COPPER AND ZINC REMOVAL FROM ACID MINE DRAINAGE USING CALCAREOUS SANDSTONE

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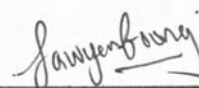## SCHOOL OF SCIENCE AND TECHNOLOGY
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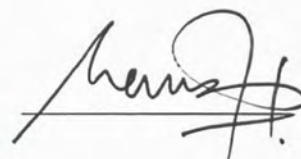been cited in reference.

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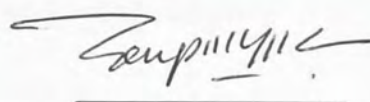LAW YEN FOONG
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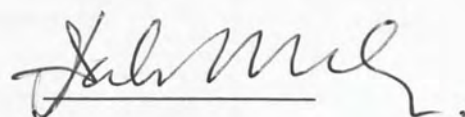# VERIFICATION

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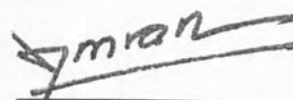
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ABSTRACT

The removal of heavy metals (i.e. Cu and Zn) from AMD using calcareous sandstone (CSS) was investigated. Batch experiments were conducted at different contact time (i.e. 1, 2, 3, 4, 5, 6 and 24 hours) and different AMD (i.e. AMD P1 and AMD P2), and the final pH and concentrations of Cu and Zn were determined. A neutralization experiment using NaOH was also carried out to evaluate the effect of pH on metal removal. The results showed that the removal of Cu and Zn by CSS was highly efficient. However, the overall percentage removal depended on contact time, type of metal and AMD. Percentage removal of metal increased with contact time and equilibrium was attained within 24 hours. The pH of the AMD-CSS mixture also showed simultaneous increase from pH 3.0 to pH > 7.0. Comparatively, percentage of metal removal and magnitude of pH increase were lower for AMD P2 compared with AMD P1. In all cases percentage removal of Cu is greater than Zn. The removal of Cu and Zn from the AMD was attributed to chemisorption and precipitation mechanisms.

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ABSTRAK

Penyingkiran logam berat, Cu dan Zn daripada saliran asid lombong (AMD) dengan menggunakan batu pasir berkapur (CSS) telah dikaji. Eksperimen kelompok dijalankan dalam masa tertentu: 1, 2, 3, 4, 5, 6 dan 24 jam, dan saliran asid lombong yang berlainan, AMD P1 dan AMD P2. Kepekatan akhir Cu dan Zn dan pH akhir adalah ditentukan. Eksperimen peneutralan dijalankan secara berasingan untuk menilai kesan pH terhadap penyingkiran logam berat. Hasil kajian menunjukkan bahawa penyingkiran Cu dan Zn oleh CSS adalah efektif. Namun ia bergantung kepada masa, jenis logam dan jenis saliran asid lombong. Peratusan penyingkiran logam meningkat dengan masa dan keseimbangan dicapai dalam masa 24 jam. Dalam masa yang sama, pH campuran AMD-CSS meningkat dari pH 3.0 hingga pH > 7.0. Secara amnya, peratusan penyingkiran logam dan peningkatan pH bagi AMD P2 adalah lebih rendah berbanding AMD P1. Dalam semua keadaan, peratus penyingkiran Cu adalah lebih tinggi daripada Zn. Penyingkiran kedua-dua logam ini daripada AMD adalah melibatkan mekanisma jerapan kimia dan pemendakan.

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AMD	Acid Mine Drainage
CSS	Calcareous sandstone
ppm	parts per million
ppb	parts per billion
Å	Ångstrom (1×10^{-10} m)
K_d	Distribution coefficient
K_{sp}	Solubility

CHAPTER 1

INTRODUCTION

1.1 Context and Relevance of Study

Acid Mine Drainage (AMD) is a world wide environmental problem associated with mining activities. AMD consists of various pollutants, including acid (i.e. H_2SO_4) and heavy metals such as copper (Cu), nickel (Ni), iron (Fe) and zinc (Zn) (Down and Stocks, 1997; Gray, 1997; Yu and Heo, 2000). Continuous discharge of AMD into the environment can cause adverse chemical, biological and physical impacts (WHO, 1998; Durkin and Herrmann, 1994; Salomons *et al.*, 1995). It is therefore important that AMD undergoes treatment prior to discharge into the receiving environment to avoid from environmental pollution (Yu and Heo, 2000; Gray, 1997).

Conventionally, wastewater treatment involves technologies such as precipitation, oxidation, ultrafiltration, adsorption, reverse osmosis, electrodialysis and ion exchange with synthetic resin (Sanzhez and Ayuso, 2002; Walton, 1995; Cheremisinoff, 1995; Hanzlik *et al.*, 2004; Gupta *et al*, 2003). Basically, techniques with low operating cost and sufficient efficiency for heavy metal removal are preferable in AMD treatment (Komnitsas *et al.*, 2003) . AMD treatment using natural

materials such as zeolite, calcareous materials, limestone, fly ash and clay is a cheaper alternative (Komnitsas *et al.*, 2003; Bailey *et al.*, 1999). The significant ability of calcareous materials such as calcite to remove heavy metals from wastewater has been reported (Lorens, 1981; Sanchez and Ayuso, 2002). However, no information is available on on the potential of calcareous sandstone (CSS) for similar purpose. This material is abundantly available in Sabah, Malaysia.

1.2 Objectives of Study

The objectives of this study are:

i.   To determine the efficiency of zinc and copper removal from AMD using CSS.

ii. To evaluate the mechanism of zinc and copper removal from AMD by CSS.

1.3 Scope of Study

In this study the removal of Cu and Zn from AMD is examined by batch experiments using 2.0g CSS and 40.0 mL AMD (i.e. solid solution ratio 1:20). The particle size of CSS is fixed at 2-4mm. The final pH and metals (Cu and Zn) concentration are determined. Subsequently, a neutralization experiment (i.e. effect of pH: 3.0 – 9.0) is carried out on the AMD sample using NaOH solution as the neutralizing agent and the final Cu and Zn concentration determined. On the other hand, the mechanism of the metal removal process is described.

CHAPTER 2

LITERATURE REVIEW

2.1 Acid Mine Drainage (AMD)

2. 1. 1   Definition

AMD is a general term given to typically acidic lechates draining from mine waste dumps or deposits. AMD can be defined as a drainage that occurs as result of sulfide oxidation in rocks exposed to air and water (Durkin and Herrmann, 1994; Hughes and Poole, 1989). It is a polluted water that contains elevated concentration of iron, aluminum and acid. The contaminated water is often reddish-brown in colour due to high level of oxidized iron (Hadley and Snow, 1974).

2. 1. 2   Formation of AMD

AMD is generated by oxidation processes involving chemical, biological and electrochemical reactions and varies with environmental condition (Salomons et al., 1995; Stumm and Morgan, 1996; Evangelow, 1995; Kleinmann et al., 1981; Singer and Stumm, 1970). It is produced when metal sulphides (pyrite or marcasite) are

exposed to air and water (Salomons *et al.*,1995). In the case of iron sulfide (pyrite), the chemical reactions of the acid-generating process can be expressed as follows:

$$FeS_2 + 3O_2 \rightarrow FeSO_4 + SO_2 \qquad (2.1)$$

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (2.2)$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (2.3)$$

$$2Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4 \qquad (2.4)$$
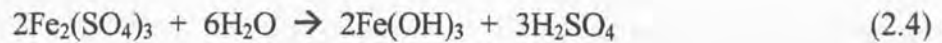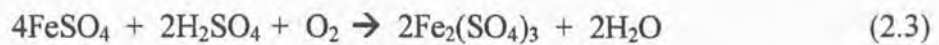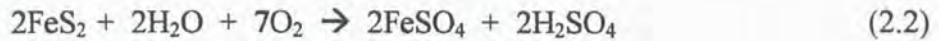
Under dry condition, oxidation of sulphide produces water-soluble ferrous sulphate and sulphide dioxide (Equation 2.1). However, in the presence of water and oxygen, pyrite undergoes oxidation process and sulphuric acid is formed (Equation 2.2). Ferrous sulphate may contribute towards further oxidation process to produce water-soluble ferric sulphate in the presence of sulphuric acid and oxygen (Equation 2.3). Ferric ion (Fe^{3+}) combines with the hydroxyl (OH^-) ion of water to form ferric hydroxide. Ferric hydroxide is insoluble in acidic condition and is precipitated (Down and Stocks, 1997) (Equation 2.4).

The overall sequence of reactions result in the production of acid:

$$4FeS_2 + 14H_2O + 15O_2 \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \qquad (2.5)$$
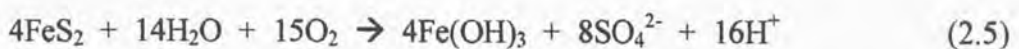
The low pH condition (i.e. pH 2-4) generated from the sulphide oxidation is capable to dissolve heavy metals in the form of carbonates, oxide and sulphide contained in the mine wastes (Down and Stocks, 1997). The acid then leaches through the mine rocks and releases heavy metals such as lead, zinc, copper, arsenic, selenium, mercury and cadmium.

2. 1. 3 Characteristic of AMD

Leachates draining mine wastes where pyrite oxidation and mineral dissolution reactions are actively taking place are generally enriched with oxidation products and dissolution products. Consequently the leachate is highly acidic (i.e pH < 4.0) with elevated concentrations of a wide variety of metal such as zinc and copper, depending on the host rock geology (Gray, 1997; Marulanda, 1999; Down and Stocks, 1997; Bowen, 1979). This leachate is commonly termed as acid mine drainage (AMD).

2. 1. 4 Environmental Impacts of AMD

Discharges of AMD into the surrounding environment are likely to cause serious environmental pollution. The most important characteristics of AMD are its high acidity and high metal concentration. The risks of high acidity and elevated heavy metal on the biological and physical environment are described and summarized in Table 2.1 (Durkin and Herrmann, 1994; Gray, 1997; WHO, 1998; Salomons et al., 1995).

Table 2.1: The risks of high acidity and elevated heavy metal.

Biological or Physical Impact	Description
Depletion of aquatic life	Aquatic species will begin to dwindle in number as the acidity of their habitat increases because the vast majority of natural life is designed to live and survive near pH 7 (neutral)
Contamination of drinking water supply	Toxic heavy metals can be ingested by humans through drinking supplies, causing severe health problem: Lead – brain, kidney and nervous system damage. Cadmium – high blood pressure, liver damage, cancer. Copper – gastrointestinal bleeding, hepatocellular toxicity, acute renal failure and oliguria.
Contamination of food chain	Heavy metals ion will be bio-accumulate in the tissue of aquatic organisms. If certain concentration of metals is accumulating in the tissues, it can be toxic to aquatic organisms and tranfer into another organism through food chain system.
Discoloration of the streambed	As AMD flows away from the acid-generating source and moves into the receiving environment where the pH is buffered, discoloration of the streambed or the material that the AMD is passing over often is caused due to precipitation of solid metal hydroxides.

2.1.5 Treatment of AMD

The main objective of AMD treatment is to neutralize the acidity and to remove heavy metal ions. The treatment of AMD consists of active treatment system and passive treatment system. The main difference between these two systems is that active treatment system requires a constant maintenance of the supply system such as lime for neutralization while passive treatment systems is designed to allow for low or no maintenance and should be self-contained with regards to treatment and waste (Ginness, 1999).

In active chemical treatment system the acidity of AMD is buffered by the addition of alkaline reagent such as calcium carbonate, sodium hydroxide, sodium bicarbonate or anhydrous ammonia (Porcella *et al.*, 1990; Walton, 1995). These alkaline reagents raise the pH to acceptable levels and decrease the solubility of dissolved metals. Heavy metal ions are precipitated from the solution in the form of metal hydroxide. In contrary, the concept behind passive treatment is to allow the naturally occurring chemical and biological reactions that aid in AMD treatment to occur in the controlled environment of the treatment system. Types of passive treatment include wetland technology, open limestone channels, anoxic limestone drains (ALD), alkalinity producing system (APS), limestone pond, and are illustrated in Figure 2.1 (Ginness, 1999).

A. Aerobic Wetlands

1-3 in. Water
1-3 ft. Organic Matter

B. Anaerobic Wetlands

1-3 in. Water
1-2 ft. Organic Matter
.5- 1 ft. Limestone

C. Alkalinity Producing Systems (APS)

3-6 ft. Water
6-12 in. Organic Matter
1-2 ft. Limestone
Drainage System

D. Anoxic Limestone Drains (ALD)

2-4 ft. Soil
20-40 mil Plastic Liner
surrounding or covering LS
Trench or bed of Limestone

E. Limestone Pond

3-6 ft. Water
1-3 ft. Limestone

F. Open Limestone Channel (OPC)

Small or large sized Limestone placed
along sides and in bottom of culverts,
diversions, ditches, or stream channels.

Figure2.1: Types of passive treatment system.

2.2 Technologies for Metal Removal from Wastewater

2. 2. 1 Introduction

Various types of wastewater treatment method such as precipitation, adsorption by
adsorbent, ion exchange, reverse osmosis (ultra-filtration) and solvent extraction have
been implemented to remove the toxic metal ions from the wastewater (Sanzhez and
Ayuso, 2002; Walton, 1995; Cheremisinoff, 1995; Hanzlik *et al.*, 2004; Gupta *et al*,
2003). However, the major choice of wastewater treatment method depends on the
effective operating cost and the efficiency of the metal ions removal (Sanzhez and
Ayuso, 2002; Peric *et al.*, 2003; Komnitsas *et al.*, 2003).

2. 2. 2 Ion –exchange

Ion exchangers are solid materials (e.g. zeolite) which are capable in exchanging cations or anions with their surroundings (Walton, 1995). A cation exchanger contains exchangeable cations (such as metal or protons). The general reaction for ion-exchange is as follows:

$$M'X_{n(aq)} + M(matrix)_{(s)} \rightarrow MX_{n(aq)} + M'(matrix)_{(s)} \qquad (2.6)$$
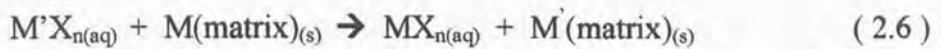
In the reaction, metal ion (M') in solution is bound to the insoluble matrix and the cation (M) is released from the insoluble matrix simultaneously (Walton, 1995). Disadvantages of ion exchange are summarized in Table 2.2.

2. 2. 3 Reverse osmosis (Ultra-filtration)

Reverse osmosis is a physical process by which the dissolved substances in a solvent are separated with the aid of a semi-permeable membrane. By applying a pressure in excess of the natural osmotic pressure to the raw water, the membrane selectively allows the solvent (e.g. water) molecules to pass through while a high proportion of the electrolyte and dissolved organic molecules are rejected (Rowe and Magid, 1995). Disadvantages of reverse osmosis are summarized in Table 2.2.

2. 2. 4 Electrodialysis

Electrodialysis is a process in which ions are conveyed through ion-selective membranes from one solution to another solution under the action of a direct current electrical potential (Rowe and Magid, 1995). The first general principle of an electrodialysis is that membranes used can be constructed to ease the passage of selective ions. Secondly, dissociation of the ions from the salt in water will produce cations and anions. Thirdly, the dissociated ions are moved and attached to the opposite charge electrode. The efficiency of electrodialysis is depends on the flow rate among the compartment and the maximum voltage that can be accepted (Rowe and Magid, 1995). Disadvantages of electrodialysis are summarized in Table 2.2.

2. 2. 5 Solvent extraction

Solvent extraction is a process in which a substance such as metal ion is transferring from solution in one solvent to another solvent without any chemical change (Manahan and Stanley, 2001). Separation by solvent extraction requires a non-aqueous solvent for its operation and it may be more toxic than the metal ion which is extracted from wastewater. Disadvantages of solvent extraction are summarized in Table 2.2.

REFERENCES

Aw Li Chuen and Marcus Jopony, 2003. Adsorption characteristics of copper and zinc on limestone. *Proceedings Malaysian Science and Technology Congress 2003 (MSTC 2003).* 23-25 September, 2003. Kuala Lumpur. pp 367-373.

American Public Health Association (APHA), 1985. Standard Methods for The Examination of Water and Wastewater, 17th ed. Washington, DC.

Bayat, B., 2002. Comparative study of adsorption properties of Turkish fly ashes I. The case of nickel (II), copper (II) and zinc (II). *Journal of Hazardous Materials* **B95**, 251-273.

Benguella, B. and Benaissa, H., 2001. Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies. *Water Research* **36**, 2463-2474.

Benhammou, A., Yaacoubi, A., Nibou, L. and Tanouti, B., 2005. Adsorption of metal ions onto Moroccan stevensite: kinetic and isotherm studies. *Journal of Colloid and Interface Science* **282**, 320-326.

Bowen, H. J. M., 1979. *Environmental Chemistry of the Elements.* Academic Press, Troy, MO.

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. *Journal of colloid and interface science* **277**, 1-18.

Cheremisinoff, P. N., 1995. *Handbook of Water and Wastewater Treatment Technology.* Marcell Dekker, Inc., New Jersey.

Crocket, J. H. and Winchester, J. W.,1966. Co precipitation of zinc with calcium carbonate. *Geochimica Cosmochimica Acta* **30**, 1093-1109.

Cyril Jinusie and Marcus Jopony, 2004. Potential application of calcareous geomaterials for neutralization of acidic wastewater: a case study on acid mine water. *Proceeding 2nd Bangi Conference on Environmental Management*, 13-14th September, 2004, Bangi, Selangor. pp 519-524.

Davis, J.A., Fuller, C.C. and Cook, A.D., 1987. A model for trace metal sorptionprocesses at the calcite surface: Adsorption of Cd^{2+} and subsequent solid solution formation. *Geochim-Cosmochim Acta* **51**, 1477-1490.

Down, C. G., and Stocks, J., 1997. *Environment Impact of Mining*. Applied Science Publishers Ltd., London.

Durkin, T. V. and Herrmann, J. G., 1994. *Managing environmental problems at inactive and abandoned metals mine sites*. U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati. (Unpublished).

EPA 402-R-99-004A, 1999. The K_d Model, Methods of Measurement and Application of Chemical Rection Codes. United States Environmental Proctection Agency. http:// www.epa.gov/radiation/cleanup/partition.htm.

Evans, J. R., Davids, W. G., MacRae, J. D., and Amirbaham, A., 2001. Kinetics of cadmium uptake by chitosan-based crab shells. *Water Research* **36**, 3219-3226.

Gray, N. H., 1997. Acid mine drainage composition and the implications for its impact on lotic systems. *Water Research* **32**, 2122-2134.

Gupta, V. K., Jain, C. K., Ali, I., Sharma, M., and Saini, V. K., 2003. Removal of cadmium and nickel from wastewater using bagasse fly ash-a sugar industry waste. *Water Research* **37**, 4038-4044.

Hanzlik, J., Jehlicka, J., Sebek, O., Weishauptova, Z. and Machovic, V., 2004. Multi-component adsorption of Ag(I), Cd(II) and Cu(II) by natural carbonaceous materials. *Water Research* **38**, 308-319.

Hadley, R. and Snow, D., 1974. *Water Resources and Problems Related to Mining.* American Water Resource Association, MN.

Harter, R. D. and Naidu, R., 2001. An assessment of anvironmental and solution parameter impact on trace-metal sorption by soils. *Soil Science Society of America Journal* **65**, 597-612.

Harvey, D., 2000. *Modern Analytical Chemistry.* McGraw Hill. Singapore.

Hautala, E., Randall, J., Goodban, A., Waiss, A. J., 1976. Calcium carbonate in the removal of iron and lead from dilute waste water. *Water Research*, **11**, 243-245.

Hughes, M. N., and R. K. Poole, 1989. *Metals and Micro-organisms.* Chapman and Hall, London.

Inglezakis, V.J. and Grigoropoulou H., 2004. Effects of operating conditions on the removal of heavy metals by zeolite in fixed bed reactors. *Journal of hazardous materials* **52**, 1-7.

Jae Young Yu and Bong Heo, 2000. Dilution and removal of dissolved metals from acid mine drainage along Imgok Creek, Korea. *Journal of Applied Geochemistry* **16**, 1041-1053.

Jain, C.K., Singhal, D.C. and Sharma, M.K., 2004. Adsorption of zinc on bed sediment of river Hindon: adsorption models and kinetics. *Journal of Hazardous Materials* **B114**, 231-239.

Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *Adv. Chem. Ser.* **73**, 337-387.

Jeong, C. H. et al., 1995. Effect of ionic strength and pH on Cs and Sr sorption of Na-Bentonite. *Journal of Korean Society of Environmental Engineering* **17**, 359-367.

Jurinak, J. and Bauer, N., 1956. Thermodynamics of zinc adsorption on calcite, dolomite and magnesium-type minerals. *Soil Science Society of America Journal* **20**, 466-471.

Kim, M.S., Hong, K.M. and Chung, J.G., 2003. Removal of Cu(II) from aqueous solutions by adsorption process with anatase-type titanium dioxide. *Water Research* **37**, 3524-2529.

Kinniburgh, D. G. and Jackson, M. L., 1981.*Adsorption of Inorganics at Solid-Liquid: Cation adsorption by hydrous metal oxides and clay Interfaces.* Ann Arbor Science, MI.

Kleinmann, R. L. P., Crerar, D.A. and Pacelli, R. R., 1981. Biogeochemistry of acid mine drainage and method to control acid formation. *Mineral Engineering* **33** (3), 300 - 305.

Komnitsas, K., Bartzas, G. and Paspaliaris, I., 2003. Efficiency of limestome and redmud barrier: laboratory column studies. *Journal of Minerals Engineering* **17**, 183-194.

Koss V. And Moller P., 1974. Surface ion exchange on calcite powder in the presence of Mn^{2+} ions. *Inorg. Nucl. Chem. Lett.* **10**, 849-854.

Lee, G., Bigham, J.M. and Faure, G., 2002. Removal of trace metals by co-precipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown mining district, Tennessee. *Applied Geochemistry* **17**, 569-581.

Lorens, R. B., 1981. Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. *Geochimica Cosmochimica. Acta* **45**, 553-561.

McKay, G. and Porter, J., 1997. Equilibrium parameters for the sorption of copper, cadmium and zinc ions onto peat. *Journal Chemistry Technology Biotechnology* 69, 309-320.

Marulanda, A. L. B., 1999. *Bioremediation of acid mine drainage by reduction of metal ion via algal biomass.* Department of Chemical Engineering. New Mexico.

McBride, M. B., 1979. Chemisorption and precipitation of Mn^{2+} at the $CaCO_3$ surface. *Soil Science Society of America Journal* **43**, 693-698.

McBride, M. B., 1980. Chemisorption of Cd^{2+} on calcite surfaces. *Soil Science Society of America Journal* **44**, 26-28.

Moller, O. and Sastri C.S., 1974. Estimation of the number of surface layes of calcite involved in Ca^{2+} Ca isotopic exchange with solution. *Z.Phys. K. Chem. Folge* **89**, 80-87.

Munk, L.A., Faure, G., Pride, D.E. and Bigham, J.M., 2002. Sorption of trace metals to an aluminium precipitate in a stream receiving acid-rock drainage; Snake River, Summit country, Colorado. *Applied Geochemistry* **17**, 421-430.

Ngah, W.S.W., Ghani S.A. and Kamari A., 2004. Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads. *Bioresource Technology* **96**,443- 450.

Papadopoulos, P. and Rowell, D. L., 1988. The reaction of cadmium with calcium carbonates surfaces. *Journal of Soil Science* **39**, 23-36.

Papadopoulos, P. and Rowell, D. L., 1989. The reaction of copper and zinc with calcium carbonate surfaces. *Journal of Soil Science* **40**, 39-48.

Peric, J., Trgo, M. and Medvidovic, N. V., 2003. Removal of zinc, copper and lead by natural zeolite- a comparison of adsorption isotherms. *Water Research* **38**, 1893-1899.

Plummer, L. N., Wigley, M. L. and Parkhurst, M. L., 1978. Chemical modeling in aqueous systems. *America Journal of Science* **278**, 179-216.

Porcella, D. B. et al. and Adriono, D. C. (eds), 1990. *Acidic Precipitation : Mitigation of acidic conditions in lake and streams.* Springer- Verlag, New York.

Rampe J.J., Runnel, D. D., 1989. Contamination of water and sediment in a desert stream by metals from an abandoned gold mine and mill, Eureka District, Arizona, USA. *Applied Geochemistry* **4**, 445-454.

Rengaraj, S., Kim, Y., Joo, C.K. and Yi, J., 2004. Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: kinetics and equilibrium. *Journal of Colloid and Interface Science* **273**, 14-21.

Rowe, D. R. and Magid, I. M. A., 1995. *Handbook of Wastewater Reclamation and Reuse.* New York.

Salomons, W., Forstner, U. and Mader, P.(eds), 1995. *Heavy Metals, Problems and Solution.* Springer-Verlag Berlin Heidelberg, New York.

Sanchez, A. G. and Ayuso, E. A., 2002. Sorption of Zn, Cd and Cr on calcite: application to purification of industrial wastewaters. *Mineral Engineering* **15**, 539-547.

Sekar, M., Sakthi, V. and Rengaraj, S., 2004. Kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell. *Journal of Colloid and Interface Science* **279**, 307-313.

Singer, P. C. and Stumm, W., 1970. Acid mine drainage: the rate determining step. *Science* **167**, 1121-1123.

Spark, K.M., Johnson, B.B. and Wells, J.D., 1995. Characterising heavy metal adsorption on oxides and oxyhydroxides. *European Journal of Soil Science* **46**, 621-631.

Stumm, W., 1992. *Chemistry of the Solid-Water Interface*. Wiley, New York.

Stumm, W. and Morgan, J. J., 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. 3rd edition. Wiley, New York.

Tan, T.C. and Teo, W.K., 1987. Combined effect of carbon dosage and initial adsorbate concentration on the adsorption isotherm of heavy metals on activated carbon. *Water res.* **21**, 1183-1188.

Theobald, Jr., Lakin H. W., Hawkins, D. B., 1963. The precipitation of aluminium, iron and manganese at the junction of Deer Creek with the Snake River in Summit Country, Colorado. *Geochimica Cosmochimica Acta* **27**, 121-132.

Tsusue, A. and Holland, H. D., 1966. The co precipitation of cations with $CaCO_3$-III. The co precipitation of Zn^{2+} with calcite between 50 and 250°C. *Geochimica Cosmochimica Acta* **30**, 439-453.

Vengris, T., Binkiene, R. and Sveikauskaite, A., 2000. Nickel, copper and zinc removal from waste water by a modified clay sorbent. *Applied Clay Science* **18**, 183-190.

Walton, A. G., 1967. *The formation and Properties of Precipitates*. John Wiley, New York.

Walton, P. H. and Clark, J. H. (eds), 1995. *Chemistry of Waste Minimization: Methods of metal capture from effluent*. Chapman and Hall, UK.

WHO, 1998. Guidelines for Drinking Water Quality. WHO, Geneva.

Xu, Y. and Schwartz, F.W., 1994. Sorption of Zn^{2+} and Cd^{2+} on hydroxyapatite surfaces. *Environmental Science and Technology* **28**, 1472-1480.

Yavuz, O., Altunkaynak Y., and Guzel F., 2002. Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. *Water Research* **37**, 948-952.

Zachara, J.M., Cowan, C.E. and Resch, C.T., 1990. Metal cation / anion adsorption on calcium carbonate: Implication to metal ion concentrations in groundwater. *Proceeding of EPA Workshop on Metal Speciation and Transport in Groundwaters*, 24-26 May, 1989, Jekyll Island, Georgia.

Zachara, J.M., Cowan, C.E. and Resch, C.T., 1991. Sorption of divalent metals on calcite. *Geochemica Cosmochimica Acta* **55**, 1549-1562.

Zhang, G., Yang, X., Liu, Y., Jia Y., Yu G. and Ouyang S., 2004. Copper (II) adsorption on Ca-rectorite and effect of static magnetic field on the adsorption. *Journal of colloid and interface science* **278**, 265-269.