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Project Summary

Bench-Scale Evaluation of Ammonia Removal from Wastewater by Steam Stripping

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The purpose of the study summarized here was to generate laboratory data to support the development of wastewater discharge standards for ammonia in nonferrous metal winning processes. Ammonia removal effected by steam stripping from synthetically compounded "wastewater" samples was studied to determine the importance of factors affecting the rate of removal and the degree of removal.

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

Results of the steam stripping study indicated that varying chemical constituents such as $SO_4^=$ and the molal strength did not significantly affect the efficiency of ammonia removal. Preheating wastewater and operating the stripping tower at high steam-to-wastewater flowrate ratios such as 4 lb/gal achieved higher removals (99.9% or more). Based on engineering unit process and operation requirements, the cost analysis indicated that lime may be more economical than caustic for pH adjustment depending on waste sludge characteristics and disposal requirement.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Extracting metal values from some ores requires the use of hydrometallurgical techniques that employ ammoniacal lixiviants. The metal values are recovered from the pregnant liquors, leaving an aqueous wastewater residual high in dissolved solids and ammonia. This wastewater requires treatment for removal of ammonia as well as 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. The purpose of this study was to determine the usefulness of steam stripping for the removal of ammonia from wastewaters generated in the metal smelting and refining industry.

Approach

The overall objective was pursued as three discrete tasks. Task 1 involved theoretical and laboratory studies to determine the effects of wastewater composition on the equilibrium of ammonia (gas) and on water and gas-liquid mass transfer rates, especially within the temperature range of interest in actual plant operations. In Task 2, laboratory tests were performed in a bench-scale steam stripping apparatus processing two representative synthetic wastewaters with pH adjustment by either lime or caustic. Task 3 involved the estimation of the capital and operating costs associated with the pH adjustment methods and the handling of the waste sludge subsequently formed. Disposal costs were not included in this analysis.

Methods

One objective of the first 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. This theoretical study was based on information given in the published literature.

The second aspect of this task involved experiments to study the effect of varying $SO_4^=$ concentration, molal strength, and pH adjustment method [NaOH or $Ca(OH)_2$] on the gas transfer rates for ammonia. Synthetic wastewater stream A (Table 1) was designed to have a high SO_4= level and molal strength. Waste stream B has a lower $SO_4^=$ level than A, whereas both A and C have the same $SO_4^=$ level. Waste streams B and C have the same molal strength and were brought to such conditions by adjusting Cl^- concentrations. The experiments were conducted in identical, completely mixed batch reactors at temperatures near 90°C. The variation of ammonia concentration with time was studied after adjusting solution pH to 12 with NaOH or $Ca(OH)_2$.

During Task 2, a laboratory-scale steam stripping unit was designed and constructed (Figure 1). The pH of two different synthetic waste streams, B and C (Table 1), was adjusted to 11.5 or greater with either NaOH or CaO. Ammonia removal was studied for the different pH adjustment methods and different steam-to-wastewater flowrates.

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 1, the wastewater flowed down over the packing material and exited through the effluent line at the column base. Steam was injected into the column at the base of the packing material. As the wastewater passed through the jet of steam, it was heated to 100°C. Flowrates for the steam and/or the influent wastewater were varied to determine the differences in ammonia removal efficiency. 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.

A total of nine steam stripping experiments were performed to explore the effects of sulfate concentration and total molal strength and to compare the use of NaOH (caustic) or CaO (lime) for pH adjustment of the solutions. The extent of ammonia removal was studied for different steam-to-wastewater flowrates.

In Task 3, the costs for chemical addition, sludge removal, and thickening were estimated for four different representative waste streams and for a variety of wastewater flowrates. 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, buildings, land, or sludge disposal—all of which are likely to vary considerably from site to site.

Results and Discussion

Task 1: Theoretical and Laboratory Studies on the Equilibrium and Mass Transfer of Ammonia in Wastewater

The analyses of the estimated Henry's Law constant and changes in solubilities of ammonia indicated that adding caustic, as compared with adding slaked lime, resulted in higher Henry's Law constants and lower solubilities for the three waste streams considered. These effects can be attributed to the relatively high ionic strength found in wastewaters when pH was adjusted with NaOH. For 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 had the highest molal strength.

Experimental studies to determine the effects of dissolved species and pH adjustment method on the mass transfer coefficient (K) indicated that those effects were relatively low and the maximum changes in mass transfer coefficient did not exceed 25%. In two of the three different solutions, however, the mass transfer coefficient was higher for the waste sream where pH was adjusted using caustic. For solutions with approximately the same $SO_4^=$ concentration but different molal strength, the mass transfer 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 indicated that, when compared with lime, addition of NaOH promoted ammonia removal for solutions with relatively low $SO_4^=$ levels (5,000 mg/L).

Task 2: Ammonia Removal Studies Using Steam Stripping Unit

The results of the steam stripping study are summarized in Table 2. The data show that when the steam-to-wastewater flowrates were low (1.3 lb/gal), the ammonia removal efficiency was as low as 93%. By increasing steam-to-wastewater flowrates to 3.8 lb/gal, removals of more than 99.9% were observed. The removal efficiency in one study was improved by 2 percentage points when the temperature of the influent waste stream was raised by about 20°C. The addition of lime increased the temperature more than 10°C because hydration of lime is an exothermic process.

For wastewater with low initial $SO_4^=$ level (5,000 mg/L), ammonia removal was 3 percentage points higher when pH was adjusted with caustic rather than with lime. These observations agreed with the trends predicted from the estimated Henry's Law constant and mass transfer coefficient. In

Table 1. Wastewater Characteristics for Gas Transfer Rate Experiments

Chemical Species	*Concentration, mg/L*		
	Wastewater A	*Wastewater B*	*Wastewater C*
NH_3-N	5,000	5,000	5,000
Mg^{++}	200	200	200
Na^+	19,127	11,939	11,939
$SO_4^=$	20,000	5,000	20,000
Cl^-	28,000	28,000	16,906

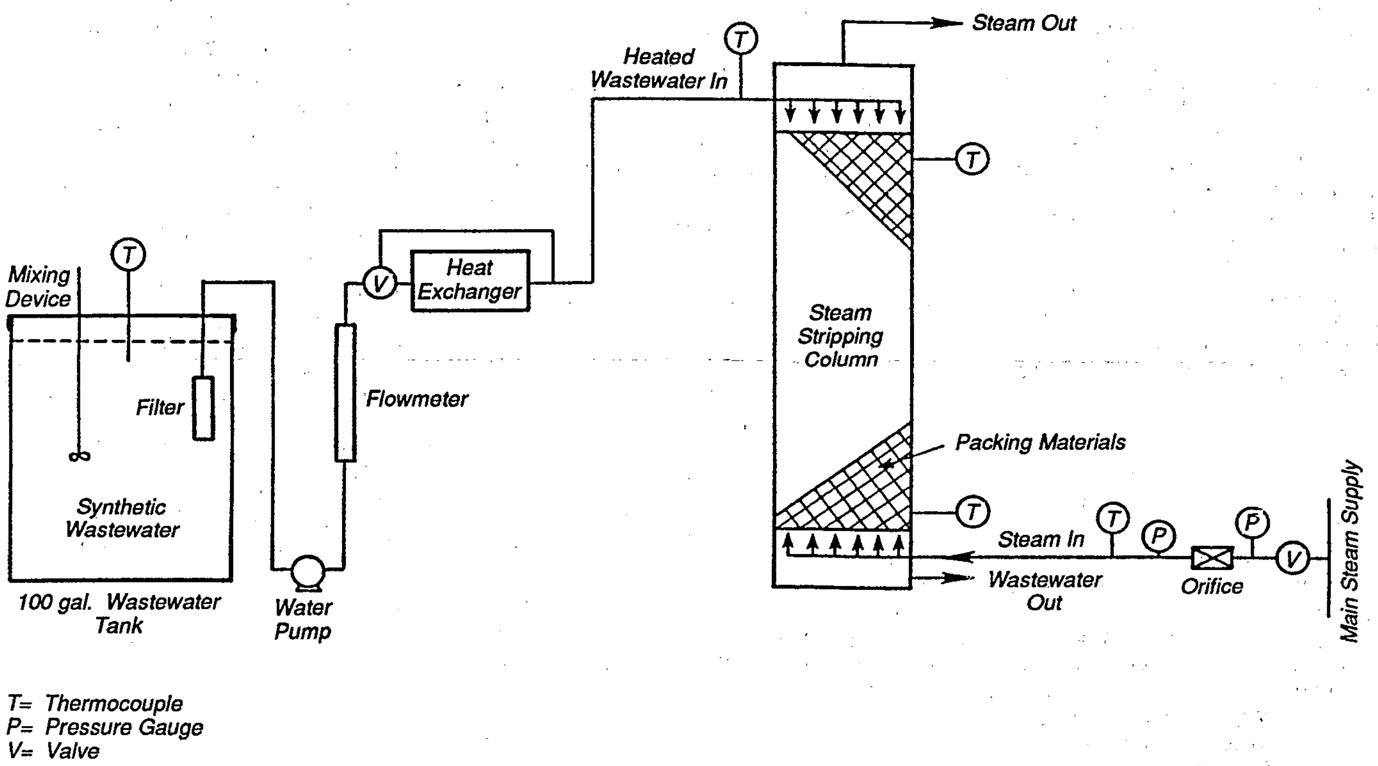

Figure 1. *Experimental setup for ammonia removal by steam stripping.*

Table 2. *Summary Results of Laboratory Study on Steam Stripping*

Wastewater	pH Adjustment Method	Wastewater Temp. °C: Column Influent	Wastewater Temp. °C: Column Effluent	Steam to Wastewater Ratio (lb/gal)	NH_3 - N conc., mg/L: Influent	NH_3 - N conc., mg/L: Effluent	Average NH_3 Removal, %
B (low $SO_4^=$)	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 $SO_4^=$)	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

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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 with caustic. These observations agreed 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% of ammonia was removed by introducing high steam-to-wastewater flowrates, such as 3.8 lb/gal. Varying chemical constituents such as $SO_4^=$ and the molal strength had only a little effect on net NH_3 removal. Preheating wastewaters and operating the stripping tower at high temperatures by increasing the steam-to-wastewater flowrate ratio resulted in higher removal efficiences.

Task 3: Engineering Cost Estimates

The cost estimates for the chemicals and equipment to adjust the pH of an ammonia-bearing, metal-winning wastewater before stripping showed that lime can be more economical than caustic. 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. There may be a different set of cost-effective processes, however, when costs for land, transport, and handling of large quantities of sludge are high.

Summary and Conclusions

The analyses of estimated Henry's Law constant and changes in ammonia solubilities indicated that adding caustic, rather than slaked lime, would result in higher Henry's Law constants and lower solubilities for the three waste streams studied. Although no significant variation of the mass transfer coefficient (K) was observed when $SO_4^=$ concentrations were varied from 5,000 to 20,000 mg/L, K was the highest for low $SO_4^=$ wastewaters when pH was adjusted with NaOH.

Results of the steam stripping study indicated that varying the chemical constituents such as $SO_4^=$ and the molal strength did significantly affect the efficiency of ammonia removal. More ammonia was removed (99.9% or more) by preheating wastewater and by operating the stripping tower at high steam-to-wastewater flowrates such as 4 lb/gal. Based on engineering unit process and operation requirements, the cost analysis indicated that lime may be more economical than caustic for pH adjustment.

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John Burckle is the EPA Project Officer (see below).
The complete report, entitled "Bench-Scale Evaluation of Ammonia Removal from Wastewater by Steam Stripping," (Order No. PB91-234 633/AS; Cost: $26.00; subject to change) will be available only from:
National Technical Information Service
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