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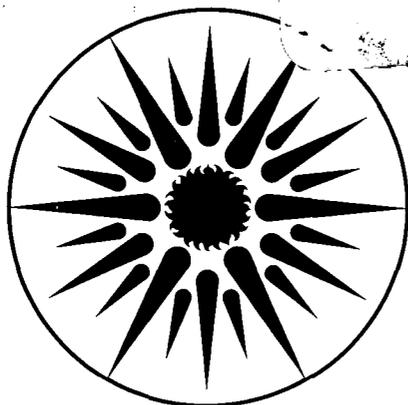
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WATERS USING TUBULAR, MICROPOROUS  
POLYTETRAFLUOROETHENE MEMBRANES

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# AMMONIA REMOVAL FROM OIL SHALE PROCESS WATERS USING TUBULAR, MICROPOROUS POLYTETRAFLUOROETHENE MEMBRANES

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## ABSTRACT

Oil shale process waters can contain high concentrations (1 to 30 g/L) of dissolved ammonia/ammonium ion, most of which must be removed prior to discharge or codisposal. Nonosmotic dissolved-gas dialysis (NOGD), a membrane separation process that uses tubular, microporous hydrophobic polytetrafluoroethene (PTFE) membranes, is being evaluated as an alternative to conventional ammonia removal methods, such as steam stripping. Unlike most conventional methods, NOGD is more selective for ammonia, and it combines both removal and recovery of ammonia in a single unit process. The PTFE membrane serves as a gaseous barrier between two aqueous phases. Dissolved ammonia diffuses from the wastewater through the gaseous interface to an acidic absorption solution (dialysate), which serves to maintain the concentration gradient of ammonia gas across the membrane wall. This separation process has been described in a numeric model based on the diffusive transport of ammonia. For an ammonium hydroxide solution, correlation between the numeric model and experimental results was greater than 90% using mass-transfer coefficients as the basis of comparison; correlation between the model and experimental data for waters from three oil shale retorts (Occidental burn #6 [Oxy-6], Geokinetics-9, and Paraho) was poorer. On the basis of hydraulic residence times (HRT), the ammonia removals attained were 56% for Oxy-6 (0.92 min HRT), 55% for Geokinetics (0.87 min HRT), and 64% for Paraho (0.83 min HRT). These results from bench-scale experiments demonstrate the potential of NOGD as a rapid ammonia removal process.

## INTRODUCTION

Ammoniac industrial and domestic wastewaters contain an equilibrium mixture of free ammonia gas and nonvolatile, protonated ammonium ion. The relative concentrations of these two species depends on the pH. The concentration of ammoniac-

nitrogen reported for any given wastewater does not distinguish between the two forms. Wastewater ammoniac-N concentrations can range over orders of magnitude: domestic sewage (typically 10 to 50 mg/L) (Metcalf and Eddy, Inc. 1979), oil refinery wastewaters (as high as 7 000 mg/L) (American Petroleum Institute 1969), and oil shale process waters (1 000 to 31 000 mg/L) (Daughton, Sakaji, and Langlois, in press).

Ammonia removal from refinery wastewaters typically depends on a packed-bed process (e.g., steam stripping). Studies by the American Petroleum Institute (API 1975) have shown, however, that steam strippers do not always meet design specifications. Removal of ammonia and carbonate alkalinity from oil shale wastewaters, using EPA-approved treatment schemes that included steam stripping, has been evaluated (Day, Desai, and Liberick, Jr. 1983). Another report on steam stripping of oil shale wastewaters (Sakaji, Persoff, and Daughton 1984) summarizes the results of pilot- and bench-scale steam strippers and concludes that this treatment process is not always successful. These limitations, coupled with the energy requirements for steam generation, suggest that alternative technologies may be desirable. One such alternative is the use of gas-permeable membrane separation devices.

This report discusses nonosmotic dissolved-gas dialysis (NOGD) as an alternative to conventional steam stripping. The process uses dialysis (i.e., ammonia diffuses from a region of high concentration to one of low concentration, the dialysate) without the concomitant osmosis of liquid water. NOGD is similar to the hollow-fiber gas membrane technology that has been used for the selective separation of ammonia from aqueous solutions (Qi and Cussler 1985), but NOGD uses a thicker and more porous, tubular polytetrafluoroethene (PTFE) membrane. The combination of hydrophobic and microporous membrane properties allows gases to volatilize from the liquid phase and diffuse through the gas-filled membrane pores while preventing the passage of liquid water; this

prevents dilution by the wastewater and allows for collection of highly concentrated dialysates. The transport of ammonia is driven by a concentration gradient maintained across the membrane by absorption of the ammonia permeate into a dilute, nonvolatile acid solution, where it is protonated to form ammonium ion; this effectively reduces the ammonia concentration at the outer membrane wall to zero. An advantage of NOGD is not only the selectivity of the process, but also the combining of stripping and resource recovery into a single unit process; this simplifies design and encourages recovery of a potentially valuable resource.

The diffusive transport model of ammonia removal was experimentally verified by NOGD treatment of an ammonium hydroxide solution. To assess the feasibility of wastewater treatment by NOGD, removals for waters containing a wide range of ammoniac concentrations were compared. Ammonia removals from both domestic sewage and an ammonium hydroxide solution were close to predicted values even though the ammonia concentrations differed by orders of magnitude. Ammonia removals from oil shale wastewaters were much poorer than predicted, although the results were comparable to those achieved by some bench- and pilot-scale steam strippers. The theory of NOGD, a description of the numeric transport model, and laboratory results are discussed in this report.

#### THEORY OF NONOSMOTIC DISSOLVED-GAS DIALYSIS

The use of PTFE membranes for dissolved-gas removal has been almost exclusively confined to chemical-analysis instrumentation. Microporous PTFE membranes have been used in continuous-flow reactors for the quantitative analysis of aqueous samples for volatile solutes such as chlorine (Aoki and Munemori 1983) and ammonia (Aoki, Uemura, Munemori 1983). One of the first uses of tubular, microporous PTFE membranes was for the selective removal of ammonia from samples of oil shale process water for the purpose of quantifying total nitrogen in the dialyzed sample as a rapid estimate of organic nitrogen (Daughton, Jones, and Sakaji 1985). From this work, it was suggested (Daughton and Sakaji 1984) that these tubes could be used in a continuous-flow process for ammonia removal, despite the noted physical limitations of the membranes (Daughton 1984, Chapter 2).

Previous studies of microporous membranes in continuous-flow operations used models based on mass-transfer coefficients. These models provide limited information on the mechanics of the NOGD process because the approximations and ambiguities inherent in this approach are concealed in a single coefficient (Cussler 1984). That approach was used to describe a process similar to NOGD that uses a microporous polypropylene membrane (Qi and Cussler 1985). The resulting model was limited

to viewing the process as a series of resistances to mass transfer: in the feed water, membrane, and dialysate (i.e., acid-capture solution); the primary resistances were demonstrated to be in the membrane and feed.

Rather than combining the separate processes of ammonia transport into a single coefficient, a detailed numeric model could be built from the equation of continuity; effects such as dispersion and diffusion can be modeled as separate transport phenomena. Such a model would improve the understanding of how ammonia is transported through microporous PTFE membranes, and it would also show the proper parameters to monitor for experimental demonstration, engineering analysis, and economic analysis.

For the continuous-flow NOGD process, an incompressible fluid (wastewater) is pumped through the tubular membrane of internal radius,  $r_i$ , and external radius,  $r_o$ , with steady laminar flow in a direction,  $z$ , parallel to the membrane wall (Fig. 1). The velocity profile is fully established and is parabolic. Ammonia is transported only by diffusion in the radial direction and by convection in the  $z$ -direction (diffusion in the  $z$ -direction is negligible in comparison). There is no chemical reaction that consumes or produces ammonia while the wastewater is in the PTFE membrane. The concentration profile of ammonia, in radial coordinates  $[c(z, r)]$ , is given by the equation:

$$D_L \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) = 2v_m \left( 1 - \frac{r^2}{r_i^2} \right) \frac{\partial c}{\partial z} \quad (1)$$

The position from the tube centerline to the membrane wall is given by the variable,  $r$ ;  $r_i$  is the inner radius of the tubing. The

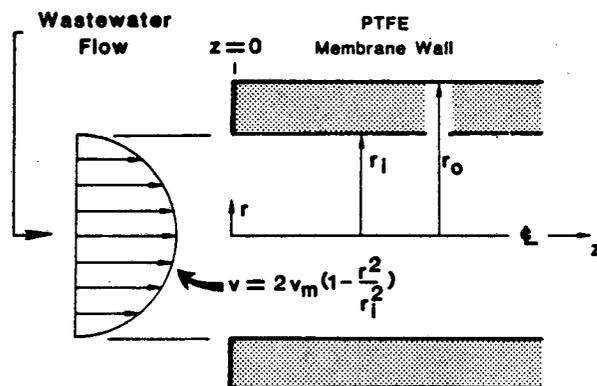


Figure 1. Tubular PTFE membrane with laminar flow. Flux of ammonia through the microporous tubular PTFE membrane starts at  $z=0$ .

average velocity through the tube is given by  $v_m$ . The diffusive transport in the radial direction is described by Fick's Law, where the diffusion coefficient,  $D_L$ , is the liquid-phase diffusivity of ammonia in water (assuming a dilute solution).

There are three boundary conditions required to solve this equation. The first two are:

$$c = c_0 \quad (\text{at } z=0, \text{ for all } r) \quad (2)$$

and

$$\frac{dc}{dr} = 0 \quad (\text{at } r=0, \text{ for all } z) \quad (3)$$

The first boundary condition (eq. 2) states that the concentration of ammonia in the wastewater is homogeneous and isotropic before it enters the tubular membrane ( $z=0$ ). The second boundary condition (eq. 3) states that the concentration profile is symmetric around the tube centerline.

The third boundary condition (see eq. 4) states that the flux of ammonia through the gaseous, microporous membrane structure is equal to the flux of ammonia from the liquid phase. Inherent in this equation is an equilibrium condition at the gas-liquid interface governed by Henry's Law. After the volatile ammonia passes through the membrane it is absorbed by the acid dialysate and immediately protonated, reducing the ammonia concentration at the external membrane wall to zero. The absence of a concentration gradient means there is no resistance to mass transfer in the dialysate. Transport through the gaseous microporous membrane structure is by diffusion, but the diffusion path is tortuous. The diffusion coefficient is therefore modified to an effective diffusivity to reflect the longer path length through the membrane wall. The effective diffusivity is given by the equation  $D_e = D_G \epsilon^{1.5}$ , where  $D_G$  is the gas-phase diffusivity, and  $\epsilon$  is the porosity of the membrane (Petersen 1965). The third boundary condition contains a gas-phase concentration gradient or resistance to mass transfer and is given by the equation:

$$\left. \frac{dc}{dr} \right|_{r=r_i} = (c_{r=r_0} - c_{r=r_i}) m D_e \frac{1}{D_L r_i \ln(r_0/r_i)} \quad (4)$$

The variables of equation 1 and the boundary conditions (eqs. 2-4) are made dimensionless by substituting the following groupings into the equations:

$$\theta = c_1/c_0, \quad \eta = r/r_i, \quad \gamma = D_L z / (2v_m r_i^2), \quad \text{and} \\ K = m D_e / (D_L \ln(r_0/r_i)).$$

In dimensionless form, eq. 1 and the boundary conditions (eqs. 2-4) are:

$$(1 - \gamma^2) \frac{\partial \theta}{\partial \gamma} = \frac{\partial^2 \theta}{\partial \eta^2} + \frac{1}{\eta} \frac{\partial \theta}{\partial \eta} \quad (5)$$

$$\begin{aligned} \theta(0, \eta) &= 1 \\ \theta'(\gamma, 0) &= 0 \\ \theta(\gamma, 1) + (1/K)\theta'(\gamma, 1) &= 0 \end{aligned}$$

Equation 5 is a form of Whittaker's equation, which belongs to a group of confluent hypergeometric equations whose solution is a confluent hypergeometric function of the second kind.

This set of dimensionless equations is identical to the "extended Graetz" problem described by Bowen, Levine, and Epstein (1976). Equation 5 is solved by using the separation-of-variables technique and the boundary conditions. A form of the general solution is assumed by splitting the radial-position ( $\eta$ ) and longitudinal-position variables into two solvable ordinary differential equations whose solutions are "particular." One particular solution is the exponential relationship between  $\theta$  and  $\gamma$ . When substituted into the general solution, the result is:

$$\theta(\gamma, \eta) = \sum_{n=1}^{\infty} B_n Y_n(\eta) e^{-\lambda_n^2 \gamma} \quad (6)$$

Bowen et al. (1976) use a confluent hypergeometric function to solve the eigenfunction,  $Y_n(\eta)$ , because the method of using a conventional power series does not converge when  $n > 7$ . In addition, they found the number of  $\lambda_n$  and  $B_n$  terms required to calculate  $\theta$  to four significant figures varied with the value of  $\gamma$ . For the values of  $\gamma$  covered by the NOGD experiments, a minimum of one hundred  $\lambda_n$  and  $B_n$  terms are required, more than can be obtained by the conventional power-series solution.

Use of the confluent hypergeometric function provides the last particular solution to the general solution (eq. 6). Inserting the general solution into the mean value theorem of calculus (Bennett and Myers 1974) and integrating across the cross-sectional area of the membrane gives the average ammonia concentration for any length of tubing. The average concentration provides a means of evaluating the accuracy of the numeric model. A disadvantage in this approach is that changes in the average concentration,  $\theta$ , over a range of  $\gamma$ 's does not follow a simple proportionality. It is therefore necessary to normalize the data so that changes in  $\theta$  with respect to  $\gamma$  do not affect the comparison of experimental and predicted data. This can be accomplished by calculating mass-transfer coefficients,  $k_{\text{expt}}$  and  $k_{\text{calc}}$ , from the experimental or predicted average concentrations. These mass-transfer coefficients can also be used for comparisons with other mass-transfer processes, such as hollow-fiber gas membranes.

The mass-transfer coefficient,  $k$ , is calculated from the equation:

$$k = 2r_i v_m \ln(c_0/c_1) \frac{1}{\epsilon z (r_i + r_0)} \quad (7)$$

This equation is the result of writing two equations, one for a mass balance on an incremental section of tubing and a second for the flux of material through the liquid phase; the two equations are then combined and integrated over the tube length to give eq. 7. To calculate  $k_{\text{expt}}$  or  $k_{\text{calc}}$ , the experimental or predicted fraction of ammonia remaining ( $\theta$ ) is used in eq. 7.

## METHODS AND MATERIALS

### Computer Model

The computer model was written on a Fortune Systems 32:16 XP (UNIX operating system). The numeric solution to equation 5 followed the protocol used by Bowen et al. (1976) except that a bisectional-root searching technique (Arfken 1985) replaced the Newton-Raphson method.

### NOGD Reactor

The tubular PTFE membranes were manufactured by W.L. Gore and Associates, Inc. (Elkton, MD) by controlled stretching or expanding of PTFE. These membranes had an internal diameter of 1.0 mm, external diameter of 1.8 mm, a maximum pore size of 2.0  $\mu\text{m}$ , and a porosity of 0.50. The lengths of tubes used in this study were 24.7, 25.0, and 50 cm.

The isothermal, countercurrent NOGD reactor used in this study consisted of three concentric tubes: an inner, PTFE membrane tube, a middle glass tube containing the acid dialysate, and an outer glass tube that served as a constant temperature water bath. Each end of the PTFE tube was connected to a short length of 19-ga stainless-steel tubing by silicone caulk. The stainless-steel tubing was inserted through a silicone stopper that was used to seal off the middle tube and hold the acid dialysate around the PTFE membrane. This assembly was held inside the water jacket with a neoprene stopper, and the temperature of the water in the water jacket was monitored continuously with thermocouples.

### Water Samples

The NOGD reactor was used to treat ammonium hydroxide solutions, three oil shale process waters, and a sample of domestic sewage. The ammonium hydroxide solutions were prepared by diluting 5.72 mL of reagent-grade ammonium hydroxide to 1-L with 0.1 N sodium hydroxide solution. These solutions yielded 700 to 800 mg-N/L, essentially all as dissolved ammonia. The oil shale process waters (Daughton 1984, Appendix I) were Oxy-6 (Occidental burn #6), Geokinetics (burn #9), and Paraho. The ammoniac-N concentrations for Paraho, Oxy-6, and Geokinetics were 24 690, 1 127, and 1 905 mg-N/L, respectively.

These wastewaters were selected because they represented two extremes in bicarbonate-carbonate buffering potential. Buffering slows the reduction in pH that results from ammonia removal and concomitant deprotonation of ammonium ion. The buffering capacity was estimated as the ratio of ammonium ion to inorganic

carbon. A ratio greater than one would indicate that more protons could be released than the buffering system could absorb; the ratio for each water was 56.8 (Paraho), 0.66 (Oxy-6), and 0.55 (Geokinetics).

An additional sample of Oxy-6 retort water was stripped of ammonia by raising the pH to 12.2 and sparging with air for several hours at 50°C. The ammonia-free sample was then spiked with ammonium hydroxide to give an ammonia concentration of 750 mg-N/L prior to NOGD treatment.

The domestic wastewater sample was collected from the effluent of a primary clarifier (settled sewage) operated by SEEHRL (Sanitary Engineering and Environmental Health Research Laboratory, University of California, Richmond Field Station). The pH of this sample was raised to 12.9 with 50% aqueous sodium hydroxide prior to NOGD treatment.

Particulate matter in each wastewater was removed by tangential-flow filtration (0.45  $\mu\text{m}$ ) to minimize pore clogging during NOGD treatment. The samples were then pumped to the NOGD reactor with a peristaltic pump using short lengths of silicone-rubber tubing. The solutions were delivered to the reactor through Teflon and stainless-steel delivery lines, minimizing loss of ammonia. The stainless steel delivery line was submerged in a water bath to preheat the reactor influent to 30°C. Sulfuric acid (1.0 N) was selected as the acid for the dialysate because it is nonvolatile. This solution was preheated to 30°C and metered to the reactor by a Mariotte reservoir through silicone-rubber tubing.

### Analysis

Samples from the ammonium hydroxide experiments were immediately analyzed for total-N by the rapid method of combustion/chemiluminescence (C/CL) (Jones and Daughton 1985). These values were equivalent to ammoniac-N since ammonia was the only nitrogenous compound present; this was confirmed with the phenate colorimetric method (Daughton, Sakaji, and Langlois, in press). The wastewaters were analyzed for ammonia by the phenate colorimetric method. The samples were stored at 4°C prior to analysis.

Composites of the effluent samples were collected after the NOGD reactor reached steady-state operation, which was verified by monitoring total-N by C/CL. For all effluent samples, the reactor was operated for 50 to 100 hydraulic residence volumes before steady-state monitoring began. Since dissolved ammonia gas rather than ammonium ion was the species of interest, ammonia concentrations were calculated from the ammoniac-N concentrations and sample pH using the  $\text{pK}_a$  of ammonium ( $\text{pK}_a = 9.3$  at 30°C).

## RESULTS AND DISCUSSION

### Numeric Model Verification

The accuracy of the equations used in the numeric ammonia-transport model were verified by evaluating  $\theta$  for a series of  $\gamma$ 's with  $K=1.0$ ; selecting a value of 1.0 was identical to a condition used by Bowen et al. (1976) for which  $\theta$  was evaluated over five decades of  $\gamma$ . Results of  $\theta$  predicted by the computer model were compared with the values of  $\theta$  calculated by Bowen et al. (1976) to determine if the NOGD model produced equivalent results (Table 1). The comparison shows an insignificant amount of deviation, only in the fourth significant digit.

### Ammonium Hydroxide Solution

Since the results of the NOGD numeric model matched those of Bowen et al. (1976), the predicted values, using  $D_e = 9.81 \times 10^{-2}$  and  $D_L = 2.75 \times 10^{-5}$  cm<sup>2</sup>/s at 30°C, were compared with experimental data obtained from treatment of the aqueous ammonium hydroxide solutions, as shown in Fig. 2. (This represented an ideal test case because the additional chemical and physical interactions of organic compounds and particulates are absent.) The results demonstrate that an increase in  $\gamma$  gives a decrease in  $\theta$ . A higher  $\gamma$  indicates either a lower velocity or longer tube length, which permits more ammonia to diffuse through the membrane. These results also demonstrate that the relation between  $\theta$  and  $\gamma$  is not a simple proportionality.

The relationship between the experimental results and predicted values can be more clearly demonstrated (Fig. 3) by plotting the experimental versus predicted fraction of ammonia remaining. A perfect correlation between predicted and experimental data would yield a line with a slope of unity and a zero intercept (broken line, Fig. 3). Since the least-squares regression line was above the ideal line, the experimental fraction remaining was slightly higher than predicted, but since the ideal line is within the 95% confidence limits of the regression line (also shown on Fig. 3), the difference between the experimental and predicted results is probably not significant.

Table 1. Comparison of Theta Values Obtained from the Numeric Model with Published Results

$\gamma$	numeric model	published model <sup>1</sup>
1.0	0.0663	0.0663
0.1	0.7496	0.7498
0.01	0.9673	0.9674
0.001	0.9964	0.9964
0.0001	0.9995	0.9996

<sup>1</sup> Bowen et al. (1976).

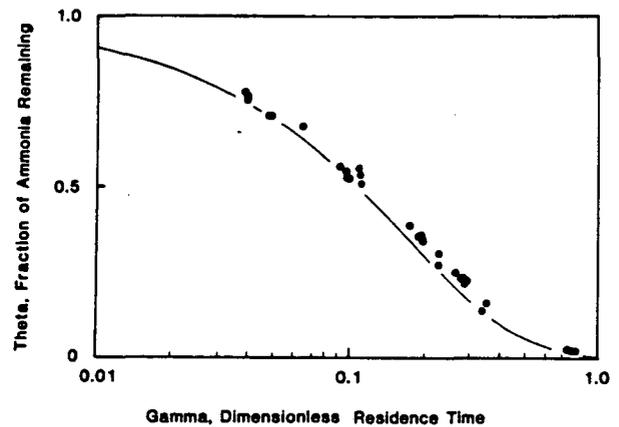


Figure 2. Fraction of ammonia remaining ( $\theta$ ) as a function of the dimensionless tube length ( $\gamma$ ) for NOGD treatment of an ammonium hydroxide solution at 30°C. The solid line represents the fraction remaining predicted by the numeric model.

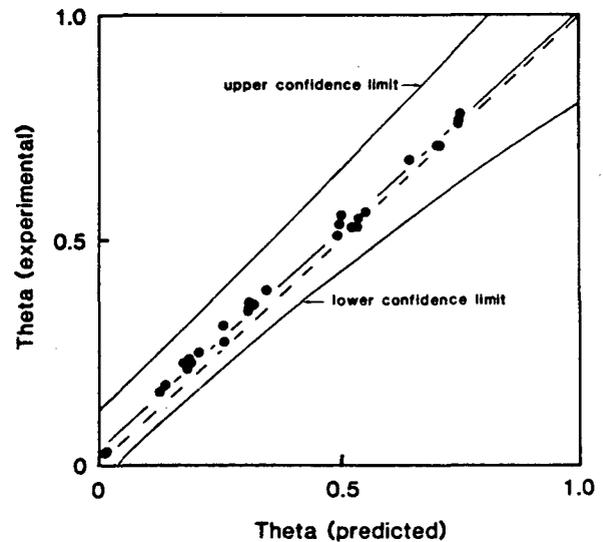


Figure 3. Regression analysis of the experimental fraction remaining ( $\theta$ ) versus the predicted fraction remaining after NOGD treatment of an ammonium hydroxide solution with the 95% upper and lower confidence limits for the regression line.

Since regression does not indicate whether the difference between the ideal line and the regression line is significant, the data were analyzed by using the normalized experimental mass-transfer coefficients calculated from eq. 7 for the experimental and predicted data,  $k_{\text{expt}}$  and  $k_{\text{calc}}$ , respectively. Each  $k_{\text{expt}}$  value was normalized by dividing it by its respective  $k_{\text{calc}}$ . This resulted in an range of values from 0.841 to 1.09 with an average of 0.913, indicating that actual process performance was 8.7% lower than predicted. This discrepancy may have resulted from chemical analysis bias or from inaccurate values for certain parameters used in the model (e.g., Henry's coefficient, membrane porosity, or diffusion coefficient). The agreement between predicted values and experimental results indicated that the proposed mechanisms of ammonia transport in the numeric model (i.e., radial diffusion, tortuous gas-phase diffusion through the membrane, and longitudinal convection in laminar flow) accounted for the major transport mechanisms during treatment of an aqueous ammonium hydroxide solution.

The close correlation between the model and experimental results also suggests similarities between NOGD and the hollow-fiber gas membranes used by Qi and Cussler (1985). In both processes, concentration gradients are associated with the resistance to mass transfer, and because gradients exist only in the wastewater and the membrane, the only resistance to mass transfer would be encountered in those two phases. This in turn means no resistance to mass transfer exists in the acid dialysate: hence, the NOGD process is not dependent on the flow rate of the dialysate. This is unlike steam stripping, whose physical operation is dependent on the gas-to-liquid ratio.

On the basis of mass-transfer coefficients, the NOGD process compares favorably with the hollow-fiber gas membrane and steam stripping processes. A typical mass-transfer coefficient for a packed-bed steam stripper, under identical conditions of flow (Cussler 1984), is an order of magnitude higher than that found herein for the NOGD reactor. The reported mass transfer coefficient for the polypropylene hollow-fiber membrane process (Qi and Cussler 1985) is an order of magnitude lower than that found herein.

The enhanced performance of NOGD relative to the hollow-fiber membrane process can probably be attributed to the greater porosity of the PTFE membranes. For example, the Knudsen number (ratio of mean free path to pore diameter) for the polypropylene membranes is four. In other words, the ratio of the mean free path for an ammonia molecule is four times longer than the membrane pore diameter. This increases the likelihood that an ammonia molecule would collide with the membrane pore wall, restricting its diffusion through the membrane. In contrast, the Knudsen number for the PTFE membranes is less than 1.0, indicating the Knudsen-diffusion effects are less important.

One physical criterion used to compare the relative economies of various stripping devices is the ratio of gas-liquid surface area to empty-bed reactor volume. For a hypothetical NOGD reactor containing 18 tubular membranes packed in a 1.5-cm internal-diameter dialysate tube, this ratio would be  $300 \text{ m}^2/\text{m}^3$  which compares favorably well with the 550 to  $820 \text{ m}^2/\text{m}^3$  reported for polypropylene hollow-fiber gas membranes (Qi and Cussler 1985) and the 62 to  $984 \text{ m}^2/\text{m}^3$  reported for packed-bed reactors (Treybal 1980).

Since the surface-area-to-volume ratios are within an order of magnitude, the relative differences between the mass-transfer rates will be determined by the mass-transfer coefficients. The mass-transfer rate in the hollow-fiber gas membrane process will be roughly two orders of magnitude below steam stripping or one order of magnitude lower than NOGD. Consideration of NOGD as an alternative to steam stripping, however, should also include the lower operating temperatures required for NOGD as well as enhanced resource recovery.

#### Wastewaters

**Oil Shale Process Waters.** Data obtained from the oil shale retort water experiments correlated with predicted values (indicated by regression analysis of the experimental  $\theta$  against the predicted  $\theta$ ) (Fig. 4). The data deviated significantly, however, from the ideal correlation (broken line, Fig. 4). It is significant to note that the regression lines all lie above the ideal case, an

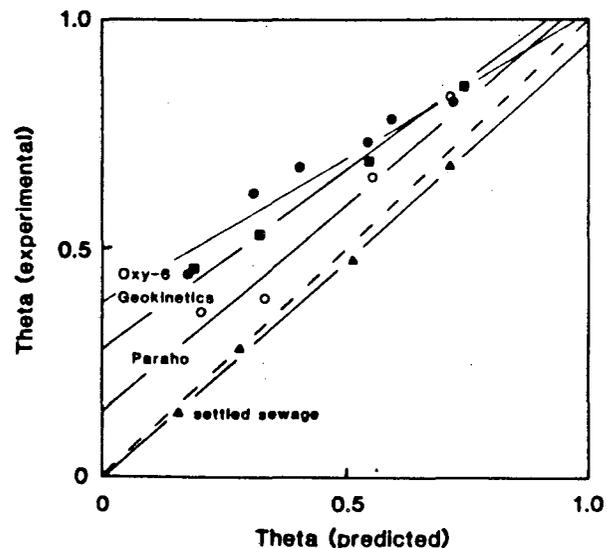


Figure 4. Regression analysis of the experimental fraction remaining ( $\theta$ ) versus the predicted fraction remaining after NOGD treatment: Oxy-6 (solid circles), Geokinetics (solid squares), and Paraho (open circles) oil shale process waters; domestic wastewater (solid triangles).

indication that performance is poorer than predicted by the numeric model.

To determine if a significant difference between the data sets existed, a one-way analysis of variance (ANOVA) was performed on the normalized mass-transfer coefficients of the data sets. The aqueous ammonium hydroxide experimental results were included as one of the data sets. At the 99% confidence level there was a significant difference between all the data sets, but the ANOVA is not able to determine, on the basis of a paired-comparison, which data sets produce the significant difference.

The Newman-Keuls test (Snedecor and Cochran 1980) was used to determine which paired comparisons of the normalized mass-transfer coefficients produced a significant difference. All possible paired comparisons except that of Oxy-6 and Geokinetics were significantly different, indicating that a single correlation was not sufficient for describing NOGD performance on oil shale wastewaters, and that NOGD treatment of oil shale process waters is different from the treatment of an aqueous ammonium hydroxide solution (ideal case). It was not surprising that the mass-transfer coefficients indicated an increased resistance to mass transfer; since the removals were less than predicted, the mass-transfer coefficients calculated from the oil shale process water data were an order of magnitude lower than those from the ammonium hydroxide experiments. The increased resistance to mass transfer was believed to be due to pH-dependent reactions (resulting in the production or consumption of ammonia) or physical barriers at the gas-liquid interface (e.g., surfactants). Neither of these factors was included in the numeric model.

Increased resistance to mass transfer at the internal gas-liquid interface could result from the presence of surfactants, which can inhibit mass transfer by as much as 25% (Sherwood, Pigford, and Wilke 1975). Oil shale retort waters often contain large quantities of amphiphatic (surfactant-like) organic compounds, a large percentage of which are fatty acids (Daughton 1986). In addition, the presence of pH-dependent reactions may also affect the removal of ammonia.

Unlike the aqueous ammonium hydroxide experiments, where the pH was four units greater than the pK of ammonia, the oil shale process waters were treated at their native pH values to determine if the wastewaters contained sufficient buffering to obviate alkali addition. Ammonia-ammonium re-equilibration during dialysis (the pH dropped 0.3 to 0.4 units after NOGD treatment) violated one of the assumptions of the model -- that ammonia was neither consumed nor produced by chemical reaction during NOGD treatment.

In an attempt to determine if poor performance could be attributed to pH, an aqueous sodium hydroxide solution was mixed with Oxy-6 retort water at the influent of the reactor. The elevated pH (14) shifted the ammonia-ammonium equilibrium so

that no ammonium was present. The results are plotted together with the data from the non-pH-adjusted Oxy-6 sample (Fig. 5). Also included in this figure is the data set from NOGD treatment of a stripped and spiked sample of Oxy-6 process water.

If these data and the results from the aqueous ammonium hydroxide experiments are compared by a one-way ANOVA using the normalized mass-transfer coefficients, a significant difference is found between the data sets at the 99% confidence level. The Newman-Keuls test indicates the results of the Oxy-6 and pH adjusted Oxy-6 data sets are not significantly different at the 99% confidence level, an indication that alkali addition did not improve NOGD performance significantly. The Newman-Keuls test also indicates that, at the 99% confidence level, the data from the stripped and spiked Oxy-6 experiment were not significantly different from the aqueous ammonium hydroxide experiments, an indication that removal of ammonia introduced artificially into the Oxy-6 process water is not affected by the presence of organic solutes.

Despite the apparent deviation from the numeric model and the results of the aqueous ammonium hydroxide solution, the ammonia removals from Oxy-6, Paraho, and Geokinetics process waters (56%, 64%, and 55%, respectively) were obtained at hydraulic residence times of 0.92, 0.83, and 0.87 min, respectively. The percentage of ammonia removed by NOGD is comparable with that of some pilot- and bench-scale steam strippers (Sakaji, Persoff, and Daughton 1984).

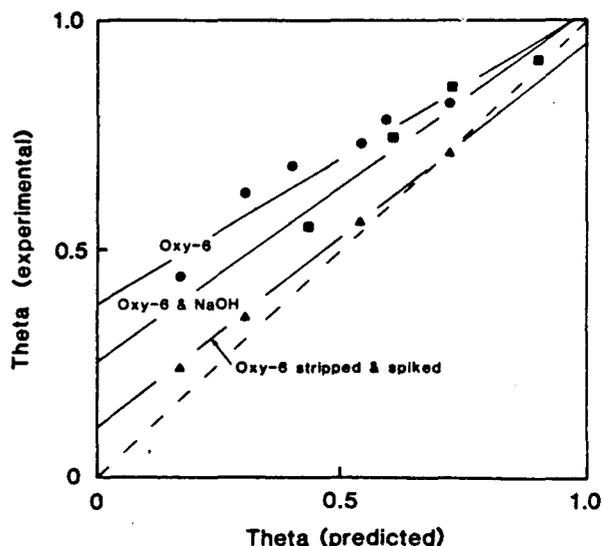


Figure 5. Regression analysis of the experimental fraction remaining ( $\theta$ ) versus the predicted fraction remaining after NOGD treatment: Oxy-6 (solid circles), Oxy-6 with sodium hydroxide (solid squares), and Oxy-6 stripped and spiked (solid triangles).

**Domestic Wastewater.** Domestic wastewaters contain ammonia concentrations that are usually about two orders of magnitude lower than oil shale process waters. Despite these lower concentrations, a maximum removal of 86% was achieved for a domestic sewage sample (residence time of 0.97 min).

Regression of the experimental versus predicted fraction of ammonia remaining (Fig. 4) shows a strong linear correlation. A one-way ANOVA on the normalized mass-transfer coefficients from the oil shale process waters, aqueous ammonium hydroxide, and settled sewage data indicates a significant difference between the data sets at the 99% confidence level. The average  $k_{\text{expt}}$  to  $k_{\text{calc}}$  ratio for the settled sewage data set was 1.09, an indication that ammonia removals were 9% better than predicted by the model. Even though a significant difference between the average ratios exists, as determined by the Newman-Keuls test, the settled sewage results were closer to the ideal case than those data obtained from the oil shale process water experiments: an indication that the NOGD process can be used as an alternative method for ammonia removal from domestic wastewaters and that the numeric model can be used to predict NOGD process performance on domestic wastewaters.

Nonosmotic dissolved-gas dialysis has potential as an alternative to steam stripping. Like steam stripping, NOGD can be used to treat both domestic wastewater and oil shale process waters. Points of comparison of the two methods are summarized in Table 2.

Table 2. Comparison of Steam Stripping with NOGD

criteria	steam stripping	NOGD
Surface Area to Volume Ratio ( $\text{m}^2/\text{m}^3$ )	62-984	300
Mass-Transfer Coefficient (cm/s)	$10^{-2}$	$10^{-3}$
Operating Temperature ( $^{\circ}\text{C}$ )	100	30
Receiving Phase	steam	aqueous acid

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## LIST OF SYMBOLS

B	a coefficient
$c_0$	influent ammonia concentration
$c_1$	effluent ammonia concentration
$D_G$	gas phase diffusivity
$D_L$	liquid phase diffusivity
$D_e$	effective gas phase diffusivity
r	radial variable
$r_i$	internal membrane radius
$r_o$	external membrane radius
m	Henry's coefficient
$v_m$	average velocity
z	tube length
$\epsilon$	membrane porosity
$\gamma$	dimensionless residence time
$\lambda$	eigenvalue
$\eta$	dimensionless radius
$\theta$	dimensionless concentration

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