

# High temperature ammonia stripping and recovery from process liquid wastes

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## Abstract

The feasibility of a process for ammonia removal and recovery from high temperature waste waters is assessed.  $\text{NH}_3$  is stripped away in a packed column by means of air which is continuously looped to a further absorption unit. Here ammonia is dissolved in an acid solution which is sent to a crystalliser for  $(\text{NH}_4)_2\text{SO}_4$  production (a fertiliser). The performance of the process was studied at varying the temperature level, the flow rate to be treated, the ammonia inlet and outlet concentrations, and the packing type used in the stripping and absorption columns. The unit treatment cost appears to be competitive compared to alternative technologies, especially for high ammonia inlet concentrations and operating temperatures. Moreover, no escape of ammonia to the atmosphere is assured, contrary to simple stripping units.

## 1. INTRODUCTION

The presence of ammonia in natural or industrial waste waters has become a major environmental problem [1]. Specific treatments are often needed either to render these waters potable [2, 3] or to avoid eutrophication [4]. Several technologies were proposed based on different chemical-physical principles: air stripping, biological denitrification, selective ion exchange, reverse osmosis, electrodialysis, electrochemical oxidation and breakpoint chlorination. The first two systems gained large application in civil sewage treatment [3, 5], while the other treatments have been applied less extensively and to more specific cases. In particular, breakpoint chlorination is often used when potable-grade water has to be produced [6].

Cost comparisons are reported in literature [7]. However, the choice of a particular route strongly depends on the nature of the water to be treated. For example, biological denitrification is hindered by low-temperature environments, the absence of carbonaceous compounds in suitable amount and the presence of toxic compounds. Ion exchange can have severe drawbacks when interfering ions are present. Breakpoint chlorination is generally too expensive for practical application unless low initial ammonia concentrations have to be removed, because of high costs and problems connected to the presence of unconverted chlorine in the processed water.

In this work attention is focused on the stripping process. This route seems particularly promising whenever an industrial waste water (i.e. from the chemical, the textile or the fibre-production industry) is characterised by comparatively high temperatures and ammonia concentrations. High temperatures enable a high gas-liquid mass transfer rate by enhancing its driving force (i.e. ammonia solubility in water is lowered). As a result the volume of the stripping units is reduced. Moreover high ammonia concentrations can be kept in the outgoing gas phase, favouring further absorption in a slightly acid solution and the production of ammonium sulphate (a widely-employed fertiliser). By these means any serious escape of ammonia either in gaseous form or in aqueous solution can be prevented.

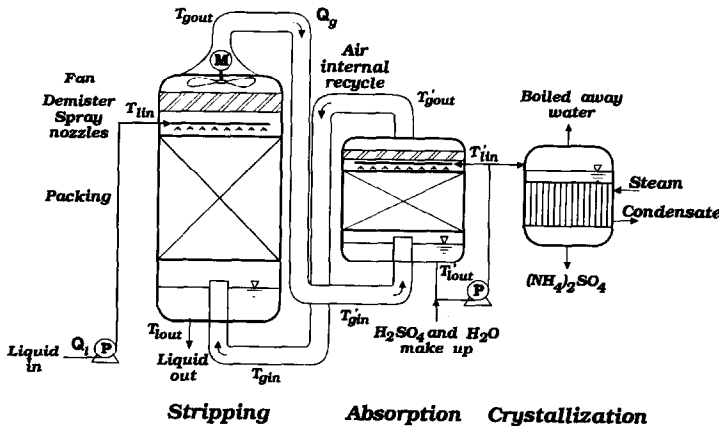


Figure 1. A scheme of the proposed plant.

Fig. 1 reports a possible scheme for an industrial-scale plant for ammonia stripping and recovery. An air internal recycle provides the ammonia stripping from the waste water in the first packed column and its absorption in a second column. A concentrate, slightly acid ammonium sulphate solution is continuously drawn off from this column and sent to a crystalliser. The air internal loop helps to keep high temperatures all over the system despite eventually rigid climates (no external air is fed to the system). Moreover, it allows to operate in the absence of  $\text{CO}_2$ , which usually promotes the massive formation of carbonate scaling on the packing used in single-pass stripping units [5,8].

A feasibility study of this process is presented.

The treatment of an industrial waste water generated in the production of cellulose-acetate fibres was considered as a case study (source: ACETATI S.p.A. - Verbania - NO - Italy). Table 1 lists its main characteristics. Such a solution is left over at the bottom of distillation columns for acetic acid recovery in the above process, hence its comparatively high temperature ( $\sim 100^\circ\text{C}$ ). The presence of ammonia is a consequence of the use of acetamide as a catalyst in the cellulose acetylation step [9].

On the basis of thermodynamic equilibrium data and on experimental interphase mass transfer measurements the effects of the packing type and of the gas and liquid flow rates on

the process performance are evaluated. The influence of ammonia inlet and outlet concentrations is also considered. The process viability is demonstrated from both technical and economic standpoints. In this last context, the overall treatment cost per cubic meter of waste water is derived at varying all the above process variables. As a final analysis the opportunity of heating up a low temperature waste water so as to improve the ammonia transfer rate will be assessed.

## 2. GAS-LIQUID EQUILIBRIUM COMPOSITIONS

The amount of  $\text{NH}_3$  that can be stripped away from the waste water or, vice versa, absorbed in the acidic solution is, to a major extent, conditioned by thermodynamic equilibrium.

The equilibrium distribution of ammonia in a gas and a liquid phase kept in contact at given operating conditions is substantially controlled by the following equilibria:

- Ammonia absorption:  $\text{NH}_3(\text{g}) = \text{NH}_3(\text{l})$ . (1)
- Ammonia hydrolysis:  $\text{NH}_3(\text{l}) + \text{H}^+ = \text{NH}_4^+$ . (2)
- Water dissociation:  $\text{H}_2\text{O} = 2 \text{H}^+ + \text{O}^{2-}$ . (3)

On the basis of data and formulas reported in [10-12], the following equation could be deduced, accounting for the variation of the gas-liquid distribution ratio  $K$  versus  $\text{pH}$  and  $T$  (this variation is plotted in Fig. 2):

$$K = \frac{y}{x} = \frac{1.441 \cdot 10^5 \cdot e^{-3513/T}}{1 + 2.528 \cdot 10^{-\text{pH}} \cdot e^{6054/T}} \quad (4)$$

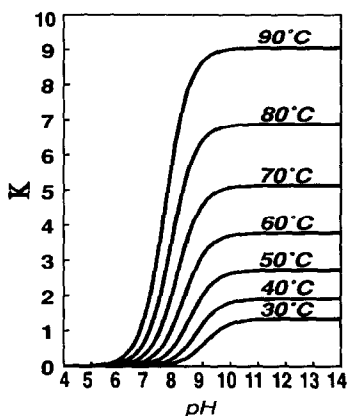


Figure 2. Variation of the distribution ratio  $K$  versus  $\text{pH}$  at different temperature levels.

Provided the  $\text{pH}$  is high enough (11 will be assumed as a project value), temperature strongly aids ammonia desorption, while ammonia absorption is clearly favoured when operating at  $\text{pH}$  values lower than 5, without almost any effect of  $T$ . This suggests to set the

pH of the two solutions at controlled, independent, optimum values. Besides, thanks to the air internal recycle, temperature can be kept at a high level all over the apparatus, with great benefits to the stripping unit and negligible influence on the absorption performance. Moreover, high temperatures allow to keep highly concentrated the acid ammonium sulphate solution without any risk of *in situ* precipitation. Further, steam consumption in the crystalliser is reduced.

Lime can be employed to reach the desired basicity. The needed amount can be easily evaluated on the basis of the composition reported in Table 1, assuming a 90% efficiency of technical CaO. NaOH could be, in principle, an alternative to lime. However, its almost five times higher cost per unit weight hampers its application despite its considerable technical advantages: scaling due to calcium salts is avoided, the basification is almost immediate and could be performed on-line with no need of specific apparatus.

Table 1.  
Characteristics of the industrial waste water taken as a case study.

Flow rate	: 50 m <sup>3</sup> /h.	Mn	: 4 ppm.
Temperature	: ca. 100 °C.	Fe	: 0.8 ppm.
NH <sub>3</sub>	: 150 ppm.	Cu	: 0.2 ppm.
SO <sub>4</sub> <sup>2-</sup>	: 2500 ppm.	C.O.D.	: 280 ppm.
HSO <sub>4</sub> <sup>-</sup>	: 2500 ppm.	Alcohols, aldehydes	: traces.
Na <sup>+</sup>	: 1000 ppm.		

### 3. CALCULATION SCHEMES AND DESIGN CRITERIA

#### 3.1 Stripping unit

A countercurrently operated packed-bed column was chosen as the ammonia stripper, equipped either with Raschig rings or with Berl saddles. The packing nominal dimension was assumed equal to 1½ inches, in line with the magnitude of calculated column diameters. For a given waste water composition and flow rate, the following calculation scheme was used:

- The inlet temperature of the waste water  $T_{lin}$  was fixed at a desired value.
- The K ratio was evaluated through equation (4).
- The desired outlet ammonia concentration was fixed and consequently the minimum air flow rate was calculated assuming the gas phase leaves the column at equilibrium. This value was cautiously increased by 20%.
- On the grounds of the experimental data deduced from the work of Fellingner [13] and plotted in Fig. 3 for both packing types, the height of the transfer unit  $H_{OG}$  [14] and the column diameter could be evaluated for a given ratio of the actual gas specific flow rate  $G$  and that at loading conditions  $G_l$ .
- The needed number of transfer units  $N_U$  was then calculated [14].
- The height of the stripping column  $H_{STR}$  could thus be evaluated as  $N_U$  times  $H_{OG}$ . The obtained value was conservatively increased by 30%.
- The pressure drop across the column was then calculated using the Leva expression reported in [15] for both packing types. The pressure drop in the demister was considered equivalent to that of 0.3 m of packed column.

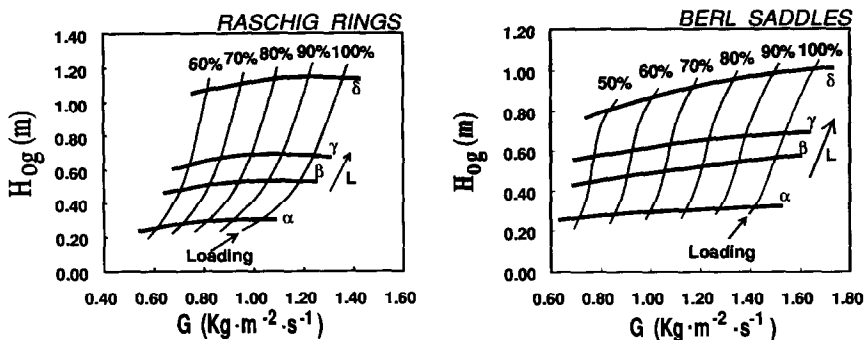


Figure 3.  $H_{Og}$  vs. the specific gas flow rate at different specific liquid flow rates ( $\alpha=2441$ ,  $\beta=4882$ ,  $\gamma=7324$ ,  $\delta=21971 \text{ Kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) for both packing types.

### 3.2 Absorption unit

The same equipment was chosen for the absorption unit, where fresh sulphuric acid has to be added so as to keep the desired acidity and produce ammonium sulphate.

The following calculation route was here employed:

- the liquid flow rate  $Q_l$ , the column diameter and the height of a single transfer unit were assumed equal to those of the stripping unit, being the gas flow rate the same (air recycle).
- Due to the extremely low  $K$  values at the chosen pH levels one transfer unit should be almost sufficient to absorb almost all the ammonia. Conservatively,  $N_u$  was set equal to 2, to possibly account for a certain reduction of the mass transfer efficiency caused by liquid channelling, or for inaccuracies due to the above assumptions. No  $\text{NH}_3$  was considered to be left in the air outlet of the absorption column.
- Pressure drops were calculated as for the stripping unit.

### 3.3 Water transport

As a consequence of thermal energy balances the temperatures of the two columns may become slightly different. Depending on these temperatures and on the compositions of the liquids, the saturation vapour pressures and enthalpies of air are generally different [17, 18]. Therefore a net water transport between the two columns may be enabled. Gas-liquid water transfer in packed columns is much more intense than ammonia transfer (see [19] for mass transfer coefficients). This implies that water saturation is in any case reached by the air flowing in both columns whose height was designed based on the slower ammonia transfer.

Temperature and enthalpy conditions along the columns can be easily derived via the well-known Mickey method [20]. Provided thermal dissipation through the ducts connecting the two columns is negligible, Fig. 4 reports a qualitative representation of the above conditions showing how saturation is rapidly approached in both columns. Once the inlet liquid temperatures are known the relative humidity of the gas phase leaving each column can be deduced and the net water transfer through the columns can be derived.

If the system is perfectly adiabatic, the sensible heat exchanged between the gas and the liquid phases in both columns is perfectly balanced by the latent heat of water evaporation or condensation respectively. Referring to Fig. 4, in this case points 1 and 2 should have the same saturation enthalpy. Therefore, if a proper thermal insulation is provided, the temperature

of the liquids remains thus constant along the columns. This is particularly useful in case heat recovery from the treated waste water is possible somewhere in the primary process.

The temperature of the absorption solution reaches a maximum value in adiabatic conditions; heat losses or dispersions lower this temperature affecting the water transport between the two columns, as later discussed.

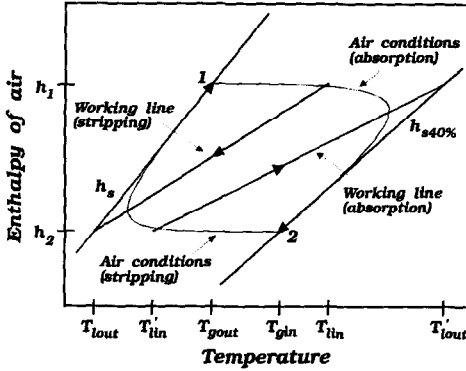


Figure 4. Mickey construction for the calculation of the enthalpy and temperature conditions in the air loop.

### 3.4 Economics

Table 2 and 3 list formulas and data used to evaluate the operating and the capital costs, respectively. Unit costs were assumed consistent with the Italian market (March 1993). Costs were updated to this datum by means of Cost Indexes whenever needed [24]. The unit treatment cost  $c_u$  was derived as follows:

$$c_u \text{ [}/m^3] = (\text{Capital Costs} + \text{Operating Costs}) / (Q_1 \cdot h_y) \tag{5}$$

As mentioned earlier, some calculations included pre-heating of the waste water. A shell-and-tube heat exchanger was chosen as the pre-heater. Operating and capital costs for this apparatus were evaluated as follows (assumed data:  $c_l = 0.682 \text{ Kcal} \cdot \text{Kg}^{-1} \cdot \text{K}^{-1}$  [25];  $\rho_l$  versus  $T$  from [26];  $U = 3000 \text{ Kcal} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{K}^{-1}$ ;  $\Delta h_{ev} = 530 \text{ Kcal} \cdot \text{Kg}^{-1}$ ):

$$\text{Operating cost (steam consumption)} = 1.1 \cdot c_{\text{steam}} \cdot h_y \cdot Q_1 \cdot \rho_l \cdot c_l \cdot \Delta T_{liq} / \Delta h_{ev} \tag{6}$$

$$\text{Capital cost (Shell: carbon steel; tube: stainless steel; steam at shell side)} [22] = \tag{7a}$$

$$= 5.963 \cdot e^{(4.5656 + 0.65 \cdot \ln(10.764 \cdot A))} \cdot (10.7639 \cdot A)^{0.1787} \quad \text{where:}$$

$$A = \text{heat exchange surface} = \frac{Q_1 \cdot \rho_l \cdot c_l}{U \cdot \Delta T_{ml}} ; \Delta T_{ml} = \frac{(100 - T_{in}) - (100 - T_{out})}{\ln\left(\frac{100 - T_{in}}{100 - T_{out}}\right)} \tag{7b}$$

**Table 2.**  
**Operating cost expressions (\$/y).**

<ul style="list-style-type: none"> <li>• <i>Chemicals</i></li> <li>• <math>\text{Ca(OH)}_2 = 0.0978 \cdot Q_1 \cdot h_y.</math></li> <li>• <math>\text{NaOH} = 0.518 \cdot Q_1 \cdot h_y.</math></li> <li>• <math>\text{H}_2\text{SO}_4 = 0.288 \cdot Q_{\text{NH}_3} \cdot h_y</math> ; <math>Q_{\text{NH}_3} = 10^{-6} \cdot Q_1 \cdot \rho_1 \cdot (x_{\text{in}} - x_{\text{out}}).</math></li> <li>• <math>(\text{NH}_4)_2\text{SO}_4 = -0.04 \cdot Q_{\text{sulph}} \cdot h_y</math> ; <math>Q_{\text{sulph}} = 7.765 \cdot Q_{\text{NH}_3}.</math></li> <li>• <math>\text{Steam} = 0.0165 \cdot h_y \cdot \frac{Q_{\text{sulph}}}{x_{\text{sulph}}} \cdot (100 - x_{\text{sulph}}).</math></li> </ul>	
<ul style="list-style-type: none"> <li>• <i>Electricity</i> [21]</li> <li>• <math>\text{Fan} = 1.338 \cdot 10^{-6} \cdot \frac{h_y \cdot Q_g \cdot \Delta P_{\text{tot}}}{E_f}</math> ; <math>\Delta P_{\text{tot}} = 1.1 \cdot (\Delta P_{\text{str}} + \Delta P_{\text{abs}}).</math></li> <li>• <math>\text{Pumps} = 1.155 \cdot 10^{-7} \cdot \frac{h_y \cdot \rho_1 \cdot Q_1 \cdot (2 + H_{\text{str}} + H_{\text{abs}})}{E_p}.</math></li> </ul>	
<ul style="list-style-type: none"> <li>• <i>Labor &amp; Supplies</i> [7] = 0.12 · Electricity.</li> <li>• <i>Maintenance</i> [7] = 0.02 · Invested capital.</li> <li>• <i>Overhead</i> [7] = 0.7 · (Labor &amp; Supplies + Maintenance).</li> <li>• <i>Contingency</i> [7] = 0.08 · (All above items).</li> </ul>	
<p><i>Assumed data:</i></p> <ul style="list-style-type: none"> <li>• <i>Unit costs :</i> <ul style="list-style-type: none"> <li>• NaOH = 0.35 \$/Kg.</li> <li>• <math>\text{Ca(OH)}_2 = 0.07</math> \$/Kg.</li> <li>• <math>\text{H}_2\text{SO}_4 = 0.1</math> \$/Kg.</li> <li>• <math>(\text{NH}_4)_2\text{SO}_4 = 0.04</math> \$/Kg.</li> <li>• Steam = 0.015 \$/Kg.</li> <li>• KWh = 0.05 \$.</li> </ul> </li> <li>• <i>Efficiencies:</i> <ul style="list-style-type: none"> <li>• <math>E_f = 0.60.</math></li> <li>• <math>E_p = 0.70.</math></li> </ul> </li> <li>• <i>Working time:</i> • <math>h_y = 8760</math> h/y.</li> </ul>	

**Table 3.**  
**Capital cost expressions (\$).**

<ul style="list-style-type: none"> <li>• <b>Equipment</b> <ul style="list-style-type: none"> <li>• Shell + Exteriors + Electricals + Piping [21] =  <math display="block">= 305.7 \cdot S \cdot \{[(H_{str} + 1.5)^{1.462} + 4.48] + [(H_{abs} + 1.5)^{1.462} + 4.48]\},</math> </li> <li>• Packing = <math>c_p \cdot S \cdot (H_{str} + H_{abs}).</math></li> <li>• Spray nozzles [21] = <math>36.25 \cdot Q_1.</math></li> <li>• Demisters [22] = <math>3163 \cdot G^2.</math></li> <li>• Fan [21] = <math>0.2911 \cdot \frac{\Delta P_{tot} \cdot Q_g}{E_f}.</math></li> <li>• Pumps [21] = <math>0.793 \cdot \{ \{641.1 \cdot [\frac{Q_1 \cdot (H_{str} + 1)}{E_p}]^{0.44} + Q_1 \cdot (H_{str} + 1)^{0.97} \} + \{641.1 \cdot [\frac{Q_1 \cdot (H_{abs} + 1)}{E_p}]^{0.44} + Q_1 \cdot (H_{abs} + 1)^{0.97} \} \}.</math></li> <li>• Crystalliser [22] = <math>5034 \cdot Q_{sulph}^{0.55}.</math></li> <li>• Instrumentation [7] = <math>0.05 \cdot (\text{All above items}).</math></li> </ul> </li> </ul>	
<ul style="list-style-type: none"> <li>• <b>Invested Capital</b> <ul style="list-style-type: none"> <li>• Equipment (see above).</li> <li>• Land &amp; Site development = <math>850 \cdot S.</math></li> <li>• Contingency [7] = <math>0.15 \cdot (\text{Equipment} + \text{Land \&amp; Site development} + \text{Packing}).</math></li> </ul> </li> </ul>	
<ul style="list-style-type: none"> <li>• <b>Total invested capital</b> <ul style="list-style-type: none"> <li>• Invested capital = Equipment + Land &amp; Site development + Contingency.</li> <li>• Start up [7] = <math>0.05 \cdot \text{Invested Capital}.</math></li> <li>• Working capital [7] = <math>0.05 \cdot \text{Invested Capital}.</math></li> </ul> </li> </ul>	
<ul style="list-style-type: none"> <li>• <b>Capital costs (\$/y)</b> <ul style="list-style-type: none"> <li>• Interest and depreciation = Annuity <math>\cdot (\text{Invested capital} + \text{Start up}).</math></li> <li>• Interest on working capital = Interest <math>\cdot \text{Working capital}.</math></li> </ul> </li> </ul>	
<b>Assumed data:</b> <ul style="list-style-type: none"> <li>• <math>c_p</math> [23] : <ul style="list-style-type: none"> <li>• Raschig rings (porcelain) = 1073 \$/m<sup>3</sup>.</li> <li>• Berl saddles (porcelain) = 444 \$/m<sup>3</sup>.</li> </ul> </li> <li>• Annuity = <math>0.15 \text{ y}^{-1}.</math></li> <li>• Interest = <math>0.08 \text{ y}^{-1}.</math></li> </ul>	



## 4. RESULTS AND DISCUSSION

### 4.1 Effect of $G/G_1$

For both Raschig rings and Berl saddles Fig. 5 shows the variation of the unit treatment cost as a function of  $G/G_1$  and  $T_{lin}$ . For higher values than 80% the effect of the above ratio on  $c_u$  is of minor importance even at low temperatures. This figure was kept constant in all further calculations, allowing a small safety margin from loading conditions. This is advisable considering the unavoidable errors in the determination of the loading curves (Fig. 3), and the possibility of a certain degree of fouling of the packing. Table 4 reports a set of input parameters which have been used as a reference for the calculations described in the next paragraphs.

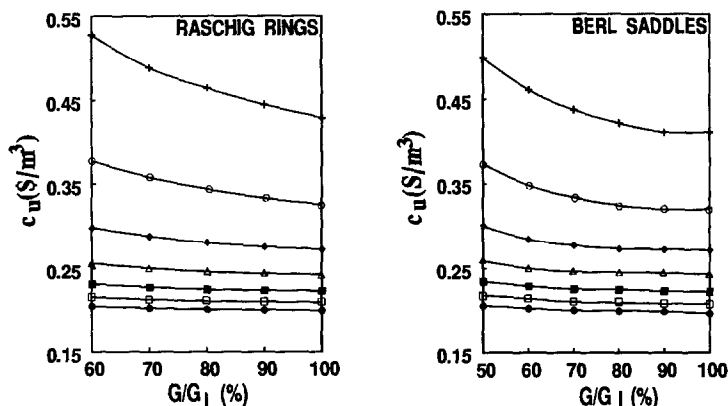


Figure 5 Effect of the  $G/G_1$  ratio on  $c_u$  for both packing types at different  $T_{lin}$  levels (+: 30°C; O: 40°C; ◆: 50°C; Δ: 60°C; ■: 70°C; □: 80°C; ●: 90°C).

Table 4.

Reference conditions (used in all the calculations unless otherwise specified).

•	Packing type	: Berl saddles;	•	$x_{in}$	: 150 ppm;
•	$Q_1$	: 50 m <sup>3</sup> /h;	•	$x_{out}$	: 15 ppm;
•	$G/G_1$	: 80 %;	•	$T_{lin}$	: 80 °C.

### 4.2 Water transport

Solubility data from [16] suggest to keep the ammonium sulphate concentration in the absorption solution equal to about 40% mass basis. At all temperatures of interest (30-90 °C), this concentration is comparatively close to the saturation limit so as to reduce the amount of water to be boiled away in the crystalliser, but still sufficiently lower to avoid  $(NH_4)_2SO_4$  precipitation within the absorption column. Depending on the temperature levels of the two columns, the water transported from the stripping column to the absorption column may be lower or higher than the total amount of water needed to keep the chosen  $(NH_4)_2SO_4$  concentration. For the reference case (Table 4) Fig. 6 shows the variation of the water flow rate to be poured in the absorption solution to keep the desired concentration level, as a function of the

temperature of the solution itself. Negative values represent an excess of water transported via the gas phase; consequently, as also reported in Fig. 6, the ammonium sulphate concentration in the absorption column would dramatically drop. This suggests to set a heater to warm up the solution whenever its concentration becomes lower than a minimum value. The energy consumption of the heater should be rather limited due to the comparatively small amount of solution continuously looping in the absorption column (less than  $1 \text{ m}^3$  for the reference case).

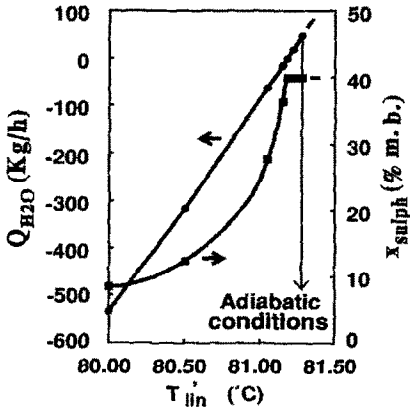


Figure 6. Variation of  $Q_{H_2O}$  with  $T_{IIin}$  and consequent  $x_{sulph}$  values ( $T_{IIin} = 80^\circ\text{C}$ ). Negative  $Q_{H_2O}$  values are not accounted for in the estimation of  $x_{sulph}$ .

#### 4.3 Effect of temperature

Fig. 7 shows the dramatic influence of  $T_{IIin}$  on the unit treatment cost at varying the purification level and the packing type. The effect of temperature is more and more marked as long as the imposed  $x_{out}$  decreases. This can be explained by the increasing importance of capital costs compared with operating costs when  $x_{out}$  is set lower and lower. The higher the K ratio, which is markedly enhanced by temperature at pH 11 (Fig. 2), the smaller the stripping column and the capital investment implied.

Fig. 8 reports the contributions to the overall capital costs for the reference conditions at  $40^\circ\text{C}$  and  $80^\circ\text{C}$ . Similarly, the contributions to the overall treatment costs are reported in Fig. 9. From these graphs a few considerations can be drawn:

- the capital costs at  $80^\circ\text{C}$  are less than a half of those at  $40^\circ\text{C}$ . This is due to the positive influence of temperature on K.
- At  $40^\circ\text{C}$ , capital costs are strongly affected by the size of the stripping and the absorption units and by those items which are in some way related to this last parameter (pumps, fan, instrumentation, contingency, etc.). The mentioned size is indeed rather large (see later Fig. 12), due to a comparatively low K value. When temperature and K increase, the contribution of the cost of the columns to the overall capital costs becomes less important since the column dimension decrease.
- At  $80^\circ\text{C}$  the crystalliser is the most expensive unit of the plant. Its size and its costs do not depend on temperature but they are directly linked to the amount of ammonia stripped away from the waste water.

- As a consequence, when operating at rather low temperatures particular attention should be focused on the design of the columns and on the choice of a proper packing material (which of course may be different from the ones considered in this work). At high temperatures the optimisation of the crystalliser becomes more important.
- Considering the treatment costs, at the chosen depreciation and interest rates, the importance of the capital costs and of those items which are strongly dependent the size of the columns is major at 40°C and minor at 80°C.
- The cost of chemicals and steam, once again related to the amount of stripped ammonia, is not a function of temperature. It controls the overall treatment costs at 80°C. It has to be noticed however that the cost of chemicals is affected to a major extent by the amount of lime employed. More than 90% of this amount is though needed, for the chosen case study, to neutralise the total acidity of the waste water, an operation that is always prescribed by environmental laws and thus not only implied by the ammonia stripping and recovery route.

Due to the positive effect of temperature on process performance and economics a pre-heating of the waste water might be beneficial. However, from an economic standpoint, the benefits linked to a stripping unit operating at higher temperatures may be overruled by the cost of pre-heating. Fig. 10 shows the variation of  $c_u$  with the stripping temperature at various  $\text{NH}_3$  abatement levels in case the temperature of the waste water was 10°C or 20°C before heating. These two situations are possibly representative of winter and summer conditions.

For the 20°C case, pre-heating is convenient only when very low  $x_{\text{out}}$  values are required. Particularly, the optimum stripping temperature is about 40°C when  $x_{\text{out}}$  is 1 ppm.

For colder waste waters (10°C) pre-heating is generally beneficial unless rather high ammonia outlet concentrations are tolerated (30 ppm). This effect is even more pronounced in case Raschig rings are used instead of Berl saddles. However,  $c_u$  remains for Raschig rings always higher than for Berl saddles.

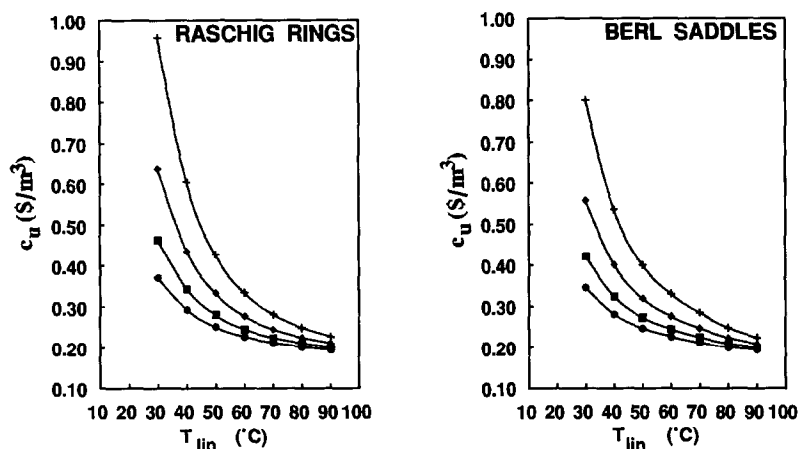


Figure 7. Effect of  $T_{\text{lin}}$  on  $c_u$  for both packing types at different  $x_{\text{out}}$  values (+: 1 ppm; ◆: 5 ppm; ■: 15 ppm; ●: 30 ppm).

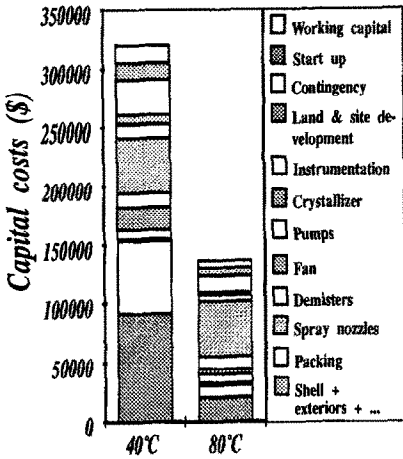


Figure 8. Contributions to the overall capital costs at 40°C and 80°C for the reference case.

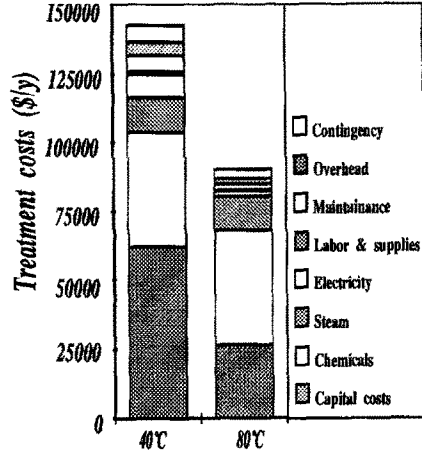


Figure 9. Contributions to the overall treatment costs at 40°C and 80°C for the reference case.

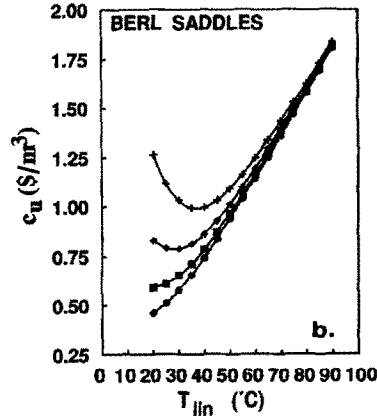
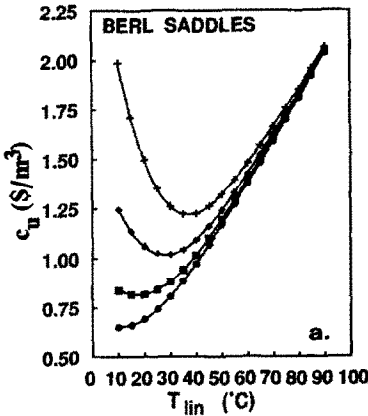


Figure 10. Variation of  $c_u$  with  $T_{lin}$  at different  $x_{out}$  values (+: 1 ppm; ◆: 5 ppm; ■: 15 ppm; ●: 30 ppm), after pre-heating from: a. 10°C; b. 20°C.

**4.4 Effect of packing type**

It can be easily noticed from figures 5 and 7 that Berl saddles outperform Raschig rings on an economic basis despite their higher unit cost (Table 3). This remains true at varying either the inlet and outlet ammonia concentrations or the flow rate. It seems therefore likely that more efficient, though more expensive packing (i.e. structured packing [27]) can even do better than Berl saddles, and lower further the unit treatment cost.

#### 4.5 Effect of $x_{out}$

$c_U$  and  $H_{STR}$  are plotted against  $x_{OUT}$  in figures 11 and 12 at different temperature levels. The unit treatment cost gets clearly lower when less severe ammonia abatements are required. However, especially at low temperatures,  $H_{STR}$  diminishes at a much higher rate than  $c_U$  when  $x_{OUT}$  is increased. This is due to the already described prominence of operating costs at high temperatures compared with capital costs, and particularly to the fact that steam and chemicals requirements are much less sensitive to  $x_{out}$  compared with the size of the stripping column.

When operating at high temperatures ( $>50^\circ\text{C}$ ), very intensive  $\text{NH}_3$  abatements (e.g. necessary to cope with very restrictive law limits) can be attained with only a marginal increase of the unit treatment cost.

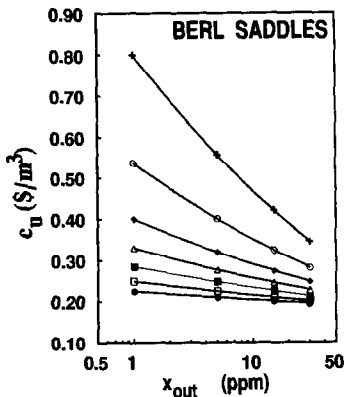


Figure 11. Variation of  $c_U$  with  $x_{out}$  at different  $T_{lin}$  levels (+:  $30^\circ\text{C}$ ; O:  $40^\circ\text{C}$ ; ◆:  $50^\circ\text{C}$ ; Δ:  $60^\circ\text{C}$ ; ■:  $70^\circ\text{C}$ ; □:  $80^\circ\text{C}$ ; ●:  $90^\circ\text{C}$ ).

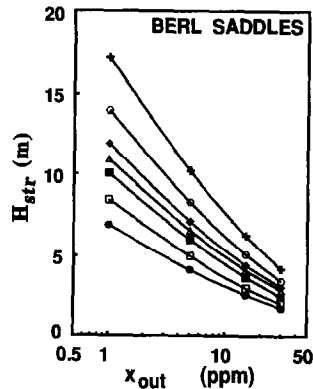


Figure 12. Variation of  $H_{STR}$  with  $x_{out}$  at different  $T_{lin}$  levels (+:  $30^\circ\text{C}$ ; O:  $40^\circ\text{C}$ ; ◆:  $50^\circ\text{C}$ ; Δ:  $60^\circ\text{C}$ ; ■:  $70^\circ\text{C}$ ; □:  $80^\circ\text{C}$ ; ●:  $90^\circ\text{C}$ ).

#### 4.6 Effect of $x_{in}$

Fig. 13 shows the variation of  $c_U$  with  $x_{in}$  at different temperature levels. It can be readily noticed from this graph how the slope of the isothermal curves decreases rapidly at first and becomes nearly constant at high  $x_{in}$  values. This is due to the fixed and variable costs related to the crystalliser, which govern  $c_U$  when comparatively large amounts of ammonia need to be converted into  $(\text{NH}_4)_2\text{SO}_4$  crystals. Once again the optimum design of the crystalliser is in this case essential.

#### 4.7 Effect of $Q_1$

When  $Q_1$  is increased an obvious decrease of the unit treatment cost can be noticed, as a consequence of a less-than-proportional increase of capital costs. However, for technical reasons, a limit to the column diameter has to be set; beyond this limit, which is here fixed equal to 3.5 m, a multiple column set-up has to be used.  $c_U$  is thus a step function of  $Q_1$ , as shown in Fig. 14. However, for sufficiently high  $Q_1$  values the unit treatment cost remains in the range 0.18-0.20  $\$/\text{m}^3$ . This can be considered a competitive value, as later discussed.

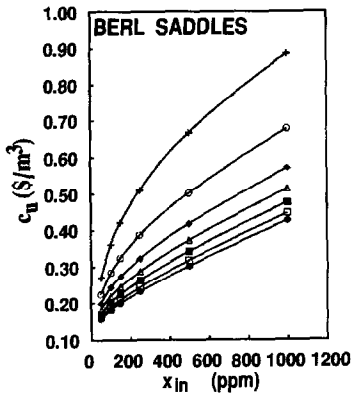


Figure 13. Variation of  $c_u$  with  $x_{in}$  at different  $T_{in}$  levels (+: 30°C; O: 40°C; ◆: 50°C; Δ: 60°C; ■: 70°C; □: 80°C; ●: 90°C).

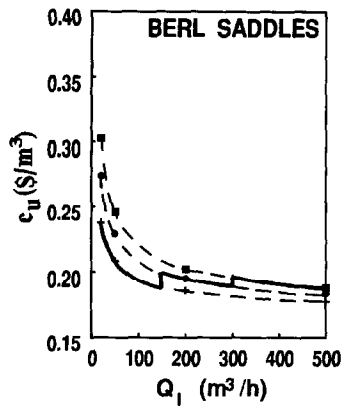


Figure 14. Variation of  $c_u$  with  $Q_l$  for multiple column setups (+: 1 column; ●: 2 columns; ■: 3 columns; maximum column diameter: 3.5 m).

## 5. CONCLUSIONS

On the basis of the obtained results, concerning both the technical and the economical profile of the studied process, the following final considerations can be drawn:

- The ammonia stripping and recovery system with internal air recycle appears technically feasible and relatively easy to control.
- When operating at high temperatures stripping is markedly favoured. Highly efficient and compact units can be used for this purpose. Therefore the studied process seems particularly promising whenever intrinsically warm waste waters have to be treated. Dealing with low temperature streams high  $T_{in}$  levels could be reached with a pre-heating system, which is though not economic unless comparatively high stripping efficiencies are required.
- Compared to traditionally employed stripping units, which have no recovery systems and thus spread the stripped ammonia in the atmosphere, the proposed process, converting  $NH_3$  into ammonium sulphate, is highly preferable from the environmental viewpoint, especially when high  $NH_3$  quantities have to be removed.
- The unit treatment cost is affected by the capital and the operating costs in a different way at varying the initial concentration level, the required removal extent, the overall flow rate to be treated and, most of all, the operating temperature. Particularly,  $c_u$  becomes more and more affected by the operating costs as long as temperature and  $x_{out}$  increase. However, a considerable part of operating costs is linked to the amount of lime needed to neutralise the waste water considered as a case study, an operation that is compulsory and independent of the specific treatment performed.
- Finally, the  $c_u$  value (equal to about 0.2 \$/m<sup>3</sup> for the chosen reference conditions) is hardly comparable to literature data on ammonia removal, since most contributions took into account only civil waste waters, having relatively low initial ammonia concentrations (a few tenths of ppm). In those conditions the cost of a simple stripping treatment is about 1/3 of

that of biological denitrification and ion exchange, about 1/4 of breakpoint chlorination, and down to 1/10 of membrane treatments [7]. In this context the additional cost implied by the recovery section of the analysed process, which allows to avoid any environmental pollution as well as the other just-quoted processes, appears fairly tolerable.

## ACKNOWLEDGEMENTS

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## NOMENCLATURE

A	heat exchange surface (m).
$c_l$	heat capacity of the liquid ( $\text{Kcal}\cdot\text{Kg}^{-1}\cdot\text{K}^{-1}$ ).
$c_p$	unit cost of packing ( $\$/\text{m}^3$ ).
$c_u$	unit treatment cost ( $\$/\text{m}^3$ ).
$E_f$	fan efficiency.
$E_p$	pump efficiency.
G	gas specific mass flow rate ( $\text{Kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ).
$G_l$	gas specific mass flow rate at loading conditions ( $\text{Kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ).
h	enthalpy of air ( $\text{Kcal}/\text{Kg}$ dry air).
$\Delta h_{cv}$	heat of evaporation of water ( $\text{Kcal}/\text{Kg}$ ).
$h_s, h_{s40\%}$	saturation enthalpy of air for the system air-water, air-40% mass basis ( $\text{NH}_4$ ) <sub>2</sub> SO <sub>4</sub> aqueous solution ( $\text{Kcal}/\text{Kg}$ dry air).
$h_y$	working time (h/y).
$H_{abs}, H_{str}$	height of the absorption, stripping column (m).
$H_{og}$	height of one transfer unit (m).
L	liquid specific mass flow rate ( $\text{Kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ).
K	gas-liquid distribution ratio at equilibrium conditions.
$N_u$	number of transfer units.
$\Delta P_{abs}, \Delta P_{str}$	pressure drop in the absorption, stripping tower (cm H <sub>2</sub> O).
$\Delta P_{tot}$	total pressure drop along the air loop (cm H <sub>2</sub> O).
$Q_g, Q_l$	gas, liquid flow rate ( $\text{m}^3/\text{h}$ ).
$Q_{H2O}$	water make-up needed to keep a 40% mass basis concentration in the absorption solution ( $\text{Kg}/\text{h}$ ).
$Q_{NH3}, Q_{sulph}$	mass flow rate of ammonia, ammonium sulphate ( $\text{Kg}/\text{h}$ ).
S	column section ( $\text{m}^2$ ).
T	temperature (K).
$T_{lin}, T'_{lin}$	liquid inlet temperature of the stripping, absorption column ( $^{\circ}\text{C}$ ).
$T_{lout}, T'_{lout}$	liquid outlet temperature of the stripping, absorption column ( $^{\circ}\text{C}$ ).
$T_{gin}, T'_{gin}$	gas inlet temperature of the stripping, absorption column ( $^{\circ}\text{C}$ ).
$T_{gout}, T'_{gout}$	gas outlet temperature of the stripping, absorption column ( $^{\circ}\text{C}$ ).
U	heat transfer overall coefficient ( $\text{Kcal}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{K}^{-1}$ ).
x	ammonia weight fraction in the liquid phase (ppm).
$x_{in}, x_{out}$	ammonia weight fraction in the liquid inlet, outlet of the stripping column (ppm).

$x_{sulph}$	ammonium sulphate weight fraction in the absorption solution (% mass basis).
$y$	ammonia weight fraction in the gas phase (ppm).
$\rho_l$	liquid density (Kg/m <sup>3</sup> ).

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