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RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

CATION-EXCHANGE REMOVAL OF COPPER FROM AMMONIACAL AQUEOUS SOLUTION

by

P.S. BULL
J.V. EVANS

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ABSTRACT

This report examines the nature of the adsorbed copper-ammine species in the resin phase, evaluates their stability constants and compares them with published data obtained in aqueous solution. It extends the study of the adsorption of copper by a strong acid-cation exchanger to solutions containing low concentrations of ammonia (0-0.032 M), and copper (10^{-4} M) and differentiates between the role of the ammonium ion and the free ammonia in the ion-exchange process.

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ADSORPTION; AMMONIA; AMMONIUM COMPOUNDS; AQUEOUS SOLUTIONS; COPPER; COPPER COMPLEXES; COPPER SULFATES; ION EXCHANGE; ION EXCHANGE MATERIALS; PURIFICATION; RESINS; TITRATION

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Figure 1 Titration of 1 mℓ of R_2Cu-form resin in 45 mℓ 5 x 10^{-4} M $(NH_4)_2SO_4$ solution (25°C).

Figure 2 Formation curves for copper-ammines in aqueous solution (Bjerrum (1957)) and ion exchange resins (this report and the measurements of Stokes and Walton (1954)).

Figure 3 The effect of ammonium ion concentration on the breakthrough curves for copper.

Figure 4 The effect of ammonia concentration on the breakthrough curves for copper.

1. INTRODUCTION

The presence of copper in the feedwater of direct cycle nuclear power reactors can lead to the deposition in the reactor core of copper oxides on the fuel element surfaces. Similarly, in conventional fossil-fuelled power plant copper in the feedwater will tend to deposit on boiler surfaces.

Copper entering the primary circuit from the copper alloy contained in feedwater systems of direct-cycle reactors has been found to be as high as 2.6 kg/month (Rocca 1966). It has been estimated that some 80% of the total copper fed to the core can deposit on the fuel elements (Pickman 1969). Copper appears to deposit in the reactor core in one of two ways; either it appears as a dense deposit of almost pure copper oxide or it deposits concurrently with iron oxides to give a layer of mixed metal oxides.

Sisson (1970) and Rocca (1966) describe how in the Dresden and Carigliano dual-cycle early generation BWRs copper oxide was found to preferentially plate-out around the fuel element orifices with adverse effects on core pressure drop and coolant flow. Hartman and Axtell (1969) have reported somewhat similar deposits of copper oxide on the bottom of fuel bundles in the Big Rock BWR.

It has been found by Charlesworth (1970) that deposits of steel corrosion products (crud) on the fuel-sheaths and other heat-transfer surfaces were porous and the deposition process reversible. The porous deposits were said to offer little resistance to heat-transfer because of the incidence of wick-boiling. However, the presence of non-ferrous alloys in the system can materially change the properties of these iron oxide deposits. Copper, nickel and zinc corrosion products can all form dense well-bonded deposits (Sisson 1970, Hazel 1968, Megerth 1968). If the products deposit concurrently with iron oxide they may consolidate the porous deposit and greatly reduce the release rate and porosity. This consolidation will in turn greatly increase the resistance to heat flow to the coolant with resultant overheating and possible failure of the fuel cladding. Examples of this behaviour have occurred in several reactors including SGHWR Prototype (Pickman 1969) and Big Rock (Holladay 1964, Howard and Duncan 1966, Worthington and Hazel 1966, Megerth 1968).

Similarly, with a fossil-fuelled power plant it has been estimated that copper, derived from the materials of the feedwater system, builds up continuously in a large boiler at the rate of 1-2 g h^{-1} (Holmes and Mann 1965). A lower rate of deposition was found by Galloway (1963) who reported a build-up over ten years' operation of > 6 kg of copper in a 1300 psig boiler. In addition to its likely effect on heat transfer and flow via deposition as the

solid oxide, copper has long been suspected of playing a role in 'on-load' corrosion of boiler tubes. However, divergent opinions are held on this point and the role of copper is not certain (Evans 1960, Hamer, Jackson and Thurston 1961, Holmes and Mann 1965). A recent report (CEGB 1971b) has briefly mentioned that deposited layers of iron and copper represent an important agency for the concentration of caustic soda and chloride solids, two prime causes of 'on-load' corrosion (Holmes and Mann 1965). With the advent of the high temperature once-through boilers the deposition of copper oxide in the turbine has caused serious reduction in turbine efficiency (CEGB 1971a, Pocock and Stewart 1963).

The high copper levels in the feed of direct-cycle reactors have been largely overcome in the early generation dual-cycle BWRs by replacing the copper alloy high pressure heaters by stainless steel (Hartmann and Axtell 1970). Later generation BWRs with their higher rating use all-ferrous feed trains and full-flow condensate polishing units. These latter are high flow-rate mixed bed ion-exchange units which remove both dissolved and suspended impurities (Applebaum 1968, Frazer 1967, CEGB 1971a). The use of condensate polishing would be particularly necessary where copper alloys, such as Admiralty or aluminium brass, were used in the condenser, this being standard practice in seawater-cooled stations, or in the low pressure feed heaters. A typical value which has been quoted for copper in the feed of direct cycle reactors during normal operation is 0.002 mg ℓ^{-1} Cu (Crits and White 1970, Pickman 1969).

Similarly with the later once-through high temperature boilers the tendency has been to all-ferrous feed trains (Sisson et al 1968) and condensate polishing (CEGB 1971a, Frazer 1967). Very low copper limits are specified; typical values quoted are 0.0015 mg ℓ^{-1} at the exit of the polishing unit (CEGB 1971a) and 0.01 mg ℓ^{-1} for the feed (Calise and Duff 1958, Sussman 1971), and measured values after polishing are quoted as less than 0.001 mg ℓ^{-1} (Frazer 1967).

Le Surf, Bryant and Tanner (1966) have suggested that the addition of ammonia at a level of 10 mg ℓ^{-1} to the circuit of a direct-cycle reactor would allow the use of mild steel for circuit construction. The CANDU-BLW reactor which started commissioning in 1971 employs carbon-steel and a coolant dosed with ammonia in the manner described. A 'zero solids' water treatment for pH and oxygen control using ammonia and hydrazine additions to boiler feedwater is very widely used in conventional fossil-fuelled plant. Typical levels of dosing are ammonia up to 1 mg ℓ^{-1} and hydrazine not less than 0.02 mg ℓ^{-1}

(CEGB 1971a). In the case of once-through steam generators utilising all-ferrous feed trains and a pH of 9.6, ammonia dosing at a level of 2 mg ℓ^{-1} is used (Sisson et al 1968, Frazer 1967).

Use of ammonia and hydrazine, particularly at the high level recommended for direct-cycle reactor systems, will result in large concentrations of ammonia appearing in the steam (approximately 30 mg ℓ^{-1} for 10 mg ℓ^{-1} water dosing (Le Surf et al 1966)) and subsequently in the condenser. The concentrations in the condenser can rise to several hundred mg ℓ^{-1} in certain areas such as the inlet of the air cooler and even higher at the gaseous extract. Where copper alloys are used in the condenser and possibly low pressure feed heater tubes these latter can corrode and give a high release of copper into the condensate (Shreir, 1963, Leidheiser 1971, Sisson 1961, Hopkinson 1964, Tice and Venizelos 1963). Thus if ammonia dosing were to be used for a seawater-cooled station then the condensate polishing unit must be able to remove copper from ammoniacal solutions down to the limits previously quoted. In an ammonia-dosed system the cation resin used for polishing would be in the ammonium form (Kennedy 1968, Sisson et al 1968, Frazer 1967).

Copper forms very stable ammine complexes in ammonia solutions (Bjerrum 1940) and information as to its cation-exchange behaviour in this form is limited. It has previously been shown that the positively charged copper-ammine complexes are adsorbed onto cation-exchange resins in the presence of high concentrations of ammonia in the range 0.56 to 5.12 $\underline{M}$ NH_3 (Tolmachev, Kolesnikova and Do Min Hong 1968). These authors state that over this range increasing ammonia concentration leads to faster kinetics for the ion-exchange reaction but a decrease in the total capacity for copper. These results are for batch ion-exchange and the authors claim that the results are due to the increase in the proportion of the more highly coordinated complex $Cu(NH_3)_5^{2+}$. However, we were interested in the effect of lower concentrations of ammonia ($\sim 10^{-3}$ $\underline{M}$ or 10-50 mg ℓ^{-1} NH_3) as may occur at the entrance to the condensate polishing unit, and where the lower-order complexes are more significant. It is also important to know how this complex formation affects the characteristics of column ion-exchange.

The nature of the copper species in the resin phase in contact with ammoniacal solutions has been investigated (Stokes and Walton 1954). Using a batch equilibration technique in which they added various amounts of ammonia to batches of resin in the cupric form, they were able to determine the formation curve for the copper-ammine complexes in the resin phase. Because the points fell near to the formation curve given for the aqueous solution complexation

of copper with ammonia (Bjerrum 1957) the authors assumed that the stability constants for the copper-ammine complexes are the same in the resin phase as in aqueous solution. However, this again tells us little about column operation and the authors did not look for leakage of copper from the resin into the solution.

The work reported here was designed:

(i) to obtain a more accurate measurement of the formation curve for the copper-ammine complexes in the resin environment, using a pH titration technique, and to derive approximate stability constants for these complexes from this curve;

(ii) to determine the effect of this complexation (and therefore of ammonia concentration) upon the characteristics of ion-exchange columns using ammonium-form cation-exchange resins for the removal of copper, under conditions of low concentrations of copper and ammonia.

2. EXPERIMENTAL

2.1 Resin and Reagents

The two resins used in these experiments were the Rohm and Haas nuclear grade cation resin, IRN77 (16 to 50 mesh) and the Dowex 50W resin (100-200 mesh).

The Rohm and Haas resin was dried overnight at 105°C and found to contain 0.44 g of dry resin per mℓ of wet resin. The exchange capacity for Na^+ and NH_4^+ was 1.6 mmol $m\ell^{-1}$ resin, found by pH titration with the appropriate base. The exchange capacity for Cu^{2+} was 0.8 mmol $m\ell^{-1}$ resin, found by measuring the dry weight gain of a measured volume of resin when saturated with copper sulphate solution. This figure was rechecked by stripping the resin with dilute acid and analysing the solution for Cu^{2+} spectrophotometrically using MHATT reagent (Corbett 1966). The Dowex resin had an exchange capacity for Cu^{2+} of 0.95 mmol $m\ell^{-1}$ resin and contained 0.42 g dry resin per mℓ of wet resin.

All reagents were of analytical grade. Solutions were prepared using triply-distilled, demineralised water of conductivity less than 0.5 μS cm^{-1}.

2.2 Titration of Copper-form Resin with Ammonia

1 mℓ of IRN77 resin was saturated batchwise with copper sulphate solution, rinsed and placed in a titration vessel with a known volume of 5×10^{-4} M ammonium sulphate solution. This mixture was then titrated with 0.14 M ammonia solution, allowing time to equilibrate between each addition. The titration was performed with magnetic stirring at 25°C in a nitrogen atmosphere, to exclude CO_2. The formation of complex ammines in the resin was followed by

measuring the change of pH in the solution (Bjerrum 1957). It was noted that at the end of the titration no copper could be detected in the solution above the resin (limit of detection 0.5 $\mu g Cu\, m\ell^{-1}$ using MHATT reagent (Corbett 1966)).

2.3 Column Experiments

The concentration of copper in the solutions used for the column experiments was kept as low as possible to avoid precipitation and to approximate possible practical conditions. This necessitated keeping the column size and bed volume as small as possible and the flowrate as high as possible to reduce the period of the runs to a workable length. In addition, condensate polishing units are typically run at a high flow per unit bed area compared to conventional ion-exchange units. Use of these conditions gave rise to potential interference by wall and channelling effects. This was overcome by using the smaller bead size resin Dowex 50W where preliminary experiments obtained using this resin gave results differing markedly from those obtained with the coarser IRN77.

Two series of column experiments were carried out to separate the effect of both ammonium ion and free ammonia concentration on copper uptake by the resin. The conditions for these runs were as follows:

Ammonium Ion Concentration

Solutions - 10^{-3} M copper sulphate in various concentrations (5×10^{-5} M to 2.5×10^{-2} M) of ammonium sulphate at pH 5.3.

Temperature - 25°C.

Column - 5 mℓ of IRN77 resin, saturated batchwise by ammonium hydroxide, rinsed and placed in a column of cross-section 1.0 cm^2. Experiments were also carried out at two concentrations (5×10^{-3} M and 5×10^{-2} M) of ammonium sulphate using Dowex 50W resin in place of the IRN77. The results were identical to those obtained with the larger resin beads so it was assumed that wall and channelling effect were not interfering significantly under these conditions.

Flowrate - 5.0 $m\ell\ min^{-1}$.

Free Ammonia Concentration

Solutions - 10^{-4} M copper sulphate in 1.5×10^{-2} M ammonium sulphate with various levels of ammonia (0-550 mg ℓ^{-1}).

Temperature - 25°C.

Column - 1 mℓ of Dowex 50W resin in the ammonium form, rinsed and placed in a column of cross-section 0.20 cm^2. A preliminary series of runs were carried out using IRN77 in a column of cross-section 0.20 cm^2. The results were similar but showed rather more scatter

and it was assumed that wall and channelling effect were significant in the earlier runs.

Flowrate - 1.0 mℓ min^{-1}.

Breakthrough curves, up to the point of 50% breakthrough ($C/C_o = 0.5$) were investigated for these solutions. C = the cupric ion activity of the effluent and C_o = the cupric ion activity of the original solution.

Cupric ion activity was measured directly on the ammoniacal solutions using an Orion solid state specific ion electrode.

3. RESULTS AND DISCUSSION

3.1 Titration of Copper-form Resin with Ammonia

The complexation reactions in aqueous solution are represented as:

$$Cu(NH_3)_{n-1}^{2+} + NH_3 = Cu(NH_3)_n^{2+} \quad (n=1, 2, \ldots 5)$$

and the stability constants

$$k_n = \frac{[Cu(NH_3)_n^{2+}]}{[Cu(NH_3)_{n-1}^{2+}] \cdot [NH_3]} \qquad \ldots(1)$$

The equilibrium depends only upon the activity of ammonia in solution and is independent of such variables as total copper concentration, pH or ammonium ion concentration. However, the ammonia must also satisfy the following equilibrium -

$$NH_3 + H^+ = NH_4^+$$

$$K_{NH_4^+} = \frac{[NH_3] \cdot [H^+]}{[NH_4^+]} \qquad \ldots(2)$$

For solutions of ammonium hydroxide and ammonium salt, mass balance and electroneutrality require that:

$$[NH_4^+]_{total} = [NH_4^+]_{initial} \cdot \frac{V_1}{V_2} + [OH^-] - [H^+]$$

where V_1 and V_2 are the initial and final volumes. For pH greater than 7.8 the last term is neglected and

$$[NH_4^+]_{total} = [NH_4^+]_{initial} \cdot \frac{V_1}{V_2} + [OH^-]$$

$$\text{or} \quad [NH_4^+]_{total} = [NH_4^+]_{initial} \cdot \frac{V_1}{V_2} + \frac{10^{-14}}{[H^+]} \qquad \ldots(3)$$

Substituting into Equation (2) and rearranging gives

$$[NH_3] = \frac{K_{NH_4^+}}{[H^+]} \cdot \left([NH_4^+]_{initial} \cdot \frac{V_1}{V_2} + \frac{10^{-14}}{[H^+]} \right) \qquad \ldots(4)$$

From Equation (4) it follows that, given $K_{NH_4^+}$ and the initial ammonium salt concentration, then the measurement of pH after a given volume of titrant addition ($V_2 - V_1$) will give the value of $[NH_3]$ at that point. The amount of ammonia complexed with the copper may then be calculated by difference.

Copper can also coordinate with ammonia in the ion-exchange resin (Nelson and Walton 1944). Similar equations may be written as:

$$R_2Cu(NH_3)_{n-1} + NH_3 = R_2Cu(NH_3)_n \quad (n=1, 2, \ldots 5)$$

$$\text{and} \quad k_n = \frac{[R_2Cu(NH_3)_n]}{[R_2Cu(NH_3)_{n-1}] \cdot [NH_3]} \qquad \ldots(5)$$

where R represents a single ion-exchange group within the resin matrix.

The ratio of activities of copper species can be approximated by the ratio of their concentrations in the same phase. We will assume that the activity of ammonia in the resin phase is the same as that in the aqueous phase as is usual in phase distribution studies. Thus pH measurement will permit us to follow the complexation reaction through Equation (4).

By choosing a value of $[NH_4^+]_{initial} = 10^{-3}$ M and titrating with approximately 0.1 M ammonia solution it was possible to keep $[NH_4^+]$ reasonably constant throughout the titration. The value of $K_{NH_4^+}$ used in these tabulations was $10^{-9.25}$ (Bjerrum 1957).

The titration curve is given in Figure 1; subsequent calculations yielded the 'formation curve' in Figure 2, the plot of $p[NH_3]$ against $\bar{n}$, where $\bar{n}$ is the average number of coordinated NH_3 groups per Cu^{2+} ion. Figure 2 also shows the formation curves obtained by Bjerrum (1957) for copper-ammine complexes in solution and by Stokes and Walton (1954) for ion-exchange resin.

Using the following procedure which is similar to that of Bjerrum, the stability constants for the copper ammines in the resin can be estimated from Figure 2.

When $\bar{n} = i - \frac{1}{2}$ ($i=1, 2, \ldots 5$) then the main species in solution will be those given by $n = i - 1$ and $n = i$. Neglecting other species:

$$\bar{n} = \frac{[R_2Cu(NH_3)_{i-1}] \cdot (i-1) + [R_2Cu(NH_3)_i] \cdot i}{[R_2Cu(NH_3)_{i-1}] + [R_2Cu(NH_3)_i]}$$

$$= \frac{[R_2Cu(NH_3)_{i-1}] \cdot (i-1 + i \cdot k_i \cdot [NH_3])}{[R_2Cu(NH_3)_{i-1}] \cdot (1+k_i \cdot [NH_3])} \qquad \text{(from (5))}$$

$$\text{i.e. } i-\tfrac{1}{2} = \frac{i-1 + i \cdot k_i \cdot [NH_3]}{1+k_i \cdot [NH_3]} \qquad \text{at } \bar{n} = i - \tfrac{1}{2}$$

This reduces to

$$k_i = \frac{1}{[NH_3]} \quad \text{at } \bar{n} = i - \tfrac{1}{2} \qquad \ldots(6)$$

Similarly at $\bar{n} = i$ the species in solution will be those given by $n = i - 1$, $n = i$ and $n = i + 1$ and it can be shown that $k_i \cdot k_{i+1} = \frac{1}{[NH_3]^2}$ at $\bar{n} = i$ ...(7)

Using Equations (6) and (7) the following estimates of the stability constants k_n (n=1, 2, ... 5) were obtained from Figure 2 and compared with those obtained by Bjerrum for the aqueous solution case.

TABLE 1

	$R_2Cu(NH_3)_n$	$Cu(NH_3)_n^{2+}$
log k_1	4.5	4.48
log k_2	3.7	3.68
log k_3	3.1	3.01
log k_4	2.5	2.16
log k_5	1.9	~-0.5

For the first four constants there is little difference. There could be a difference in the fifth coordination position however. According to Bjerrum the ratio between consecutive stability constants k_n and k_{n+1} in a stepwise reaction is, from statistical considerations, proportional to the expression $\frac{(N-n+1) \cdot (n+1)}{(N-n) \cdot n}$ where N is the number of equivalent positions (i.e. the total number of equivalent steps in the reaction). Table 1 shows that the constants for the aqueous solution case conform approximately to this relationship when N = 4. Thus the first four coordination positions are equivalent whereas the fifth differs. This behaviour, along with the Jahn-

Teller effect, has been observed in other copper complexes (Cotton and Wilkinson 1962). Indeed there are some square planar, four-coordinate copper complexes (Cox et al 1936).

These constants estimated for the complexes in the resin phase show no large change for the fifth position. The ratios of the consecutive formation constants fit the above relationship more closely if N is made equal to 6. This suggests that in the environment of the high fixed charge density of the resin phase all six octahedral positions around the Cu^{2+} ion are equivalent and copper may coordinate five or even six ammonia molecules equivalently under these conditions.

Substantiation of this hypothesis was not possible due to the inaccuracy of the method at high ammonia concentrations. Furthermore, these concentrations are outside the range of interest for this investigation. However, it was confirmed that the ammine-complexes of copper participate in ion-exchange on sulphonic cation-exchange resin and that the nature of the species in the resin phase are the same as those in the aqueous phase at the levels of ammonia likely to be encountered in the feedwater of a direct-cycle reactor.

3.2 Column Experiments

In evaluating the effect on copper ion-exchange of varying the free ammonia concentration, early problems were encountered with precipitation of hydroxo-compounds of copper. These were overcome by (i) adjusting solutions to a constant, high ammonium ion concentration with ammonium sulphate so that the required ammonia concentration could be obtained at lower pH, and (ii) lowering the total copper concentration. The latter was possible because the ion-exchange breakthrough curves were determined using an Orion solid state specific ion electrode for measuring the effluent Cu^{2+} activity. This electrode was found to give a linear millivolt response to the logarithm of cupric ion activity down to very low levels, measurements to below 10^{-11} M being made satisfactorily in this work. (The manufacturer claims an ability to measure to 10^{-20} M in systems buffered with copper ions (Orion Research Inc. 1968).) The measurements were found to be free from interference from other ions in this system. A change of one unit in the log of cupric ion activity gave a 30 millivolt change in response.

Using the ammonium form of the cation exchanger the selectivity of this resin for copper may be influenced by the concentrations of both the ammonium ion and free ammonia in solution. In order to separate these two effects the first measurements were made at pH 5.3 in various concentrations of ammonium sulphate only and therefore negligible free ammonia.

The results are given in Figure 3. Ammonium ion concentration $\leqslant 5 \times 10^{-3}$ M had no effect on the amount of copper removed by the resin. A concentration of 5×10^{-2} M caused 25% loss in capacity for copper to a point of 50% breakthrough.

It was shown that with a total copper concentration of 10^{-4} M the addition of 1.5×10^{-2} M ammonium sulphate was sufficient to prevent precipitation over the required range of free ammonia concentration. Figure 3 shows that this ammonium ion concentration is sufficient to cause some reduction in the breakthrough capacity for copper (the total copper concentration here being only one tenth of that in Figure 3). Since the ammonium ion concentration was maintained constant while the ammonia concentration was varied the influence of the latter could be ascertained. High ammonium ion concentrations also simplify the determination of $[NH_3]$ from pH measurement by reducing Equation (4) to

$$[NH_3] = \frac{K_{NH_4^+}}{[H^+]} \cdot [NH_4^+]_{initial} \qquad \ldots(8)$$

The amount of ammonia complexed with the copper is also a negligible fraction of the total concentration of ammonia plus ammonium ion.

The results of the column experiments in which the ammonia concentration was varied in 1.5×10^{-2} M ammonium sulphate are summarised in Figure 4 and although there is a slight spread of the results there is no definite trend over the ammonia concentration range of 0 to 550 mg ℓ^{-1}. Using Bjerrum's stability constants the composition of the copper species in these solutions varied from 100% Cu^{2+} at 0 mg ℓ^{-1} NH_3, to 83% $Cu(NH_3)_4^{2+}$ and 16% $Cu(NH_3)_3^{2+}$ at 550 mg ℓ^{-1} NH_3. Therefore, it is concluded that the presence of this concentration of ammonia has no significant effect on the ion-exchange removal of copper from solution.

Figure 3 and Figure 4 show that significant sorption of copper occurs at high concentrations of ammonium ion in solution. The selectivity of the resin for $Cu(NH_3)_n^{2+}$ species is similar to that for Cu^{2+} but much greater than that for NH_4^+.

The observation that the formation of copper-ammine complexes has little or no effect on the cation-exchange behaviour of copper is not unexpected since these complexes of copper are similar in size to the hydrated copper ion. They are better represented by the formula $Cu(H_2O)_{5-n}(NH_3)_n^{2+}$ in which it is seen that the hydrated copper ion is simply the first member of the series (n = 0).

4. CONCLUSION

Laboratory scale experiments have shown that the ability of the cation-exchange resin of a condensate purification plant to remove copper down to very

low levels is not likely to be impaired by the presence of ammonia at the expected concentrations. The actual performance of a purification plant could only be found by full-scale or pilot-scale experiments. It was found that the presence of ammonia at concentrations between 0 to 550 mg ℓ^{-1} (0-0.032 M) has no effect on the ability of a cation-exchange column to remove dissolved copper from 10^{-4} M copper sulphate solution. The complex ammine species formed in this aqueous ammoniacal environment are adsorbed onto cation-exchange resins as readily as the uncomplexed cupric ion and are held as strongly. Whilst the presence of ammonium ion at a concentration of 5×10^{-2} M caused a 25% loss in capacity for copper at 50% breakthrough, a concentration of 5×10^{-3} M had negligible effect.

In the resin environment the copper-ammine species appear to be of the same form as those found in aqueous solution. There is evidence that the fifth coordination position on copper is equivalent to the first four, contrary to the situation in aqueous solution. This suggests the existence of six coordinate copper in the resin environment but this was not confirmed.

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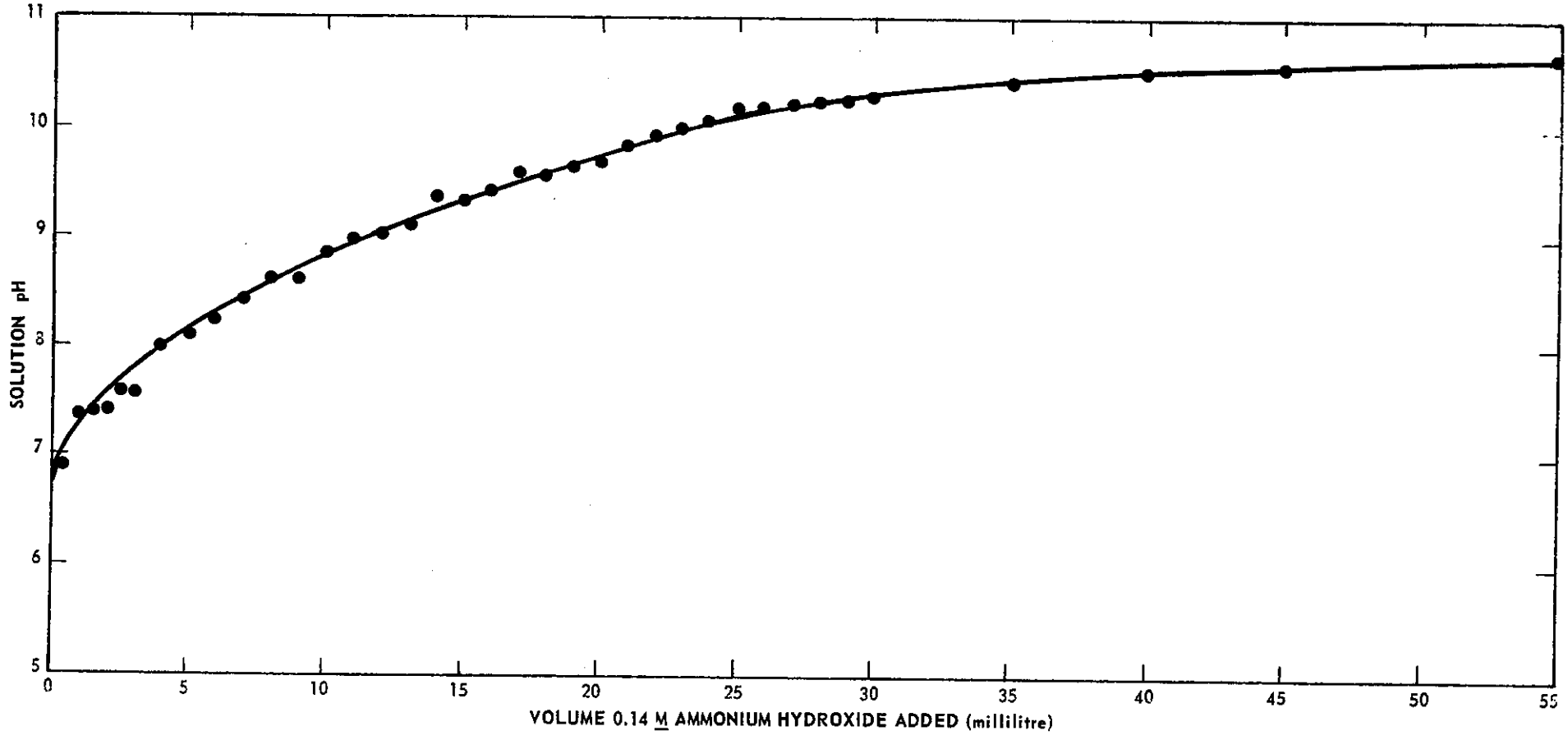

FIGURE 1. TITRATION OF 1 mℓ OF R_2Cu-FORM RESIN IN 45mℓ OF 5×10^{-4} M $(NH_4)\,SO_4$ SOLUTION (25°C)

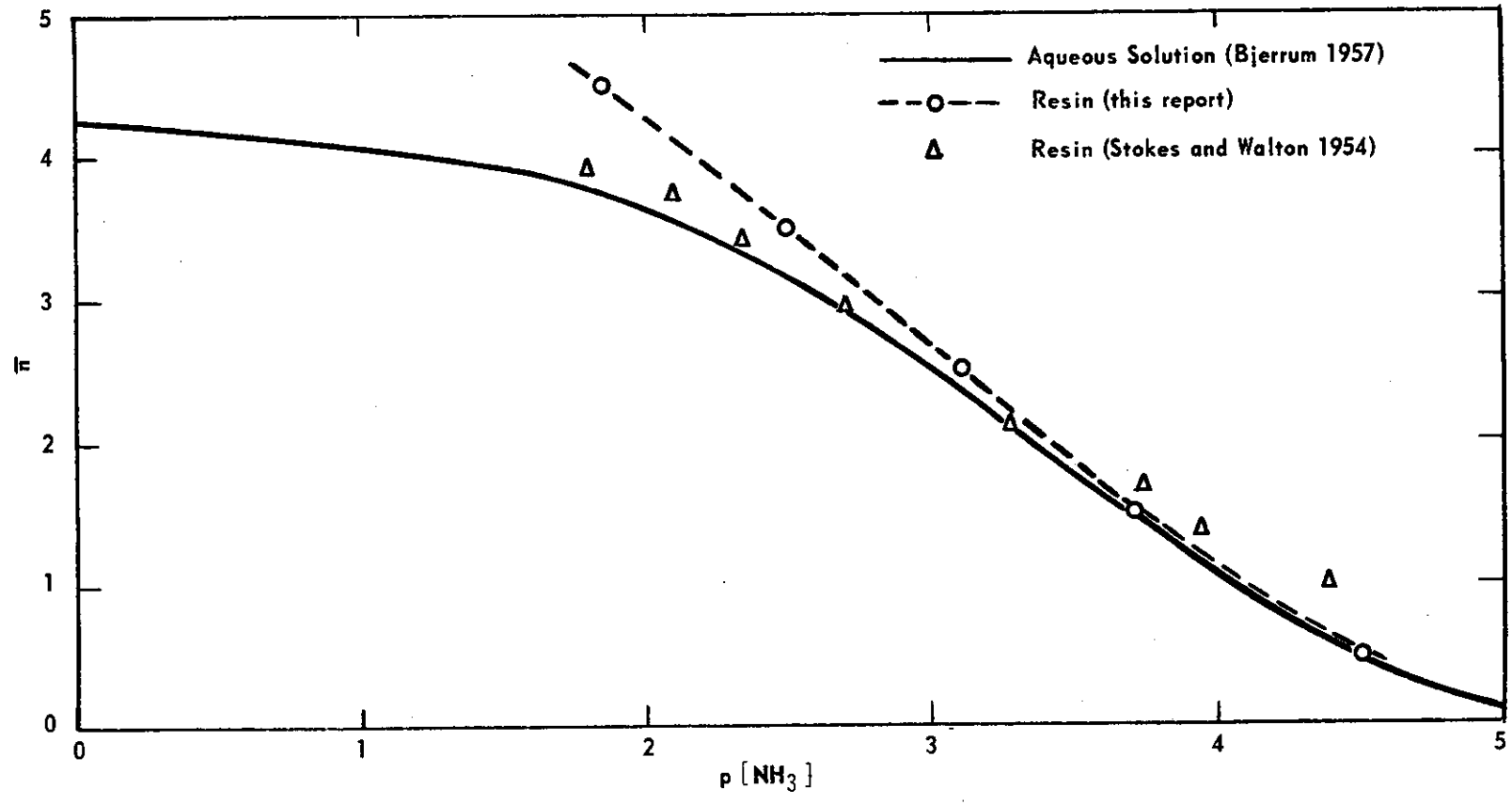

FIGURE 2. FORMATION CURVES FOR COPPER-AMMINES IN AQUEOUS SOLUTION (BJERRUM (1957)) AND ION EXCHANGE RESINS (THIS REPORT AND THE MEASUREMENTS OF STOKES AND WALTON (1954))

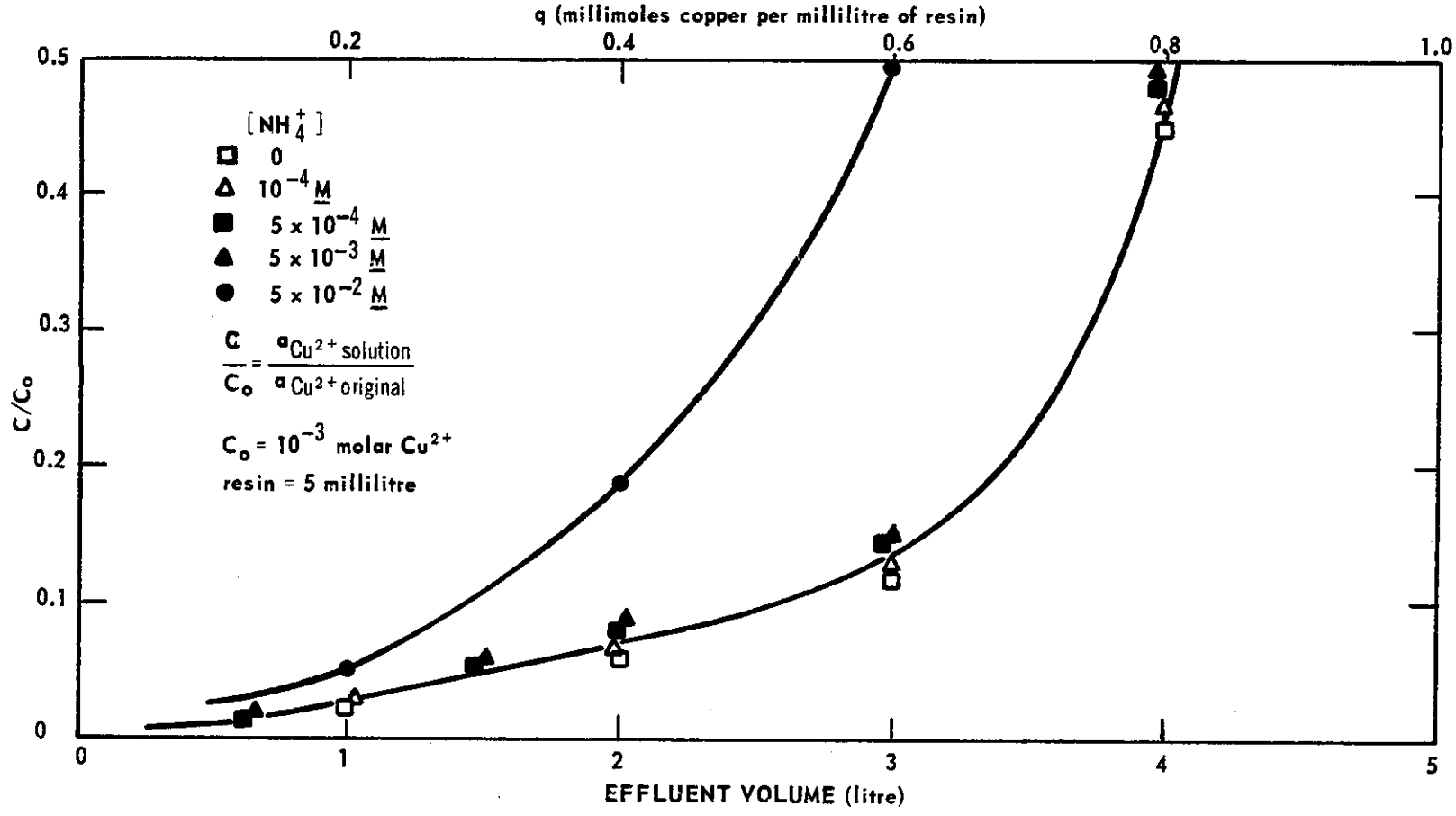

FIGURE 3. THE EFFECT OF AMMONIUM ION CONCENTRATION ON THE BREAKTHROUGH CURVES FOR COPPER

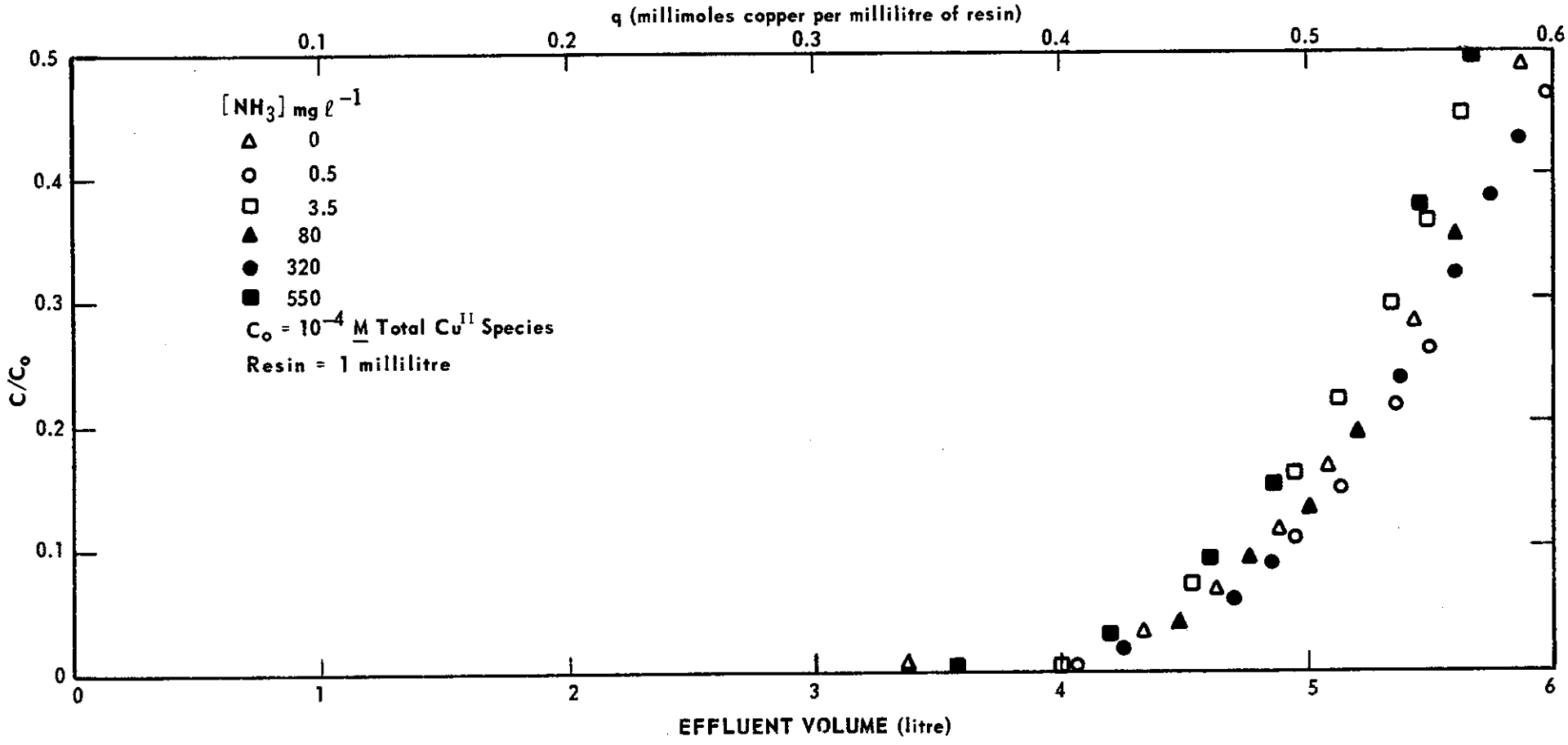

FIGURE 4. THE EFFECT OF AMMONIA CONCENTRATION ON THE BREAKTHROUGH CURVES FOR COPPER