*k13)/dummy
    b2=k13/dummy
    CHK(k)=(-b1-(b1**2-4.*b2)**0.5)/2.

c      write(*,*) dummy,b1,Ref(k),CHK(k)

    J1(k)=high1
    J2(k)=high2
    J3(k)=high3
    if(high1.GT.0.) then
        if(high2.GT.0) then
            Jt(k)=high3
        else
            if(high3.LE.CHK(k)) then
                Jt(k)=high2
            else
c              write(*,*) 'high1 > 0 : CHK, high2,high3'
c              WRITE(*,716) CHK(k),high2,high3
                Jt(k)=high2
            end if
        end if
    else
        if(high3.LE.CHK(k)) then
            if(high2.LE.CHK(k)) then
                Jt(k)=high1
            else
c              write(*,*) 'high3 < Jmin : CHK, high1, high2'
c              write(*,716) CHK(k),high1,high2
                Jt(k)=high1
            end if
        else
c          write(*,703) k, CHK(k),high1,high2,high3
703  format (1x,'k=',i3,' Chk=',e12.4,' J1=J3:',3e12.4)
            Jt(k)=high1
        end if
    end if

c      if(high1.LT.0.) then
c          Jt(k)=high1
c      else
c          if(high2.LT.0.) then
c              Jt(k)=high2

```

```

c          else
c          Jt(k)=high3
c          end if
c          end if

c          end if
c          write(*,*) Jt(k)

C----- Calculate variables at z=z -----

Os(k) =Os(k-1)-2.*Jt(k)/Qs
Osm(k)=Os(k) +2.*Jt(k) /k2
Cs(k) =Cs(k-1)+ Jt(k)/Qs
Csm(k)=Cs(k) - Jt(k) /k3

Otm(k)=Osm(k) +2.*Jt(k) /k4
Csm(k)=Csm(k) - Jt(k) /k5

Ht(k) =Ht(k-1)-2.*Jt(k)/Qt
Htm(k)=Ht(k) -2.*Jt(k) /k7
Mt(k) =Mt(k-1)+ Jt(k)/Qt
Mtm(k)=Mt(k) + Jt(k) /k6

alfa(k)=Otm(k)/Htm(k)
Rrex(k)=1./(alfa(k)*ke)
Rshe(k)=Ri/(Ro*Keq*alfa(k)**2*ksC)
Rmem(k)=Ri/(Rlm*Keq*alfa(k)**2*kmC)
Rtub(k)=1./ktM(k)
Rw(k)=Rrex(k)+Rshe(k)+Rmem(k)+Rtub(k)
c Jc(k)=-2.*Pi*Ri*dz*Nf*(Mt(k)-Cs(k)/(Keq*alfa(k)**2))/Rw(k)

dumj1(k)=-Cs(k-1)/((k3+k5)/(k3*k5)+k9*Cs(k-1))
dumj2(k)=-1./k8
dumj3(k)=-1/k10
dumj4(k)=-Ht(k-1)/(2./k7+k11)

C----- go to the next increament -----

180 continue

C ***** check your mass balance *****

y=Mt(nz+1)-Mtout
yy=Mtout
Remove=100.*(Mtin-Mt(nz+1))/Mtin
error=1.-Mt(nz+1)/Mtout
c write(*,720) iter,Qt,Remove,Mt(nz+1),error
write(*,720) iter,Qs,Remove,Mt(nz+1),error
if(dabs(error) .LT. 1.d-6) go to 900
if(iter.GE.2) then
    if(x-y .EQ. 0.) then
        write(*,*) 'error for Total Mass Balance = 0'
        go to 900
    end if
    Mtout=x*(yy-xx)/(x-y)+xx
else
    Mtout=Mtout+0.01*(Mt(nz+1)-Mtout)
end if

C-----

if(iter.EQ.1000) then
    write(*,*) 'Total mass balance does not converge.'
    go to 900
end if

```

```

x=y
xx=yy
iter=iter+1
go to 90

```

C***** Computer Output Control Statement *****

```

900      continue
c        do k=1,nz+1,nnz
c          write(10,700) k,Ht(k),Htm(k),Otm(k),Osm(k),Os(k),
c            &      Mt(k),Mtm(k),Ctm(k),Csm(k),Cs(k),
c            &      Rrex(k),Rshe(k),Rrm(k),Rtub(k),alfa(k),Rw(k),Jt(k)
c        end do

      aktH=0.
      aktM=0.
      aRw=0.
      aRrex=0.
      aRshe=0.
      aRmem=0.
      aRtub=0.
      aalfa=0.
      do k=2, nz+1
        aktH=aktH + ktH(k)
        aktM=aktM + ktM(k)
        aRw=aRw + Rw(k)
        aRrex=aRrex + Rrex(k)
        aRshe=aRshe + Rshe(k)
        aRmem=aRmem + Rmem(k)
        aRtub=aRtub + Rtub(k)
        aalfa=aalfa + alfa(k)
      end do
      aktH=aktH/Float(nz)
      aktM=aktM/Float(nz)
      aRw=aRw/Float(nz)
      aRrex=aRrex/Float(nz)
      aRshe=aRshe/Float(nz)
      aRmem=aRmem/Float(nz)
      aRtub=aRtub/Float(nz)
      aalfa=aalfa/Float(nz)

      ExitCt=Mt(nz+1)*63.55*1000000.
c      write(10,730) Qt,ExitCt,Remove
c      write(11,740) Qt,aktH,aktM,ExitCt,Remove
c      write(12,750) Qt,aRw,aRrex,aRshe,aRmem,aRtub,aalfa

c      write(10,735) Qs,ExitCt,Remove
c      write(11,740) Qs,ksO,ksC,ExitCt,Remove
c      write(12,750) Qs,aRw,aRrex,aRshe,aRmem,aRtub,aalfa

c      do k=1,nz+1,nnz
c        write(13,760) Qt,Jt(k),Jc(K)
760        format(5x,f8.4,2e14.5)

c        ExMt=Mt(k)*63.55*1000000.
c        write(13,701) k,ref(k),chk(k),J1(k),J2(k),J3(k),ExMt
c      end do

      write(13,701) Qt,(k,Jt(k),dumj1(k),dumj2(k),dumj3(k),
&      dumj4(k), k=1,nz+1,nnz)
701      format(3x,'Qt =',f8.5/6(5x,i3,5e12.4/))

950      continue

```

C----- Output Statements Format -----

```
700      format(1x,80('-')/1x,'k=',i3,'Ht=',e11.4,'Htm=',e11.4,'Otm=',  
    &          e11.4,'Osm=',e11.4,'Os=',e11.4/,2x,'Mt=',e11.4,'Mtm=',  
    &          e11.4,'Ctm=',e11.4,' Csm=',e11.4,' Cs=',e11.4/2x,  
    &          'Rrex=',e11.4,' Rshe=',e11.4,' Rmem=',e11.4,' Rtub=',  
    &          e11.4/5x,'alfa=',e11.4,'Rw=',e11.4,' Jt=',e11.4)
```

```
720      format(1x,'iter =',i3,1x,f6.4,2x,'%R=',e12.4,' Mt(nz+1)=' ,  
    &          e13.5,' error=',e13.5)
```

```
730      format(1x,80('-')/5x,'Qt',f8.5,' ml/sec Exit Conc.=' ,f9.4,  
    &          ' mg/l % Removal=',e12.4,' %'/1x,80('-'))
```

```
735      format(1x,80('-')/5x,'Qs',f8.5' ml/sec Exit Conc.=' ,f9.4,  
    &          ' mg/l % Removal=',e12.4,' %'/1x,80('-'))
```

```
740      format(12x,f8.5,3x,2e14.4,3x,f9.4,3x,f10.4)
```

```
750      format(1x,f7.5,e12.4,5e11.4)
```

C----- Stop Program Running -----

```
stop  
end
```