



## Effect of temperature on sorption of metals by silica-supported 2-(aminomethyl)pyridine. Part I: Binding equilibria

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### ABSTRACT

The effect of temperature on acid and metals binding was studied using a commercial chelating adsorbent CuWRAM® (by Purity Systems Inc., USA) which contains 2-(aminomethyl)pyridine (AMP) ligands on a polyamine–silica composite. The binding equilibria in synthetic copper and nickel sulfate solutions and authentic multimetal process solutions were measured at 25–90 °C in batch experiments using potentiometric and spectroscopic methods. Experimental data were correlated with a non-ideal competitive adsorption (NICA) model.

According to the results, the binding enthalpy is negative for both sulfuric acid and metal sulfates. Basicity and metals binding strength of the adsorbent thus decrease with temperature. The affinity for copper remains sufficiently high even at 90 °C to ensure high uptake selectivity from a concentrated ZnSO<sub>4</sub> solution. At the same time the amount of metal adsorbed remains constant or even increases with increasing temperature.

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### 1. Introduction

Chelating adsorbents and ion exchangers have good selectivity for transition metals and thus find applications in hydrometallurgy. The markets offer a wide selection of commercial chelating separation materials. Iminodiacetic acid (IDA) [1–4], aminophosphonate (AP) [5,6] and bis-(pyridylmethyl)amine (PMA) [7–15] are examples of extensively studied ligands used on chelating separation materials. The chelating ligand acts as a donor and metal cation as an acceptor of electrons.

The basicity of chelating ligands on solid adsorbents is of importance in hydrometallurgical metal separation and purification applications. We have earlier reported [16–18] precipitation problems when using relatively basic branched poly(ethyleneimine) (BPEI) adsorbent, WP-1® by Purity Systems Inc. On the other hand, elution of the metals from the adsorbent has been observed to be a problem when using Dowex-4195, which contains bis-(2-pyridylmethyl)amine functionality [18]. According to an earlier study [18], these problems can be avoided using a chelating adsorbent functionalized with 2-(aminomethyl)pyridine (AMP) groups. AMP is a bidentate weakly basic chelating ligand, which contains one aliphatic amine group and one pyridyl group [19–22].

*Abbreviations:* AMP, 2-(aminomethyl)pyridine; CuWRAM, silica-supported commercial AMP adsorbent; NICA, non-ideal competitive adsorption model.

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The effect of temperature on the behavior of solid separation materials has been investigated to some extent but most of the studies deal with simple ion exchange. Influence on ion exchange equilibria has been studied since 1950s [23–28]. According to Helfferich [29], ideal ion exchange reaction does not depend on temperature. Bonner and Smith [23], on the other hand, have shown that equilibrium constant of sodium–hydrogen exchange decreases with increasing temperature, whereas for copper–hydrogen exchange it increases with increasing temperature. This effect was attributed to change of activity coefficients of the ions in the solid phase. Some studies on temperature effect on the behavior of chelating ion exchangers [30–37] and adsorbents [32] are also available. Muraviev et al. [30] have studied temperature response selectivity of IDA resin with copper and zinc. They have reported that increasing temperature increases copper capacity of IDA and also the selectivity of copper over zinc. Furthermore, copper can be stripped selectively from the resin with decreasing temperature and by pre-equilibrating the resin with same solution as used in loading (dual-temperature technique) [30]. Zagorodni et al. [32] have also studied dual-temperature technique using different chelating resins with IDA, picolinic acid and thiourea as the functional group. According to their results, the resin functionalized with picolinic acid has higher capacity and selectivity for copper than the IDA resin. However, the exchange kinetics was too slow for practical purposes [32].

Nevertheless, the effect of temperature on acid and metal binding properties of chelating adsorbents deserves more attention as

### Nomenclature

$c$	stoichiometric electrolyte concentration, mol/L	$T$	temperature, K or °C
$h$	empirical parameter (Eq. (1)), –	$\alpha$	selectivity coefficient, –
$\Delta H_b$	binding enthalpy, J/mol		
$I_s$	ionic strength of the supporting electrolyte, mol/L	<i>Subscripts and superscripts</i>	
$K$	affinity constant, L/mol	a	sulfuric acid
$p$	heterogeneity parameter (Eq. (1)), –	i, j	component
$q$	amount adsorbed on the solid phase, mmol/g	Me	metal
$q^*$	total amount of the nitrogen groups, mmol/g		
$R$	gas constant, J/Kmol		

temperature is a significant factor in hydrometallurgical separation applications. Our previous studies with AMP-functionalized adsorbents were carried out at ambient temperature and the aim of this work is to elucidate the effect of temperature on binding properties and complex formation abilities of copper and nickel by soluble AMP and by AMP supported on a porous silica composite (CuWRAM®). Previously the temperature dependency of protonation and metal complexation of the AMP ligand has been studied e.g. by Goldberg and Fernelius [19] and by Garcia-Espana et al. [21,22]. According to these data, soluble AMP is very selective for transition metals but increasing temperature decreases the stability constants [19]. However, no studies on AMP-functionalized solid adsorbents appear to be available.

The objective of this first part of the present study is to establish the effect of temperature on equilibrium binding properties of chelating adsorbent, which contains AMP groups supported on silica. The material is a commercially available adsorbent CuWRAM® obtained from Purity Systems Inc. Acid–base properties as well as copper and nickel binding equilibria of CuWRAM and soluble AMP are measured using potentiometric titration and batch uptake experiments. Complex formation is measured using UV–Vis spectroscopy. The experimental data are correlated with a non-ideal competitive adsorption (NICA) model reported by Kinniburgh et al. [38].

## 2. Experimental

### 2.1. Materials

The silica-supported porous chelating adsorbent CuWRAM® was obtained from Purity Systems Inc., USA. The synthesis of CuWRAM has been described in a patent by Rosenberg and Fischer [39]. The corresponding soluble chelating ligand AMP (99%) was supplied by Sigma–Aldrich. Because of its silica matrix, CuWRAM does not swell significantly under ordinary conditions, whereas its chemical stability poses problems in some cases. However, according to preliminary tests, CuWRAM have been noticed to endure both 5 M H<sub>2</sub>SO<sub>4</sub> and 4 M NH<sub>4</sub>OH. Furthermore, no problems in mechanical durability were found in this study.

Before all measurements the adsorbent was pretreated first with 2 M H<sub>2</sub>SO<sub>4</sub>, water, 4 M NH<sub>4</sub>OH, and water. After this cycle adsorbent was extracted over-night with methanol in order to remove the colored substances observed in preliminary tests. After methanol-extraction the H<sub>2</sub>SO<sub>4</sub>–water–NH<sub>4</sub>OH pretreatment cycle was repeated twice and finally the adsorbent was rinsed with generous amount of water and then dried in vacuum. Physical characteristics of the pretreated material were measured as described in our previous article [18]. The specific surface area was 145 m<sup>2</sup>/g, while pore volume and average pore size were 0.57 mL/g and 16 nm. Density of the material was 0.75 g/mL and a value of 0.43 was obtained for the particle porosity. The nitrogen content of

the adsorbent was 2.88 mmol/g. The nitrogen content of the adsorbent was 2.88 mmol/g. This value gives the total number of amine groups.

The solutions were prepared from reagent-grade metal salts (CuSO<sub>4</sub>·5H<sub>2</sub>O, NiSO<sub>4</sub>·6H<sub>2</sub>O), sodium hydroxide, sulfuric acid and ammonium hydroxide. The supporting ionic strength of the synthetic sulfate solution was 2 mol/L and it was adjusted with reagent-grade Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O.

### 2.2. Methods

#### 2.2.1. Sorption equilibrium measurements

All experiments were made at temperatures of 25, 60, and 90 °C. Titration curves of soluble AMP were measured at a constant supporting ionic strength of 2 mol/L and using 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> as titrant. Titration curves and binding isotherms were determined in separate batches for copper and nickel both in synthetic sulfate solutions and in the zinc process solutions I and II shown in Table 1. Metal ion concentrations were determined by plasma emission spectroscopy (Iris Intrepid II XDL ICP–AES). A constant amount of the adsorbent (about 0.2 g) was weighed in glass vials containing different concentrations of sulfuric acid and metal salts. The liquid volume of all samples was 10 mL. The samples were shaken at 25 and 60 °C for at least 2 days. After separation of the solids, the equilibrium solutions then kept several hours at 25 °C before measurement of the equilibrium pH.

The pH values were converted to stoichiometric acid concentrations by calibrating the glass electrode against known acid concentrations. Measurements at 90 °C were made in a similar way, except that the samples were kept in an oven at 90 °C and shaken twice per day. The adsorbed amount of metals was calculated from

**Table 1**  
Composition of the process solutions.

Metal	Concentration (mol/L)	
	Solution I	Solution II
Zn	2.5	2.2
Mg	0.5	0.4
Mn	0.1	0.1
Cu	$1.1 \times 10^{-2}$	n.d.
Ca	$7.8 \times 10^{-3}$	$6.5 \times 10^{-3}$
Cl	$4.0 \times 10^{-3}$	$4.0 \times 10^{-3}$
Cd	$3.3 \times 10^{-3}$	$2.2 \times 10^{-3}$
Al	$2.8 \times 10^{-4}$	$1.1 \times 10^{-4}$
Co	$2.4 \times 10^{-4}$	$3.6 \times 10^{-4}$
Ni	$2.1 \times 10^{-4}$	$3.1 \times 10^{-4}$
Pb	$4.2 \times 10^{-5}$	$7.5 \times 10^{-5}$
Fe	$3.2 \times 10^{-5}$	n.d.
As	$7.5 \times 10^{-6}$	n.d.
pH	4.9	4.9

n.d., not detected.

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