A Novel Electrochemical Process for Aqueous Oxidation of Acid Mine Drainage using Advanced Power Electronics and Real time Control

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Abstract An electrochemical treatment process using an external power supply connected to an electrical circuit consisting of oxidising electrodes immersed in an acid mine drainage (AMD) source water offers a simple, efficient, effective, chemical-free active treatment for removal of iron. In trials, electrochemical oxidation measured by an ORP meter produced clear water and recoverable iron sludge without the need for pH adjusting chemicals for some AMD source waters. This paper presents an overview of the electrochemical oxidation process, their reactions steps and scale-up for a commercial electrochemical reactor incorporating advanced power electronics and real time control.

Keywords Acid Mine Drainage, electrochemical treatment, advanced oxidation.

Introduction

Acid mine drainage (AMD) can contain high concentrations of dissolved (semi)-metals and sulphate, often with very low pH values. Unless treated, such waters may not be discharged into the natural environment. The acid water is formed as a result of bacterial oxidation when pyrites are exposed to oxygen and water after or during mining processes (Maree *et al.* 2004). Currently, the favoured industrial methods of treating acid water are pH neutralisation using lime, biological neutralisation-adsorption in natural or man-made wetland systems, oxidation using aeration, ozone, or hydrogen peroxide and more recently reverse osmosis (RO). However, many of these processes have limitations, for example, lime neutralisation requires the quarrying, production of un-slaked or slaked lime which produces large quantities of unstable iron rich sludge, wetlands require specially constructed sites occupying large areas of land while iron precipitates irreversibly on RO membrane filters, thus requiring complex chemical backwashing and frequent replacement.

Oxidation of untreated pyrite by bacteria (Silverman 1967; *e.g. Ferrovum myxofaciens sp*; Hendrick and Johnson 2012) is achieved by two mechanisms: direct oxidation (electron transfer) between the pyrite particles and bacterial cells, and indirectly by further oxidation of ferrous ions to the ferric state, thereby regenerating the ferric ions required for chemical oxidation of pyrite. Such reactions can be regarded as electrochemical. An electrochemical oxidation process can similarly be achieved by oxidising AMD using oxygen over potential electrodes, to become electron deficient to favour the higher oxidation state of the ferric ion.

Electrochemical water treatment is achieved by passing AMD water between two or more oxidising electrodes. Excitation of the electrodes is controlled by an advanced programmable power electronic system, which can provide a variable AC/DC power source. In addition, real time monitoring of key physico-chemical-electrical parameters such as ORP and electrical impedance important to both water treatment process and stability of power electronics process, provides the knowledge base for automatic feed-back control, adjustment to fluctuating changes in feed water quality to maintain optimum treatment performance and electrical energy usage. Such systems have already been applied successfully to large scale remediation of aluminium rich contaminated groundwater, drinking water treatment (removal of humic/fulvic acids and contaminant metals), wastewater treatment (phosphate) and general industrial effluent as whole (Khanniche *et al.* 2001).

Electrochemical Approach

The electrochemical treatment of AMD water has been reviewed with reference to the aqueous oxidation of pyrite by molecular oxygen produced by the electrolysis of water employing oxidising electrodes.

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad (1)$$

The electro-oxidation path is considered a consequence of two steps:

1. The oxidation of pyrite by molecular oxygen to sulphate and ferrous iron;
2. The oxidation of pyrite by hydrogen peroxide as result of the corresponding cathodic reduction of molecular oxygen.

$$O_2 + 2\,H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$

Step (i)

$$FeS_2 + {}^7\!/_2 O_2 \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2\,H^+ \qquad (3)$$

$$Fe^{2+} + {}^1\!/_4 O_2 + H^+ \rightarrow Fe^{3+} + {}^1\!/_2 H_2O \qquad (4)$$

$$Fe^{3+} + 3\,H_2O \rightarrow Fe(OH)_{3(s)} + 3\,H^+ \qquad (5)$$

This is a heterogeneous in-direct reaction with respect to oxygen produced from an oxidising electrode, acting as the anode. The rate of reaction is a function of current density (Am^{-2}) applied to the electrode and production of oxygen. Other oxidising derivatives and radicals *e.g.* ozone, hydroxyl radical [$\bullet OH$], superoxide anion radical [$\bullet O_2$] and hydro-peroxyl radical [$\bullet OH_2$] have not been considered in this paper. The reactions were carried out at the natural pH of the AMD source waters.

Step (ii)

$$FeS_2 + {}^{15}\!/_2 H_2O_2 \rightarrow Fe(OH)_{3(s)} + 2\,H_2SO_4 + 4\,H_2O \qquad (6)$$

This is a heterogeneous in-direct reaction with respect to the reduction of oxygen produced from an oxidising electrode by the corresponding cathode. Likewise the reactions were carried out at the natural pH of the AMD source waters.

The limiting rate in Step (i) is the formation of molecular oxygen sufficient to oxidise the pyrite. An intermediate $Fe_3O_4\bullet xH_2O$ green/black hydrated magnetite was observed during the oxidation of pyrite to $Fe(OH)_3$ ferric hydroxide during start-up.

Power Electronics, Controls and treatment process

The power electronics system comprises an AC to DC converter and a universal programmable matrix converter which feeds power to the oxidising electrodes housed in a reactor cell (Fig. 1):

Modern closed-loop control techniques are used to deliver the required voltage, current and frequency to initiate electrochemical oxidation from the surfaces of the oxidising electrodes housed in an insulated reactor. The reactor is described as an ‘open cell’ whereby the anodes and corresponding cathodes have no cell or membrane partitioning allowing oxidation-reduction reactions to occur simultaneously within the reactor housing.

An industrial example of the above treatment process is shown Fig. 2.

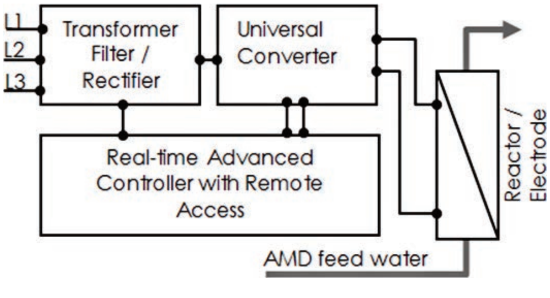

***Fig. 1** Treatment process schematic*

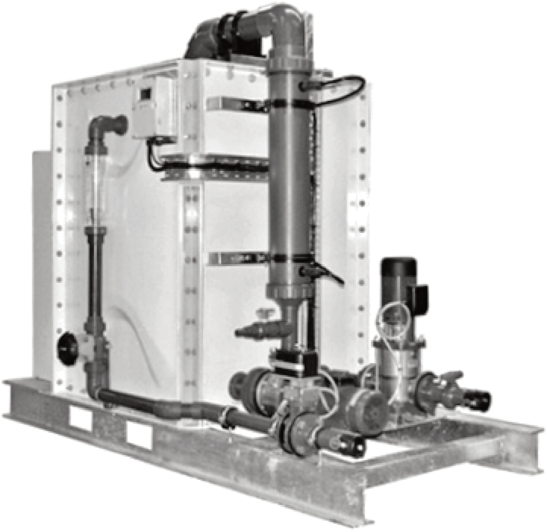

Fig. 2 *Example of an industrial electro-oxidation treatment unit (10,000 Lh^{-1})*

Results

Fig. 3 below shows photographs taken before, during and after the treatment of an AMD sample using electro-oxidation process. Samples and trials were conducted on 4 source AMD discharges (coal mine sites) in the UK and included:

- Open cast coal field site, Merthyr Tydfil, S.Wales, UK;
- Disused mine discharge, Ynysarwed, S.Wales, UK;
- Disused mine pumping schemes, Blenkinsopp, UK
- Disused mine pumping scheme, Dawdon, UK.

The electro-oxidation reaction time for all samples was 4 minutes.

Fig. 3A shows untreated samples of high clarity with pyrite in soluble form. Fig. 3B shows formation of ferrous iron leading to the formation of insoluble ferric floc (Fig. 3C) under slow stirring conditions (10 minutes). Fig. 3D shows dense settled ferric sludge following 30 minutes of unhindered settlement. Samples taken from Ynysarwed, Blenkinsopp were pH neutral and fresh water sources. The sample from Merthyr was a fresh water source but pH 4.0 whereas the Dawdon sample was high salinity and low pH 4.2. All samples precipitated ferric sludge; however the saline sample produced a very fine floc with hindered settlement. pH of this sample showed a decrease in pH to 3.5 units. Samples from Ynysarwed and Blenkinsopp showed no variation in pH after treatment whereas the more acidic sample from Merthyr showed an increase of pH to 6.4 after treatment.

A further laboratory based experiment was conducted using Ynysarwed mine water to determine the current density most effective for Fe (II) removal by electrochemical oxidation. Fig. 4 below shows that with a set two minute treatment time. Fe concentration decreases with an increase in current density. Five amps were sufficient to decrease Fe (II) concentrations from 73.4 mg/L to 0.2 mg/L (European drinking water quality standard).

Table 1 shows the changes in measurable parameters at increasing current densities.

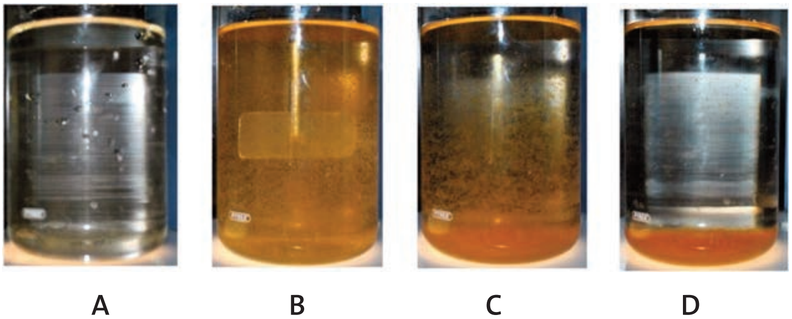

Fig. 3 *Treatment reaction stages of AMD water*

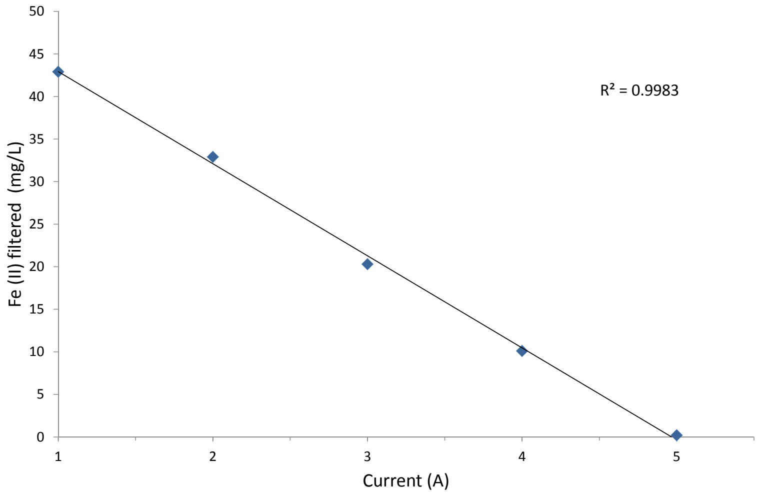

Fig. 4 *Fe (II) concentrations after two minute treatment time at increasing current densities*

Discussion

The results from the 4 trials at Ynysarwed, Blenkinsopp, Merthyr and Dawdon show that electrochemical oxidation offers a potential treatment process to precipitate ferric sludge for AMD discharges over a range of pH values and source waters without the need for pH correction.

The more detailed study at Ynysarwed shows a positive correlation between the conversion of Fe^{2+} to Fe^{3+} and its subsequent precipitation and removal with an increase in current densities applied to the oxidising electrodes ($r^2 = 0.99$). An increase in current density *i.e.* production of molecular oxygen and hydrogen peroxide increased the ORP (mV) potential of the AMD source water ($r^2 = 0.95$). The increase in ORP with increasing current density and reduction in pH supports the hydrolysis of water to molecular oxygen and Steps (i) and (ii) for oxidation of pyrite by oxygen and hydrogen peroxide. ORP would appear to offer a simple and effective control to monitor and control the treatment process via feed-back loop to the AC-DC and universal matrix controllers to optimise both treatment performance and energy efficiency.

In common with the water and wastewater sector, other examples of electrochemical water treatment are relatively scant. In part this has been due to over-simplification of what is a complex treatment reaction and scale-up from laboratory based reactors to industrial based electrochemical reactors leading to the conclusion that electrochemical treatment processes as being uneconomical at the laboratory stage.

Current	**Untreated**	**1 A**	**2 A**	**3 A**	**4 A**	**5 A**
pH	6.69	6.81	6.17	5.9	5.64	4.62
Temperature (°C)	16.81	18.36	17.69	18.41	17.46	17.89
Dissolved Oxygen (%)	31.2	50.3	54.4	54.4	56.5	57.8
Conductivity (µs/cm)	1813	1736	1651	1726	1280	1341
ORP (mV)	-15.7	-10.5	26.1	42.7	70.7	151.6
Fe II (mg/L)	73.4	42.9	32.9	20.3	10.1	0.2
Fe III (mg/L)	0.3	0.1	0.2	0.1	0.2	0.2

Table 1 *Measured parameters for the Ynysarwed electrochemical oxidation experiment*

Recent advances in industrial electrochemical reactor design and operation (Dunne 2009) have demonstrated typical operating costs for iron and aluminium removal from upland groundwater supplies at 0.2 $kWhm^{-3}$. Benefits over conventional treatment processes included small footprint, low sludge volume, reduced chemical requirement, wide ranging and effective treatment compared to chemical precipitation, membrane filtration and RO treatment processes.

Conclusions

Electro-chemical oxidation to precipitate iron sludge from pyrites employing advanced power electronics and instrumentation offers an economically viable alternative process to lime neutralisation, ozone and hydrogen peroxide dosing, biological wetland treatment and RO treatment systems. Precipitation of ferrous hydroxide is via oxygen formed by oxidation of water at the anode and hydrogen peroxide via reduction of oxygen at the cathode. Iron sludge precipitated from AMD samples appeared independent of source and pH.

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