

## **COPPER AND COBALT EXTRACTION FROM SULPHATE SOLUTION USING NATURAL CLINOPTILOLITE**

Antoine F. Mulaba-Bafubiandi<sup>1</sup>, D. Nyembe<sup>1,2</sup> and B. Mamba<sup>2</sup>

1: Minerals Processing and Technology, Department of Extraction Metallurgy, Faculty of Engineering and the Built Environment, University of Johannesburg, POBox 526, Wits 2050

2: Department of Chemical Technology, Faculty of Science, University of Johannesburg, POBox 17011, Doornfontein, South Africa

*Email: amulaba@uj.ac.za*

### **Abstract**

Copper and cobalt are generally electro-won from their aqueous sulphate solutions. After optimised leaching of their ores, concentrates or calcine bearing minerals, the leachate is clarified and suitably purified prior to the electrolytic extraction of the metal of pursuit (Percy, 2006). Solvent extraction (SX) using appropriate organic solvents and ion exchange (IX) with relevant resins are known purification processes used for copper and cobalt recovery (Stanely, 1970). As zeolites in general and natural zeolites in particular, demonstrate ion exchange properties (Korkuna et al., 2005), an attempt has been made to use Southern African natural clinoptilolite in the recovery of copper and cobalt from their aqueous sulphate solutions. Initially, synthetic Co and Cu solutions were prepared. Preceded by laboratory ore leachate, plant solutions are to be used. AAS, XRF, XRD, Mossbauer spectroscopy and BET were characterization techniques used. Natural clinoptilolite was used as-received as well as acid activated; and cobalt and copper extractions were performed at room temperature.

### **Introduction**

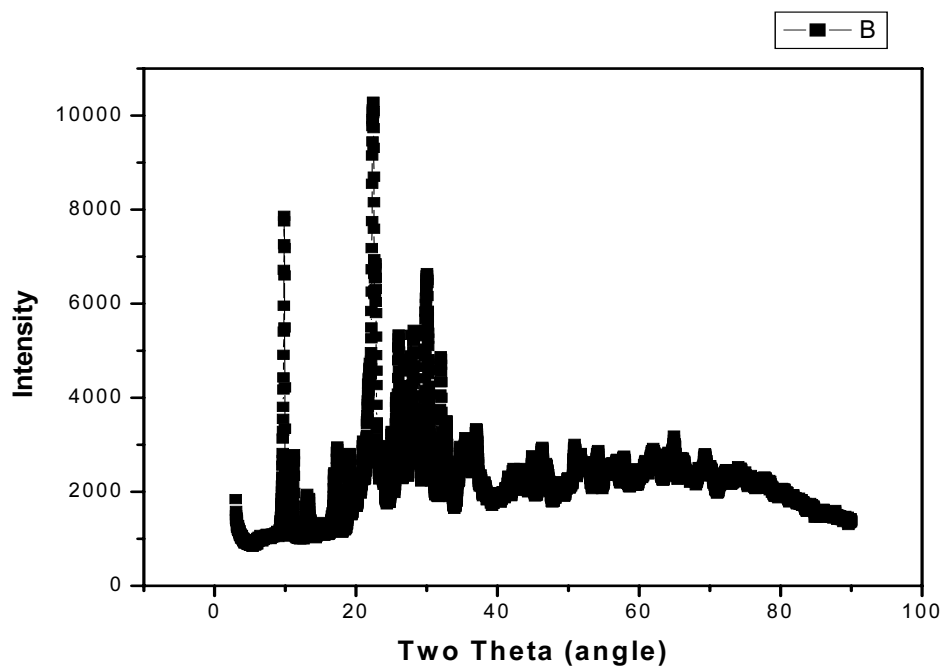
Natural zeolites, discovered in the 18th century, are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminium, silicon, and oxygen in their regular framework. Cations and water are located in the pores. The silicon and aluminium atoms are tetrahedrally coordinated with each other (Korkuna, 2005). Zeolites are thus natural minerals mined in many parts of the world, southern Africa is one of them. Some zeolites are synthetically produced (Sherry; 1979). Zeolite structures have channels that can accommodate cations, water, or other molecules. As far as ion exchange properties are concerned, zeolites may exchange the structural and the interstitial sodium for external cations such as copper and cobalt, as in this study; and calcium and magnesium present in hard water (Kuronen et al., 2006).

## Experimental

### Materials and method

Natural clinoptilolite found in the Vulture Creek, Kwazulu Natal, South African geological formation was used. It was examined using X-ray powder diffractometer Phillips X'pert Model 0993. As indicated in the XRD pattern Figure 1, a typical crystallite composition of 70 %SiO<sub>2</sub>, 12%Al<sub>2</sub>O<sub>3</sub>, 2%Na<sub>2</sub>O, 5%K<sub>2</sub>O, 2%CaO, 2.5%Fe<sub>2</sub>O<sub>3</sub> with traces of other elements was observed. It was ground and grains -2cm +1cm were selected as ions exchangers. Their elemental composition was determined using X-ray fluorescence (XRF, Phillips Magix Pro), and their BET surface area analysed. 2 g of sample was first degassed by passing nitrogen gas for 4 hours at 120 °C before porosity and surface area analysis. Sulphate solutions containing copper and cobalt ions were prepared using CoSO<sub>4</sub>.7H<sub>2</sub>O and CuSO<sub>4</sub>.5H<sub>2</sub>O respectively. The crushed natural clinoptilolite samples were further rinsed with distilled water, subsequently air dried and/or oven dried at 50 °C for 24 hours prior to the extraction. Laboratory batch ion exchange process was conducted using a 2cm diameters columns where copper and cobalt bearing solutions were passed through two types of natural clinoptilolite (as received and acid site activated) for the extraction of these metals. The solutions obtained from the extraction were assayed using AAS.

### Results and discussion



**Figure 1:** Mineralogical pattern of the natural clinoptilolite.

The following composition was found for the aluminosilicate natural clinoptilolite studied:  $0.2\text{Ti}^{2+}$ ,  $74\text{Si}^{2+}$ ,  $1.3\text{Na}^+$ ,  $1.1\text{Mg}^{2+}$ ,  $3.8\text{K}^+$ ,  $1.5\text{Fe}^{3+}$ ,  $1.5\text{Ca}^{2+}$ ,  $12.4\text{Al}^{3+}$

The measured BET surface areas and pore sizes for the air and oven dried natural clinoptilolite were ( $26.03\text{ m}^2/\text{g}$ ,  $0.081\text{ cm}^3/\text{g}$ ) and ( $20.88\text{ m}^2/\text{g}$ ,  $0.068\text{ cm}^3/\text{g}$ ) respectively. This showed that oven drying started already to close up the zeolite structure, Figure 2.

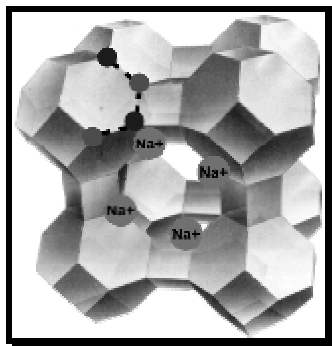


Figure 2: Zeolite structure to be used as ion exchangers and or sieves(Themistocleous, 1990)

## Copper and cobalt percentage extraction.

### As receive natural clinoptilolite as ion exchanger

Ion exchange has been performed with the as received natural clinoptilolite and with the acid treated zeolite. Figure 3 (a) and figure 3 (b) show the trend in copper and cobalt percentage extraction respectively.

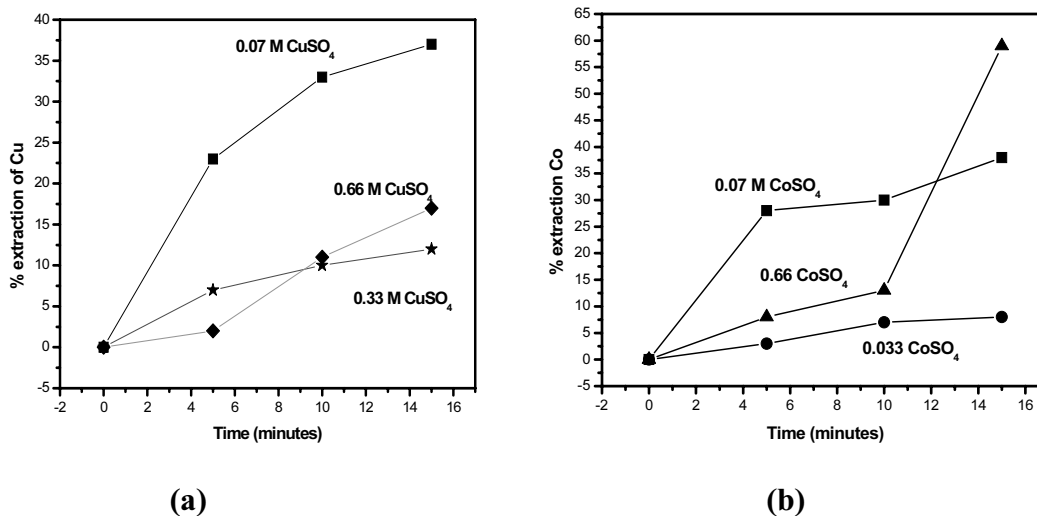


Figure 3: Percentage extraction of copper figure 3 (a) and of cobalt figure 3 (b) by natural clinoptilolite.

Copper up take has been seen inversely proportional to the initial concentration of  $\text{Cu}^{2+}$  in the solution. After 15 minutes 37% of Cu has been loaded onto the natural zeolite structure from an initial solution of 0.07 M while only 17 % has been loaded from a solution of 0.66 M. Although an outsider reading was observed for the cobalt up-take from 0.66M solution after 15 minutes, the above trend seems to be maintained. IN general, the natural clinoptilolite seems to have a greater affinity for Cobalt with respect to copper.

The natural zeolite was further acid activated with different concentrations of HCl (0.02M; 0.04 M; 0.1M; and 0.15M) and the percentage copper and cobalt extracted has been determined.

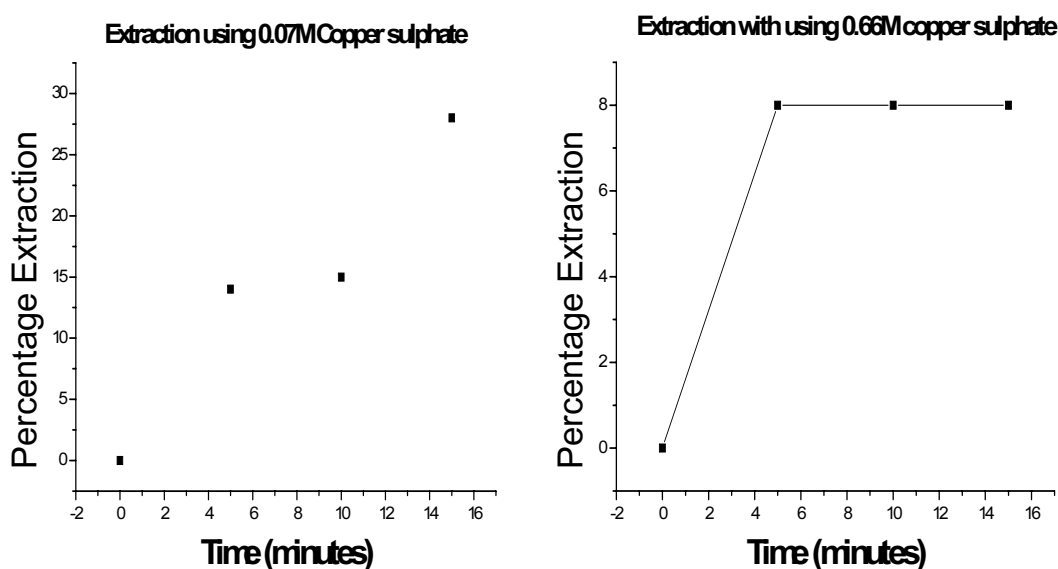


Figure 4: percentage extraction of copper by 0.02M HCl activated clinoptilolite. Figure 4 (a) from 0.07 M copper sulphate and figure 4(b) from 0.66M.

## conclusion

Modified or activated zeolites have been found much more metal up-takers than untreated. Due to the presence of alumina, zeolites exhibit a negatively charged framework, which is counter-balanced by positive cations resulting in a strong electrostatic field on the internal surface. These cations can be exchanged to fine-tune the pore size or the adsorption characteristics. 30 % up take was observed for copper while 40% for cobalt in a 0.02 M HCl activated natural clinoptilolite. It seemed that the stronger the activating acid the lower the metal up take efficiency. Irregularities experimental data observed could be attributed to uneven particle size or air bubbles that were seen to hinder full exposure of the solution to the whole surface area of the

clinoptilolite. These air bubbles can be minimized if extraction can be performed under slightly raised temperature and pressure or completely rinsed particles.

### **Acknowledgements**

The authors wish to thank Prattley (South Africa) for providing the natural clinoptilolite used in this work.

### **References**

Korkuna O. (2006) 87 243-254. Microporous and Mesoporous Materials. Clays and Clay Minerals, Vol. 27, No. 3, pp. 231-237, 1979.

Sherry. H. Ion Exchange Properties of the Natural zeolite, Erionite. P. Q. Corporation, P.O. Box 258, Lafayette Hill, Pennsylvania 19444

Kuronen , M., Weller M, Townsend R., Harjula R. (2006). Ion exchange selectivity and structural changes in highly aluminous zeolites. Reactive & Functional Polymers 66 1350–1361 Polymers

<http://www.elsevier.com/locate/react>

Peacey, J. G. "Copper metallurgy", in AccessScience@McGraw-Hill, <http://www.accessscience.com>, DOI 10.1036/1097-8542.161350, last modified: November 14, 2001.

SMI Analytical Laboratory Services (Access date 14/03/2007) Main page. Analytical Chemistry Services. X-Ray Diffraction Services South Africa.

