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Indicator Parameters for Metals of Potential Concern in South African Acid and Circum-Neutral Mine Waters

Ansu van der Walt[1], Christian Wolkersdorfer[1,2]

[1]South African Research Chair for Acid Mine Drainage Treatment, Department of Environmental, Water and Earth Sciences, Tshwane University of Technology (TUT),
[2]Lappeenranta University of Technology, Laboratory of Green Chemistry

ABSTRACT

Costly and partly time consuming chemical analysis including ICP-MS, ICP-OES, ion chromatography or photography are usually used to analyse metals in mine influenced water (MIW). This paper introduces a new, effective method for estimating metal concentrations in MIW, by using titration curves and their inflection points. Based on a range of South African mine waters a new indicator method for this purpose will be established. The mine water chemistry will be predicted by a still to be developed, automated method using the inflection points to correlate the distribution of the inflection points to the mine water chemistry. In addition to the inflection points of the acid-base reaction, the reactions taking place during neutralization are identified, as each inflection point and plateau relates to a metal buffer reaction. These titration data is used to identify the buffer systems in the MIW, the acidity of the corresponding pH values within the titration and the concentrations of dissolved iron and aluminium in MIW. In the future, acid-base titrations of MIW shall replace routine chemical mine water analysis, which shall only be conducted when the indicators show a statistically significant change in metal concentrations.

1 Introduction

Mining activities might be responsible for different sets of environmental effects on water resources. One of the effects include the acidification of mine water that is produced by the oxidation of Fe-sulfide, particularly pyrite (Huang et al. 2005). Pyrite-rich materials associated with mining activities are exposed to atmospheric conditions. The exposure of these materials results in acid mine drainage (AMD) which is characterized by low pH values, high sulfate concentrations, and concentrations of Fe, Al or Mn that may act as buffering systems (Totsche et al. 2006). Before treatment of mining influenced water (MIW) can commence, the major metal ions and their concentrations must be determined. Usually, to analyse the metals in MIW, costly chemical analysis, either by ICP-MS, ICP-OES, ion chromatography or photometry are used. For decades, the mining industry is searching for cheap and reliable *indicator methods* for analysing environmental relevant chemical water parameters.

The purpose of this study is therefore to introduce an effective indicator method for estimating metal concentrations in MIW. This method will use the inflection points of titration curves as indicator points to identify the water's metal concentrations and determine its acidity. Determining the acidity of a system provides information of the sample water's capacity to neutralise a strong base to a specified pH. Constructing titration curves from titration data can indicate each titrant increments, their equivalent pH values, help to determine the inflection point of the acid-base reaction and enable more clarity on the reactions taking place during neutralization. These titration curves can be used to identify buffer limits in the water system, the acidity of corresponding pH values within the titration curve limit, and to determine the concentration of iron and aluminium in MIW. The acid-base titration method is a rapid, cost-effective, diagnostic tool to identify the presence of major metal ions (Kalin & Liu 1992).

2 Materials and Methods

The study was performed at different South African sites containing acid and circumneutral mine water. At each site, three samples were collected for further analysis. As the temporal development of the mine influenced water is not relevant for this study, duplicate samples over a period are not required. Samples were collected in 1.5 L, 1 L and 250 mL PTFE bottles which had its own function for sampling: samples collected in the 250 mL bottles, were filtered (0.45 cellulose nitrate filter) and acidified with nitric acid in the field.

The 1-L-containers were used for the acid-base titration and to determine the total iron and ferrous iron concentrations using a HACH DR900 Colorimeter in the field. Samples collected in the 1.5 L and 250 mL PTFE bottles were delivered to an accredited laboratory to determine the water's chemical composition. On-site parameters were measured with a HACH HQ40d with its corresponding probes during sampling. These parameters included; pH, electrical conductivity (µS/cm), redox (mV), temperature (°C), oxygen concentration (mg/L), oxygen saturation (%) and pressure (hPa). The pH and electrical conductivity probes were calibrated daily, and the samples were stored below 6 °C.

Samples were titrated with either 0.05 mol/L HCl for 1N NaOH or 0.005 mol/L HCl for 0.1 N NaOH depending on the water chemistry of each sample. The initial volume of each sample before titration was 50 mL. Each acid-base titration curve was simulated in triplicate by using the HACH Titralab TM1000 with its Titramaster 1000 software and a HACH photometer which enabled metal concentration detection. The chemical analysis data was captured with all the relevant fieldwork data into one MS Excel spreadsheet which enabled the calculation of each sample's acidity manually using MS Excel functions.

The curve fitting software Table Curve 2D was used to construct the titration curves of each sample from the Titramaster 1000 data obtained. Each curve was smoothed, and the inflection points of each curve were manually determined. Multivariate statistical analysis was applied to all the data by using a predictive analytic software, SPSS. The inflection points as a function of pH was used for cluster analysis.

3 Results and Discussion

The acid-base titration method uses the pH change at each addition of NaOH. The resultant titration curve of the acidic mine water is shaped like staircases (Figure 1). The titrations curves of each sample were smoothed with an automated smoothing algorithm, namely cubic spline functions. Various smoothing algorithms were studied and applied to the data, but the results from the cubic smooth algorithm could be best interpreted and had a regression of nearly one. The inflection points of each curve where identified as either a change in concavity (1st derivative) or where the 2nd derivative equals 0 to the x-axis of the smoothed data sets. Each inflection point has its own unique coordination. The concentration values (x) of each inflection point, was determined manually from the second derivative ($x = 0$). The pH values (y) of each inflection point, were identified by an automated table using the concentration values obtained. The lower the resolution of the titrant increments, the more difficult it was to identify the inflection points. These points where plotted into the smoothed data, and visual outliers where removed.

The pH increase within the curve is caused by the neutralization of the H^+-ions by the OH^--ions in solution. As the metal ions are precipitated by the OH^--ions in solution, a horizontal plateau is present within the titration curve (gradient = 0), indicating the formation of metal hydroxides. The inflection points as a function of pH was used for K-mean cluster analysis. The cluster groups per titration curve was manually identified. An overall cluster analysis was done on all the inflection points, and 5 cluster centres where identified. These cluster centres have a direct relation to the metal hydroxides within each specified pH range as discussed by various research (Figure 2).

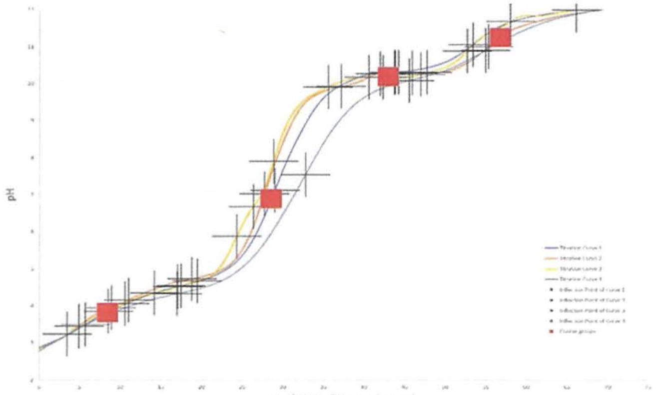

Figure 1: Example of an acid mine water titration curve with its corresponding inflection points and cluster groups (location Kromdraai L Colliery, Emalahleni).

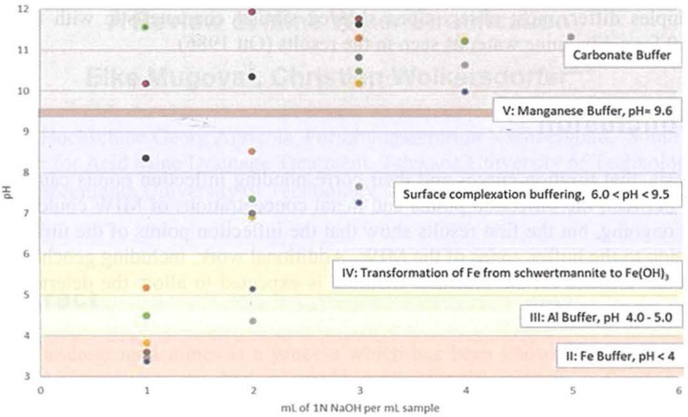

Figure 1: Example of all the cluster groups of the mine water in the specified buffer regions. The cluster groups were interpreted as a function of the pH.

Titration curves of MIW usually show five plateaus (I to V). Plateau I relates to the hydrogen sulfate buffer. An increase in slope before plateau I (pH < 3) is due to free hydrogen and hydrogen sulfate buffering. With the addition of NaOH to the solution the hydrogen sulfate ion forms a sulfate ion which causes a gradual change in pH. At the transition plateau of I to II, there is still hydrogen sulfate in the solution and therefore the buffering continues into the buffer plateau II. During titration, the titrated base is neutralised until most of the HSO_4^- ions and protons are used up (Xin et al. 2011):

$$H^+ \leftrightarrow H_2O - OH^- \qquad \log K = 14.00 \tag{1}$$

$$HSO_4^- \leftrightarrow SO_4^{2-} + H^- \qquad \log K = -1.978 \tag{2}$$

Plateau II relates to the iron buffer (pH < 4). In this plateau the dissolved ferric iron (Fe^{3+}) acts as the acid and the precipitating iron hydroxide ($Fe(OH)_3$) as the base. Dissolution and precipitation of iron hydroxide and precipitation of hydroxy sulfate such as schwertmannite are responsible for the buffering in plateau II and the high concentrations of ferric iron are responsible for the orange to brown-red colour of MIW. The following reactions take place in this buffer plateau (Xin et al. 2011):

$$Fe(OH)_3(s) \rightarrow Fe_3^+ + 3H_2O - 3H^+ \qquad \log K = 4.90 \tag{3}$$

$$Fe_8O_4(OH)_{12}(SO_4)_{2(s)} \rightarrow 8Fe^{3+} + 2SO_4^{2-} + 16H_2O - 2OH^- \qquad \log K = 12.00 \tag{4}$$

Plateau III is classified as the trivalent aluminium buffer (pH 4.0 – 5.0) which functions like the iron buffer and is associated with the dissolution/precipitation of aluminium minerals (Ott 1988). Plateau IV (pH ≈ 6.0) results from the Fe transformation from schwertmannite to $Fe(OH)_{3(s)}$. It depends on the concentration of the dissolved Fe: is the concentration high, the plateau will be present, is it moderately low, the buffer plane will not be present. The slow slope increase between plateaus IV and V (6.0 < pH < 9.5) can be explained by surface complexation buffering. Plateau V is classified as the manganese buffer (pH ≈ 9.6).

Total acidity is defined as titrations to a pH of 8.3, which signifies the upper limit of the carbonate buffer concentration (Totsche et al. 2006). Though acidity and ionic concentrations from previous research samples differ, most observations showed similar characteristic with two buffer zones below pH 6.0 for acidic mine water as seen in the results (Ott 1986).

4 Conclusion

The hypothesis, that titration curves and their corresponding inflection points can be used to draw correlations between the inflection points and metal concentrations of MIW could be verified. The work is still ongoing, but the first results show that the inflection points of the titration curves have a direct relation to the buffer zones of the MIW. Additional work, including geochemical modelling and correlation statistics on the indicator method, is expected to allow the determination of metal concentration ranges in MIW.

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