SUSTAINABLE PURIFICATION OF MINE WATER USING ION EXCHANGE TECHNOLOGY

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ABSTRACT

Water polluted as a consequence of mining is the single largest environmental challenge facing the industry. This is due to the fact that the problem is persistent and costly to remediate and tends to be a liability for mines long after closure. Water re-use is essential in water scarce regions and current technologies for treatment of mine water are capable of producing acceptable potable, agricultural and industrial grade water. However, no commercial process has yet demonstrated the ability to do this in a substantially zero effluent manner as all processes produce significant quantities of solid or concentrated waste. Mine water purification solutions need to be developed that make economic sense and that minimize the solid waste produced. This paper details a case study for an almost zero-effluent, economically-viable and patented approach, using ion exchange (IX) technology, in the purification of mine water for discharge or re-use as agricultural, process, industrial or potable water.

Key enabling features of the proposed treatment approach are;

- use of nitric acid and ammonia (regenerants in the ion exchange circuit) to produce saleable products directly and with good control over the product mix;
- considerable flexibility to influent quality; and
- use of a proprietary IX technique to significantly increase eluate concentrations and eliminate waste.

The technical and economic performance of the process has been evaluated at pilot scale on a typical water quality from a gold mine in South Africa and financial projections indicate that the proposed treatment approach is competitive with existing approaches. An additional benefit of the proposed treatment approach is that it lends itself to modular implementation.

1. INTRODUCTION

The issue of mine water release is considered to be of national significance and a major impact to the state of the environment (Oelofse, 2008) in South Africa and elsewhere (www.inap.org). In the current paper we focus on South Africa however the conclusions are generally applicable. Water polluted due to mining is continuously extracted from operational mines to prevent flooding of equipment, infrastructure and mining areas. In closed mines this effluent is either continuously pumped to maintain a critical level underground or it is allowed to decant at surface. The gradual acidification of mine-water is the result of natural leaching of pyrite resulting in the release of sulfur from the rock exposed by mining. The sulfur in the rock forms dilute sulfuric acid in the presence of water and atmospheric oxygen. The acidified water is an ideal lixiviant for metals also contained in the exposed rock thus forming a mixture of metal sulfate salts. The process of dissolution of pyrite and other metal species is accelerated by biological activity. Mine water polluted in this way is commonly referred to as acid mine drainage (AMD).

The composition of polluted mine waters is a function of mine-water acidity as well as the rock mineralogy in a given location. These waters usually contain high levels of sulfates, calcium and magnesium and sometimes sodium and chlorides. Toxic metals such as iron, aluminium, uranium, manganese, nickel, zinc, cadmium, lead and copper also occur. Corrosive attack by AMD can have a costly impact on mining equipment and infrastructure. This is often controlled through the addition of a solution of limestone and/or lime to the mine water prior to reticulation and extraction from the mine. Neutralization of the AMD results in the formation of a gypsiferous precipitate containing the insoluble metals in the form of a sludge that is stored in a waste facility. The neutralized mine water extracted from mines still requires further treatment prior to disposal to meet discharge standards suggested by the South African Department of Water and Environmental Affairs (DWEA) (reference at end the DWEA publication source for this standard 2009). In particular the new discharge standards require that the sulfate levels are reduced to below 350mg/ℓ and uranium levels are reduced to below 50µg/ℓ.

The ion exchange treatment method for mine water is invariant to whether the AMD is treated before or after neutralization. A case study is presented that indicates the performance of an ion-exchange based process for the treatment of neutralized mine water discharged from an operational underground gold mine and neutralized to pH 7 with lime. This polluted stream contains elevated levels of calcium (±300mg/ℓ), sodium (±300mg/ℓ), magnesium (±100mg/ℓ) and uranium (±100µg/ℓ) in association with sulfates (±1300mg/ℓ).

2. CASE STUDY – TREATMENT OF NEUTRALIZED ACID MINE WATER IN THE WITWATERSRAND WESTERN BASIN

An underground gold mine, located in the Western Basin of the Witwatersrand Goldfield in Gauteng, South Africa, is currently extracting a significant volume of neutralized water from three operating shafts. Some of this volume is recycled to the mine for ongoing mining activities, a quantity is used in the processing plant and the balance is discharged into the local river system after neutralization. Although neutralizing with lime improves mine water quality it does not meet discharge or re-use standards. Table 1 compares the neutralized mine water quality with the required discharge water quality standard. It is evident that additional treatment is required particularly for removing sodium, uranium and sulfates.

Table 1. Quality of neutralized mine water and discharge standard

Parameter	Units	Neutralized mine water quality	DWEA[*] discharge standard
pH		7	5.5 – 9.5
Calcium	mg/ℓ	295	300
Magnesium	mg/ℓ	104	100
Sodium	mg/ℓ	306	150
Potassium	mg/ℓ	3.1	-
Iron	mg/ℓ	0.4	200
Uranium	µg/ℓ	105	50
Sulfate	mg/ℓ	1290	350
Chloride	mg/ℓ	8.5	150

[*] Department of Water and Environmental Affairs (DWEA)

Environmental and Remedial Technology Holdings (Earth) (Pty) Ltd have developed a patented ion-exchange based process (Howard and Grobler, 2009) to treat the neutralized mine water to bring it within standards required for discharge. The process was first investigated at bench-scale and then tested at pilot scale. The on-site pilot trials generated the data for input to a full-scale plant cost estimate conducted by TWP Projects. The trials showed the process to be zero-effluent with respect to the removal of both uranium and sulfate. Figure 1 shows a schematic of the flow sheet employed to treat the neutralized AMD.

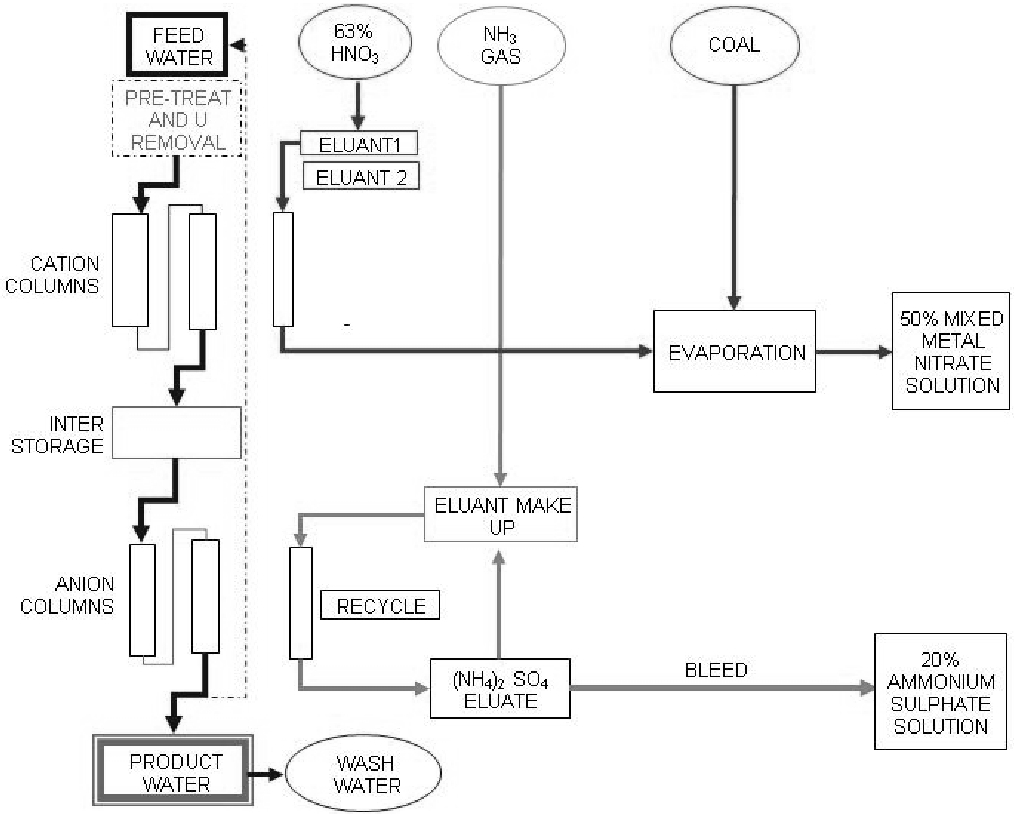

Figure 1. Schematic of neutralized AMD treatment process

A separate ion-exchange step was developed for the removal of uranium prior to the ionic demineralisation plant. This approach ensured that the main IX plant was not exposed to radioactive uranium and reduced the risk of uranium contamination of the process byproducts.

The mixed-metal nitrate product from the extraction of the cations is a high-purity nitrate solution of sodium, calcium and magnesium. The low impurity levels make this a suitable product for use in the explosives industry. The high purity (>99%) of the ammonium sulfate product from the extraction of the anions, makes it suitable for chemical grade applications.

Process Description

It is necessary to first filter the neutralized mine water since solids and organics are deleterious to the ion-exchange process. Sand filters are used for clarification and activated carbon for the removal of organics. As the pre-treatment steps do not have the benefit of chemical regeneration for controlling bacterial growth it is necessary to continually dose a bacterial disinfectant into the forward stream. Low levels of dissolved chlorine are maintained by dosing hypochlorite solution made up from granulated chlorine (calcium hypochlorite) and IX effluent water. As a back-up measure treatment with lye solution can be used.

The stream is split to feed two parallel banks of sand filters. Build up of solids in the sand beds is controlled by periodic backwashing with filtrate. Backwash slurry is returned to the mine process plant. The solution exiting the sand filters passes through columns charged with granular activated carbon to remove traces of organic prior to uranium IX. When spent the activated carbon is removed and replaced with a fresh charge of absorbent. The spent carbon can be used to supplement the carbon fuel used for water evaporation in the elution product concentration steps.

After filtration the solution is fed in two parallel streams to sets of uranium IX columns arranged in a lead-lag configuration with a fifth column for polishing. At all times one of the columns will be out of the loading cycle and subject to elution. A strong-base anion resin is used. In this instance, sulfuric acid is used for elution of uranium loaded on the resin. The uranium-bearing eluate is suitable for sale to uranium processors. The uranium IX barren solution reports to a storage tank. A portion is fed to the cation IX system and the remainder is diverted to be combined with final IX barren before discharge.

A strong-acid IX resin is used to remove cations from the solution. Four fixed-bed IX columns are used and at all times three are in the loading cycle and one in elution. The loading of cations onto the resin displaces protons into the solution. This enables pH to be used to control the loading cycle as the termination of cation loading is registered as an increase in solution pH. When this occurs the column is taken out of the loading cycle and the solution is drained by gravity and using air displacement.

The loaded resin is eluted with diluted nitric acid solution made up from weaker acid solutions from prior elutions and concentrated nitric acid from storage. The concentrated portion of the eluate stream exiting the column is advanced to product concentration and the weaker portions (the ends of the characteristic bell-shaped eluate concentration profile) are recycled. In this way reagent usage and concentration of the final eluate are maximized. The product stream is concentrated further to 50% moisture by evaporation using a stream of hot gas in counter-current flow to the solution introduced via spray nozzles into the top of the evaporation tower. The concentrated product is pumped continuously from the sump at the bottom of the tower via a chamber filter press to remove coal-based solids to storage prior to dispatch.

The anions in solution (primarily sulfate) are removed using a weak-base anion exchange resin. Four fixed-bed IX columns are used and at all times three are in the loading cycle and one in elution. The conductivity of the exiting solution is used to control the loading cycle as the termination of anion loading is registered as an increase in solution conductivity. When this occurs the column is taken out of the loading cycle and the solution is drained by gravity and using air displacement.

The loaded resin is eluted with diluted aqueous ammonia solution made up from weaker solutions from prior elutions and concentrated ammonia from storage. The concentrated portion of the eluate stream exiting the column is advanced to product concentration and the weaker portions are recycled. In this way reagent usage and concentration of the final eluate are maximized.

Experimental Program

The experimental program was planned and executed in three distinct stages to address specific process issues.

- Dynamic experiments on bench-scale using 800mℓ IX columns
- Steady state experiments on pilot scale (4m^3/d) using 20ℓ IX columns
- Optimisation trials on pilot scale using 20ℓ IX columns

Dynamic experiments

The objective of the dynamic experiments was the bench-scale simulation of the conceptual process flow sheet. During this stage the regeneration of the uranium column with sulfuric acid was modified to instead use sodium sulfate to ensure the conversion of the resin to the sulfate rather than the bi-sulfate form. The experimental setup consisted of six columns connected in series.

Steady-state pilot trials

Accurately controlled week-long trials were executed on the pilot plant to assess the technical viability of the process, determine process efficiencies and generate data for the full-scale plant cost estimate and for financial modeling and economic evaluation. The target parameters for the trials (e.g. flow-rates, eluant concentrations, split elution ratios, sampling regimes, etc) were selected based on the findings of the dynamic experiments.

Optimization pilot trials

Optimization trials were conducted to explore an optimisation matrix for the primary economic parameters; flow rate, reagent consumption and product concentrations. The pilot plant was operated for 12 hours to attain “steady state” conditions before the commencement of optimization trials that entailed operation of the entire system for a further 72 hours.

Standard operating procedures and appropriate parameter logs for areas of operation were developed to ensure competency levels of the operating team for operational control, process monitoring and logging of process parameters. Routine analysis, calibration of instruments and standard analytical procedures were instituted to ensure accuracy of the data produced that included analyses easily executed in the on-site laboratory for control and comprehensive analyses of composite samples by accredited off-site laboratories. Figures 2 and 3 show views of the pilot plant set up and arrangement.

Figure 2. “Containerized” Earth pilot plant at site

Figure 3. IX column and manifold arrangement for Earth pilot plant

Pilot Trial Results

Initial experiments at laboratory scale yielded excellent water quality with <1mg/ℓ total dissolved solids and conductivity around 4mS. This water quality is better than most demineralized water sold for analytical purposes by chemical suppliers.

Tables 2 to 4 summarize product qualities achieved in the pilot trials. Table 2 gives the quality of final product water achieved at steady state operation at a flowrate of 4m^3/d.

Table 2. Product water quality achieved in steady-state pilot trial

Parameter	Units	Value
pH		7.5
Calcium	mg/ℓ	7.1
Magnesium	mg/ℓ	2.4
Sodium	mg/ℓ	56
Potassium	mg/ℓ	0.5
Iron	mg/ℓ	0.1
Uranium	µg/ℓ U	5
Sulfate	mg/ℓ	50
Chloride	mg/ℓ	57

Excellent product qualities were achieved for both the cationic (Table 3) and anionic (Table 4) IX circuits. Purity levels were in excess of 99%.

Table 3. Composition of cationic mixed-metal nitrate solution product

Parameter	[g/ℓ]
Calcium nitrate	80.4
Magnesium nitrate	42.2
Sodium nitrate	75.3
Potassium nitrate	0.53

Table 4. Composition of anionic ammonium sulfate solution product

Parameter	[g/ℓ]
Ammonium sulfate	198.6
Ammonium chloride	1.4

Preliminary Economic Assessment

The basis for the mass balance was 20000m^3/d. Table 5 indicates reagent consumption and final product generation rates. The calculated water recovery efficiency for the process is 98.7%.

Table 5. Material consumption and production rates

Reagents	[tpd]
Nitric acid (100%)	59.1
Ammonia	10.9

Products	[tpd]
Ammonium sulfate	35.8
Calcium nitrate	24.2
Sodium nitrate	29.3
Magnesium nitrate	12.7

Table 6 gives a summary of the operating expenditure per cubic metre of water treated.

Table 6. Summary of operating costs

	[ZAR/m^3]
Nitric acid (100%)	7.53
Ammonia	2.08
Electricity	0.29
Coal	1.58
Salaries and wages	0.97
Resin	0.19
Admin and expenses	0.09
Maintenance and spares	0.19
Total operating cost	**12.94**

TWP Projects produced a factored cost estimate in accordance with the requirements of an AACE (Association of the Advancement of Cost Engineering) Class 4 estimate for a 20000m^3/d plant Table 7 gives a summary of the cost of capital associated with this scale of plant.

Table 7. Summary of cost of capital calculation

Capex	[ZARm]	141
Finance period	[years]	20
Interest rate	[per annum]	15%
Cost of capital	[ZAR/m^3]	2.68

Table 8. Summary of revenue streams

Product	**[ZAR/m^3]**
Ammonium sulfate solution (20% m/m)	3.05
Mixed metal nitrate solution (50% m/m)	8.05
Total revenue	**11.10**

Table 8 indicates the projected revenues that the process can achieve for the product spectrum that has been selected. Based on the data in Tables 6 to 8 it is projected that the process can be operated at a cost of ZAR4.53/m^3 of water treated.

3. CONCLUSIONS

The required quality for discharge of mine water within the current standards was achieved using a patented process developed by Earth. The process has no effluent other than a small volume of solid waste from backwashing the sand filters because the products generated by eluting the cation and anion columns are saleable in the form produced. This ion-exchange based process did not yield any effluent in the treatment of neutralized AMD. In particular the process reduced the uranium and sulfate levels to within the specified standards. TWP Projects did the factored cost estimate for a 20000m^3/d processing plant for inclusion in the preliminary economic assessment of the process. The pilot trials have demonstrated the technical and economic viability of the process. Future work will be focussed on alternative product ranges, treatment of raw AMD directly using IX and development of a patented continuous counter-current ion exchange contactor with the option of resin-in-pulp operation. This is intended to extend the range of waste effluents that can be treated and extend the concept to the retreatment of past residues and low grade resources.

4. REFERENCES

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