

EFFECT OF THE PRESENCE OF DISSOLVED METALS, Fe AND Al, ON NEUTRALIZATION OF ACIDIC AQUEOUS SOLUTION

Ho, Stella Yen Ling and Marcus Jopony

School of Science and Technology, University Malaysia Sabah

Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia

Email: stellahyl@gmail.com

Abstract: The efficacy of neutralization of an acidic aqueous solution is generally dependent on the type of alkaline material used. However, another limiting factor but often overlooked is the presence of dissolved metals. In this study, the effect of Fe^{3+} and Al^{3+} on the neutralization of acid aqueous solutions was investigated. Potentiometric titrations using 0.01 M NaOH were performed on aqueous acidic solutions, with initial pH pre-adjusted to 3.0, in the absence and presence of 10 mg/L and 100 mg/L Fe^{3+} or Al^{3+} . The results showed that the presence of Fe^{3+} or Al^{3+} resulted in a strong buffering at pH 3.0-3.5 and 4.0-4.5, respectively. Meanwhile, no significant pH buffering was observed for the non-metal acidic aqueous solutions. Consequently, more alkalinity (base) is required to increase the solution pH from pH 3.0 to the prescribed value (pH=7.0), particularly at high metal concentration. At a similar concentration, the presence of Al^{3+} resulted in more intense pH buffering and thereby more alkalinity is required for neutralization compared with Fe^{3+} .

Keywords: Neutralization; dissolved metals; hydrolysis; pH buffering.

INTRODUCTION

Neutralization by the addition of an alkaline material is a standard technique for treatment of acidic water and wastewater. Typical alkaline materials used include caustic soda, quick or hydrated lime, magnesium hydroxide and ammonium hydroxide [14, 18, 20]. The used alkaline generating materials such as limestone, fly ash, olivine, serpentinite, lignite have also been reported [2, 8, 11, 14]. Neutralization raises the pH of the water or wastewater to a desired value (e.g pH ~ 7.0), thereby reducing its' acidity. However, the efficacy of this process depends on several factors including the type of alkaline material used, particle size (if the material is solid in nature), contact time as well as on the characteristics of the water or wastewater [14].

*Received Mar 8, 2014 * Published April 2, 2014 * www.ijset.net*

In general, the acid characteristic of an aqueous solution can be expressed either by its pH value and/or total acidity value. pH is a measure of free acidity (H^+) present in solution while total acidity is represented by the combination of free acidity and mineral acidity. This mineral acidity associated with dissolved metals in particular Fe^{3+} and Al^{3+} . These metal ions readily undergo hydrolysis at pH 3.5-4.0 and 4.0-4.5, respectively to produce additional H^+ [4, 9]. In many common aqueous systems such as groundwater and surface water where the acid character is dominated by free acidity, neutralization process (i.e. increase in pH) can proceed in the usual manner as expected for a typical acid-base neutralization reaction. However, in acidic metal-rich aqueous systems such as acid mine drainages and industrial wastewater where mineral acidity predominates, *in situ* generation of H^+ attributed to Fe^{3+} or Al^{3+} hydrolysis can cause a sluggish increment in pH despite addition in the amount of alkalinity [3, 6, 10]. This pH buffering characteristic inevitably hinders or reduces the neutralization process efficiency. This factor however is often disregarded since the design of neutralization treatment process is usually based on the initial pH of the acid water or wastewater rather than its' total acidity value. In this study the effect of dissolved Fe^{3+} and Al^{3+} on acid neutralization efficacy was investigated and compared.

MATERIALS AND METHODS

Aqueous stock solutions (1000 mg/L) of Fe^{3+} and Al^{3+} were prepared from $FeCl_3 \cdot 6H_2O$ and $Al_2(SO_4)_3 \cdot 16H_2O$, respectively. Subsequently, metal solutions with initial concentrations of 10 mg/L and 100 mg/L were prepared and their initial pH adjusted to 3.0 with 1M H_2SO_4 . Additionally, an aqueous solution with initial pH \approx 3.0 was also prepared. All aqueous samples (50 mL) were titrated potentiometrically with 0.01 M NaOH to pH > 7.0 [6, 22].

RESULTS AND DISCUSSION

Effect of Fe^{3+} on neutralization

In the absence of Fe^{3+} , the titration graph is typical for a strong acid-strong base reaction (**Fig. 1**), whereby a sharp increase in pH was observed at equivalent point. In the presence of 10 mg/L Fe^{3+} , a similar trend in the increase of pH was also observed but slightly higher amount of alkalinity was required to raise the solution pH to 7.0. By contrast, in the presence of 100 mg/L Fe^{3+} a strong *pH buffering* was evident at pH 3.0-3.5. The pH value showed a very small increase from pH~ 3.0 despite the increasing amount of base (alkalinity) added. After a specific lag time, the pH eventually increased to the desired value.

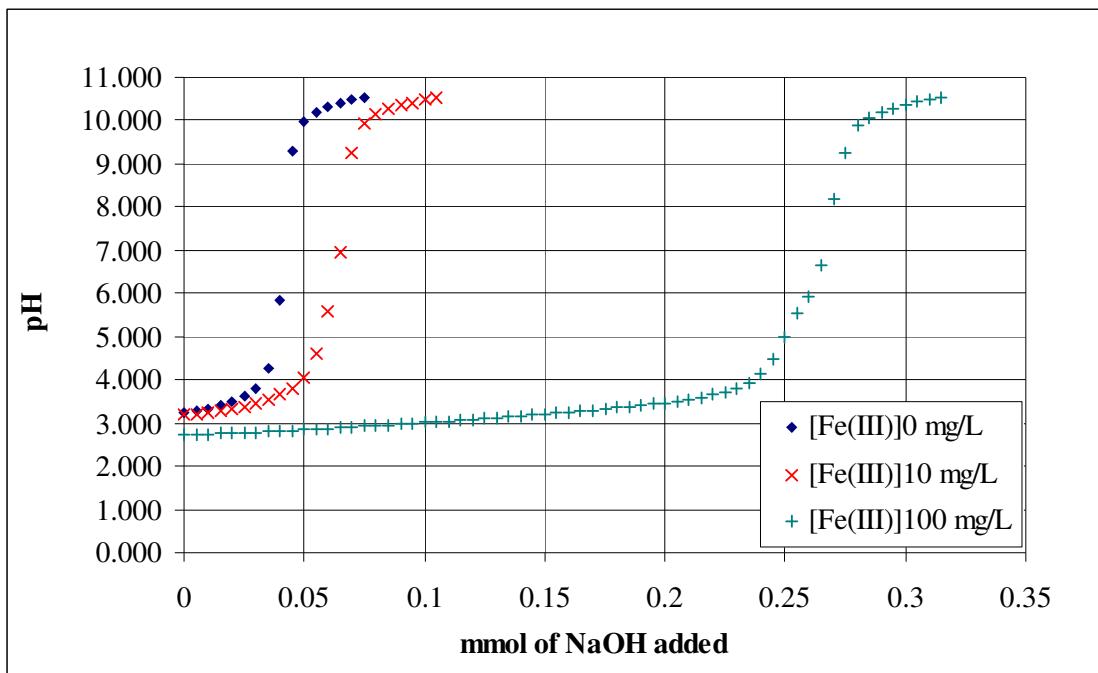


Fig. 1 Titration curves in the absence and presence of Fe³⁺ in acidic aqueous solution

During the titration, the added OH⁻ react rapidly with the H⁺ in solution, resulting in an increase in pH from pH ~ 3.0 (Eq. 1) [10]. In the presence of Fe³⁺, however, the increase in pH triggers the hydrolysis of Fe³⁺ (Eq. 2). This hydrolysis produces acidity which temporarily suppresses the increase in pH.



The amount of mineral acidity generated can also be greater at higher Fe³⁺ concentration. Consequently, the pH buffering effect at 3.0-3.5 is more pronounced at highest concentration of Fe³⁺. The pH only increases above 3.5 when all the Fe³⁺ ions have undergone hydrolysis or its' mineral acidity is depleted. Comparatively, the amount of alkalinity required to increase the pH to 7.0 is about 4 times higher for 100 mg/L Fe³⁺ compared to 10 mg/L Fe³⁺ (**Fig.2**).

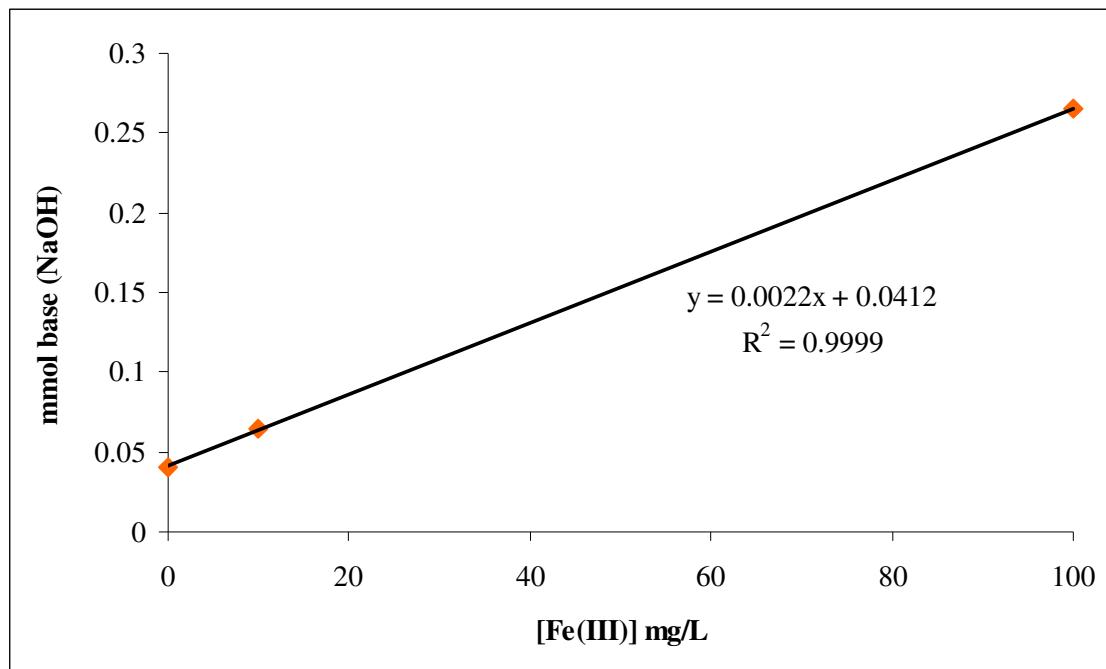


Fig. 2 Effect of Fe^{3+} concentration, on the amount of base required for neutralization (pH 7.0) of acidic aqueous solution

Effect of Al^{3+} in neutralization

In the presence of 10 mg/L of Al^{3+} , the increment in the solution pH (>3.0) at initial stage also displayed a similar trend to a strong acid-strong base titration curve (Fig. 3). However, as soon as pH approached 4.0, the graph displayed a small plateau before it starts to increase sharply to pH 7.0. Also, the amount of alkalinity required for the increment is relatively higher than acidic aqueous solution without the presence of Al^{3+} . However, at the highest concentration of Al^{3+} (i.e. 100 mg/L), a very conspicuous pH plateau was observed at pH 4.0–4.5. Only a small increment in pH was observed despite the amount of base added was increased.

The increased in pH to pH~4.0 following the addition of base prompted the hydrolysis reaction of Al^{3+} [9, 10, 22].



The rapid release of H^{+} inevitably causes a lagtime because every liberated mole of H^{+} during hydrolysis is quickly counteracted with a mole of the added base. Hence, the pH value of solution remained fairly constant as indicated by the pH plateau in the titration graph.

This buffering reaction continued until the mineral acidity has been depleted. Subsequent addition resulted in sharp increment in pH. Comparatively, the presence of 100 mg/L of Al^{3+} in acidic aqueous solution required 5.2 times more alkalinity than 10 mg/L to increase the

solution pH to 7.0 (**Fig.4**). By comparison with acidic aqueous solution without the presence of Al^{3+} , this value became more significant where it requires 13.6 times more alkalinity to attain pH 7.0.

Comparatively, the magnitude of pH buffering in the presence of Al^{3+} was significantly higher and more prominent than in the presence of Fe^{3+} . At similar concentrations 10 mg/L and 100 mg/L, acidic aqueous solution in the presence of Al^{3+} would require 1.6 and 2.1 times more alkalinity, respectively to attain a similar pH at 7.0 (see **Fig. 5**). This can be attributed to a higher ionic potential (i.e. charge/size ratio) in Al^{3+} compared to Fe^{3+} . Higher ionic potential gives a greater inductive effect during hydrolysis to attract electron density from oxygen atom in water molecule [7]. This substantially weakens the O-H bond of an attached water molecule making the release of a proton, H^+ relatively easier and faster. Ultimately, high intensity of hydrolysis reaction is expected for acidic aqueous solution containing significant presence of Al^{3+} rather than Fe^{3+} . As a result, neutralization process (i.e. increment in pH) becomes sluggish and inefficient.

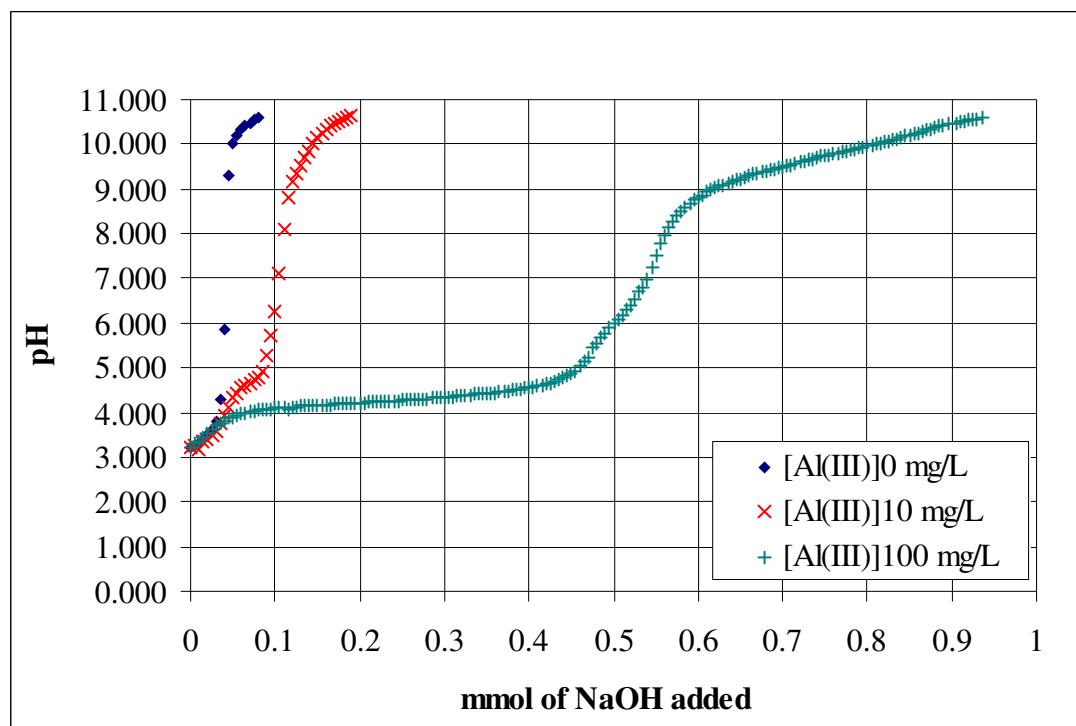


Fig. 3 Titration curves in the absence of Al^{3+} and presence of different concentrations of Al^{3+}

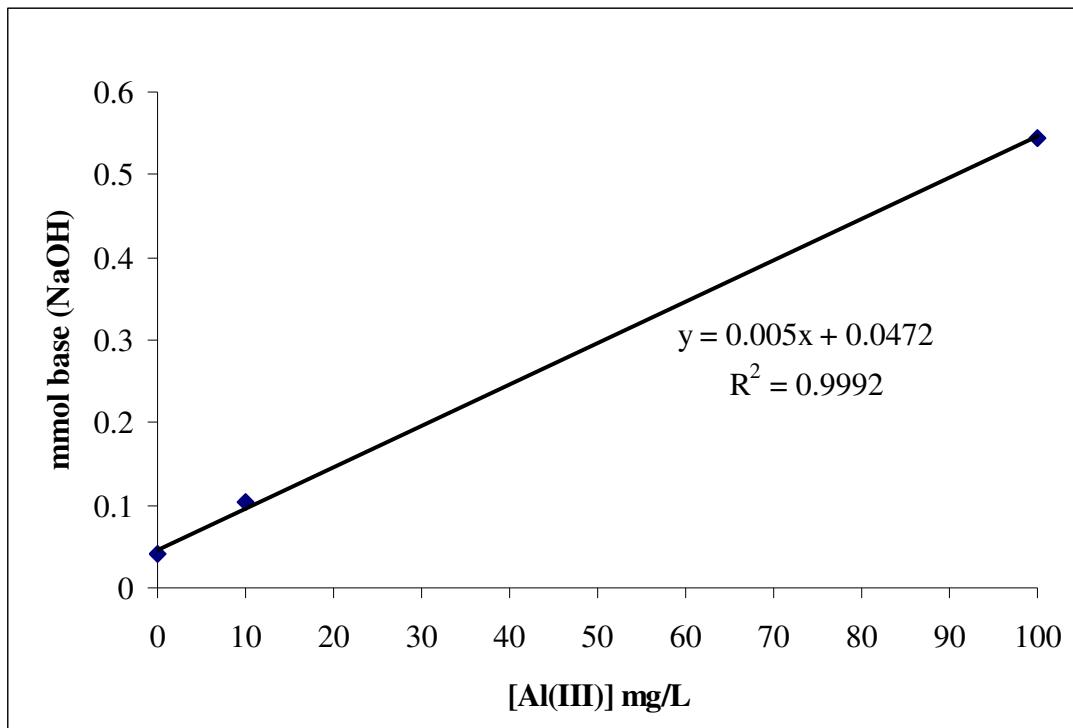


Fig. 4 Effect of concentration of Al^{3+} on the amount of base required for neutralization of acidic aqueous solution to pH 7.0

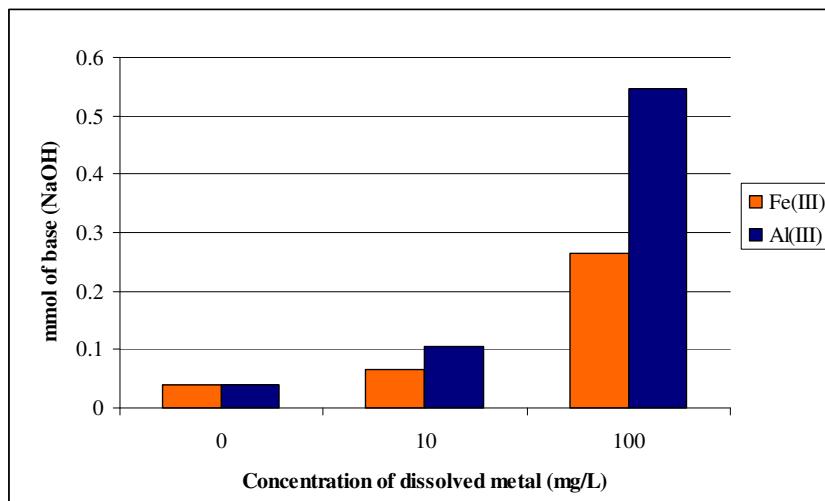


Fig. 5 Effect of Fe^{3+} vs. Al^{3+} concentration on the amount of base required for neutralization of acidic aqueous solution to pH 7.0

CONCLUSION

The presence of Fe^{3+} and/or Al^{3+} in an acidic aqueous solution can inhibit the increase in pH thereby reducing the efficacy of neutralization process. This effect is more apparent at high

concentration in particular for Al^{3+} . It is therefore crucial that neutralizing of an aqueous acidic solution needs to take into consideration the presence of dissolved metals (i.e. mineral acidity) instead of solely on the apparent pH value.

Acknowledgement

The authors would like to thank the Education of Higher Learning of Malaysia for MyPhD scholarship assistant during the entire project. Special thanks go to UMS School of Science and Technology for providing all the necessary materials and instruments for the analysis.

REFERENCES

- [1] Barton, P. (1978). The Acid Mine Drainage. In Nriagu, J.O. (ed.). *Sulfur in the Environment Part II: Ecological Impacts*. California: John Wiley and Sons, 318-254.
- [2] Bernier, L.R. (2005). The potential use of serpentinite in the passive treatment of acid mine drainage: Batch experiments. *Environmental Geology* **47**, 670-684.
- [3] Chon, H.-T. & Hwang, J.-H. (2000). Geochemical characteristics of the acid mine drainage in the water system in the vicinity of the Dogye Coal Mine in Korea. *Environmental Geochemistry and Health* **22**, 155-172.
- [4] Cravotta III, C.A. & Trahan, M.K. (1999). Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. *Applied Geochemistry* **14**, 581-606.
- [5] Doye, I and Duchesne, J. (2003). Neutralisation of acid mine drainage with alkaline industrial residues: laboratory investigation using batch leaching tests. *Applied Geochemistry* **18**, 1197-1213.
- [6] España, J.S, Pamo, E.L., Pastor, E.S., Aduvire, O., Andrés, J. R. & Barrettino, D. (2005). Acid mine drainage in the Iberian Pyrite Belt (Odiel River watershed, Huelva, SW, Spain). *Applied Geochemistry* **20**, 1320-1356.
- [7] Fergusson, J.E. 1982. *Inorganic chemistry and the earth: chemical resources, their extraction, use and environmental impact*. Pergamon series on environmental impact volume 6. Oxford: Pergamon Press.
- [8] Gitari, W.M, Petrik, L.F., Etchebers, O., Key, D.L., Okujeni, C. (2008). Utilization of fly ash for treatment of coal mines wastewater: Solubility controls on major inorganic contaminants. *Fuel* **87**, 2450–2462.
- [9] Hedin, R.S. 2006. The use of measured and calculated acidity values to improve the quality of mine drainage datasets. *Mine Water and the Environment* **25**: 146-152.

- [10] Kirby, C.S. & Cravotta III, C. A. (2005a). Net alkalinity and net acidity 1: Theoretical considerations. *Applied Geochemistry* **20**, 1920-1940.
- [11] Kleiv, R.A. & Thornhill, M. (2004). Adsorptive retention of copper from acidic mine water at the disused sulphide mine at Lokken, central Norway-initial experiments using olivine. *Minerals Engineering* **17**, 195-203.
- [12] Mackie, A.L. and Walsh, M.E. (2012). Bench-scale study of active mine water treatment using cement kiln dust (CKD) as a neutralization agent. *Water Research* **46**, 327-334.
- [13] Madzivire, G., Gitari, W.M., Vadapalli, V.R.K., Ojumu, T.V., Petrik, L.F. (2011). Fate of sulphate removed during the treatment of circumneutral mine water and acid mine drainage with coal fly ash: Modelling and experimental approach. *Minerals Engineering* **24**, 1467–1477.
- [14] Maree, J.P. & du Plessis, P. (1994). Neutralization of acid mine water with calcium carbonate. *Water Science Technology* **29**, 285-296.
- [15] Munk, L. and Faure, G., Pride, D.E. and Bigham, J.M. (2002). Sorption of trace metals to an Aluminium precipitate in stream receiving acid rock-drainage: Snake River, Summit County, Colorado. *Applied Geochemistry* **17**, 421-430.
- [16] Pérez-López, R, Castillo, J., Quispe, D., and Nieto, J.M. (2010). Neutralization of acid mine drainage using the final product from CO₂ emissions capture with alkaline paper mill waste. *Journal of Hazardous Materials* **177**, 762–772.
- [17] Potgieter-Vermaak, S.S., Potgieter, J.H., Monama, P. & Grieken, R.V. (2006). Comparison of limestone, dolomite, and fly ash as pre-treatment agents for acid mine drainage. *Minerals Engineering* **19**, 454-462.
- [18] Sengupta, M. (1993). *Environmental Impacts of Mining: Monitoring, Restoration, and Control*. Florida: Lewis Publishers.
- [19] Singh, G. & Rawat, N.S. (1985). Removal of trace elements from acid mine drainage. *International Journal of Mine Water* **4**, 17-21.
- [20] Skousen, J.G., Sexstone A., and Zimkiewicz, P.F. (2000). Acid Mine Drainage Control and Treatment. In: *Reclamation of Drastically Disturbed Lands*, 2nd Ed. American Society of Agronomy and American Society for Surface Mining and Reclamation. Madison: WI.
- [21] Sun, Q. (2000). *Iron and Acid Removal from Acid Mine Drainage in Open Limestone Systems*. Ph.D thesis, West Virginia University.

- [22] Totsche, O., Pothig, R., Uhlmann, W., Buttcher, H. & Steinberg, C.E.W. (2004). Buffering mechanisms in Acidic Mining Lakes- A Model-Base analysis. *Aquatic Geochemistry* **9**, 343-359.
- [23] Uhlmann, W., Buttcher, H. Totsche, O. & Steinberg, C.E.W. (2004). Buffering of acidic mine lakes: The relevance of surface exchange and solid bound sulphate. *Mine water and the Environment* **23**, 20-27.