

Application of coal fly ash to circumneutral mine waters for the removal of sulphates as gypsum and ettringite

Godfrey Madzivire^{a,*}, Leslie F. Petrik^a, Wilson M. Gitari^a, Tunde V. Ojumu^b, Gillian Balfour^a

^a University of the Western Cape, Chemistry, Modderdam Road, Cape town, Western Cape 027, South Africa

^b Department of Chemical Engineering, Cape Peninsula University of Technology, P.O. Box 652, Cape Town 8000, South Africa

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ABSTRACT

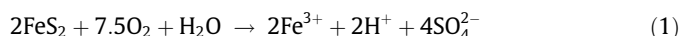
South African power stations generate large amounts of highly alkaline fly ash (FA). This waste product has a serious impact on the environment. Acid mine drainage (AMD) is another environmental problem associated with mining. AMD has high heavy metal content in addition to high sulphate concentrations. Several studies have shown that 80–90% of sulphates can be removed when FA is co-disposed with AMD rich in Fe and Al. In South Africa, sources of contaminated mine waters, unlike AMD have circumneutral pH and much lower concentrations of Fe and Al, but rich in Ca and Mg. Treatment of such waters with FA resulted in no significant removal of sulphates when treated to pH less than 10. Subsequent treatment of circumneutral mine water to pH greater than 11 resulted in more than 60% sulphate removal. Treatment of circumneutral mine water to pH greater than 11 with FA followed by seeding with gypsum crystals and the addition of amorphous Al(OH)₃ resulted in removal of sulphate to levels below the Department of Water Affairs and Forestry (DWAF) water quality effluent limit (500 ppm).

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1. Introduction

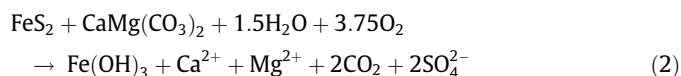
Clean water is recognized around the world as a crucial element in the battle against poverty and a limiting factor to growth (Barson et al., 1997). The freshwater resources in South Africa are under stress due to the increasing population coupled with pollution as a result of industrial and domestic activities. Typical pollutants include industrial effluents, domestic and commercial sewage, mine waters, agricultural runoff (Davies et al., 1993). Moreover, mine water is recognized to be contributing significantly to the country's water pollution problems. A proper disposal approach requires that mine water be treated to remove sulphates to less than 500 ppm and also achieves toxic metal removal (DWAF, 1996).

The biological oxidation of pyrites (FeS₂) – a major constituent of mine tailings – usually result in AMD formation as shown in Eq. (1). This water is characterised by high acidity, and high level of metals such as Fe, Mn, Mg and Al in sulphate form (Eby, 2004 and Younger et al., 2002).



Circumneutral mine waters, often referred to as Ca–Mg rich waters are produced when AMD undergoes partial neutralization due to the surrounding geology as the AMD flows past dolomite

rich mineral (Eq. (2)). In the process some metal contaminants will precipitate, while sulphates precipitate as gypsum or may be adsorbed on precipitating metal hydroxides.



As a result, circumneutral mine water contains lower sulphate levels than acid mine water and has near neutral pH. Unlike acid mine water, the concentrations of toxic metals in circumneutral mine water are near or below the acceptable effluent quality limit but such mine waters still contain a considerable amount of sulphate (Banks et al., 1997; Younger et al., 2002).

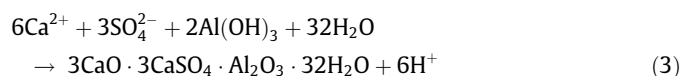
Many treatment technologies have been developed to decontaminate mine waters to produce potable and industrial waters. They can be broadly classified as passive and active treatment methods (Bosman et al., 1990). These technologies and their applications have been reviewed extensively by several authors (Mukhopadhyay et al., 2007; Neculita et al., 2007; Mare, 1988; Mattson and Lew, 1982; Geldenhuys et al., 2001 and Bosman et al., 1990). Due to high costs associated with treatment of mine water, cheaper ways which involve the use of fly ash (FA), a waste material produced from coal fired power stations, are currently being developed (Petrik et al., 2003). FA is a by-product obtained during the combustion of coal in coal burning power generation plants; its composition has been widely reported (Adriano et al., 1980). Although its disposal constitutes an environmental problem (Van den Berg et al., 2001), its potential use for the treatment of

* Corresponding author. Tel.: +27 82 593 1436; fax: +27 21 959 3878.

E-mail address: gmadzivire@uwc.ac.za (G. Madzivire).

acid mine water has been explored recently (Petrik et al., 2003; Hammack et al., 2006; Gitari et al., 2001; Gitari et al., 2008). The potential to use FA can be attributed to the fact that the aqueous extracts from FA are strongly alkaline (pH = 12) due to the presence of free soluble lime components (CaO and MgO) (Gitari et al., 2008). It has been shown that treatment of acid mine water with FA reduces the sulphate concentration considerably.

Although treatment of circumneutral mine water with FA results in approximately 60% sulphate removal (Madzivire et al., 2008) the sulphate concentration is still greater than the acceptable limit of less than 500 ppm prescribed by Department of Water Affairs and Forestry (DWAF, 1996). However, it has been shown in a SAVMIN process using lime that at pH >11, addition of amorphous Al(OH)₃ can reduce sulphates to a level below the effluent limit of 250 ppm (Smit, 1999). Those authors showed that in addition to gypsum formation, sulphate is also precipitated as ettringite with Al(OH)₃ as shown in Eq. (3).



This study presents the steps carried out to remove sulphates from circumneutral mine water to below the allowed effluent limit using FA. This study would have a significant implication, in addition to providing an outlet for FA usage, because the process would be more economically viable than the traditional chemical methods in a scale-up operation, given that FA is readily available in bulk quantities and is available close to the coal mines releasing the circumneutral mine water.

2. Materials and methods

2.1. Sampling

The materials used in this study are circumneutral mine water and fly ash (FA). The mine water was collected from a coal mine in Mpumalanga, South Africa. The mine water was filtered through a 0.45 µm nucleopore membrane and cation samples were acidified with concentrated HNO₃ to pH <2. The samples were sealed in plastic containers and kept at 4 °C until analysis by inductive-coupled plasma-atomic emission/mass spectrometry (ICP-AES/MS) and Ion Chromatography (IC) for cations and anions respectively. FA was collected from a nearby coal combustion power station in Mpumalanga, South Africa. The power station uses pulverized coal to generate electricity. The FA was collected directly from the precipitators and kept in sealed plastic bags devoid of air to avoid carbonation of free lime to calcite.

2.2. Experimental procedure

Simulated circumneutral mine water was used in this study. The simulated mine water was formulated based on the analysis of mine water samples collected from the field in Mpumalanga. It was made by dissolving the following salts in MilliQ water (1000 ml): MgSO₄ · 7H₂O (8.622 g), CaSO₄ (1.698 g), KNO₃ (0.09 g), NaCl (0.076 g) and MnCl₂ · 4H₂O (0.097 g). All the chemicals that were used for the simulated mine water solution were analytical grade except the MnCl₂ · 4H₂O which was a commercial grade. The simulated mine water was analysed to confirm the exact concentrations.

FA (125 g) and simulated circumneutral mine water (250 ml) were mixed together using an overhead stirrer. The mixture was stirred while monitoring the progress of the reaction by measuring electrical conductivity (EC) and pH using Hanna HI 991301 portable pH/EC/TDS/temperature pH meter. The reaction was allowed to proceed until the pH was >12. Thereafter, gypsum seed (0.1360 g)

and 96% (w/w) purity amorphous Al(OH)₃ (0.196 g) were added and mixed for 15 min. This procedure follows the SAVMIN process (Smit, 1999), but replaces lime with FA in the procedure. After adding Al(OH)₃ the mixture was filtered through 0.45 µm nucleopore membrane filter paper and the water analysed for cations and anions. The samples for cation analysis were preserved by acidifying with concentrated HNO₃ to pH <2. The samples were kept at 4 °C prior to analysis using inductively coupled plasma (ICP) and ion chromatography (IC) for cations and anions respectively. This experiment was done three times to verify reproducibility. The FA and solid residues were analysed using X-ray diffraction (XRD) and X-ray fluorescence (XRF) techniques after treatment of mine to pH >12 and after gypsum seeding and addition of Al(OH)₃.

2.3. Analytical techniques

Mine water samples and process water (mine water after treating with FA) were analysed using inductively coupled plasma-mass spectrometer/atomic emission spectrometer (ICP-MS and ICP-AES) for cations and ion chromatography (IC) for anions. Trace cations were analysed using Agilent 7500CE ICP-MS using a High Matrix Introduction (HMI) accessory and helium as collision gas. Major cations were analysed using a Varian Radial ICP-AES.

XRD was performed using PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and fixed receiving slits with Fe filtered Co Kα radiation. The XRD machine step size (2θ) was set at 0.02 and the time per step was set at 0.5. The SEM images were taken using the HITACHI X-650 Scanning Electron Microanalyzer.

3. Results and discussion

The chemical compositions of Mpumalanga coal mine water and simulated mine water are shown in Table 1. The composition of the simulated mine water used in this study is comparable to Mpumalanga coal mine water, for the major elements. It contains high concentrations of Ca and Mg with very low concentrations of Fe and Al but contains sulphate concentration much above the required effluent limit of 500 ppm.

The coal FA used in this study was analysed with XRF and % weight of the oxides are shown in Table 2. According to the

Table 1
Composition of Mpumalanga coal mine water and simulated mine water.

Element	Mpumalanga coal mine water concentration (ppm)	Simulated mine water concentration (ppm)
pH	6.9 ± 0.49	6.6 ± 0.21
Al	0.016 ± 1.1 × 10 ⁻³	0.13 ± 1.2 × 10 ⁻³
B	0.16 ± 1.1 × 10 ⁻³	0
Ba	0.013 ± 3.5 × 10 ⁻⁵	0
Ca	540 ± 2.9	570 ± 3.3
Co	0.29 ± 2.8 × 10 ⁻⁴	0
Fe	0.074 ± 6.2 × 10 ⁻⁴	1.9 ± 1.7 × 10 ⁻³
K	29 ± 0.014	34 ± 0.021
Mg	860 ± 15	847 ± 10
Mn	25 ± 0.085	27 ± 0.022
Mo	0.015 ± 7.1 × 10 ⁻⁶	0
Na	21 ± 0.036	24 ± 0.021
Ni	0.21 ± 1.4 × 10 ⁻⁴	0
Sr	1.8 ± 0.033	1.4 ± 0.011
Zn	0.16 ± 2.1 × 10 ⁻⁴	0
Cl ⁻	120 ± 8.5	82 ± 5.5
F ⁻	0.79 × 0.014	0
NO ₃ ⁻	120 ± 0.014	55 ± 0.51
PO ₄ ³⁻	5.6 ± 0.071	0
SO ₄ ²⁻	4600 ± 28	4700 ± 21

Number of samples, n = 3.

Table 2

Chemical composition of FA and SR analysed using XRF.

Major oxides	% w/w (FA)	% w/w (SR1)	% w/w (SR2)
SiO ₂	54.01 ± 0.28	53.16 ± 0.18	54.13 ± 0.37
Al ₂ O ₃	29.01 ± 0.14	26.17 ± 0.21	25.94 ± 0.17
CaO	4.63 ± 0.09	4.61 ± 0.10	4.97 ± 0.13
Fe ₂ O ₃	3.99 ± 0.07	4.3 ± 0.06	4.66 ± 0.07
TiO ₂	1.79 ± 0.03	1.45 ± 0.04	1.44 ± 0.06
MgO	1.12 ± 0.03	1.93 ± 0.03	1.9 ± 0.06
K ₂ O	0.78 ± 0.01	0.76 ± 0.01	0.78 ± 0.01
P ₂ O ₅	0.54 ± 0.02	0.55 ± 0.03	0.55 ± 0.12
SO ₃	0.24 ± 0.01	0.65 ± 0.04	0.89 ± 0.04
Na ₂ O	0.14 ± 0.01	0.04 ± 0.001	0.01 ± 0.0002
MnO	0.038 ± 0.001	0.06 ± 0.001	0.06 ± 0.001
LOI	3.7 ± 0.54	4.73 ± 0.24	3.92 ± 0.35
Total	99.99 ± 0.13	99.28 ± 0.08	99.60 ± 0.10

Loss on ignition (LOI); Fly ash (FA); Solid residue obtained after mixing FA with mine water to pH 12.35 (SR1) and Solid residue obtained after mixing FA to pH 12.35 and then gypsum seeding and Al(OH)₃ addition (SR2).

American Society for Testing and Materials (ASTM) classification method, the FA used in this study is Class F since the summation of SiO₂, Al₂O₃ and Fe₂O₃ is greater than 70% (Manz, 1999). XRD analysis showed that FA is made up of mullite, quartz, hematite and lime (Fig. 1).

From the XRF results obtained for the solid residues recovered after contact with the minewater, the % weight of SO₃ increased (Table 2). This means that the sulphate sink was the FA. The % weight of SO₃ was greater for the solid residues after seeding and addition of Al(OH)₃ (SR2) compared to before seeding (SR1).

XRD spectra obtained show that gypsum was formed during the treatment of mine water with FA. The lime phases in the FA disappear during the treatment of mine water and a new gypsum peak appeared in SR1 XRD spectrum (Fig. 1). After addition of Al(OH)₃ an ettringite peak was observed in SR2 XRD spectrum, meaning that a further decrease in sulphate concentration was due to ettringite formation.

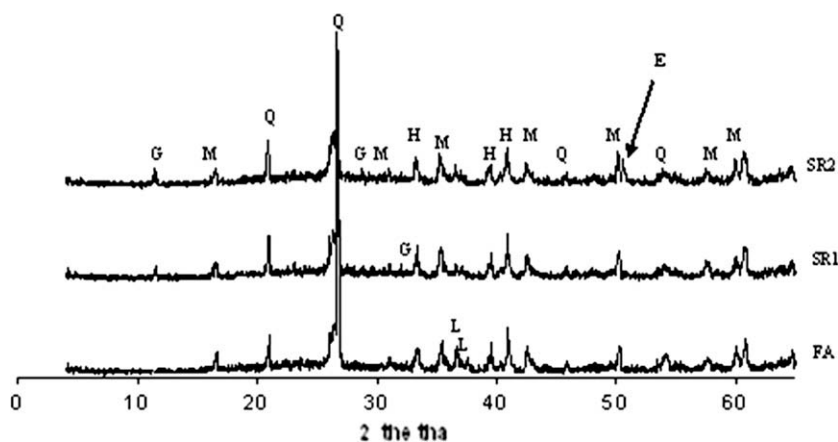


Fig. 1. XRD spectra for fly ash SR1 and SR2 (L-lime, G-gypsum, M-mullite, Q-quartz, H-hematite and E-ettringite).

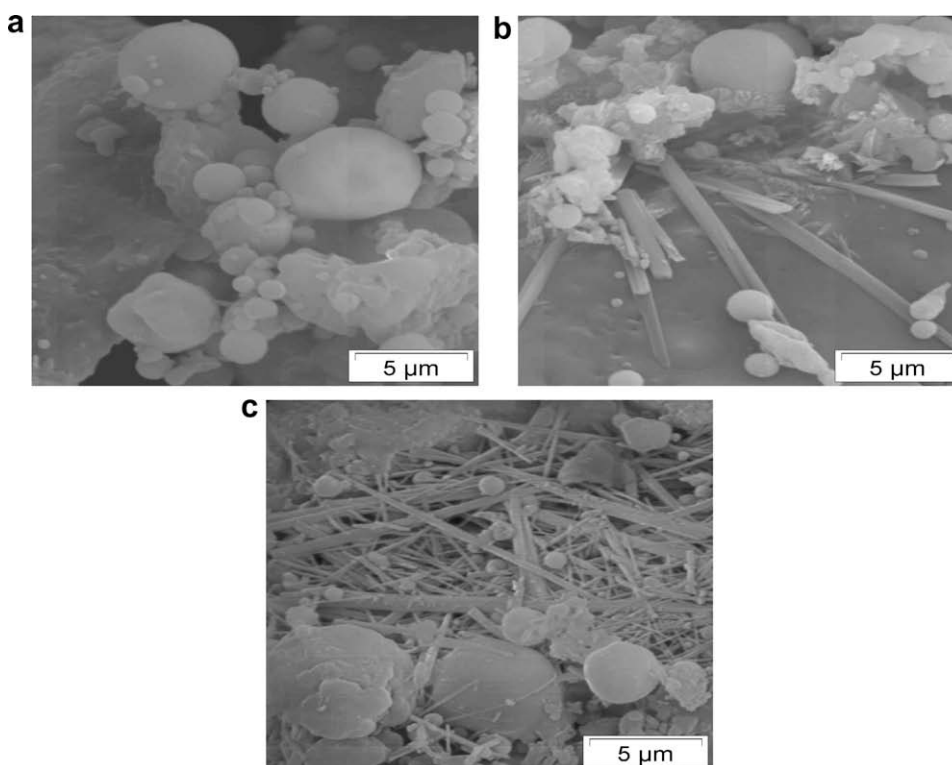


Fig. 2. SEM images of FA (a), SR1 (b) and SR2 (c) (magnification 5000×).

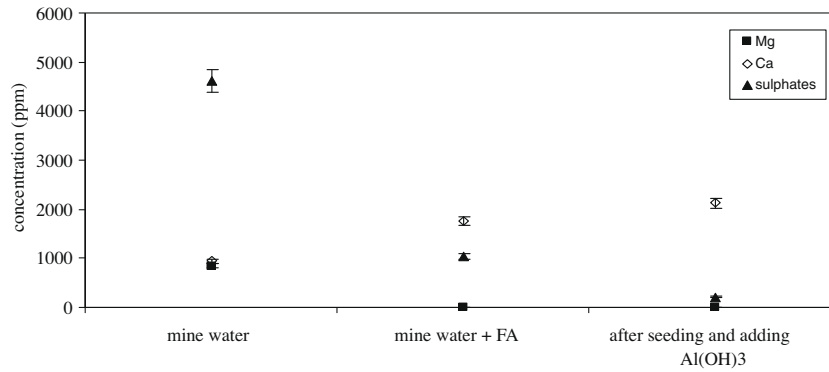


Fig. 3. Comparison of the concentration of Mg, Ca and sulphates after treatment of mine water with FA followed by addition of Al(OH)₃.

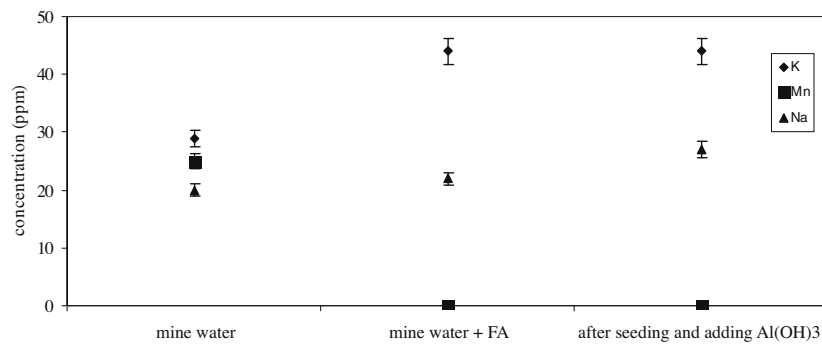


Fig. 4. Comparison of the concentration of K, Mn and Na after treatment of mine water with FA or with FA and Al(OH)₃.

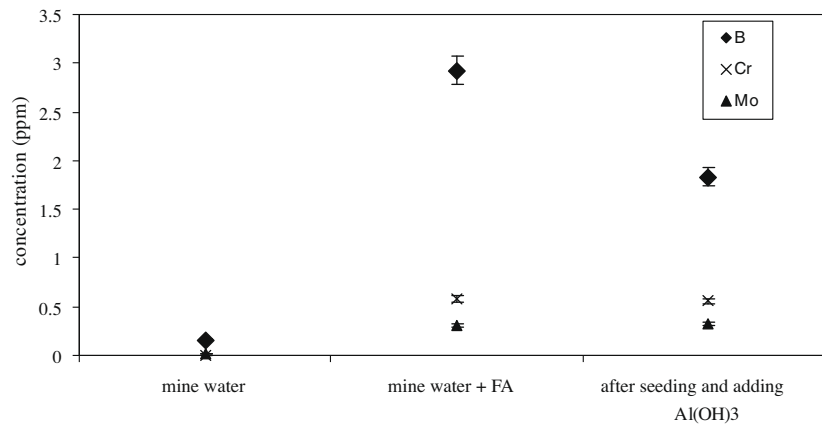
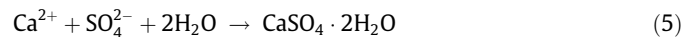


Fig. 5. Concentration of B, Cr and Mo during treatment of mine water with FA and Al(OH)₃.

SEM images obtained show that FA is made of spherical particles of less than 10 µm and irregular shaped particles (Fig. 2a). A SEM image of SR1 shows the presence of rod shaped (gypsum). The SEM image for SR2 show the presence of rod shaped (gypsum) and needle shaped (ettringite) phases which are not present in the FA sample. This offered further confirmation that gypsum and ettringite were the mineral phases that were responsible for sulphate precipitation when FA and Al(OH)₃ were added respectively during mine water treatment.

Treatment of circumneutral mine water with FA to pH 12.25 reduced the sulphates from 4800 ppm to 1043 ppm as shown in Fig. 3, due the dissolution of CaO from FA. The free lime in FA dissolves and then reacts with SO₄²⁻ in the mine water (Eqs. (4) and (5)).



However, once the amorphous Al(OH)₃ was added the sulphate concentration was further reduced from 1043 ppm to 213 ppm (Fig. 3) which is well below the DWAF effluent limit of 500 ppm. This is due to the formation of ettringite (Smit, 1999) as described by Eq. (3).

The concentration of Mg decreased to below detectable limit when the pH was increased to 12.25 due to the formation of Mg(OH)₂. Precipitation of Mg(OH)₂ at pH greater than 11 has been reported in the literature (Geldenhuis et al., 2001). The % weight of MgO increases in the solid residues meaning that the FA was the sink of Mg during treatment of mine water (Table 2).

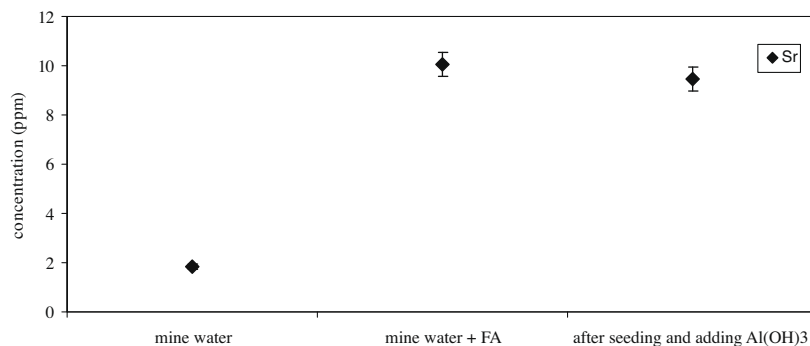


Fig. 6. Concentration of Sr during treatment of mine water with FA and then Al(OH)₃.

It can be observed that the removal of the sulphates correlated with the Mg removal. The presence of Mg ions decreased the amount of gypsum incipient nuclei because of MgSO_{4(aq)} complexation, which reduces the availability of sulphate ions for nucleus formation (Le Gouvellec and Elimelech, 2002). Although a significant amount of sulphate was removed, discharging water of such a high pH to the environment would remain a challenge. However, sparging CO₂ into the solution could be used to lower the pH and at the same time reducing the high Ca level by precipitation of CaCO₃ (Smit, 1999).

Treatment of mine with FA to pH 12.25 removed Mn to below the detection limit and the weight of MnO increases in the solid residue (Table 2). Mn precipitates as Mn(OH)₂ at pH 8.5–9.5 (Gurdeep and Narendra, 1985). K and Na levels increased in the mine water recovered after contact with FA. It can be inferred from Fig. 4 that the increase in K and Na was due to leaching of these elements into solution after contact with FA since the % weight of K₂O and Na₂O in the solid residues decreases (Table 2). However, the concentration of Na (42.07 ppm) and K (44.18) are still below the DWAF water quality limit of 70 and 50 ppm respectively (DWAF, 1996).

In Figs. 5 and 6, it is shown that the concentrations of B, K, Cr, Mo and Sr increased in the treated water. The increased levels observed after treatment under the specified conditions can only be attributed to their leaching from FA.

Of concern were B (1.833 ppm), Cr (0.5598 ppm) and Mo (0.328 ppm) levels which are increased to above the required DWAF target water quality effluent limit of 0.5, 0.1 and 0.01 ppm, respectively (DWAF, 1996). Previous work has shown the potential of zeolite adsorbents synthesized from coal FA to remove these toxic elements (Somerset et al., 2005; Somerset et al., 2008; Petrik et al., 2006; Moreno et al., 2001). It is thus proposed that these trace elements should be removed via adsorption with zeolites to make this treatment option viable.

4. Conclusion

This study has shown that sulphate can be removed from circumneutral mine water by treating with FA to a pH greater than 11, followed by seeding with gypsum and adding amorphous Al(OH)₃ with subsequently precipitation of sulphate as ettringite. The pH was increased to greater than 12 with fly ash to precipitate out Mg²⁺; thereby enhancing the precipitation of CaSO₄ · 2H₂O, but the water was still saturated with respect to gypsum. The saturated water was then seeded with gypsum crystals to initiate the precipitation of gypsum from the saturated solution. The solution was then mixed with Al(OH)₃ to precipitate out sulphate as ettringite. Once the amorphous Al(OH)₃ was added the sulphate concentration was further reduced from 1043 ppm to 213 ppm (Fig. 3) which is well below the DWAF effluent limit of 500 ppm. This is due to the formation of ettringite. The resulting high levels

of B and Mo due to leaching from fly ash may be removed from the mine water using zeolites synthesised from fly, and the post process water pH can be lowered to acceptable limits by bubbling CO₂ which would also reduce the Ca concentration in the treated water.

References

- Adriano, D.C., Page, A.L., Elseewi, A.A., Chang, A.C., Straughan, I., 1980. Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: a review. *Journal of Environmental Quality* 9, 333–344.
- Banks, D., Younger, P.L., Arnesen, R.L., Egil, R., Iversen, E.R., Banks, S.B., 1997. Mine-water chemistry: the good, the bad and the ugly. *Environmental Geology* 32 (3), 157–174.
- Barson, M.S., Van Niekerk, P.H., Van Rooyen, J.A., 1997. Overview of water resources availability and utilization in South Africa. Department of Water Affairs and Forestry, Pretoria.
- Bosman, D.J., Clayton, J.A., Maree, J.P. and Adlem, C.J.L., 1990. Removal of sulphates from mine water with sulphide. In: *Proceedings of the Lisbon 90 International Symposium: Acidic Mine Water in Pyritic Environments*, p. 16.
- Davies, B.R., O'Keefe, J.H., Snaddon, C.D., 1993. A Synthesis of the Ecological Functioning, Conservation and Management of South African River Ecosystem WRC report #TT 62/93. Water Research Commission, Pretoria.
- Department of Water Affairs and Forestry, 1996. South African Water Quality, Guidelines, second ed., Domestic Use, vol. 1. Department of Water Affairs and Forestry, Pretoria, South Africa.
- Eby, G.N., 2004. Principles of Environmental Geochemistry, first ed. Brooks/Cole Cengage Learning, USA.
- Geldenhuys, A.J., Mare, J.P., De Berr, M., Hlabela, P., 2001. An integrated limestone/lime process for partial sulphate removal. In: *Conference on Environmentally Responsible Mining in South Africa*, 2001, CSIR.
- Gitari, M.W., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E., Okujeni, C., 2001. Treatment of acid mine drainage with fly ash: removal of major contaminants and trace elements. *Journal of Science Health A: Toxic Hazardous Substances* 41, 1729–1747.
- Gitari, W.M., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E., Okujeni, C., 2008. Utilization of fly ash for treatment of coal mines waste water: solubility controls on major inorganic contaminants. *Fuel* 87, 2450–2462.
- Gurdeep, A., Narendra, S.R., 1985. Removal of trace elements from acid mine drainage. *International Journal of Mine Water* 4 (1), 17–23.
- Hammack, R.W., de Vegt, A.L., Schoeneman, A.L., 2006. The removal of sulfates and metals from mine waters using bacterial sulfate reduction: pilot plant results. *Mine water and the Environment* 10, 1–10.
- Le Gouvellec, Y.A., Elimelech, M., 2002. Calcium sulfate (gypsum) scaling in nanofiltration of agricultural drainage water. *Journal of Membrane Science* 205 (1–2), 279–291.
- Madzivire, G., Leslie, L.F., Vadapalli, V.R.K., Gitari, W., 2008. Optimization of sulfate removal from circumneutral mine water using fly ash. In: *39th SACI National Convention*, 2008, Stellenbosch University, p. 162.
- Manz, O.E., 1999. Coal fly ash: a retrospective and future look. *Fuel* 78 (2), 133–136.
- Mare, J.P., 1988. Sulphate Removal from Industrial Effluents. University of the Orange Free State, Bloemfontein.
- Mattson, M.E., Lew, M., 1982. Recent advances in reverse osmosis and electrodialysis membrane desalting technology. *Desalination* 41 (1), 1–24.
- Moreno, N., Querol, X., Ayora, C., Pereira, C.F., Janssen-Jurkovičová, M., 2001. Utilization of zeolites synthesized from coal fly ash for the purification of acid mine waters. *Environmental Science and Technology* 35, 3526–3534.
- Mukhopadhyay, B., Bastias, L., Mukhopadhyay, A., 2007. Limestone drain design parameters for acid rock drainage mitigation. *Mine Water and the Environment* 26, 29–45.
- Neculita, C.M., Zagury, G.J., Brussie, B., 2007. Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria: critical review and research needs. *Journal of Environmental Quality* 36, 1–36.

- Petrik, L.F., White, R.A., Klink, M.J., Somerset, V.S., Burgers, C.L., Fey, M.V., 2003. Utilization of South African fly ash to treat acid coal mine drainage, and production of high quality zeolites from the residual solids. In: Proceedings of the International Ash Utilization Symposium. University of Kentucky, Centre of Applied Energy Research, pp. 1–26.
- Petrik, L.F., Hendricks, N., Ellendt, A., Burgers, C., 2006. Toxic element removal from water using zeolite adsorbents made from solid residues. WRC Research Report No. K1546/1/07. WRC, South Africa. ISBN: 978-1-77005-464-6.
- Smit, J.P., 1999. The purification of polluted mine water. In: International Symposium of Mine Water and Environment for the 21st Century, 1999.
- Somerset, V., Petrik, L., Iwuoha, E., 2005. Alkaline hydrothermal conversion of fly ash filtrates into zeolites 2: utilization in wastewater treatment. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering* 40 (8), 1627–1636.
- Somerset, V., Petrik, L., Iwuoha, E., 2008. Alkaline hydrothermal conversion of fly ash precipitates into zeolites 3: the removal of mercury and lead ions from wastewater. *Journal of Environmental Management* 87, 125–131.
- Van Den Berg, J.J., Cruywagen, L., De Necker, E., Hodgson, F.D.I., 2001. The suitability and impact of power station fly ash for water quality control in coal opencastmine rehabilitation: acid mine drainage neutralization, conditioning and partial. Report No. 745/1/01. VINNICOMBE, D.A, 2000.
- Younger, P.L., Banwart, S.A., Hedin, R.S., 2002. *Mine Water: Hydrology, Pollution, Remediation*. Dordrecht Kluwer Academic Publishers.