then be drawn through these *localized* K-values to cover the entire *TBP* range. The calculations also indicate that the variation of the liquid concentrations of the heavy *components* contribute much less to the error in the K-values from the pseudocomponent treatment than the variation in the y value across the same cut. For example for the 533.15-560.95K fraction, at 533.15K and 10.335 MPa, the x-value of the heavy *component* varies from 0.8483 to 0.8473 while the y-value varies from 0.003834 to 0.007884.

Once the basic data for the equilibrium liquid and vapor compositions of acceptable accuracy have been obtained to represent the K-values as a function of pressure, temperature and composition, the latter assigned along the true boiling point cut, then the calculations can be conducted using size of cuts more consistent with the new experimental accuracy, hopefully, much smaller than are inherent in the present treatment.

NOTATION

LV% = volume percent of liquid boil off
L/V = liquid to vapor molar ratio
P_c = critical pressure
T_c = critical temperature
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek Letters

γ = activity coefficient in the liquid phase
ν^o = fugacity coefficient in the liquid phase
ϕ = fugacity coefficient in the vapor phase
ω = acentric factor

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Nitric Oxide Gas Absorption in A Limestone Packed Column

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INTRODUCTION

Absorption of nitrogen oxides into aqueous solution is an important process industrially in the manufacturer of nitric acid, and environmentally in the removal of these oxides from combustion gases and the aqueous reprocessing of nuclear fuels (Counce and Perona, 1979). Prior to the development of the Haber-Bosch process for the production of ammonia, processes in which nitrate fertilizers were produced from atmospheric air employing various types of electric arcs were widely used (Waesser, 1926). The production of nitrate fertilizer employing electric arc processes (Treharne et al, 1978) has recently received attention as a possible technique for small scale farm produced fertilizer powered by alternate energy sources (solar, wind, hydro).

In the systems being studied nitric oxide is produced by the arc from atmospheric air, oxidized to nitrogen dioxide, and subsequently absorbed into an aqueous solution containing lime of limestone. The resulting solution of calcium nitrate can be directly tied to the irrigation system during growing season, or stored for later use in the winter. The concentration of nitric oxide produced by the arc is low (1-2%), making the gas absorption process difficult. Because of the proposed farm location of the process it is desired that the system be relatively simple and inexpensive. Studies of nitric oxide gas absorption were, therefore, performed employing a column packed with limestone chips in conjunction with a gas holding tank to provide for the oxidation of nitric oxide to the more soluble nitrogen dioxide (hence N_2O_4). The studies were conducted in order to evaluate the effect of gas flow velocity, input nitric oxide partial pressure, packing height and holding tank volume on the absorption of nitric oxide—air mixtures at concentrations below 2%.

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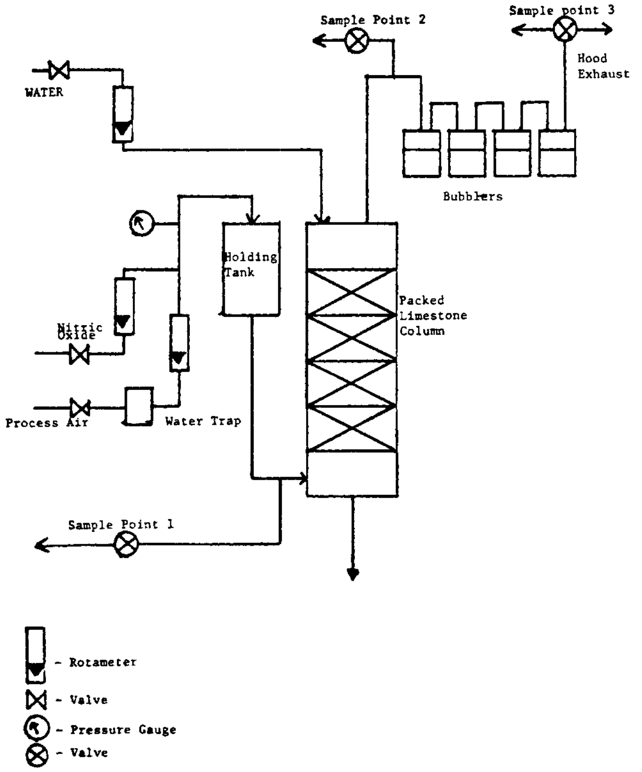

Figure 1. Schematic diagram of packed limestone NO_x gas absorption system.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The flow sheet for the experiment is shown in Figure 1. The packed column consists of a 0.106 m i.D. × 1.52 m long section of PVC pipe packed with 0.0191 m limestone chips. The packing was suspended by a 9.53×10^{-3}m thick sheet of PVC which had 4.76×10^{-3}m wide slots placed 3.18×10^{-3}m apart to provide space for gas and liquid flow. Even liquid distribution was provided by a specially designed liquid distribution plate containing a large number of holes drilled by a #60 drill bit set inside 4.76×10^{-3}m grooves. The holding tank consisted of 0.1018 m i.D. PVC pipe which was varied in length when it was desired to change the holding tank volume. Gas exiting the column passed through four static bubblers (0.1016 m i.D. PVC pipe 0.305 m long) containing aqueous solution to remove remaining nitrogen oxides prior to venting.

The gas handling equipment consisted of nitric oxide and air rotameters, as well as stainless steel valves, fittings and connecting tubing. Pure nitric oxide supplied by Air Products and Chemicals was mixed with process air to form a gas mixture of the desired concentration. Gas samples could be obtained at three points in the system; before and after the column, or after the bubblers.

Gas analysis was accomplished employing a Perkin Elmer model 450 double beam spectrophotometer at a wavelength of 4.6×10^{-7}m at a temperature of 22°C. A cell of pathlength of 0.1 m was employed. Samples were held for a sufficient time prior to analysis to allow for the complete oxidation of nitric oxide to nitrogen dioxide.

Employing data obtained from Sherwood (1937) for 6.35×10^{-3}m, 1.27×10^{-2}m, and 1.9×10^{-2}m broken stone with a superficial liquid flow rate (expressed as mass of water per unit time per unit of cross sectional tube area without solids) of 6.78×10^{-1} kg/sec/m^2 indicate that the superficial gas velocities at the flooding point were 0.45, 0.85, and 1.10 m/sec, respectively. It was found that over the range of gas and liquid flow rates used (4.72×10^{-3}m^3/sec gas flow and 1.25×10^{-5}m^3/sec liquid flow) it was impossible to get the column to flood.

Experimental data were not taken until the system had reached steady state as indicated by no changes in the column outlet nitrogen oxide concentrations for 30 minutes.

PREVIOUS WORK

The absorption of nitrogen dioxide into water or dilute solutions of nitric acid can be represented by the following reactions:

$$2\ NO_2\ (g) = N_2O_4\ (g) \qquad (1)$$

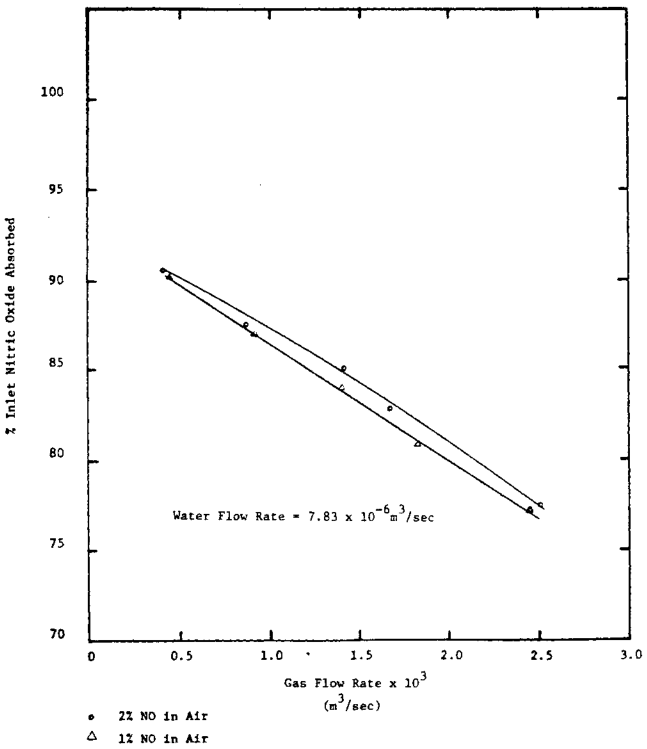

Figure 2. Gas flow velocity vs. NO_x absorption.

$$2\ NO_2\ (\text{or } N_2O_4) + H_2O = HNO_3 + HNO_2 \qquad (2)$$

$$N_2O_4 = NO_3^- + NO^+ \qquad (3)$$

$$4\ HNO_2 = 2\ NO + N_2O_4 + 2\ H_2O \qquad (4)$$

Previous investigators (Kameoka and Pigford [1977], Wendel and Pigford [1958], Caudle and Denbigh [1953], Denbigh and Prince [1947], Peters et al [1955]) have reported that Reaction (4), the decomposition of nitrous acid, takes place slowly at low concentrations. It has also been reported that Reaction (2) is the rate determining step and is first order with respect to N_2O_4 concentration.

The oxidation of gaseous nitric oxide to nitrogen dioxide is a third order gas phase reaction with a negative temperature dependence (Greig and Hall [1967], Ashmore et al [1962]). The formation of N_2O_4 from NO_2 is also favored with decreasing temperature.

The absorption of nitrogen dioxide into aqueous sulfuric acid, sodium hydroxide and alkaline sodium sulfide solutions has been studied (Kameoka and Pigford [1977]) with the latter increasing the rate of absorption compared with water by a factor of 2.5. Other investigators (Kobayashi et al [1977]) have studied nitrogen oxide absorption in aqueous solutions containing a variety of organic and inorganic salts and indicated that NO_2 absorption efficiency increases with increasing redox potential of the reagent present in the aqueous solution.

RESULTS

Initial studies were conducted employing 1.52 m of packing and a holding tank volume of 0.037 m^3. Results are presented in Fig. 2 for the absorption of feed mixtures containing from 1% to 2% nitric oxide as a function of gas flow rate. The results indicate a steady linear decrease in nitric oxide (nitrogen dioxide) absorption with increasing gas flow rate in the range studied (4.16×10^{-4}m^3/sec − 2.5×10^{-3}m^3/sec). It was felt that this decrease in absorption with increasing flow rate was the result of the decreased residence time of the nitric oxide air mixture in the holding tank resulting in decreased nitrogen dioxide concentration (hence decreased N_2O_4). To test this hypothesis, experiments were conducted to determine the effect of holding tank volume on the absorption. Holding tank volume was varied

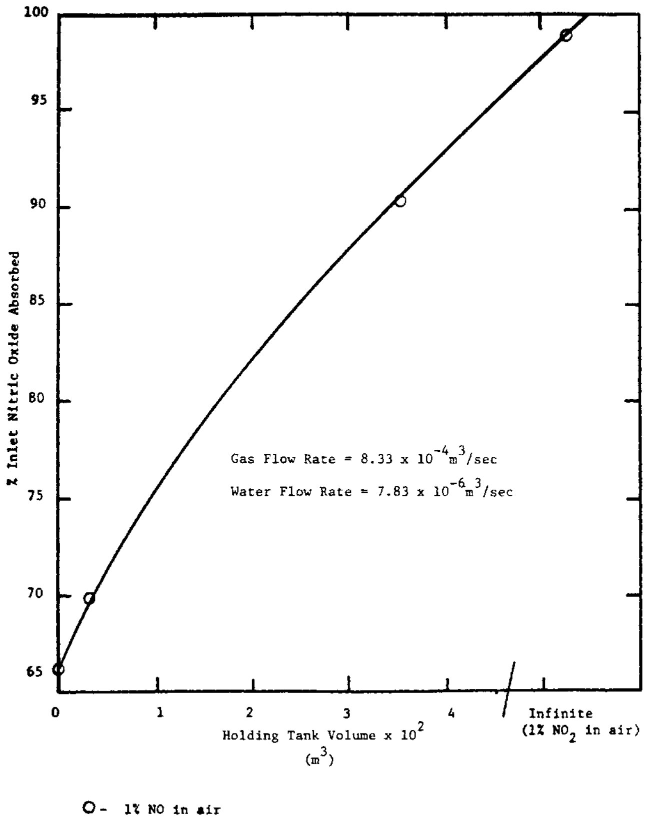

Figure 3. Holding tank volume vs. NO_x absorption.

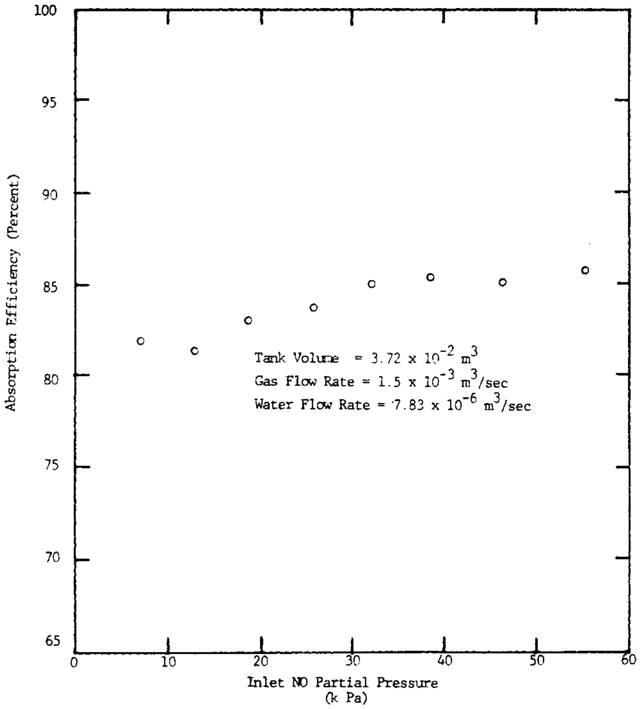

Figure 4. Absorption efficiency vs. inlet NO partial pressure.

employing 1% nitric oxide in air mixtures. To simulate a very large tank (one in which NO and NO_2 were able to reach equilibrium) a feed of 1% nitrogen dioxide in air was used. Results at a gas flow velocity of 8.33 × 10^{-4}m³/sec are presented in Fig. 3 and indicate a rapid increase in absorption with increased holding tank volume.

The effect of input nitric oxide partial pressure, at a fixed gas flow velocity and holding tank volume, on absorption efficiency is presented in Fig. 4. Efficiency was defined by the following relation (Levenspiel [1972])

$$X\ NO_x = \frac{1 - P\ NO_x\text{out}/P\ NO_x\ \text{in}}{1 + E\ P\ NO_x\text{out}/P\ NO_x\ \text{in}} \tag{5}$$

where $X\ NO_x$ is the efficiency of nitrogen oxide removal, $P\ NO_x$ is the partial pressure of the nitrogen oxides, and E is the fractional change in volume of the gas due to absorption. At low NO_x concentrations, the product $E\ P\ NO_x$ out/$P\ NO_x$ is much less than one so that Equation (5) reduces to:

$$X\ NO_x = 1 - \frac{P\ NO_x\text{out}}{P\ NO_x\text{in}} \tag{6}$$

The results indicate an increase in absorption efficiency with increasing NO_x partial pressure until a partial pressure of 38 k Pa after which the efficiency remains unchanged with increasing partial pressure.

Variation of the height of limestone packing in the column was found to have a significant effect on the absorption. Absorption dropped from 82% with 5 ft. of packing to 55% with 3 ft of packing at identical conditions (1.66 × 10^{-3}m³/sec gas flow, 7.83 × 10^{-6}m³/sec water flow).

Variation of the water flow velocity from 4 × 10^{-6}m³/sec to 1.25 × 10^{-5}m³/sec had no observable effect on the absorption efficiency.

DISCUSSION AND CONCLUSIONS

The results of this study indicate that oxidation of nitric oxide to nitrogen dioxide is crucial in obtaining high absorption efficiencies, thus making the size of the holding tank prior to the column an important design criterion. The absorption efficiency was also found to be a function of gas flow velocity and of NO_x partial pressure (at low partial pressures).

The amount of limestone packing present in the column was found to significantly affect the absorption efficiency. Limestone is consumed during the absorption process so that the amount of limestone in the column (hence the absorption efficiency) will decrease with time. This problem can be minimized by use of two columns, each containing significantly more limestone packing than required for the minimum acceptable absorption efficiency. The first column would operate until the absorption efficiency declined to the minimum acceptable value, after which the second column would be put into operation while the first column was repacked. Employing typical results obtained in this study, a column containing 50 kg. of limestone operating with a gas flow rate of 8.33 x 10^{-4}m³/sec of 1% NO_x in air (water flow rate = 7.83 × 10^{-6}m³/sec) could operate for approximately 558 hours at an efficiency of 90% or greater before repacking was necessary.

The results presented in this study were for an absorption system with no liquid recycle. The introduction of a recycle would decrease the absorption efficiency because of HNO_2 buildup and its subsequent dissociation to nitric oxide and as the result of decreased $CaCO_3$ dissolution because of calcium ion build-up in the solution. The planned small scale fertilizer manufacturing system, however, will be equipped with a recycle for use at times when irrigation is not needed so that the more concentrated fertilizer solution can be made and stored.

ACKNOWLEDGMENT

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Calculation of Critical Points from Cubic Two-Constant Equations of State

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Evaluation of critical points for multicomponent mixtures based on an equation of state has attracted considerable attention in recent years. The first general procedure for direct determination of critical temperature and pressure was developed by Peng and Robinson (1977), who used a criterion based on the Gibbs free energy, while a later method by Heidemann and Khalil (1979) is based on the Helmholtz free energy. Indirect methods, where the critical point is found from a phase envelope construction, have also been suggested (Assilineau et al, 1979, Michelsen, 1980).

The direct methods result in two complex non-linear equations. The method of Heidemann and Khalil is far superior, since it requires a computational effort proportional to n^3 (n being the number of components) as compared to n^5 in the procedure of Peng and Robinson. The partial derivatives required using the Helmholtz free energy are much more rapidly evaluated than those using the Gibbs free energy.

The present paper describes a computational modification of the method of Heidemann and Khalil, applicable to simple, two-constant Cubic Equations of State such as the SRK-equation (Soave, 1972) and the PR-equation (Peng and Robinson, 1976). This modification reduces the computing time by a factor of 5-10.

For systems where the unlike binary interaction parameters may be calculated from the pure-component parameters using the geometric mean values, a further simplification is given, whereby computing times are reduced to a few milliseconds, almost irrespective of the number of components.

Method of Heidemann and Khalil

Using a Taylor series expansion of the Helmholtz free energy, Heidemann and Khalil derived the following criterion: At the critical point a mixture of total composition $\mathbf{N}$ must satisfy

$$\mathbf{Q}\Delta\mathbf{N} = 0, \quad \Delta\mathbf{N}^T\Delta\mathbf{N} = 1 \tag{1}$$

and

$$C = \sum_i \sum_j \sum_K \Delta N_i \Delta N_j \Delta N_K \left(\frac{\partial^3 A}{\partial N_i \partial N_j \partial N_K}\right)_{T,V} = 0 \tag{2}$$

where A is the Helmholtz free energy, and

$$Q_{ij} = \left(\frac{\partial^2 A}{\partial N_i \partial N_j}\right)_{T,V} = RT\left(\frac{\partial \ln f_i}{\partial N_j}\right)_{T,V} \tag{3}$$

To evaluate T_c and v_c nested iterations were used. Newton iteration at a fixed value of v is used to determine a temperature where the set of homogeneous equations (1) have a nontrivial solution. The elements ΔN_i are calculated, and evaluation of the cubic form C is used to correct v in an outer loop. For simple cubic equations of state the evaluation of C requires essentially only one or two double summations, and for general equations numerical evaluation as described in (Michelsen, 1980) is inexpensive. The computationally expensive part is that of solving (1). The solution technique suggested in the following takes advantage of the specific temperature dependence in the SRK- and PR-equations of state.

Two-Constant Cubic Equations of State

We shall consider Cubic Equations of State of the form

$$P = \frac{RT}{v - b} - \frac{a}{(v + \delta_1 b)(v + \delta_2 b)} \tag{4}$$

where the mixture constants a and b are given by the mixing rules

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{5}$$

$$b = \sum_i y_i b_i \tag{6}$$

$$a_{ij} = (a_{ii} a_{jj})^{\frac{1}{2}}(1 - k_{ij}) \tag{7}$$

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