EPA/600/2-91/046 September 1991

BENCH-SCALE EVALUATION OF AMMONIA REMOVAL FROM WASTEWATER BY STEAM STRIPPING

.

..

.

bу

.

G.B. Wickramanayake (Work Assignment Leader) D. Evers, J.A. Kittel, and A. Gavaskar

> BATTELLE Columbus Division

Columbus, Ohio 43201-2693

EPA Contract No. 68-03-3248

Project Officer

J. O. Burckle Water and Hazardous Waste Treatment Research Division Risk Reduction Engineering Laboratory Cincinnati, Ohio 45268

> RISK REDUCTION ENGINEERING LABORATORY OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY Cincinnati, Ohio 45268

DISCLAIMER

This material has been funded wholly or in part by the United States Environmental Protection Agency under contract 68-03-3248 to Battelle Memorial Institute, Columbus Division. It has been subject to the Agency's review and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementation, and management of research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the research and the user community.

This work was requested by the Office of Water Regulations and Standards for data to be developed on a bench-scale which would support the development of a regulation for removal of ammonia from waste streams originating from the extraction of metals, particularly tungsten, using ammoniacal lixivants.

> E. Timothy Oppelt, Director Risk Reduction Engineering Laboratory

ABSTRACT

The purpose of this study was to generate laboratory data to support the development of discharge standards for ammonia in nonferrous metal winning process wastewaters. The objective was accomplished by studying the removal of ammonia from synthetically compounded "wastewater" samples using a bench-scale steam stripping apparatus.

The analyses of estimated Henry's Law constant and changes in ammonia solubilities indicate that addition of caustic, when compared with slaked lime, can result in higher Henry's Law constants and lower solubilities for the three waste streams studied. Although no significant variation of mass transfer rate coefficient (K) was observed when SO_4^{-} concentrations were varied from 5,000 to 20,000 mg/L, K was highest for low SO_4^{-} wastewaters when pH was adjusted using NaOH.

The results of the steam stripping study indicated that the variation of chemical constituents such as SO_4^- and the molal strength did not have a significant effect on the efficiency of ammonia removal. Higher removals such as 99.9 or more can be achieved by preheating wastewater and operating the stripping tower at high steam to wastewater flowrates such as 4 lb/gallon. The cost analysis based on the requirements for engineering unit processes and operations indicated that lime can be more economical than caustic for pH adjustment.

CONTENTS

-

		<u>Page</u>
Foreword Abstract Figures Tables Acknowledgem	nents	iii iv vii ix xi
1. SUMMARY		1
1.1	INTRODUCTION	1
1.2	OBJECTIVES AND SCOPE	. 1
	in Wastewater.	. 1
	1.3.2 Task 2: Ammonia Removal Studies Using Steam Stripping Unit	2 4
2. INTRODUC	TION AND OBJECTIVES	5
2.1	INTRODUCTION	5
2.2	OVERALL PROJECT OBJECTIVES	5
3. TASK 1:	THEORETICAL AND LABORATORY STUDIES ON EQUILIBRIUM AND MASS-TRANSFER	7
3.1	OBJECTIVES AND SCOPE	7
3.2	METHODS	7 7 7
3.3	RESULTS AND DISCUSSION	9 9 16
3.4	SUMMARY	30

CONTENTS (continued)

١

-

4.	TASK 2:	AMMONIA REMOVAL STUDIES USING STEAM STRIPPING UNIT	33
	4.1	OBJECTIVE AND SCOPE	33
	4.2	DESIGN AND CONSTRUCTION OF THE STEAM STRIPPING UNIT4.2.1Characteristics of the Column4.2.1.1Flow-Mode4.2.1.2Column Packing4.2.1.3Column Material4.2.2Design of the Stripping Unit4.2.2.1Henry's Law Constant4.2.2.2Number of Transfer Units4.2.2.3Diameter of the Column4.2.2.4Height Equivalent to a Transfer Unit4.2.3Scale-Up	33 33 34 35 35 35 36 40
	4.3	EXPERIMENTAL PROCEDURES	41
	4.4	RESULTS AND DISCUSSION	50
	4.5	SUMMARY AND CONCLUSIONS	60
5.	ENGINEER	ING COST ESTIMATES	62
	5.1	OBJECTIVE AND SCOPE	62
	5.2	METHODS 5.2.1 Equilibria Modelling 5.2.2 Cost Estimates 5.2.3 Process Design	67 67 67 73
	5.3	RESULTS AND DISCUSSION	75
	5.4	SUMMARY AND CONCLUSIONS	83
6.	QUALITY	ASSURANCE/QUALITY CONTROL	84
7.	REFERENC	ES	86

.

FIGURES

.

-

<u>FIGURE</u>		<u>Page</u>
3.1	Variation of ammonia concentration with time: Wastewater A and NaOH	. 24
3.2	Variation of ammonia concentration with time: Wastewater A and Ca(OH) ₂	. 25
3.3	Variation of ammonia concentration with time: Wastewater B and NaOH	. 26
3.4	Variation of ammonia concentration with time: Wastewater B and Ca(OH) ₂	. 27
3.5	Variation of ammonia concentration with time: Wastewater C and NaOH	. 28
3.6	Variation of ammonia concentration with time: Wastewater C and Ca(OH) ₂	. 29
4.1	Dependence of NTU on removal efficiency and stripping factor .	37
4.2	Generalized correlation for flooding and pressure drop in packed columns	. 38
4.3	Flowrates and packing size	44
4.4	Stripping factors and height of column	. 46
4.5	Experimental set up for ammonia removal by steam stripping.	. 48
4.6	Calibration of steam flow rate across the orifice	. 49
5.1	Calculated pH for Plants 1, 2, 3, and 5 for lime addition.	. 68
5.2	Calculated pH for Plants 1, 2, 3, and 5 for sodium hydroxide addition.	. 69

vii

FIGURES (continued)

.

_

.

.

.

FIGURE	l	<u>'aqe</u>
5.3	Calculated sludge production for Plants 1, 2, 3, and 5 for lime addition.	70
5.4	Calculated sludge production for Plants 1, 2, 3, and 5 for sodium hydroxide addition.	71

TABLES

.

-

<u>TABLE</u>		<u>Page</u>
1.1	SUMMARY RESULTS OF LABORATORY STUDY ON STEAM STRIPPING	. 3
3.1	WASTEWATER CHARACTERISTICS FOR GAS TRANSFER RATE EXPERIMENTS .	. 8
3.2	REPORTED VALUES FOR h, AND h	12
3.3	CHEMICAL CHARACTERISTICS OF SYNTHETIC WASTEWATER USED IN MASS-TRANSFER STUDIES	13
3.4	ESTIMATES OF HENRY'S LAW CONSTANT FOR SYNTHETIC WASTEWATER	14
3.5	RESULTS OF MASS-TRANSFER EXPERIMENT A-NaOH	17
3.6	RESULTS OF MASS-TRANSFER EXPERIMENT A-Ca(OH) ₂	18
3.7	RESULTS OF MASS-TRANSFER EXPERIMENT B-NaOH	19
3.8	RESULTS OF MASS-TRANSFER EXPERIMENT B-Ca(OH) ₂	20
3.9	RESULTS OF MASS-TRANSFER EXPERIMENT C-NaOH	21
3.10	RESULTS OF MASS-TRANSFER EXPERIMENT C-Ca(OH) ₂	22
3.11	MASS TRANSFER RATE COEFFICIENTS FOR AMMONIA IN DIFFERENT WASTE STREAMS	31
4.1	COLUMN DIAMETER FOR $1/2$ -INCH PACKING AND R=5	42
4.2	EFFECT OF PACKING SIZE	43
4.3	DIMENSIONS OF THE COLUMN FOR VARIOUS VALUES OF R FOR 5/8-INCH PACKING	45
4.4	RESULTS FOR PILOT RUN NO. P-1 FOR WASTEWATER B AND NaOH	51
4.5	RESULTS FOR PILOT RUN NO. P-2 FOR WASTEWATER B AND NaOH	52
4.6	RESULTS FOR PILOT RUN NO. P-3 FOR WASTEWATER B AND CaO	53

.

TABLES (continued)

TABLE		<u>Page</u>
4.7	RESULTS FOR PILOT RUN NO. P-4 FOR WASTEWATER B AND CaO	54
4.8	RESULTS FOR PILOT RUN NO. P-5 FOR WASTEWATER C AND NaOH	55
4.9	RESULTS FOR PILOT RUN NO. P-6 FOR WASTEWATER C AND NaOH	56
4.10	RESULTS FOR PILOT RUN NO. P-7 FOR WASTEWATER C AND NaOH	57
4.11	RESULTS FOR PILOT RUN NO. P-B FOR WASTEWATER C AND CaO	58
4.12	RESULTS FOR PILOT RUN NO. P-9 FOR WASTEWATER C AND CaO	59
4.13	SUMMARY RESULTS OF LABORATORY STUDY ON STEAM STRIPPING	61
5.1	CHEMICAL AND PHYSICAL CHARACTERISTICS OF METAL PROCESSING WASTEWATERS CONTAINING AMMONIA: CONCENTRATION IN mg/L	63
5.2	CHARACTERISTICS OF REPRESENTATIVE WASTEWATER STREAMS	66
5.3	SUMMARY OF CHEMICAL AND SLUDGE DATA	72
5.4	ASSUMED CONSTANT VALUES	74
5.5	DESIGN EQUATIONS	76
5.6	CONVERSION FACTORS	77
5.7	SUMMARY OF COST ESTIMATES FOR PLANT 1	78
5.8	SUMMARY OF COST ESTIMATES FOR PLANT 2	79
5.9	SUMMARY OF COST ESTIMATES FOR PLANT 3	80
5.10	SUMMARY OF COST ESTIMATES FOR PLANT 5	81

.

-

ACKNOWLEDGEMENTS

Battelle Columbus Division (BCD) prepared this document for the Risk Reduction Engineering Laboratory (RREL), U.S. Environmental Protection Agency (U.S. EPA). Numerous people contributed to the research and writing of this report. The authors wish to thank these individuals for their contributions. John O. Burckle, U.S. EPA Project Officer, and Jeff Means, BCD Project Manager, in particular, are gratefully acknowledged for their direction and support. Ron Clark of BCD also contributed significantly at the initiation of this project. Ernie Hall of U.S. EPA is acknowledged for providing guidance and required additional information. Greg Headington, Larry Smith, and E. Voudrias of BCD are thanked for their assistance during this study, Robert Hinchee for technical review, Tom Bigelow for editorial assistance, and Cleta Richey for text processing support.

1.1 INTRODUCTION

Some industrial wastewaters, such as nonferrous metal industry wastewaters, are high in dissolved solids (e.g., 140,000 ppm total dissolved solids) and ammonia (e.g., 22,000 mg/L). These wastewaters require treatment for removal of the ammonia, as well as the dissolved solids, to meet the discharge standards. The practical methods of removing ammonia-nitrogen from wastewaters include biological nitrification-denitrification, breakpoint chlorination, evaporation, reverse osmosis, ion exchange, air stripping, and steam stripping. The purpose of this study was to generate data to support the development for the limitation of the discharge standards for the ammonia content of wastewaters from certain nonferrous metal smelting and refining processe by employing steam stripping, which is an effective ammonia removal and recovery method.

1.2 OBJECTIVES AND SCOPE

The overall objective, which was to generate laboratory data to support the development of effluent standards for high-strength ammonia wastewaters, was pursued as three discrete tasks. Task 1 involved performing theoretical and laboratory studies to determine the effects of wastewater composition on the equilibrium of ammonia (gas) and water and gas-liquid mass transfer rates, especially within the temperature range of interest in actual plant operation. In Task 2, laboratory tests were performed using a bench-scale steam stripping apparatus. Experiments were conducted using two representative synthetic wastewaters; pH adjustment was accomplished using lime and caustic. Task 3 involved analysis and estimation of capital and operating costs of the pH adjustment methods, and of the handling and disposal of waste sludge.

1.3 SUMMARY

1.3.1 <u>Task 1: Theoretical and Laboratory Studies on the Equilibrium and</u> <u>Mass Transfer of Ammonia in Wastewater</u>

The analyses of the estimated Henry's Law constant and changes in solubilities of ammonia indicate that addition of caustic, compared with slaked lime, can result in higher Henry's Law constants and ammonia lower

solubilities for the three waste streams considered. These effects can be attributed to the relatively high ionic strength resulting in wastewaters when pH was adjusted with NaOH. Between solutions B and C, where the sulfate concentration was varied without changing the solution strength (total number of moles), no significant difference in Henry's Law constant or solubility could be seen for either of the two pH adjustment methods. The highest Henry's Law constant and corresponding lowest ammonia solubility were observed in solution A which has the highest molal strength.

Experimental studies to determine the effects of dissolved species and pH adjustment method on the mass transfer rate coefficient (K) indicate that those effects are relatively low and the maximum changes in mass transfer rate coefficient do not exceed 25 percent. In two of the three different solutions, however, the mass transfer rate coefficients were higher for the waste stream where pH was adjusted using caustic. For solutions with approximately the same $SO_4^{=}$ concentration but different molal strength, the mass transfer rate coefficients were comparable when NaOH was used as the pH adjustment method. For Ca(OH)₂, however, the K values were comparable for those where both the molal strength and $SO_4^{=}$ level were different. The overall analysis of data indicate that, when compared with lime, addition of NaOH can promote the ammonia removal for solutions with relatively low $SO_4^{=}$ levels (5,000 mg/L).

1.3.2 Task 2: Ammonia Removal Studies Using Steam Stripping Unit

The results of the steam stripping study are summarized in Table 1.1. Data show that when the steam to wastewater ratios are low (1.3 lb/gal), the ammonia removal efficiency was as low as 93 percent. By increasing the steam to wastewater ratio to 3.8 lb/gal, removals of over 99.9 percent have been observed. The removal efficiency in one study was improved by 2 percentile points when the temperature of influent waste stream was raised by about 20°C. The addition of lime resulted in more than a 10°C increase in temperature since the hydration of lime is an exothermic process.

		Wastewate	r Temp. °C				
Wastewater	pH Adjustment Method	Column Influent	Column Effluent	Steam to Wastewater Ratio (1b/gallon)	<u>NH3-N con</u> Influent	Effluent	Average NHg Removal, %
B (10w SO4)	NaOH	26	101	1.9	5,200	32-102	99.1
	NaOH	26	101	1.3	5,200	255-420	93.1
	CaO	38	101	1.9	5,100	188-288	95.3
	CaO	39	101	3.8	5,000	12-16	99.7
C (high S04)	NaOH	26	101	1.9	4,750	121-198	96.9
_	NaOH	26	101	3.8	4,700	3.9-4.5	99.91
•	NaOH	47	101	1.9	3,950	2.0-80	98.8
	CaO	39	101	1.9	3,950	87-92	97.7
	CaO	39	101	3.8	3,825	1.1-2.2	99.96

•

.

TABLE 1.1. SUMMARY RESULTS OF LABORATORY STUDY ON STEAM STRIPPING

ω

•

For wastewater with low initial SO_4 = level (5,000 mg/L), ammonia removal was 3 percent higher when pH was adjusted with caustic rather than lime. These observations agree with the trends predicted from the estimated Henry's Law constant and mass transfer rate coefficient. In the experiments conducted with wastewaters using higher initial $SO_4^{=}$ levels (20,000 mg/L), ammonia removal was slightly higher when pH was adjusted with lime instead of caustic. These observations agree with the conclusions reached from the corresponding mass transfer rate studies, which did not agree with the theoretical estimates of solubilities based on Henry's Law constant.

In summary, more than 99.9 percent removal of ammonia can be achieved by introducing high steam to wastewater ratios such as 3.8 lb/gallon. Variation of chemical constituents such as $SO_4^{=}$ and the molal strength have only a little effect on net NH₃ removal. Higher removal efficiencies can be achieved by preheating wastewaters and operating the stripping tower at high temperatures by increasing steam to wastewater ratios.

1.3.3 Task 3: Engineering Cost Estimates

Cost estimates for the chemicals and equipment to adjust the pH of an ammonia-bearing, metal-winning wastewater prior to stripping show that lime can be more economical than caustic for pH adjustment. In addition, the most cost-effective method for disposal of the sludge solids generated is dewatering in a lagoon followed by landfill disposal of the solids. However, there may be a different set of cost-effective processes when costs for land, transport, and handling of large quantities of sludge are high.

2. INTRODUCTION AND OBJECTIVES

2.1 INTRODUCTION

Extracting metal values from some ores requires the use of hydrometallurgical techniques which employ ammoniacal lixiviants. The metal values are recovered from the pregnant liquors, leaving an aqueous wastewater that is high in dissolved solids and ammonia. This wastewater requires treatment for removal of the ammonia as well as the dissolved solids, to meet the discharge standards required under the Effluent Guidelines for the nonferrous metals industry.

The practical methods of removing ammonia-nitrogen from wastewaters include biological nitrification-denitrification, breakpoint chlorination, evaporation, reverse osmosis, ion exchange, air stripping, and steam stripping (Struzeski, 1978). The present study focused on steam stripping, which is also being identified as a very effective ammonia removal method for the metal smelting and refining industry (USEPA, 1976). The purpose of this work assignment was to generate data to support the development of discharge standards for such wastewaters by employing the steam stripping technique.

2.2 OVERALL PROJECT OBJECTIVES

The purpose of this project was to generate laboratory data to support the development of discharge standards for ammonia in nonferrous metal winning process wastewaters. The objective was accomplished by studying the removal of ammonia from synthetically compounded "wastewater" samples using a bench-scale steam stripping apparatus.

This overall objective was pursued as three discrete tasks. Task 1 involved performing theoretical and laboratory studies to determine the effects of wastewater composition on the equilibrium of ammonia (gas) and water and gas-liquid mass transfer rates, within the temperature range of interest in actual plant operation. In Task 2, laboratory tests were performed using a bench-scale steam stripping apparatus. Experiments were conducted using two representative synthetic wastewaters; pH adjustment was

accomplished using lime and caustic. Task 3 involved analysis and estimation of capital and operating costs of the pH adjustment methods, and of the handling and disposal of waste sludge.

3. TASK 1: THEORETICAL AND LABORATORY STUDIES ON EQUILIBRIUM AND MASS-TRANSFER

3.1 OBJECTIVES AND SCOPE

One of the objectives of this task was to investigate how the distribution of inorganic species and changes in temperature affect the equilibrium of ammonia (gas) and the wastewaters. Effects of different electrolytes, such as Na⁺, Mg⁺⁺, Ca⁺⁺, SO⁺₄, and Cl⁻, on the Henry's Law constant (H_e) were evaluated.

The second part of Task 1 involved conducting laboratory experiments to determine how the differences in wastewater characteristics would affect the overall gas-liquid mass transfer rates. These experiments were conducted in identical completely mixed batch reactors at temperatures near 90°C.

3.2 METHODS

3.2.1 Laboratory Studies

The second part of Task 1 involved experiments to study the effect of varying SO_4^{-1} concentration, molal strength, and pH adjustment method [NaOH or $Ca(OH)_2$] on the gas transfer rates for ammonia. These characteristics of the synthetic wastewaters that were used in this study are given in Table 3.1. Waste stream A was designed to have a high SO_4^{-1} level and a high total molal strength. Waste stream B has a lower SO_4^{-1} level than A, whereas both A and C have the same SO_4^{-1} level. Waste streams B and C have the same molal strength and were brought to such conditions by adjusting Cl⁻¹ concentrations.

3.2.1.1 Experimental Procedures--

The gas mass transfer experiments were conducted using 1.5-L samples. The batch reactor was a 2-L beaker placed in a constant temperature hot-water bath. Heated synthetic wastewater was first added to the reactor. Then a predetermined amount of either heated NaOH solution (10 N) or $Ca(OH)_2$ powder was added to the wastewater sample. The amount of base required to raise the pH to 12 was determined by mixing an aliquot of wastewater with the base at room temperature. For the mass transfer experiments, the base was added at elevated temperatures, otherwise, if the pH was raised first, a significant

	C	oncentration, mg/L	
Chemical Species	Wastewater A	Wastewater B	Wastewater C
NH3-N	5,000	5,000	5,000
Mg ⁺⁺	200	200	200
Na ⁺	19,127	11,939	11,939
S0 4	20,000	5,000	20,000
C1 TDS	28,000 72,127	28,000 50,139	16,906 54,045

.

-

.

TABLE 3.1.	WASTEWATER CHARACTERISTICS	SELECTED	FOR	MASS
	TRANSFER RATE EXPERIMENTS			

•

fraction of ammonia can be lost during the heating process. A sample was withdrawn from the reactor, for pH and chemical analyses, prior to initiating the test. Then an aliquot of 1 mL was taken at regular time intervals for ammonia analysis. These samples were immediately dispensed to volumetric flasks containing 99 mL of diluted HCl at room temperature. The acid treatment was performed to convert ammonia to ammonium ion, thus avoiding further loss of ammonia. All ammonia analyses were performed using an ion specific electrode (Orion 95-12 ammonia probe and Orion 701A Ionalyzer).

The contents in the reactor were continuously mixed using a mechanical stirrer rotating at a constant speed. The temperature in the water bath was kept at 90°C. The corresponding reactor temperature was approximately 88°C. Temperatures typical for ammonia stripping units are higher than these values (approximately 100°C), but such temperatures are not feasible in the mass transfer experiments because of the rapid loss of reactor contents by evaporation.

The wastewaters were analyzed for sodium, magnesium, calcium, sulphate, and chloride before and after the pH adjustment. If the final wastewater pH was found to vary beyond 10 percent of its starting value, the experiments were repeated.

3.3 RESULTS AND DISCUSSION

3.3.1 Theoretical Studies on Ammonia/Water Equilibrium

The solubility of ammonia in water depends on the partial pressure of ammonia in gaseous phase, temperature, and the distribution of dissolved species in the aqueous system. The dependency of solubility on partial pressure can be expressed as:

where

 $p = H_e C$

(1)

p = partial pressure of ammonia C = ammonia concentration in water H_p = Henry's Law constant.

The Henry's Law constant is an increasing function of temperature as given in the following equation (Danckwerts, 1970):

$$\frac{d \ln H_e}{d (1/T)} = \frac{H}{R}$$
(2)

where

T = absolute temperature

R = gas constant

H = heat of absorption of the gas.

Wastewaters from the nonferrous metals industry contain a variety of electrolytes. Distribution of these electrolytes affects the solubility of NH_3 and, thus, the Henry's Law constant. The relationship between the ionic strength (I) and H_e is given by (Danckwerts, 1970):

$$\log_{10} (H_e/H_e o) = hI$$
(3)

where

H_eo = Henry's Law constant for water h = Setchenow constant I = ionic strength.

The ionic strength of the solution is given by

$$I = \frac{1}{2} \Sigma C_{i} Z_{i}^{2}$$
(4)

where C_i is the concentration of ions of valency Z_i .

The Setchenow constant is the sum of contributions of the positively (h_{+}) and negatively (h_{-}) charged ionic species and the gaseous (h_{G}) species in solution.

$$h = h_{+} + h_{-} + h_{c}$$
 (5)

Some reported values for h_{\perp} and h_{\perp} are given in Table 3.2. These values reported by Barrett (1966) and Onda et al. (1970) agreed well for most of the species.

In mixed electrolytes, it may be supposed that the value of H_e will be given by an expression of the form (Danckwerts, 1970):

$$\log_{10} (H_{e}/H_{e}0) = h_{1}I_{1} + h_{2}I_{2} + \dots$$
 (6)

where I_1 is the ionic strength attributable to species of electrolyte No. 1 and h_1 is the Setchenow constant for that electrolyte. Based on Equation 6, the Henry's Law constant can be estimated for the solutions with different composition.

Analytical results of the synthetic wastewaters (A, B, and C) used in this study are given in Table 3.3. Using these data and Equations 4, 5, and 6, the H_e/H_e o were calculated. The estimated H_e/H_e o values are given in Table 3.4. The h_+ and h_- for corresponding species were obtained from Barrett (1966) as given in Table 3.2. The value of h_g used in Equation 5 is -0.054 liters per gram ion at 25°C (Danckwerts, 1970).

Since the reciprocal of H_e can be used to compare the change in solubility of ammonia, the results presented in Table 3.4 indicates how the different wastewaters affect the solubility of NH_3 when pH was adjusted by either NaOH or Ca(OH)₂. When compared to Ca(OH)₂, addition of NaOH to adjust the wastewater pH resulted in relatively low solubility of NH_3 in wastewater. This can be attributed to the relatively high ionic strength resulting in wastewater when pH was adjusted with NaOH. Overall, change in $SO_4^$ concentration does not appear to have a significant effect on the Henry's Law constant. Between solutions B and C where the sulfate concentration was varied without changing the solution strength (total number of moles), no significant difference in Henry's Law constant or solubility could be seen for either of the two pH adjustment methods. Highest H_e values and corresponding lowest in ammonia solubility was observed in solution A which has the highest molal strength.

	<u>h+ (</u>	L/g_ion)		h_ (L/g-ion)		
Solute	Barrett (1966)	Onda et al. (1970)	Solute	Barrett (1966)	Onda et al. (1970)	
н+	0.000	-0.0017	F	-	_	
Li ⁺	-	0.0677	c1 ⁻	0.021	0.021	
Na ⁺	0.091	0.091	Br ⁻	0.012	0.0104	
к+	0.074	0.0731	1-	0.005	-0.0082	
Rb ⁺		0.0644	S0	0.022	0.0240	
Cs ⁺	-	0.0509	NO	-0.001	0.0024	
Mg ⁺⁺	0.051	0.0525	co ² -	0.021	0.0548	
Ca ⁺⁺	0.053	0.0546	он	0.066	0.0669	
Sr ⁺⁺	-	0.0648	CNS ⁻	-	-0.0594	
Ba ⁺⁺	0.060	0.0620	P0	-	0.0059	
Cr ⁺⁺⁺	-	0.0107	s03-	-	0.0069	
Mn ⁺⁺	0.046	0.0468	HSOZ	-	0.0663	
Fe ⁺⁺	0.049	0.0491	HS	-	0.0512	
Co ⁺⁺	0.058	0.0559	C107	-	-	
Ni ⁺⁺	0.059	0.0573	4			
Cu ⁺⁺	-	-				
Zn ⁺⁺	0.048	0.0503				
Cd++	-	0.1011				
A1+++	-	0.0367				
NH4	0.028	0.0356			-	

TABLE 3.2. REPORTED VALUES FOR h+ AND h.

.

12

.

Concentration, mg/L						
Si	ample	Sulfate	Chloride	Magnesium	Sodium	Calcium
AA	[initial] [initial] (duplicate)	22,000 25,500	28,000 27,750	184 180	19,000 20,000	<10 <10
A	[pH adjusted with NaOH]	19,000	30,500	<10	31,000	<10
A A	[initial] [pH adjusted with Ca(OH)2]	66,000a 5,300	27,500 31,500	365 <10	19,000 21,000	<10 1,500
B B	[initial] [pH adjusted with NaOH]	8,200 6,500	28,750 29,500	184 <10	17,500 24,000	<10 <10
B B	[initial [pH adjusted with Ca(OH)2]	8,20 0 <4	28,750 29,500	184 <10	17,500 15,000	<10 5,000
C C	[initial] [pH adjusted with NaOH]	24,033 25,000	20,376 975 ^b	193 <10	17,764 24,000	<10 <10
C C	[initial] [pH adjusted with Ca(OH)2]	24,000 5,500	17,750 19,500	181 <10	13,000 14,000	<10 1,100
D	istilled Water [control]	<4	<50	<10	11	<10

TABLE 3.3. CHEMICAL CHARACTERISTICS OF SYNTHETIC WASTEWATER USED IN MASS-TRANSFER STUDIES

.

a Error in analytical results. For H_e calculations 22,000 mg/L was used. b Error in analytical results. For H_e calculations 19,500 mg/L was used.

13

.

Sample(a)	Electrolyte	Concentration M(b)	h(c) 1/g ion	[(d) g ion/L	ΣhI(e)	H _e /H _e o(f)	H _e (g)	% Decrease in NH3 solubility(h
A/NaOH	NaOH	0.093	0.103	0.093		<u> </u>		
	Na2SO4	0.198	0.059	0.594				
	Naci	0.859	0.058	0.859	0.0944	1.24	8.6x10-4	19
A/Ca(OH)2	NaC1	0.812	0.058	0.812				
	Na2504	0.055	0.059	0.165				
	CaČ12	0.038	0.02	0.057				
	-				0.0578	1.14	7.9X10-4	12
B/NaOH	NaC1	0.831	0.058	0.831				
	Na2SO4	0.067	0.059	0.201				
	NaÕH	0.079	0.103	0.079			_	
					0.0682	1.17	8.13x10-4	15
B/Ca(OH)2	NaC1	0.652	0.058	0.652				
	CaC12	0.089	0.02	0.134				
	Ca(0H)2	0.036	0.065	0.054			_	
					0.044	1.11	7.7x10-4	10

TABLE 3.4. ESTIMATES OF HENRY'S LAW CONSTANT FOR SYNTHETIC WASTEWATER

Sample(a)	Electrolyte	Concentration M(b)	h(c) 1∕g ion](d) g ion/L	Iti(e)	H _e /H _e o(f)	He(g)	% Decrease in NH3 solubility(h)
C/NaOH	NaC1 Na2SO4	0.053 0.260	0.058 0.059	0.563 0.78	0.0787	1.20	8.3x10-4	17
C/Ca(OH) ₂	NaC1 Na2SO4 CaSO4	0.549 0.029 0.028	0.058 0.059 0.021	0.549 0.087 0.07	0.0318	1.09	7.6×10-4	8

15

(a) Solution and the pH adjustment method [NaOH or Ca(OH)2] are indicated.

- (b) Concentration estimated from data given in Table 3.3.
- (c) Estimated using Equation 5 and data given in Table 3.2 (Barrett, 1966) $h_G = -0.054$ (Danckwerts, 1970).
- (d) Ionic strength estimated using Equation 4.
- (e) Summation of hI values for all electrolytes.
- (f) Estimated from Equation 6.
- (g) Assuming $H_{eo} = 6.95 \times 10^{-4}$ at 25°C (Powers, 1987).
- (h) Percent decrease is with respect to NH3 solubility in pure water.

3.3.2 Laboratory Studies on Mass Transfer

A number of experiments were conducted in order to estimate the rate of transfer of ammonia from solution. These studies were conducted with synthetic, ammonia-bearing wastewaters of known composition. The composition of the wastewaters was restricted to three cations, NH_4^+ , Mg^{++} , Na^+ , and two anions, SO_A^{\pm} and Cl^{-} . The relative proportions of these ions were adjusted to provide solutions of constant NH₃-N concentration but varying ionic strength. Solutions were adjusted to pH 12 or greater with slaked lime $(Ca(OH)_2)$ or sodium hydroxide (NaOH). The high pH promotes dissociation of NH_a^+ to NH_3 . The wastewater compositions along with the chemical used for pH adjustment are summarized in Tables 3.5 through 3.10. Also given in these tables are NH_3-N concentrations measured during the course of each mass transfer experiment. These values were normalized by dividing each by the initial NH_3-N_1 concentration, C_{r} . Further manipulation consisted of calculating the natural logarithm of each normalized value. The natural logarithm of the normalized values is also compiled in the tables and was used to determine the overall mass transfer rate coefficient.

The rate at which the NH_3 -N concentration decreases in solution can be expressed by the following first order differential equation:

$$\frac{dC}{dt} = K(C_s - C)$$
(7)

where

 $C = NH_3$ -N concentration at time t

 $C_s = equilibrium NH_3 - N$ concentration

K = overall mass transfer rate coefficient.

The solution to this equation is

$$\frac{C_s - C}{C_s - C_o} = e^{-Kt}$$
(8)

where $C_o = initial NH_3-N$ concentration. Since the NH₃-N concentration in the atmosphere can be assumed to be approximately 0, C_s can be assumed to be 0 by Henry's Law.

Wastewater Comp	osition	Solution A	
	Conc	centration, mg/L	
<u>cations</u>	<u>initial</u>	after pH adjustment	
NH4	5,000	4,250	(Reported as nitrogen)
Mg ²⁺	184	<10	
Na ⁺	19,000	31,000	
<u>anions</u>			
s04 ²⁻	22,000	19,000	
C1 ⁻	28,000	30,500	
Solution pH	= 12.02	l	
Temperature (°C	2) = 86.3		
pH adjustment w	with NaOH		
Time (min)		NH3-N (mg/L)	ln (C/C _o)
0 2 4 6 8 10 12 14 16 18 21 24 27 30 33 36 41 46 51		4,250 4,100 4,050 4,000 3,850 3,750 3,650 3,550 3,450 3,400 3,350 3,100 2,950 2,700 2,650 2,550 2,350 2,200 1,950	0 -0.0359 -0.0482 -0.0606 -0.0988 -0.125 -0.152 -0.152 -0.180 -0.209 -0.213 -0.238 -0.316 -0.365 -0.454 -0.454 -0.472 -0.511 -0.593 -0.659 -0.779

TABLE 3.5. RESULTS OF MASS-TRANSFER EXPERIMENT A-NaOH

.

TABLE 3.6.	RESULTS OF	MASS-TRANSFER	EXPERIMENT	A-Ca(OH)2
------------	------------	---------------	------------	-----------

·

Wastewater Co	omposition S	Solution A	
	Conce	entration, mg/L	
<u>cations</u>	<u>initial</u>	<u>after pH adjustment</u>	
NH4	5,000	3,600	(Reported as nitrogen)
Mg ²⁺	365	<10	
Na ⁺	19,000	21,000	
<u>anions</u>			
s0 ²⁻	66,000	5,300	
C1-	27,500	31,500	,
Solution pH	= 11.90		
Temperature ((°C) = 88.2		
pH adjustment	t with Ca(OH)2		
Time (min))	NH3-N (mg/L)	ln (C/C _O)
0 2 4 6 8 10 13 16 19 22 25 30 35 40 45 50 55 60	_	3,600 3,450 3,400 3,250 3,100 3,050 2,950 2,800 2,650 2,550 2,500 2,500 2,200 2,200 2,000 1,900 1,750 1,650 1,600	0 -0.043 -0.057 -0.102 -0.150 -0.166 -0.199 -0.251 -0.306 -0.345 -0.365 -0.448 -0.492 -0.588 -0.639 -0.721 -0.780 -0.811

Contraction in concernment of the local data and th				
Wastewater Compo	sition	Solution B		
	Conc	entration, mg/L		
<u>cations</u>	<u>initial</u>	after pH adjustment		
NH4	5,000	4,150	(Reported	as nitrogen)
Mg ²⁺	184	<10		
Na ⁺	17,500	24,000		
<u>anions</u>				
so ₄ ²⁻	8,200	6,500		
C1 ⁻	28,750	29,500		
Solution pH	= 11.93			
Temperature (°C)	= 88.6			÷
pH adjustment wi	th NaOH			
Time (min)		NH3-N (mg/L)		$ln (C/C_0)$
0 2 4 6 8 10 13 16 19 22 25 33 38 43 48 53 58		4,150 3,850 3,650 3,550 3,450 3,350 3,250 3,100 2,900 2,700 2,600 2,200 2,000 1,850 1,650 1,500 1,300	.	0 -0.0750 -0.128 -0.156 -0.185 -0.214 -0.244 -0.292 -0.358 -0.430 -0.468 -0.635 -0.730 -0.808 -0.922 -1.018 -1.161

TABLE 3.7. RESULTS OF MASS-TRANSFER EXPERIMENT B-NaOH

	• • •		
Wastewater Composi	tion Solu	tion B	
	Conc	entration, mg/L	
<u>cations</u>	<u>initial</u>	after pH adjustmen	<u>t</u>
NH4	5,000	3,450	(Reported as nitrogen)
Mg ²⁺ .	184	<10	
Na ⁺	17,500	15,000	
anions			
s0 ₄ ²⁻	8,200	<4	
C1 ⁻	28,750	29,500	
Solution pH	= 11.63		
Temperature (°C)	= 89		
pH adjustment with	Ca(OH)2		
Time (min)		NH3-N (mg/L)	ln (C/C _o)
0 2 4 6 8 10 13 16 19 22 25 30 35 40 45 50 55 60		3,450 3,200 3,150 3,100 2,950 2,850 2,750 2,650 2,500 2,250 2,100 2,050 1,950 1,800 1,650 1,550 1,500 1,400	0 -0.0753 -0.0910 -0.107 -0.157 -0.191 -0.227 -0.264 -0.322 -0.427 -0.496 -0.521 -0.571 -0.651 -0.738 -0.800 -0.833 -0.902

TABLE 3.8. RESULTS OF MASS-TRANSFER EXPERIMENT B-Ca(OH)2

Wastewater Composit	<u>tion</u> Solu	tion C		
	Conc	entration, mg/L		
<u>cations</u>	<u>initial</u>	after pH adj	ustment	
NH4	5,000	3,950	(Reported	as nitrogen)
Mg ²⁺	193	<10		
Na ⁺	17,700	24,000		
anions				
s0 ²⁻	24,000	25,0 00		
C1 ⁻	20,300	97 5		
Solution pH	= 12.13			
Temperature (°C)	= 88.7			
pH adjustment with	NaOH			
Time (min)		NH3-N (mg/L)		ln (C/C ₀)
0 2 4 6 8 10 13 16 19 22 25 30 35 40 45 50 55 60		3,950 3,650 3,600 3,450 3,250 3,150 2,900 2,800 2,500 2,500 2,550 2,000 1,800 1,650 1,550 1,400		0 -0.0789 -0.0928 -0.135 -0.195 -0.226 -0.226 -0.309 -0.344 -0.457 -0.438 -0.541 -0.656 -0.681 -0.786 -0.873 -0.936 -1.037

TABLE 3.9. RESULTS OF MASS-TRANSFER EXPERIMENT C-NaOH

.

•

.

			•
Wastewater Composi	<u>tion</u> Soluti	on C	
	Concer	tration, mg/L	
cations	<u>initial</u>	<u>after pH_adjus</u>	tment
NH4	5,000	3,250	(Reported as nitrogen)
Mg ²⁺	181	<10	
Na ⁺	13,000	14,000	
anions			
so ₄ ²⁻	24,000	5,500	
C1 ⁻	17,750	19,500	
Solution pH	= 12.18		
Temperature (°C)	= 88.8		
pH adjustment with	Ca(OH)2		
Time (min)	1	H3-N (mg/L)	ln (C/C ₀)
0 2 4 6 8 10 13 16 19 22 25 30 35 40 45 50 55 60		3,250 2,950 2,750 2,700 2,650 2,500 2,400 2,300 2,200 2,100 1,950 1,800 1,650 1,500 1,500 1,400 1,250 1,200 1,100	0 -0.0968 -0.167 -0.185 -0.204 -0.262 -0.303 -0.346 -0.390 -0.437 -0.511 -0.591 -0.678 -0.773 -0.842 -0.956 -0.996 -1.083

TABLE 3.10. RESULTS OF MASS-TRANSFER EXPERIMENT C-Ca(OH)2

$$p = H C_s$$
(9)

where

p = partial pressure of NH₃-N in atmosphere H = Henry's Law constant.

Therefore Equation 8 can be simplified to the following form:

$$\frac{C}{C_0} = e^{-Kt}$$
(10)

or by calculating the natural logarithm of each side to linearize the equation

$$\ln(C/C_{\rm o}) = -Kt \tag{11}$$

Figures 3.1 through 3.6 show the results plotted according to Equation 11.

It is apparent from Figures 3.1 through 3.6 that the data do not follow a first order rate law across the time span given. However, the curves consist of an initial shoulder followed by a linear portion. The overall mass transfer rate coefficients were determined by applying linear regression to the straight portion of the curve. The straight portion of the curve was generally found to be that portion of the graph that began at a point corresponding to an NH_3 -N concentration of 2500 mg/L and continuing to lower concentrations. The estimated mass transfer rate coefficients are given in Table 3.11.

The nonlinearity of the data can best be explained as experimental limitations. At high NH₃-N concentrations the partial pressure of NH₃-N above the reactors was not necessarily zero due to limitations in the ability to move gas away from the liquid surface. As NH₃-N gas accumulates over the liquid, the equilibrium concentration, C_s , increases. Since the calculations were performed assuming $C_s = 0$, the data were not expected to be linear until the partial pressure exerted by ammonia is zero.



Figure 3.1. Variation of ammonia concentration with time: Wastewater A and NaOH.



Figure 3.2. Variation of ammonia concentration with time: Wastewater A and $Ca(OH)_2$.


Figure 3.3. Variation of ammonia concentration with time: Wastewater B and NaOH.



Figure 3.4. Variation of ammonia concentration with time: Wastewater B and $Ca(OH)_2$.



Figure 3.5. Variation of ammonia concentration with time: Wastewater C and NaOH.



Figure 3.6. Variation of ammonia concentration with time: Wastewater C and Ca(OH)₂.

·

As can be seen in the Table 3.11, the mass transfer rate coefficient does not vary significantly with both solution composition and the base used for pH adjustment. In two of the three cases, however, the mass transfer rate coefficient was higher for the waste stream where pH was adjusted using NaOH. Also, for solutions A and C where the initial $SO_4^{=}$ concentrations were approximately the same, the mass transfer rate coefficients were also comparable. Solution B with the lowest $SO_4^{=}$ concentration appeared to have the highest mass transfer rate coefficient. However, the calculation of Henry's Law constant (see Table 3.4) indicates that the highest ammonia solubility is expected to occur in the solution with the lowest $SO_4^{=}$ concentration when NaOH was used for pH adjustment.

The mass transfer rate coefficients for solutions A and B were approximately the same when pH was adjusted using $Ca(OH)_2$. The relatively low K values found in these two cases indicates that addition of NaOH may have a slight advantage.

No correlation between ionic strength and mass transfer rate coefficient can be found.

3.4 SUMMARY

Analyses of the estimated Henry's Law constant and changes in solubilities of ammonia (as given in Table 3.4, page 14) indicate that addition of a caustic, compared with slaked lime, can result in higher Henry's Law constant and lower ammonia solubilities for the three waste streams considered. These effects can be attributed to the relatively high ionic strength that occurred in wastewaters when pH was adjusted with NaOH. Between solutions B and C, where the sulfate concentration was varied without changing the solution strength (total number of moles), no significant difference in Henry's Law constant or solubility could be seen for either of the two pH adjustment methods. The highest Henry's Law constant and corresponding lowest ammonia solubility were observed in solution A, which has the highest molal strength.

Experimental studies to determine the effects of dissolved species and pH adjustment method on the mass transfer rate coefficient (K) indicate that those effects are relatively low and the maximum changes in mass transfer rate

	pH Adjustment w	vith NaOH	pH Adjustment with Ca(OH);		
Solution	Ionic Strengtha (g ion/L)	K ^b (min-1)	Ionic Strengtha (g ion/L)	K ^b (min−1)	
A	1.546	0.0165	1.034	0.0132	
В	1.111	0.0199	0.840	0.0138	
C	1.343	0.0158	0.706	0.0170	

TABLE 3.11. MASS TRANSFER RATE COEFFICIENTS FOR AMMONIA IN DIFFERENT WASTE STREAMS

• • 1

· •

^a Ionic strength is the summation of I values given in Table 3.4 for a given solution.

^b K is mass transfer rate coefficient.

coefficient do not exceed 25 percent. In two of the three different solutions, however, the mass transfer rate coefficients were higher for the waste stream where pH was adjusted using caustic. For solutions with approximately the same $SO_4^{=}$ concentration but different molal strength, the mass transfer rate coefficients were comparable when NaOH was used as the pH adjustment method. For Ca(OH)₂, however, the K values were comparable where both the molal strength and $SO_4^{=}$ level were different. The overall analysis of data indicate that, when compared with lime, addition of NaOH can promote ammonia removal for solutions with relatively low $SO_4^{=}$ levels (5,000 mg/L).

4. TASK 2: AMMONIA REMOVAL STUDIES USING STEAM STRIPPING UNIT

4.1 OBJECTIVE AND SCOPE

The purpose of this task was to study the removal of ammonia from synthetic wastewaters using a steam stripping apparatus. A laboratory scale steam stripping unit was designed and constructed. Experiments were conducted using two different synthetic waste streams. The pH of each waste stream was adjusted using NaOH or CaO. Ammonia removal was studied under different pH adjustment methods and different steam to wastewater ratios.

4.2 DESIGN AND CONSTRUCTION OF THE STEAM STRIPPING UNIT

Steam stripping is used to process wastewater containing high concentrations of ammonia, e.g., from steel, petrochemical, fertilizer, organic chemical, and nonferrous metal-manufacturing operations. The cost of steam production is partly offset by the recovery and reuse of ammonia.

Efficiency of ammonia removal by steam stripping is governed by the following factors (Patterson, 1985):

- 1. Proper design of the stripper
- 2. Control of hydraulic flowrates
- 3. Adequate steam
- 4. pH levels of 11 or above
- 5. Temperatures of 200°F or above in the stripper
- 6. Sufficient droplet detainment space.

These factors were taken into consideration during the design of the steam stripping unit.

4.2.1 Characteristics of the Column

4.2.1.1 Flow

Gas transfer can be effected by various devices including tray columns, cross-flow packed columns, and counter current packed columns. Counter current packed columns are generally used for removing ammonia, hydrogen sulfide, and carbon dioxide because of the continuous and thorough contact of the liquid with the gas. Counter current flow also minimizes the thickness of the water layer on the packing, thus enhancing mass transfer. A counter current column was chosen for this study.

4.2.1.2 Column Packing--

Packing is available in different shapes (e.g., saddles, Pall rings, tellerettes), materials (e.g., ceramic, steel, plastic), and sizes (e.g., 1/2 in., 1 in., 2 in.). Packing material suitability is determined by evaluating its operating characteristics and cost. For this high temperature and high pH application, certain plastic materials like Teflon and Kynar (PVDF) were found suitable. Kynar appears to be more cost effective. Kynar has a maximum operating temperature of 302°F and a heat distortion temperature of 250°F. It is also compatible with a large number of chemicals. Hence, Kynar was selected as the packing material.

Packing material shape and size are characterized by packing factor (ft^{-1}) and surface area $(ft^2/ft^3 \text{ of column})$. Larger packings are less expensive on a unit volume basis and allow higher wastewater loading rates. Smaller packings provide larger mass transfer rate coefficients and hence smaller column heights. Therefore, for a high degree of removal, smaller packings can be more economical. It is recommended that the column diameter should be at least 8 to 10 times the nominal size of the packing in order to avoid poor liquid distribution due to wall effects. For a column of 7 in. diameter, 5/8-in. Pall rings (which have a packing factor of 97 ft⁻¹ and a surface area of 104 ft²/ft³) can be used. This size of Pall ring has a smaller surface area than 1/2-in. Berl saddles (surface area = 142 ft²/ft³), but a greater capacity (packing factor for 1/2 in. Berl saddles is 140 ft⁻¹). 4.2.1.3 Column Material--

The column material should be able to stand high temperatures and pH conditions. Kynar, Teflon, crystal glass, and stainless steel are some of the materials that can be used for stripping column. Glass was chosen as the column material because (a) it is economical and (b) the flow characteristics and scaling can be observed from outside.

4.2.2 Design of the Stripping Unit

The design of the counter current packed bed column involved the following steps:

- 1. Determination of the Henry's Law constant for NH_3 at the temperature of the column (100°C)
- Determination of the steam-wastewater ratio and the NTU (number of transfer units)
- Calculation of the steam mass flowrate (lb/ft²-hr) and a suitable column diameter
- 4. Calculation of the HTU (height of a transfer unit), and hence the height of the packing.

The column was designed for a temperature of 100 °C. The wastewater was adjusted to a pH of 11 or more. Raising the pH to 11 transforms most of the NH_4^+ to NH_3 .

4.2.2.1 Henry's Law Constant--

Henry's constants are strongly influenced by temperature. Most available data lists the Henry's constant (H) for ammonia to be 0.76 atm L/moles at 20°C. If the enthalpy change caused by dissolution of a contaminant in water is considered independent of temperature, the relation

$$\log H = \frac{-H^{0}}{RT} + K$$
(12)

can be used to determine H at 100°C (Kavanaugh and Trussell, 1980). Here R = universal gas constant = 1.987 kcal/kmol-°K; T = temperature (°K); H^o = change in enthalpy due to dissolution; and K = constant. For ammonia, H^o = 3.754 x 10³ kcal/kmol and K = 6.31. At 100°C (373°K) for ammonia, H is calculated to be 17.6 atm.

4.2.2.2 Number of Transfer Units--

The height of the column packing, Z = (HTU)x(NTU), where HTU is the height of a transfer unit and NTU is the number of transfer units. NTU is equivalent

to the number of theoretical trays required to bring about a certain degree of removal. NTU also depends on the stripping factor, R, which is given by the following equation:

$$R = H(G/L)$$
(13)

Here, G = mass velocity of steam (moles/ft²-sec), and L = mass velocity of wastewater (moles/ft²-sec). The dependence of NTU on removal efficiency and stripping factor is plotted by Treybal (1980). This graph (Figure 4.1) shows very little increase in efficiency for R > 5. For 99.9 percent removal at R = 5, the NTU = 8. These values of R and NTU were taken in the design.

The steam-wastewater ratio can then be calculated from R = 5 and H = 17.6 atm L/moles. Hence, G/L = 0.284 x (molar ratio)

= 0.284 x
$$\frac{\text{mol. wt. NH}_3}{\text{mol. wt. H}_20}$$
 = 0.284 x (17/18)
= 0.27 (mass ratio)

4.2.2.3 Diameter of the Column--

In a packed column, for a given liquid loading rate, gas pressure drop increases approximately as the square of the gas velocity. At very high gas flowrates, flooding may occur. This can be characterized by a rapid increase in gas pressure drops. Packed columns are usually designed to operate well below flooding conditions (about 40 to 50 percent). A generalized pressure drop correlation for a packed column is shown by McCabe and Smith (1984) in (Figure 4.2). Here the abscissa is

$$(L/G) \times (d_g/d_l)^{0.5}$$

and the ordinate is

$$\frac{G^2 F_p (62.3/d_L) \mu_L^{0.2}}{g_c d_L d_g}$$
(14)

where
$$F^{p}$$
 = packing factor, ft^{-1}
 d_{t} = density of wastewater, lb/ft^{3}
 d_{g} = density of steam, lb/ft^{3}



Figure 4.1. Dependence of NTU on removal efficiency and stripping factor.

(Source: Montgomery, 1985)



Figure 4.2. Generalized correlation for flooding and pressure drop in packed columns.

(Source: McCabe and Smith, 1984)

 μ_{I} = viscosity of wastewater, cP

 $g_c = Newton's-Law proportionality factor, 32.174 ft-lb/lbf-s²$

- \tilde{L} = mass velocity of wastewater, lb/ft^2 -hr
- $G = mass velocity of steam, lb/ft^2-hr.$

For $5/8^{m}$ Pall rings, $F^{p} = 97$. The densities of wastewater (assumed as water) and steam for the column temperature (100°C) are $d_{L} = 59.8$ lb/ft³ and $d_{a} = 0.03731$ lb/ft³. The viscosity of water at 100°C is $\mu_{I} = 0.284$ cP.

The abscissa is, therefore, $(L/G)x(d_q/d_L)^{0.5} = (1/0.27)x(0.03731/59.8) = 0.09$

From the graph, the ordinate for flooding is 0.14.

$$\frac{G^2 F_p}{g_c d_l d_g} \begin{pmatrix} 62.3/d \\ \mu \end{pmatrix} \mu^{0.2}}{g_c d_l d_g} = 0.14$$

$$\frac{G^2 (97) (62.3/59.8) (0.284)}{(32.174) (59.8) (0.03731)} = 0.14$$
Thus, G at flooding = 0.358 lb/ft²-s

 $= 1288 \text{ lb/ft}^2 \text{-hr}$

If the column is operated at 50 percent of flooding, then the designed steam capacity becomes G = (0.5) (1288) = 644 lb/ft²-hr. At this design capacity, the mass velocity of the liquid would be

 $L = 644/0.27 = 2385 \ 1b/ft^2$ -hr.

If a wastewater flowrate of 600 lb/hr is desired, the required crosssectional area of the column is 600/2385 = 0.252 ft². This corresponds to a diameter of 6.8 inches. For this study a column diameter of 7 inches was chosen. Thus, the designed capacity of this 7-inch diameter column is as follows:

Wastewater flowrate = 600 lb/hr = 1.2 gallons per min (gpm) Steam flowrate = 644 x (area of column)

- $= 644 \times 0.252$
- $= 162 \ lb/hr$
- = 72 ft^3/min (cfm)

Steam wastewater ratio = 2.25 lb steam/gallon of wastewater. 4.2.2.4 Height Equivalent to a Transfer Unit--

Often, the values of individual mass transfer rate coefficients vary rapidly with flowrates. Hence, the quantity obtained by dividing each mass transfer rate coefficient by the flowrate is more nearly constant than the coefficient itself (Perry, 1973). This new quantity is called the height of one transfer unit (HTU). From Perry (1973),

$$HTU = (1/a) \times (L/\mu_{L})^{n} \times [\mu_{L}/ (d_{L}D_{L})]^{0.5}$$
(14)

For 5/8-inch Pall rings, a and n are approximately 150 and 0.28 respectively. Here μ_{l} is given in lb/ft-hr. Thus, μ_{l} = 0.284 cP, = 0.687 lb/ft-hr.

D_L is the diffusion coefficient of NH₃ in the wastewater expressed in ft²/hr. For the NH₃-H₂O system at 25°C, D = 2.0 x 10⁻⁵ cm²/s. The value at 100°C is calculated by using the relationship D μ/T = constant. Thus, D at 100°C is 7.651 x 10⁻⁵ cm²/s or 2.965 x 10⁻⁴ ft²/hr.

Using this value of D, HTU = 0.39 ft. This gives a packing depth, Z = $(NTU) \times (HTU) = 8 \times 0.39 \stackrel{L}{=} 3.12$ ft. Thus, the designed column is 7 inches in diameter and has a 3 foot packing depth.

The column is made of glass to facilitate observing the flow characteristics and solid deposition/scaling in the column. Mechanical strength is provided by four external steel bars. Liquid distribution is by means of a 4armed liquid stream device. About 6 inches of space is provided above and below the packing. Two thermocouples are installed to monitor temperatures near the top and bottom of the packing. A heat exchanger is provided to preheat the wastewater before entering the column.

4.2.3 Scale-Up

Columns with larger diameters will be required for increased wastewater flowrates. If the same packing is used, the variation of column diameter with loading rate is given in Table 4.1. The calculation procedure given in the previous section was used and the stripping factor (R) was assumed to be the same. The 5-fold increase in wastewater flowrate (1.2 to 6 gpm) resulted in an approximately 2-fold diameter increase.

Larger sized packing may be used for higher capacity, i.e. smaller diameters for a given flowrate as seen in Table 4.2 and Figure 4.3. The ratio of diameter of column to size of parking should be maintained at 10. Higher capacity is slightly offset however, by the increase in height of packing. For larger columns, a 1-inch packing may be the most efficient.

Table 4.3 and Figure 4.4 show the effect of different stripping factors on column size. With increasing R, the diameter increases. The height of the column however decreases.

Even though the general procedure is the same for design of commercialscale columns, pilot studies are often necessary for establishing scale-up factors and estimating costs.

4.3 EXPERIMENTAL PROCEDURES

This section describes the methods used to operate the bench scale steam stripping unit used in Task II of this study. The design and construction of the steam stripping column is discussed in Section 4.2. The system was designed to pump a high pH synthetic wastewater influent to the top of the packing material in the column casing. As shown in Figure 4.5, the wastewater flows down over the packing material and exits through the effluent line at the column base. Steam is injected into the column at the base of the packing material. As the wastewater passes through the jet of steam, it is heated to 100°C. Flowrates for the steam and/or the influent wastewater are varied to determine the variation of ammonia removal efficiency. Wastewater was pumped to the stripping unit using 1/8 hp MAC: variable flowrate pump. The flowrate for the influent was adjusted using valves and monitored using a Brooks! flow meter. The steam flowrate was measured by condensing steam entering the column and measuring changes in the flowrate of column effluent. The steam flow entering the column was controlled using a valve/orifice unit (Figure 4.5) and monitored using two pressure gauges located on either side of the orifice. The column hood vent was sealed to prevent steam from escaping the column. Iced tap water was used as influent to ensure complete condensation of the

<u>Wastewater Flowrate</u> gpm) (lb/hr)		Column Diameter (inches)
1.2	600	7
3	1500	11
4	2000	12
б	3000	15
10	5000	20
20	10000	28

TABLE 4.1. COLUMN DIAMETER FOR 1/2-INCH PACKING AND R=5

Wastewater Flowrate	Diameter of Column (in.)			Height of Column (ft)		
(1b/hr)	Pac	cking Siz	e	Packing Size		
	5/8 in.	1 in.	2 in.	5/8 in.	1 in.	2 in.
600	7	-	•	3.0	-	.
1500	11	-	-	3.0	3.0	3.58
2000	12	11	-	3.0	-3-0	3.58
3000	15	13	-	3.0	3.0	3.58
5000	20	17	-	3.0	3.0	3.58
10000	28	24	21	3.0	3.0	3.58

TABLE 4.2. EFFECT OF PACKING SIZE

·



Figure 4.3. Flowrates and packing size.

Wastewater Flowrate (1b/hr)	<u>Diame</u> Si	<u>ter of C</u> tripping	<u>column (in.)</u> Factor	<u>Height of column (ft)</u> Stripping Factor		
	R=1	R≈3 R=5		R=1	R=3 R=	
600	6	7	7	4.3	, 3.5 8	3.0
1500	7	9	11	4.3	3.58	3.0
2000	8	11	12	4.3	3.58	3.0
3000	9	13	15	4.3	3.58	3.0
50 00	12	17	20	4.3	3.58	3.0
10000	17	24	28	4.3	3.58	3.0

 TABLE 4.3.
 DIMENSIONS OF THE COLUMN FOR VARIOUS VALUES

 OF R FOR 5/8-INCH PACKING

.



Figure 4.4. Stripping factors and height of column.

steam. The effluent flowrate was verified by direct measurement of flow volume per unit time prior to turning on the steam. Three different pressure settings were used to supply steam to the column. The column effluent flowrate was compared to the steam pressure. The calibration curve was derived by plotting changes in effluent flow against the corresponding pressure gauge settings (see Figure 4.6).

A total of nine steam stripping experiments were performed to compare two synthetic wastewater compositions and to compare the use of NaOH or CaO (lime) for pH adjustment of the solutions. The two wastewater compositions used for this study are as follows:

<u>Chemical Species</u>	Concentration in <u>Wastewater B (mg/l)</u>	Concentration in Wastewater C (mg/l)		
NH3-N	5,000	5,000		
Mg⁺⁺	200	200		
Na⁺	11,939	11,939		
S0 ₄ ⁼	5,000	20,000		
C1 ⁻	28,000	16,906		

Solutions were prepared in 50- or 100-gallon batches, and actual species concentrations were verified by analysis.

In each experiment the influent was prepared from Baker Analyzed Reagents and dissolved in tap water. Then the pH was adjusted to approximately 12 with either 10N NaOH or bulk dry CaO and the solution was mixed gently. Wastewater was pumped to the stripping column by a variable flowrate pump that could be adjusted to set a desired flowrate. Steam was turned on and the pressure gauges were adjusted to steam flowrate at the desired flow. When the column conditions had equilibrated, as indicated by the effluent and column temperatures, effluent samples were taken at regular time intervals and measured for ammonia concentration. Samples were also taken from the influent for initial ammonia concentration, pH, and other dissolved species both before and after pH adjustment. Wastewater influent and effluent temperatures and steam temperature were also recorded.



- T = Thermocouple
- P = Pressure Gauge
- V = Valve



Figure 4.6. Calibration of steam flowrate across the orifice. (Note: Each data point is an average of 3 or more flowrate measurements.)

4.4 RESULTS AND DISCUSSION

The experimental results of the steam stripping of ammonia are given in Tables 4.4 through 4.12. Since the maximum steam flowrate attainable from the system was 1 lb/min, the wastewater flowrate was maintained at or below 2 L/min (0.53 gal/min). The preliminary studies with solution B and pH adjustment with NaOH (A-NaOH system) indicated that if the steam to wastewater ratio is 1.3 lb/gal, the removal of ammonia from a stream with 5,200 ppm of NH₃-N was as low as 93 percent. Increased steam-wastewater ratios resulted in higher removals (Tables 4.4 and 4.5).

Addition of CaO to solution A resulted in 12°C increase in temperature due to the exothermic nature of CaO dissolution (Tables 4.6 and 4.7). Even with the increased influent temperatures, the ammonia removal efficiency was over 3 percent less for B-CaO system when compared to that of B-NaOH system. Results given in Table 3.4 on Henry's Law constant and the mass transfer rate coefficient for B-NaOH (0.0199 min⁻¹) is higher than that for the B-Ca(OH)₂ system (0.0138 min⁻¹). The solubility of NH₃ in the B-NaOH system is lower than that for the B-Ca(OH)₂ system (Table 3.4). These data indicate that pH adjustment with caustic can improve the ammonia removal slightly over the lime in waste streams with relatively low SO₄⁻⁻ levels (5,000 mg/L).

The experiments conducted with solution C showed that the ammonia removal was slightly higher for those where pH was adjusted with CaO than those where it was adjusted with NaOH (Tables 4.8, 4.9, 4.11, and 4.12). However, these differences were smaller than those observed for solution B. It is important to note that the differences in mass transfer rate coefficient followed a similar trend (Table 3.11). The K value for the C-Ca(OH)₂ system was slightly higher than that for the C-NaOH system. In contrast, the Henry's Law constant was slightly higher for the C-NaOH system (8.3 x 10^{-4}) when compared to the C-Ca(OH)₂ system.

Comparison of data in Tables 4.8 and 4.10 indicate that wastewater preheating can also improve the ammonia removal efficiency. The increase in influent wastewater temperature by 19°C resulted in a 2 percentile increase in the ammonia removal efficiency. More than 99.9 percent removal can be achieved by increasing the steam-wastewater ratios up to 3.8 lb/gal.

TABLE 4.4. RESULTS FOR PILOT RUN NO. P-1 FOR WASTEWATER B and NaOH

•

	Wastewater	Cha	<u>racteristic</u>	<u>s</u>	
	Concentration, mg/L				
<u>Species</u>	Before pH adjus	tme	nt	After pH adjustment	
NH4	5,600			5,200	
S04	11,200			10,900	
c1 -	35,200			32,500	
Mg++	201			<10	
Na+	16,000			26,000	
Ca++	40			<10	
<u>Test Conditi</u>	ons				
wastewater f steam flow r steam temper wastewater i wastewater i base used to	low rate ate ature nfluent temperature ffluent temperature nfluent pH adjust pH		2 L/min 1 1b/min 114°C 26°C 101°C 12.5 NaOH		

Test Results of Column Effluent Analysis

Time <u>(min)</u>	Effluent NH3-N Concentration (mg/L)	Percent Removal
5	79	98.5
10	32	99.4
15	7.8	9 9.8
20	7.4	99.9
25	102	98.0

average percent removal of ammonia = 99.1 steam to wastewater flow rate ratio = 1.9 lb steam/1 gallon wastewater

TABLE 4.5. RESULTS FOR PILOT RUN NO. P-2 FOR WASTEWATER B and NaOH

	Concentrat	Concentration, mg/L			
<u>Species</u>	Before pH adjustment	After pH adjustment			
NH4	5,600	5,200			
S04	11,200	10,900			
c1 ⁻	35,200	32,500			
Mg++	201	<10			
Na+	16,000	26,000			
Ca++	40	<10			

Test Conditions

wastewater flow rate	= 2 L/min
steam flow rate	= 0.7 lb/min
steam temperature	= 114°C
wastewater influent tem	nperature = 26°C
wastewater effluent tem	perature = 101°C
wastewater influent pH	= 12.5
base used to adjust pH	= NaOH

Test Results of Column Effluent Analysis

Time (min)	Effluent NH3-N Concentration (mg/L)	Percent Removal
5	255	95.1
10	330	93.7
15	380	92.7
20	420	91.9
25	400	92.3

average percent removal of ammonia = 93.1 steam to wastewater flow rate ratio = 1.3 lb steam/1 gallon wastewater

TABLE 4.6. RESULTS FOR PILOT RUN NO. P-3 FOR WASTEWATER B and CaO

	<u>stics</u>	
	Concentrat	ion, mg/L
Species	Before pH adjustment	<u>After pH adjustment</u>
NH4	6,600	5,100
S0 4	6,300	2,100
C1 ⁻	38,500	32,500
Mg++	271	<10
Na ⁺	20,000	15,000
Ca++	30	6,000

Test Conditions

•

.

wastewater flow rai	e	=	2 L/min
steam flow rate		=	1 lbs/min
steam temperature		=	115°C
wastewater influent	: temperature	=	38°C
wastewater efflueni	temperature	=	101°C
wastewater influent	; pH	=	11.72
base used to adjust	: pH	=	CaO
	•		

.

Test Results of Column Effluent Analysis

Time	Effluent NH3-N Concentration	
<u>(min)</u>	(mg/L)	Percent Removal
17	288	94.3
22	270	94.7
27	260	94.9
32	200	96.1
37	188	96.3

average percent removal of ammonia = 95.26 steam to wastewater flow rate ratio = 1.9 lb steam/1 gallon wastewater

TABLE 4.7. RESULTS FOR PILOT RUN NO. P-4 FOR WASTEWATER B and CaO

.

	Wastewater Characteri	stics
Species	Concentrat	ion, mg/L
	Before pH adjustment	After pH adjustment
NH4	6,600	5,000
S0 4	6,300	2,100
C1 ⁻	38,500	32,500
Mg++	271	<10
Na+	20,000	15,000
Ca++	30	6,0 00

Test Conditions

•

wastewater flow rate	=	1 L/min
steam flow rate	=	l lbs/min
steam temperature	=	115°C
wastewater influent temperature	=	39°C
wastewater effluent temperature	=	101°C
wastewater influent pH	=	11.72
base used to adjust pH	=	CaO

Test Results of Column Effluent Analysis

Time <u>(min)</u>	Effluent NH3-N Concentration (mg/L)	Percent Removal
2	16	99.7
5	13	99.7
8	13	99.7
11	13	99.7
14	12	99.8

average percent removal of ammonia = 99.7 steam to wastewater flow rate ratio = 3.8 lb steam/1 gallon wastewater

54

TABLE 4.8.RESULTS FOR PILOT RUN NO. P-5 FOR
WASTEWATER C and NaOH

	<u>Wastewater Characteri</u>	stics
	Concentrat	ion, mg/L
Species	Before pH adjustment	After pH adjustment
NH4	4,850	4,750
S0 4	39,000	41,000
C1 ⁻	20,500	21,500
Mg++	223	<10
Na ⁺	14,300	30,000
Ca++	40	30

Test Conditions

wastewater flow rate	E	2 L/min
steam flow rate	=	1 1bs/min
steam temperature	=	115°C
wastewater influent temperat	ure =	25°C
wastewater effluent temperat	ure =	101°C
wastewater influent pH	=	11.67
base used to adjust pH	E	NaOH

Test Results of Column Effluent Analysis

	Effluent NH3-N	
Time <u>(min)</u>	Concentration (mg/L)	Percent Removal
5	198	95.8
10	175	96.3
15	121	97.4
20	125	97.4
25	126	97.4

average percent removal of ammonia = 96.9 steam to wastewater flow rate ratio = 1.9 lb steam/1 gallon wastewater

55

•

TABLE 4.9. RESULTS FOR PILOT RUN NO. P-6 FOR WASTEWATER C and NaOH

.

.

	Wastewater Character	istics
	Concentra	ation, mg/L
Species	Before pH adjustment	After pH adjustment
NH4	4,850	4,700
S04	39,000	41,000
cı ⁻	20,500	21,500
Mg++	223	<10
Na+	14,300	30,000
Ca++	· 40	30
<u>Test Conditi</u>	ons	
wastewater f steam flow r steam temper wastewater i wastewater i base used to	The set of	nin s/min C 7
	Test Results of Column Effl	uent Analysis
Time <u>(min)</u>	Effluent NH3-N Concentration (mg/L)	Percent Removal
5	4.4	99.91
10	4.5	99.90
15	4.2	99.91
20	4.2	99.91
25	3.9	99.92

average percent removal of ammonia = 99.9 steam to wastewater flow rate ratio = 3.8 lb steam/1 gallon wastewater

56

.

. -

TABLE 4.10. RESULTS FOR PILOT RUN NO. P-7 FOR WASTEWATER C and NaOH

.

	Concentrat	tion, mg/L
<u>Species</u>	Before pH adjustment	<u>After pH adjustment</u>
NH4		3,950
S0 [‡]	30,000	8,800
c 1 ⁻	18,500	18,500
Mg++	186	<10
Na+	11,800	14,000
Ca++	30	1,700
Test Conditi	ons	,
wastewater e wastewater i	nfluent pH = 10.51	
base used to	adjust pH = CaO	
base used to	adjust pH = CaO Test Results of Column_Efflu	ent Analysis
base used to	adjust pH = CaO <u>Test Results of Column Efflu</u> Effluent NH2-N	ent Analysis
base used to	adjust pH = CaO <u>Test Results of Column Efflu</u> Effluent NH ₃ -N Concentration	ent Analysis
Dase used to Time <u>(min)</u>	adjust pH = CaO <u>Test Results of Column Efflu</u> Effluent NH3-N Concentration <u>(mg/L)</u>	<u>ent Analysis</u> <u>Percent Removal</u>
Dase used to Time <u>(min)</u> 5	adjust pH = CaO <u>Test Results of Column Efflu</u> Effluent NH ₃ -N Concentration <u>(mg/L)</u> 79	<u>ent Analysis</u> <u>Percent Removal</u> 98.0
Time (min) 5 10	adjust pH = CaO <u>Test Results of Column Efflu</u> Effluent NH3-N Concentration <u>(mg/L)</u> 79 80	<u>ent Analysis</u> <u>Percent Removal</u> 98.0 98.0
Time (min) 5 10 15	adjust pH = CaO <u>Test Results of Column Efflu</u> Effluent NH3-N Concentration <u>(mg/L)</u> 79 80 80	<u>Percent Removal</u> 98.0 98.0 98.0 98.0
Time (min) 5 10 15 20	adjust pH = CaO <u>Test Results of Column Efflu</u> Effluent NH3-N Concentration <u>(mq/L)</u> 79 80 80 2	<u>Percent Removal</u> 98.0 98.0 98.0 98.0 99.95
Time (min) 5 10 15 20 25	adjust pH = CaO <u>Test Results of Column Efflu</u> Effluent NH3-N Concentration (mg/L) 79 80 80 2 2 2	<u>Percent Remova</u> 98.0 98.0 98.0 99.95 99.95

.

.

TABLE 4.11.RESULTS FOR PILOT RUN NO. P-8 FOR
WASTEWATER C and CaO

	Wastewater Characteri	stics
	Concentrat	tion, mg/L
<u>Species</u>	Before pH adjustment	After pH adjustment
NH4		3,950
S04	30,000	8,800
c1 ⁻	18,500	18,500
Mg++	186	<10
Na+	11,800	14,000
Ca++	30	1,700

Test Conditions

wastewater flow rate	2	=	2 L/min
steam flow rate		=	1 lbs/min
steam temperature		=	115°C
wastewater influent	temperature	=	39°Ç
wastewater effluent	temperature	=	101°C
wastewater influent	рН	=	.11.91
base used to adjust	рН	=	CaO

Test Results of Column Effluent Analysis

Time	Effluent NH3-N Concentration	
<u>(min)</u>	(mg/L)	Percent Removal
5	87	97.8
10	91	97.7
15	90	97.7
20	92	97.7
25	92	97.7

average percent removal of ammonia = 97.7 steam to wastewater flow rate ratio = 1.9 lb steam/1 gallon wastewater

TABLE 4.12.RESULTS FOR PILOT RUN NO. P-9 FOR
WASTEWATER C and CaO

Species	Concentration, mg/L			
	Before pH adjustment	After pH adjustment		
NH4		3,8 25		
S04	30,000	8,800		
c1_	18,500	18,500		
Mg++	186	<10		
Na+	11,800	14,000		
Ca++	30	1,700		

wastewater flow rate = 1 L/min steam flow rate = 1 lbs/min steam temperature = 115°C wastewater influent temperature = 39°C wastewater effluent temperature = 101°C

wastewater ettluent	temperature	=	101-C
wastewater influent	рН	=	11.91
base used to adjust	рH	=	Ca0

Test Results of Column Effluent Analysis

Time (min)	Effluent NH3-N Concentration (mg/L)	Percent Removal		
5	2.2	99.94		
10	1.5	99.96		
15	1.3	99.97		
20	1.3	99.9 7		
25	1.1	99.97		

average percent removal of ammonia = 99.96steam to wastewater flow rate ratio = 3.8 lb steam/1 gallon wastewater

4.5 SUMMARY AND CONCLUSIONS

The results of the steam stripping study are summarized in Table 4.13. Data show that when the steam-wastewater ratios are low (1.3 lb/gal), the ammonia removal efficiency was as low as 93 percent. By increasing steamwastewater ratios to 3.8 lb/gal, removals of over 99.9 percent have been observed. The removal efficiency in one test study was improved by 2 percentile points when the temperature of the influent waste stream was raised by about 20°C. One of the advantages of using lime is its ability to raise the wastewater temperature during pH adjustment because hydration of lime is an exothermic process.

For wastewater with low initial $SO_4^{=}$ level (5,000 mg/L), ammonia removal was 3 percent higher when pH was adjusted with caustic rather than lime. These observations are in agreement with the trends predicted from the estimated Henry's Law constant and mass transfer rate coefficient. In the experiments conducted with wastewaters using higher initial $SO_4^{=}$ levels (20,000 mg/L), ammonia removal was slightly higher when pH was adjusted with lime instead of caustic. These observations are in agreement with the conclusions reached from the corresponding mass transfer rate studies that did not agree with the theoretical estimates of solubilities based on the Henry's Law constant.

In summary, over 99.9 percent removal of ammonia can be achieved by introducing a high steam-wastewater ratio such as 3.8 lb/gallon. Variation of chemical constituent such as SO_4^{-} and the molal strength have only a little effect on net NH_3 removal. Higher removal efficiencies can be achieved by preheating wastewaters and operating the stripping tower at high temperatures by increasing the steam-wastewater ratios.

Wastewater		Wastewate	<u>r Temp. °C</u>				
	pH Adjustment Method	Column Influent	Column Effluent	Steam to Wastewater Ratio Ib/gallon	<u>NH3-N con</u> Influent	Effluent	Average NH3 Removal, %
B (10w SO4)	NaOH	26	101	1.9	5,200	32-102	99.1
	NaOH	26	101	1.3	5,200	255-420	93.1
	Ca0	38	101	1.9	5,100	188-2 88	95.3
	CaO	39	101	3.8	5,000	12-16	99.7
C (high SO4)	NaOH	26	101	1.9	4,750	121-198	96.9
	NaOH	26	101	3.8	4,700	3.9-4.5	99.91
	NaOH	47	101	1.9	3,950	2.0-80	98.8
	Ca0	39	101	1.9	3,950	87-92	97.7
	Ca0	39 [°]	101	3.8	3,825	1.1-2.2	99.96

TABLE 4.13. SUMMARY RESULTS OF LABORATORY STUDY ON STEAM STRIPPING
5. ENGINEERING COST ESTIMATES

5.1 OBJECTIVE AND SCOPE

The physical and chemical characteristics of waste streams, from 9 nonferrous metals processing plants, containing high levels of ammonia are given in Table 5.1. The waste characteristics varied significantly from one plant to the other; establishing one stream with "typical characteristics for high-strength ammonia wastewater" was not seem practical. Consequently four waste streams were selected to represent the whole range of ammonia wastewaters. These are Plants 1, 2, 3, and 5. The distribution of chemical species after addition of the base was estimated by employing the geochemical equilibrium and reaction path models EQ3/EQ6 (Wolery, 1979, 1983, 1987). The wastewater characteristics used for the input of EQ3/EQ6 are listed in Table 5.2. Data on the quantity of alkali, either lime or sodium hydroxide, needed to raise the pH of metal winning wastewaters to 11.5 was generated. High pH favors the formation of ammonia, NH₃, which can be stripped from aqueous solutions. The program showed that alkali addition would produce precipitate which must be removed before stripping.

In this task the costs of a number of common wastewater treatment unit processes were investigated. Estimates of the costs for chemical addition, sludge removal, and thickening were made using the wastewater characteristics of Plants 1, 2, 3, and 5. Included in these estimates were costs for mixing facilities, chemicals, and sludge removal, concentrations, handling, and transport. Not included were costs for chemical storage facilities or buildings, land, or costs for disposal of sludge--all of which are likely to vary considerably from site to site. These cost values were generated for a variety of wastewater flowrates.

Chemical Species	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6	Plant 7	Plant 8	Plant 9
MH3	1,000-6,000	5,300-11,000	2,300	4,300	6,500-13,000	13,000-16,000	2,800	3400	22,000
Ca	18,000	21	9,600	_b	10-15	500	NR ^C	NR	MR
C1	1,300	>19,000	45,000	-	3,700-19,000	66,000	NR	16,000	150
F	55,000	2.2	-	5,600	2	-	-	42	30,000
Hg	1,300	395	21	-	150-180		NR	NR	NR
Na	810	21,000	16,000	56	13,000-20,000	NR	NR	NR	NR
50 ₄	21,000	34,000	1,000-2,500	130	400-4,800	-	NR	170	-
co3	NR	NR	NR	MR	NR .	NR	NR	NR	36,000
56	⊲0.003	0.14	NR	MR	NR	NR	NR	NR	NR
As	0.47	0.0037	NR	NR	NR	NR	NR	NR	NR
Be	550	<0.02	NR	NR	NA	NR	NR	NR	NR
Cđ	0.23	40.01	NR	NR	NR	NR	NR	NR	NR
Cr	13	⊲0.10	NR	NR	NR	NR	NR	NR	NR
Cu	13	0.56	NR '	NR	NR	NR	NR	NR	RM
CN"	21	0.036	NR	NR	NR	NR	NR	NR	NR

TABLE 5.1. CHEMICAL AND PHYSICAL CHARACTERISTICS OF METAL PROCESSING WASTEWATERS CONTAINING AMMONIA: CONCENTRATION IN mg/L^a

Chemical Species	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6	Plant 7	Plant 8	Plant 9
РЬ	2.3	18.0	NR	NR	NR	NR	NR	MR	NR
Hg	⊲0.0002	0.0091	NR	NR	NR	NR	NA	NR	NR
Ni	3.9	1.2	NR	NR	NR	NR	NR	NR	NR
Se	⊲0.003	0.08	NR	NR	NA .	NR	NR	NR	NR
Te	⊲0.002	0.081	NR	NR	NA	NR	NR	NR	NR
Zn	4,1	⊲0.1	NR	NR	NR	NR	NR	NR	NR
A1	69	2.4	NR	NR	NR	NR	NR	MR	NR
Ba	3.3	0.15	NR	NR	MR	NR	NR	ĦR	NR
8	29	27	NR	NR	NR	NR	NR	NA	NR
Co	0.23	18	NR	NR	NR	NR	NR	NR	ĦR
fe	630	2.3	NR	NR	NR	NR	NR	NR	NR
Hn	8.1	0.21	NR	NR	NR	NR	NR	MR	NR
Ho	0.53	44	NR	NR	NR	NR	NR	MR	MR
TS	150,000	170,000	93,000	4,200	47,000-150,00	0 110,000-120,000	NR	46,000	NR
TOS	20,000	140,000	NR .	3,800	38,000-140,00	0 -	NR	44,600	15,00

TABLE 5.1. (continued)

.

.

٠

.

.

-

•

Chemical Species	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6	Plant 7	Plant 8	Plant 9
TSS	130,000	230	2,300	34	180-280	300-400	40-60	82	110
рН ^đ	9.28-11.2	3.0	10.	8.0	1.0-2.0	8.4-8.8	0.8-1.2	NR	9.75

TABLE 5.1. (continued)

.

•

.

All the values are in mg/L except pH.
 b -, Negligible.
 C NR, not reported.
 d Standard pH wnits.

Chemica]		Concentration,	mg/L	
Species	Plant 1	Plant 2	Plant 3	Plant 5
Cr	13	-	-	-
Cu	13	-	-	-
Pb	2.3	18	-	-
Ni	3.9	1.2	-	-
Zn	4.1	-	-	-
A1	6.9	2.4	-	-
NH3	5,000	10,000	2,300	12,000
Ba	3.3	-	-	-
В	29	27	-	-
Ca	20	21	50	15
C1	1,300	20,000	45,000	18,000
Co	-	18	-	-
F	55,000	2.2	-	2
Fe	630	2.3	-	-
Mg	1,300	395	21	180
Mn	8.1	-	-	
Na	810	21,000	16,000	18,000
S04	21,000	34,000	2,500	4,800
рН ^а	4.5	4.5	4.5	4.5

TABLE 5.2. CHARACTERISTICS OF REPRESENTATIVE WASTEWATER STREAMS.

.

a pH is in standard units.

ς...

5.2 METHODS

5.2.1 Equilibria Modelling

The data given in Table 5.2 are the wastewater characteristics that were entered into the computer program EQ3/EQ6. The program simulates equilibrium conditions in single or multicomponent solutions, calculating the distribution of the chemical species once equilibrium has been established. This distribution will include the species concentration in solution as well as the quantity of chemical species that may have been precipitated. The program's internal data base contains information on the hydrolysis constants and solubility products of many of the chemical species that appear in high-strength ammonia wastewaters. Variations of the equilibrium constants with temperature and pressure were also calculated.

Figures 5.1 through 5.4 are plots of the output from the EQ3/EQ6 program. Figures 5.1 and 5.2 show the variation in pH as a function of the lime and sodium hydroxide added, respectively. When the solution pH reached 11.5, the temperature was raised to simulate heating of the solution before stripping. The temperature was changed from 25°C to 95°C with a corresponding drop in pH due to changes in the values of the hydrolysis constants. Figures 5.3 and 5.4 show the sludge production as a function of lime and sodium hydroxide added, respectively. The temperature change also is apparent in Figures 5.3 and 5.4 as a drop in the sludge production. The chemical dose required to adjust the pH to 11.5 and the sludge produced at 25°C were interpolated from these figures and are summarized in Table 5.3.

5.2.2 <u>Cost Estimates</u>

Process design and cost estimates were done using a spreadsheet. Inputs included chemical quantity used, sludge produced (both given in Table 5.3), wastewater flow rate, and unit costs for chemicals, energy, labor, fuel, and construction. The project life and a rate of return were also used to allow amortization of the construction costs. The final inputs were the Construction Cost Indices, calculated by Engineering News Record (1988), one for the year for which the estimate is being prepared and one for the year in which the costs are based. The output is a listing of the yearly costs for the unit processes over the project life.



Figure 5.1. Calculated pH for Plants 1, 2, 3, and 5 for lime addition, in grams of lime added per kilogram of solution.



Figure 5.2. Calculated pH for Plants 1, 2, 3, and 5 for sodium hydroxide addition, in grams of sodium hydroxide added per kilogram of solution.



Figure 5.3. Calculated sludge production for Plants 1, 2, 3, and 5 for lime addition. (grams of solid per kilogram of solution)



Figure 5.4. Calculated sludge production for Plants 1, 2, 3, and 5 for sodium hydroxide addition. (grams of solid per kilogram of solution)

TABLE 5.3. SUMMARY OF CHEMICAL AND SLUDGE DATA

(Data are for 1 L of Wastewater)

..

•

	Adjustment of pH to 11.5 With:								
		Lime	NaOH						
Plant	Lime Added (g)	Sludge Produced (g)	NaOH Added (g)	Sludge Produced (g)					
1	21	35	31	4.3					
2	18	45	23	,0.9					
3	3.8	0.6	5.5	0.1					
5	18	5.4	26	0					

Table 5.4 is a listing of the values, i.e. energy, cost, labor cost, etc., used in the analysis. These values are quotes or estimates and are meant to be representative of the costs that may be incurred. However a site-specific analysis should be performed using the actual costs along with those costs mentioned above which have not been included in these analyses. Appropriate safety factors should be employed as necessary.

The chemical costs were calculated on a yearly basis using the following formula:

chemical costs
$$(\$/yr) = Q * d_c * \$_c$$
 (15)

where

Q = wastewater flow rate
d_c = chemical dose
\$_c = chemical unit cost.

The Capital Recovery Factor, CRF, is the fraction of the cost of an expenditure that is realized each year. The CRF also accounts for the lost interest income that would have been earned had the money been invested at the chosen rate of return and not spent. The CRF can be calculated as follows:

$$CRF \frac{i(1+i)^{n}}{(1+i)^{n-1}}$$
(16)

where

i = rate of return in decimal form
n = project life in years.

5.2.3 Process Design

The size of any particular wastewater treatment operation is determined by the amount of material, either wastewater or sludge, it must treat in a given time period. Typically, operation size can be reduced to one design value, usually a volume or an area, which best represents the size and therefore the cost of the process. The equations used to arrive at this value are given in

TABLE 5.4. ASSUMED CONSTANT VALUES

.

··· .

Lime Cost	\$70/dry ton
Alum Cost	\$305/dry ton
Project Life	10 yr.
Rate of Return	9%
ENR Construction Cost Index (CCI) for 1988	4493.2
ENR Construction Cost Index (CCI) for 1978	2653.8
Energy Unit Cost	\$0.03/KW-hr
Wage Detention Times: Rapid Mix Tank	\$18/hr. 10 min.
Circular Clarifier	30 min.
Gravity Thickener	10 days
Dewatering Lagoon	30 days
Filter Press Depths:	10 min.
Gravity Thickener Wet Sludge Solids Content	4 ft. 4 ft. 2%
Dry Sludge Solids Content	20%
Landfill Distance	40 mi.
Vacuum Thickener Loading Rate	2 lbs. solids/ft ² /hr.
Fuel Cost	\$1/gal.

. -

.

• •

Table 5.5. A further explanation of these equations or any of the unit processes can be found in a water or wastewater treatment design text such as Water Treatment Principles and Design (James M. Montgomery, Consulting Engineers, Inc., 1985) or Wastewater Engineering Treatment, Disposal, Reuse (Metcalf and Eddy, Inc., 1979). Table 5.6 lists the factors used for both conversion between SI and English units as well as within any system of units. 5.3 RESULTS AND DISCUSSION

Tables 5.7 through 5.10 show the estimated yearly costs for the unit treatment processes for Plants 1, 2, 3, and 5, respectively. Yearly costs for each of the unit processes costs are shown for use of either lime or sodium hydroxide to adjust the pH. Those processes denoted by "*" represent the lowest cost treatment system for chemical addition, mixing, sludge removal, and sludge disposal based on the factors of this analysis.

In some instances when sodium hydroxide is used to adjust the pH, the sludge production was negligible. Cost estimates for sludge thickening processes in these instances have not been reported since the small size of these units makes accurately estimating the cost difficult. In other instances with sodium hydroxide, the sizes of various unit processes became so large that costs could not be estimated with accuracy and again no cost estimates have been reported.

For each of the plants, at any of the flowrates studied, the most costeffective treatment system was the same. This system consisted of lime addition for pH adjustment, followed by precipitate removal with a clarifier and sludge thickening in a dewatering lagoon, followed by disposal of the dewatered sludge in the landfill. However, the high moisture content of sludge in dewatering lagoons can offset some of the beneficial savings in subsequent processes such as sludge handling and disposal.

The overall cost of this set of processes was relatively less than the cost of any other combination of processes. Included in these estimates was recalcitrating of the lime when higher doses are used (i.e. with 200,000 and 500,000 gallons of wastewater per day). The presence of heavy metal residues in the sludge, which may be released to the atmosphere during the reducing process, may prevent the reclamation of the lime due to environmental and economic concerns. If so, the cost for chemical addition would increase,

```
Chemical Feed Rate = Q + d_C
Rapid Mix Tank Volume = Q + t_r
Clarifier Plan Area = Q + t_r / h
Gravity Thickener Plan Area = Q + t_r / h
Vacuum Thickener Area = Q + p_C / L_r
Dewatering Lagoon Volume = Q + t_r
Filter Press Volume = Q + t_r
Sludge Dry Weight = Q + p_S
Sludge Wet Weight = Q + p_S / c_S
```

where

Q = wastewater flowrate dc = chemical dose tr = detention time h = depth Lr = loading rate ps = sludge production cs = solids content TABLE 5.6. CONVERSION FACTORS

3.785 L/gal. 7.84 gal./ft3 8.34 lbs. water/ft3 2.2 lbs./Kg 1000 g/Kg 60 min./hr. 24 hr./d. 365 d./yr. 62.4 lbs. water/ft3

TABLE	5.7.	SUMMARY	OF	COST	ESTIMATES	FOR	PLANT	1
			(\$/yr)	-			

Flowrate (gal/d)	50,000	100,000	200,000	500,000
Chemical: Lime	122,000*	245,000*	489,000*	1,220,000*
Mixing Operations: Chemical Feeder Mixing Tank	29,000* 11,000*	33,000* 11,000*	27,000* 12,000*	32,000* 14,000*
Separation Process: Clarifier	12,000*	12,000*	13,000*	17,000*
Thickening Processes: Gravity Thickener Vacuum Thickener Dewatering Lagoon Filter Press	121,000 250,000 18,000* 202,000	213,000 383,000 32,000* 171,000	383,000 637,000 62,000* 172,000	1,140,000 1,080,000 134,000* 200,000
Disposal Operations: Dry Sludge Disposal Wet Sludge Disposal	93,000* 871,000	157,000* 1,800,000	306,000* 3,850,000	917,000* 9,260,000
Chemical: NaOH	718,000	1,440,000	(1)	(1)
Mixing Operations: Chemical Feeder Mixing Tank	31,000 10,000	146,000 11,000	(1) (1)	(1) (1)
Separation Process: Clarifier	13,000	146,000	(1)	(1)
Thickening Processes: Gravity Thickener Vacuum Thickener Dewatering Lagoon Filter Press	32,000 86,000 4,000 166,000	55,000 115,000 6,000 166,000	(1) (1) (1) (1)	(1) (1) (1) (1)
Disposal Operations: Dry Sludge Disposal Wet Sludge Disposal	26,000 97,000	37,0 00 231,000	(1) (1)	(1) (1)

Notes: * Flags the most cost effective set of processes.

•

. .

 The size of the unit became so large with given design parameters that an accurate estimate of the costs could not be made.

Flowrate (gal/d)	50,000	100,000	200,000	500,000
Chemical: Lime	96,000*	191,000*	383,0 00*	957,000*
Mixing Operations: Chemical Feeder Mixing Tank	27,000* 11,000*	31,000* 11,000*	24,0 00* 12,000*	31,000* 14,000*
Separation Process: Clarifier	12,000*	12,000*	13,000*	17,000*
Thickening Processes: Gravity Thickener Vacuum Thickener Dewatering Lagoon Filter Press	55,000 284,000 21,000* 166,000	274,000 445,000 38,000* 166,000	378,000 737,000 73,000* 177,000	2,890,000 1,390,000 167,000* 213,000
Disposal Operations: Dry Sludge Disposal Wet Sludge Disposal	108,000* 1,100,000	199,000* 2,240,000	386,000* 4,380,000	931,000* 1,125,000
Chemical: NaOH	533,000	(1)	(1)	(1)
Mixing Operations: Chemical Feeder Mixing Tank	27,000 10,000	(1) (1)	(1) (1)	(1) (1)
Separation Process: Clarifier	12,0 00	(1)	(1)	(1)
Thickening Processes: Gravity Thickener Vacuum Thickener Dewatering Lagoon Filter Press	21,000 58,000 2,000 166,000	(1) (1) (1) (1)	(1) (1) (1) (1)	(1) (1) (1) (1)
Disposal Operations: Dry Sludge Disposal Wet Sludge Disposal	19,000 41,000	(1) (1)	(1) (1)	(1) (1)

TABLE 5.8.SUMMARY OF COST ESTIMATES FOR PLANT 2(\$/yr)

Notes: * Flags the most cost effective set of processes.

(1) The size of the unit became so large with given design parameters that an accurate estimate of the costs could not be made.

Flowrate (gal/d)	50,000	100,000	200,000	500,000
Chemical: Lime	20,000*	40,000*	81,000*	202,000*
Mixing Operations: Chemical Feeder Mixing Tank	19,000* 11,000*	24,000* 11,000*	27,000* 12,000*	30,000* 14,000*
Separation Process: Clarifier	12,000*	12,000*	14,000*	17,000*
Thickening Processes: Gravity Thickener Vacuum Thickener Dewatering Lagoon Filter Press	18,000 59,000 500* 166,000	24,000 64,000 2,000* 166,000	29,000 72,000 2,000* 166,000	43,000 97,000 13,000* 166,000
Disposal Operations: Dry Sludge Disposal Wet Sludge Disposal	8,000* 32,000	18,000* 45,000	21,000* 68,000	32,000* 165,000
Chemical: NaOH	127,000	255,000	510,000	(1)
Mixing Operations: Chemical Feeder Mixing Tank	10,000 10,000	14,000 11,000	25,000 12,000	(1) (1)
Separation Process: Clarifier	12,000	13,000	14,000	(1)

TABLE 5.9. SUMMARY OF COST ESTIMATES FOR PLANT 3 (\$/yr)

Notes: * Flags the most cost effective set of processes.

(1) The size of the unit became so large with given design parameters that an accurate estimate of the costs could not be made.

50,000	100,000	200,000	500,000
95,000*	191,000*	383,000*	957,000*
28,000* 10,000*	31,000* 11,000*	24,000* 12,000*	31,000 * 14,000*
13,000*	13,000*	13,000*	-17,000*
40,000 92,000 4,000* 151,000	61,000 127,000 7,000* 161,000	91,000 181,000 11,000* 161,000	173,000 321,000 26,000* 161,000
29,000* 146,000	41,000* 302,000	62,000* 561,000	133,000* 1,350,000
602,000	(1)	(1)	(1)
30,000 10,000	(1) (1)	(1) (1)	(1) (1)
12,000	(1)	(1)	(1)
	<u>50,000</u> 96,000* 28,000* 10,000* 13,000* 13,000* 40,000 92,000 4,000* 161,000 29,000* 146,000 602,000 30,000 10,000 12,000	$\begin{array}{c ccccc} \underline{50,000} & \underline{100,000} \\ \hline 96,000^{*} & 191,000^{*} \\ \hline 28,000^{*} & 31,000^{*} \\ 10,000^{*} & 11,000^{*} \\ \hline 13,000^{*} & 13,000^{*} \\ \hline 13,000^{*} & 13,000^{*} \\ \hline 40,000 & 61,000 \\ 92,000 & 127,000 \\ 4,000^{*} & 7,000^{*} \\ 161,000 & 161,000 \\ \hline 29,000^{*} & 41,000^{*} \\ \hline 161,000 & 101 \\ \hline 146,000 & (1) \\ \hline 30,000 & (1) \\ \hline 10,000 & (1) \\ \hline 12,000 & (1) \\ \hline \end{array}$	$50,000$ $100,000$ $200,000$ $96,000^{*}$ $191,000^{*}$ $383,000^{*}$ $28,000^{*}$ $31,000^{*}$ $24,000^{*}$ $10,000^{*}$ $11,000^{*}$ $12,000^{*}$ $13,000^{*}$ $13,000^{*}$ $13,000^{*}$ $40,000$ $61,000$ $91,000$ $92,000$ $127,000$ $181,000$ $4,000^{*}$ $7,000^{*}$ $11,000^{*}$ $161,000$ $161,000$ $161,000^{*}$ $29,000^{*}$ $41,000^{*}$ $62,000^{*}$ $146,000$ $302,000$ $561,000$ $602,000$ (1) (1) $30,000$ (1) (1) $12,000$ (1) (1)

TABLE 5.10. SUMMARY OF COST ESTIMATES FOR PLANT 5 (\$/yr)

Notes: * Flags the most cost effective set of processes.

(1) The size of the unit became so large with given design parameters that an accurate estimate of the costs could not be made. possibly doubling. However, if recalcitrating is possible, many of the sludge dewatering and handling costs would decrease. Estimates were based on reclamation of lime from sludge, substantially decreasing the volume of sludge to be treated.

A number of factors for which no information was available or no representative price could be established may have a profound effect on the relative cost effectiveness of these processes. For other inputs, estimates were made from characteristics of municipal wastewaters. These estimates may not be representative of the wastewaters generated by metal winning facilities.

One factor that will govern the size, and ultimately the cost, of the clarifier is the particle-settling velocity. The higher the settling velocity, the smaller and less expensive the facilities. The cost estimates are based upon settling velocities of municipal wastewaters treated with lime, which may be on the same order of magnitude as those for industrial wastewaters.

A second factor is the dewatering characteristics of the sludge. A sludge in which the excess water is readily removed will require smaller dewatering facilities than a sludge that tightly holds excess water. The design is based upon characteristics of a typical municipal sludge, which will have a much different dewaterability. The dewatering characteristics of the ammoniastripper sludge could be different and may require larger or smaller facilities.

Another factor is the cost of the land necessary for each of the individual processes. Gravity thickeners and dewatering lagoons are area- intensive processes and will be least cost-effective in areas with high land values. Since no land value was figured into this analysis, the land- intensive but mechanically simple processes were favored over the mechanical processes such as vacuum dewatering and the filter press. A reevaluation, considering land costs for a specific site, may favor the use of other less land-intensive processes.

The sludge disposal costs are estimates of time and material needs only and do not include the actual cost-per-unit-volume for ultimate disposal of sludge in a landfill. The cost of transport and disposal of sludge varies

considerably based upon geographical origin of the waste, location of the landfill, and classification of the waste (i.e. hazardous, radioactive, nonhazardous, etc). Also, the disposal of unstabilized sludge regulated under Title C of RCRA is likely to be prohibited in the future. Therefore, no estimate of the cost of ultimate disposal or landfilling was made.

5.4 SUMMARY AND CONCLUSIONS

Cost estimates for the chemicals and equipment to adjust the pH of an ammonia-bearing, metal winning wastewater prior to stripping show that lime can be more economical than caustics for pH adjustment. In addition, the most cost-effective method for disposal of the sludge solids generated was dewatering in a lagoon followed by landfill disposal of the solids. However, there may be a different set of cost-effective processes when costs for land, transport, and handling of large quantities of sludge are high.

6. QUALITY ASSURANCE/QUALITY CONTROL

The following additional analytical tests were performed or instrument calibration was checked for QA purposes.

 (a) Two aliquots from the same sample were submitted for chemical analyses without indicating that they were duplicates. These samples are from solution A (see Table 3.3).

Analytical results:

		Loncentration, m	ю/L	
_Species	<u>Sample_A</u>	<u>Sample A</u>	<u>Average</u>	Percent <u>Variation</u>
Sulfate Chloride	22,000 28,000	25,500 27,750	23,750	±7.4
Magnesium	184	180	182	±1.1
Sodium	19,000	20,000	19,500	±2.6
Calcium	<10	<10	<10	-

(b) Also submitted was a distilled water sample for chemical analysis.

Analytical results:

<u>Species</u>	<u>Concentration, mq/L</u>
Sulfate	<4
Chloride	<50
Magnesium	<10
Sodium	11
Calcium	<10

(c) Ammonia analyses: The ammonia electrode was calibrated everyday using standard solution to assure that the slope did not exceed -57 (±3) mV. Also, the instrument reading was frequently checked after the ammonia analyses of test samples to assure that the variation in accuracy did not exceed ±10 percent. Instrument sensitivity was verified using two different sources of analytical grade ammonium salts.

- (d) pH analyses: The pH probe was standardized using pH 4, 7, and 10 buffer solutions on the mass-transfer rate studies. If the difference between initial and final solution pH exceeded 10 percent, the experiments were repeated.
- (e) The calibration information for thermocouples and flow meter is given in the laboratory notebook. The flow meter readings were checked with a laboratory in-line flow measurement and found that the flow meter reading was within 2 percent of the average of 4 measured values.
- (f) Steam flowrate was measured at least three times for each setting of the valve openings. The variation of measured steam flowrates at a given opening did not vary by more than ±1.8 percent. The calibration curve is given in Figure 4.6.

The performance audits for laboratory studies were conducted by the QA unit of Battelle's Biological Sciences Technical Center and an external QA officer appointed by the U.S. EPA.

7. REFERENCES

Barrett, P. V. L. Gas absorption on a sieve plant. Ph.D. Thesis. University of Cambridge, U.K. 1966. As cited <u>in</u>: P.V. Danckwerts. Gas-Lighted Reactions, McGraw-Hill Book Co., NY. 1970.

Danckwerts, P. V. Gas-Liquid Reactions. McGraw-Hill Book Company, New York, New York. 1970.

Engineering News Record, Market Trends, 220(22):40, 1988.

.

Gumerson, R. C., R. L. Culp, and S. P. Hansen. Estimating Water Treatment Costs, United States Environmental Protection Agency, Municipal Environmental Research Laboratory, Cincinnati, OH, EPA 600/2-79-162a and EPA 600/2-79-162b, 1979.

Kavanaugh, M. C. and R. R. Trussell. 1980. Design of aeration towers to strip volatile contaminants from drinking water. Journal AWWA. December 1980.

McCabe, W. L., and J. C. Smith. 1984. Unit Operations of Chemical Engineering, Third edition. McGraw-Hill, New York.

Metcalf and Eddy, Inc., Wastewater Engineering Treatment, Disposal, Reuse, 2nd. ed., McGraw-Hill Book Co., New York, 1979.

Montgomery, J. M., Consulting Engineers, Inc. Water Treatment Principles and Design. John Wiley & Sons, New York. 1985.

Onda, L., E. Sada, T. Kobayashi, S. Kito, and K. Ito. Salting-out Parameters of Gas Solubility in Aqueous Salt Solutions. Journal of Chemical Engineering of Japan 3:18-24, 1970.

Patterson, J. W. Industrial Wastewater Treatment Technology, Second edition. Butterworth Publishers, Massachusetts. 1985.

Perry, R. E., and C. H. Chilton, eds. Chemical Engineers Handbook, 5th ed. McGraw-Hill, New York. 1973.

Powers, S. E. Optimization of an Ammonia Stripping Process for a Semiconduction Manufacturing Wastewater. Master's thesis. Clarkson University. 1985.

Treybal, R. E. 1980. Mass Transfer Operations. McGraw-Hill, New York.

Struzeski, Jr., E. J. Ammonia Stream Stripping at Miscellaneous Nonferrous Metals Plants; Case Histories. In Proc. 33rd Industrial Waste Conference, Purdue Univ., Lafayette, IN. p. 204. 1978. Wolery, T.J. Calculation of Chemical Equilibrium betwen Aqueous Solutionand Minerals: The EQ3/EQ6 Software Package. Technical Report UCRL-52658, Lawrence Livermore Laboratory, February, 1979.

4

Wolery, T.J. EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: UCRL-5314, Lawrence Livermore Laboratory, April, 1983.

Wolery, T.J. EQ6, A Computer Program for Reaction-Path Modeling of Aqueous Geochemical Systems: User's Guide and Documentation. Technical Report UCRL-53788, Lawrence Livermore Laboratory, April 1987. in preparation.

U.S. Environmental Protection Agency. Draft Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Miscellaneous Nonferrous Metal Segment of the Nonferrous Metals Point Source Category, EPA-440/1-76-067. Effluent Guidelines Division, U.S. EPA, Washington, D.C. 1976.

TECHNICAL REPORT DATA		
T. REPORT NO.	p.	
EPA/600/2-91/046		
A. TITLE AND SUBTITLE	B. REPORT DATE	
Bench-Scale Evaluation of Ammonia Removal Wastewater by Steam Stripping	From September 1991	
G.B. Wyckramanayake, D.P. Evers, J.A. Kit A. Gavaskar	tel, and	
Battelle Memorial Laboratories	10. PROGRAM ELEMENT NO.	
Columbus Division	11. CONTRACT/GRANT NO.	
Columbus, OH 43201-1693	68-03-3248	
12. SPONSORING AGENCY NAME AND ADDRESS Risk Reduction Engineering Laboratory	13. TYPE OF REPORT AND PERIOD COVERED Final Report	
Office of Research & Development	14. SPONSORING AGENCY CODE	
U.S. Environmental Protection Agency Cincinnati, Ohio 45268	EPA/600/14	
15. SUPPLEMENTARY NOTES Project Officer: John O. Burckle FTS 684-7506; (513)569-7506		
The purpose of this study was to gen development of wastewater discharge st winning processes. The objective was from synthetically compounded "wastewa stripping apparatus. Although no significant variation of observed when SO_4^{-} concentrations were the highest for low SO_4^{-} wastewaters w Results of the steam stripping study constituents such as SO_4^{-} and the mola effect on the efficiency of ammonia re more) can be achieved by preheating wa tower at high steam-to-wastewater flow on engineering unit process and operation indicated that lime may be more econom	erate laboratory data to support the andards for ammonia in nonferrous metal accomplished by studying ammonia removal ter" samples using a bench-scale steam "mass transfer rate coefficient (K) was varied from 5,000 to 20,000 mg/L, K was hen pH was adjusted using NaOH. indicated that varying chemical I strength did not have a significant moval. Higher removals (99.9 percent or stewater and operating the stripping wrate ratios such as 4 lb/gallon. Based ton requirements, the cost analysis nical than caustic for pH adjustment,	
depending upon waste sludge character	SLICS and disposal regariemental	
TZ. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b.IDENTIFIERS/OPEN ENDED TERMS C. COSATI Field Group	
waste water, ammonia	wastewater discharge, ammonia removal, steam stripping	
18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (Thus Report) 21. NO. OF PAGES	
RELEASE TO PUBLIC -	20. SECURITY CLASS (This page) 22. PRICE	
	Unclassified	

.

EPA For 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

.