Final Treatment Trials on Cwm Rheidol - Ystumtuen mines discharges, Wales, using Sono-electrochemistry (Electrolysis with assisted Power Ultrasound)

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Abstract

Results of the successful 2019 Sono-electrochemistry Soneco© final pilot trials using a magnesium electrode are presented. The preferred pH range was 8.8 to 9.0 removing 90.0%, 95.7% and 95.1% total lead, zinc and cadmium.

Full-scale treatment plant would utilise 3.1 kW/m^3/h, a clarification area of 57 m^2 (enabling the lamella to fit in the existing filter beds) generating a sludge volume of 4.8 m^3/day at 2% w/w (further dewaterable by press). CapEx for a comparable high-density sludge process has an appealing ratio of 1:3. Reducing electrode costs will make OpEx more competitive whilst planned process enhancements will lower CapEx and OpEx further.

Keywords: Sono-electrochemistry, electrochemistry, liquid chemical free treatment, Soneco, reactor

Introduction

The Cwm Rheidol metal mine complex comprises of six separate mines including Ty'n y Fron a satellite mine connected by a former tramway. Four mines Ystumtuen, Penrhiw, Bwlchgwyn and Llwynteifi on the upland plateau are hydraulically connected with the Cwm Rheidol mine. Two adits drain mine water towards the Afon Rheidol. It is currently classified as one of the top-ten most polluting mine waters in Wales, discharging highly acidic mine water rich in dissolved metals (e.g. lead, zinc and cadmium) that accounts for almost half of the metals loading into the Afon Rheidol damaging the ecosystem and further adding to water body derogation to the tidal limit some 18 km downstream. The combined metal load is approximately 9 tonnes/year consisting of approximately 4.8 tonnes of zinc, 160 kg of lead, 11 kg of cadmium and 4.0 tonnes of iron. The river is also impacted with yellow ochre staining from the iron rich water (NRW 2016). Adits 6 and 9 are situated at two different heights in the Rheidol valley, Adit 6 is located at approximately 110 m and Adit 9 approximately 60 m above the Afon Rheidol. Both adits serve different mine areas and yield different water quality, flow, heavy metal concentration and metal solubility. **Adit 6** the uppermost on the mountain has a higher volume of metal mine water (30 m^3/h) yet lower concentrations of soluble metals in acidic conditions. **Adit 9** is less elevated in height and of lower volume of mine water (2 m^3/h), but higher concentrations of dissolved metals and more acidic. In 2009, the adit discharges were collected into two pipes that conveyed the discharges safely down the side of the narrow steep sided valley to a manifold before collectively discharging into the existing filter beds at a fairly constant ratio of 14:1.

The original limestone filter beds from the mid 1960's have been ineffective. Cwm Rheidol poses a challenging topology for traditional passive treatment processes or large treatment plants capable of dealing with the varying levels of water which can flow from the mines as they would require considerable area of relatively flat land (0.8 Ha) to operate adequately and cope with both high and low levels of flow to operate effectively. Natural Resources Wales (NRW) has a completed feasibility study on long-term Mine Water Treatment Plant (MWTP) for Cwm Rheidol. Due to the location and access issues the MWTP will need to be compact and with a small footprint, require minimal operational input, traffic movements and reduced risk to watercourse. Optioneering is the next stage.

Sono-electrochemistry

An alternative to adding hydroxides via traditional liquid chemicals (that can result in increased infrastructure, access requirements for delivery, safety implications, and increased risk to adjacent watercourse through uncontrolled release) hydroxides can be added using sacrificial anode electrochemistry. Here the anode is made from high purity magnesium (>98% Mg). Though the use of liquid magnesium hydroxide is common in mine water treatment the production of magnesium hydroxide via sacrificial dissolution of a magnesium electrode by electrolysis and ultrasound to electro-generate magnesium hydroxide is a novel process.

By combining power ultrasound with electrolysis in the Soneco© (Morgan 2014) sono-electrochemistry system can reduce the build up of the passivation layers (Stern and Helmholtz layers) that can develop on the electrode surface during the operation of conventional electrochemistry systems. Eliminating the formation of the passivation layer lowers the electrical resistance of reactor circuit, reduces the power requirement, increases treatment efficiency and effectiveness (Morgan 2014). This makes the Soneco© a viable alternative to conventional liquid chemical-based systems for the treatment of acid mine water drainage (AMD).

Methods

Original trials were undertaken during March and August 2018 (Rose 2019) that successfully showed the Soneco© is a suitable alternative treatment to liquid chemical dosing for treatment of mine water generated at the Cwm Rheidol - Ystumtuen mines. A third and final set of trials were undertaken during December 2019 and designed to: Re-Confirm that the proposed water limits stated can be achieved by the proposed treatment process, confirm the proposed treatment plants inputs and generate data that can be used to undertake concept sizing of a proposed MWTP.

Materials: Trial Pilot plant treatment system

The pilot plant, shown schematically in Figure 1 and in the photograph presented in Figure 2, was configured as a continuous process to minimise, as far as possible, scale up error, by matching the pilot plant operating parameters with those anticipated for the proposed full-scale plant. The process stream consists of: Mine water feed pumping system, Stage I: Soneco© DB1 Reactor, Stage II: Flocculation tank and Stage III: Lamella Clarifier.

Ancillary equipment comprised of a 50 mm flowmeter and a clarifier de-sludge pump. Conductivity and pH probes were mounted in the feed sump, another pH probe was mounted in the flocculation tank. Two $1m^3$ IBC tanks were also positioned on site to store sludge produced.

Mine water was pumped to the pilot plant from a collection tank installed where combined adit flows enter the existing reed bed system. The volume of mine water treated was recorded by a magnetic flow meter on the feed line, with flow rate regulated by a manual diaphragm valve. The operating flow rate varied between 0.95–1.1 m^3/h over the course of the trial. The mine water pH and conductivity were continuously measured in the collection tank.

Stage 1 of the process consisted of a Soneco© DB1 Reactor where magnesium hydroxide was generated electrochemically by applying a current to the magnesium anode. The current (and hence dose rate) was controlled via a pH probe located at the inlet of the Stage II Flocculation Tank. The amount of magnesium released (and hence magnesium hydroxide added) in the Stage I Reactor was controlled via a proportional integral derivative (PID) control loop. The reactor was built from SS316 with: 1No Magnesium Anode, 2No Stainless Steel Cathodes, and 8No ultrasonic transducers for removing passivation layers.

pH corrected mine water overflowed

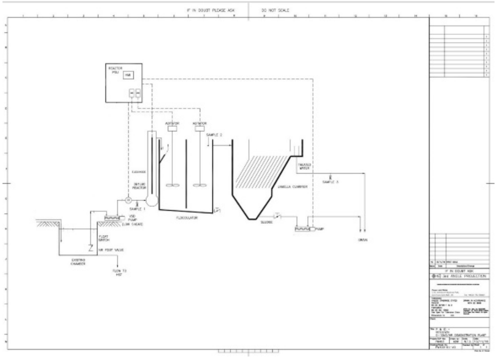

Figure 1 *P&ID of Trial System.*

Figure 2 *Photograph of the Trial System.*

from the Stage I Reactor into the Stage II flocculation tank. The 4 m^3 tank was fitted with a top mounted mixer to keep the solids in suspension, degas the metal hydroxide formed and aid floc formation. A pH probe was fitted within the flocculation tank providing a PID feedback loop that would achieve the required treatment via an inputted setpoint.

Flocculated mine water overflowed from the Stage II Flocculator into the Stage III Lamella Clarifier (combined with inlet floc mixer) where metal hydroxide floc settled and thickened. Solids/liquid separation was achieved in a lamella clarifier with an effective settling area of 10.0 m^2. Supernatant water was discharged into the filter beds prior to release to the environment.

Thickened separated solids from the clarifier were transferred via gravity back to sludge holding tanks (1 m^3 IBC tanks) and removed from site to be analysed. Supernatant water from the IBCs were decanted back to the filter beds.

Samples were taken from the: feed pit, DB1 reactor weir overflow and the final treated water. Samples were analysed (by Wheal Jane Laboratories, Truro, Cornwall England) for: pH, TSS, conductivity, sulphate, calcium, magnesium, potassium, chloride, sodium, alkalinity, carbonate, copper, arsenic, aluminium and Total and dissolved: lead, zinc, iron, cadmium, manganese. The following parameters were monitored to assess the performance of the pilot plant: volume of water treated, energy consumption, water quality (influent and effluent), magnesium consumption, sludge generation, and solids settlement characteristics (settling velocity and settled solids).

Results

The operating flow rate varied between 0.95–1.1 m3/h, measured using a magnetic type flow meter, over the course of the trial.

Table 1 presents a summary of the total metal results from the analysis undertaken on the feed mine water. These values show that as the trial proceeded the metal concentrations, i.e. zinc and cadmium, reduced in concentration due to heavy rainfall.

The results of analysis of samples undertaken on Stage 1 (Soneco©) treated water showed that the dissolved metals vary as the treatment pH varies. Once the weir discharge pH was >8.5 the dissolved zinc, lead and cadmium concentrations reduced to 0.10 mg/L, 0.10mg/L and 0.001mg/L respectively and hence this confirms that the use of magnesium electrodes is an appropriate way of raising the pH of the mine water and precipitating the dissolved metals as metal hydroxides.

Table 2 presents a summary of the total metal results from the analysis undertaken on the treated mine water. The results show that the potential treated water limits were met when the pilot plant was operated at a pH of >8.8.

Table 3 presents the total metal removal rates across the whole pilot plant during the trials. Lead, zinc and cadmium removal rates for when the operating pH was >8.8 were >86%, 91% and 90%.

Table 1: Mine water total metal concentrations

	pH	Pb mg/L	Zn mg/L	Fe mg/L	Cd mg/L	Mg mg/L	Ca mg/L	Mn mg/L
03/12/2019	2.9	0.47	22.29	2.36	0.041	15.10	35.82	0.930
04/12/2019	3.0	0.62	22.91	2.70	0.041	15.50	----	----
05/12/2019	2.9	0.48	22.28	4.56	0.041	14.85	35.12	0.940
06/12/2019	3.0	0.48	20.80	2.00	0.041	14.43	----	----
09/12/2019	3.0	0.71	15.19	5.65	0.030	10.62	27.68	0.580
10/12/2019	3.1	0.68	14.50	4.22	0.028	10.17	----	----
11/12/2019	3.0	0.89	14.37	4.16	0.028	9.93	26.94	0.510
Max		0.89	22.91	5.65	0.041	15.50	35.82	0.940
95%ile		0.84	22.72	5.32	0.041	15.38	35.72	0.938
Average		0.62	18.91	3.66	0.036	12.94	31.39	0.740
Min		0.47	14.37	2.00	0.028	9.93	26.94	0.510

Table 2 *Treated Water Discharge Total Metal Concentrations.*

	pH	Pb mg/L	Zn mg/L	Fe mg/L	Cd mg/L	Mg mg/L	Ca mg/L	Mn mg/L
03/12/2019	8.8	0.05	0.96	0.87	0.002	42.12	34.97	0.280
04/12/2019	6.1	0.06	5.06	1.22	0.022	38.46	----	----
05/12/2019	5.6	0.09	10.65	2.57	0.034	35.56	35.36	0.820
06/12/2019	5.9	0.06	9.29	1.93	0.031	34.68	----	----
09/12/2019	9.1	0.10	1.32	2.04	0.003	34.80	25.28	0.096
10/12/2019	6.1	0.19	4.91	1.23	0.019	23.86	----	----
11/12/2019	6.0	0.19	6.72	1.29	0.023	24.31	25.48	0.440
Max		0.19	10.65	2.57	0.034	42.12	35.36	0.820
95%ile		0.19	10.24	2.41	0.033	41.02	35.30	0.763
Average		0.11	5.56	1.59	0.019	33.40	30.27	0.409
Min		0.05	0.96	0.87	0.002	23.86	25.28	0.096

The conductivity measurement was recorded during the trial using the on-line meter. Due to an average mine water conductivity of 562 µS/cm the water can be termed as having low conductivity. During the trial the mine water conductivity dropped from an initial 657 µS/cm to a concentration of 437 µS/cm at the end of the trial.

Settlement tests (also termed mudline tests) were undertaken on the clarifier feed (Stage II discharge). The data derived from these tests have been used to calculate: the initial settling velocity and the final settled solids concentration. The settlement velocity of 0.6 $m^3/h/m^2$ was required to ensure a TSS limit of <30 mg/L was met. Using a rise rate of 0.6 $m^3/h/m^2$ and a total treatment flow rate of 9.4 L/s (34 m^3/h) total effective clarification area of 57 m^2 has been calculated.

Figure 3 presents an unedited photograph of the mine water, precipitate generated and treated water off the lamella clarifier.

Table 3 *Total Metal Removal Rates.*

	pH	Pb	Zn	Fe	Cd	Mn
		%	%	%	%	%
03/12/2019	8.8	90.0	95.7	63.1	95.1	69.9
04/12/2019	6.1	90.3	77.9	54.8	46.3	
05/12/2019	5.6	80.4	52.2	43.6	17.1	12.8
06/12/2019	5.9	87.3	55.3	3.5	24.4	
09/12/2019	9.1	86.1	91.3	63.9	90.0	83.4
10/12/2019	6.1	72.1	66.1	70.9	32.1	
11/12/2019	6.0	78.7	53.2	69.0	17.9	13.7
Max		90.3	95.7	70.9	95.1	83.4
95%ile		90.2	94.4	70.3	93.6	81.4
Average		83.5	70.3	52.7	46.1	45.0
Min		72.1	52.2	3.5	17.1	12.8

Minewater Precipitate Treated water

Figure 3 *Photograph of the Mine Water as it passes through the Treatment System.*

Magnesium was added via applying a current to the anode proportional to the pH in the inlet to the floc tank. Due to the chemical reactions this was converted to magnesium hydroxide with the hydroxides then used to precipitate the dissolved metals as metal hydroxides. Using a measured magnesium increase of 27 mg/L the magnesium hydroxide usage was calculated at a dose rate of 64 mg/L, this will equate to a daily plate usage of 22 kg/day of electrode in the full-scale plant when treating 34 m^3/h.

The solids generation rate, mg of solids per litre of mine water treated, has been calculated from the mine water inlet iron concentrations and the percentage of iron in the dry solids removed from the system. This calculated the sludge generation rate was 120 mg/L of water treated. Using 120 mg/L equates to a daily solids production of 98 kg of dried solids per day or 0.93 m^3/day (6.5 m^3/week) of 10% w/w solids (dewatered sludge). Sludge composition as key components as a % of the solids: Iron 17.4%, zinc 10.8%, Hydroxide 29.3%, Carbonate 9.4%.

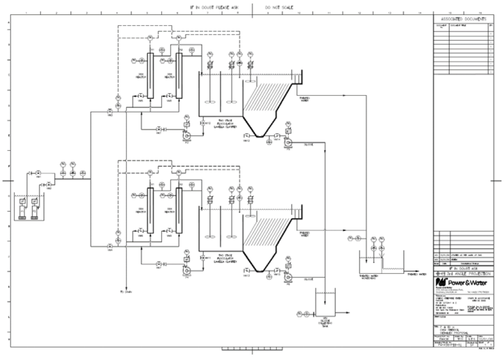

Figure 4 P&ID of Full-Scale System.

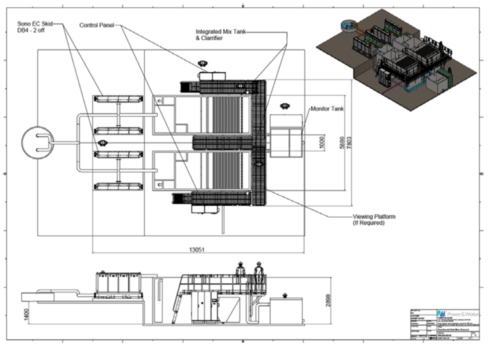

Figure 5 GA of Full-Scale System.

Full Scale Design

The trial has again successfully shown that the sono-electrochemistry process can remove the required metals, e.g. lead, zinc and cadmium, and enabled the proposed full-scale MWTP concept design to be completed. The proposed plant would consist of: a single feed system with overflow to river, two process streams each consisting of 2No DB4 reactors with automated pH control, 1No flocculation tank, 1No lamella clarifiers with 40 m^2 of clarification area and sludge transfer pumps. Common ancillaries will consist of sludge treatment via 1No sludge storage tank, 1No automated filter press, 1No sludge cake skip and treated Water Monitoring equipment, Table 4 presents a summary of the outline concept design parameters. Figures 4 and 5 show the P&ID and general Arrangement of the proposed full-scale plant.

The concept design has enabled the CapEx and OpEx costings to be undertaken enabling a comparison with a traditional high-density sludge (HDS) plant.

Table 4 The Outline Concept Design of the Full-Scale Plant.

	Item	Unit	Valve
System Design	Soneco Reactor	Name	4 No DB4
	Flash Mix	m^3	1
	Floc Mix	m^3	2
	Clarification area	m^2	57
Alkali Dose	Magnesium Hydroxide Dose Efficiency	%	92
	Actual Magnesium Hydroxide Dose	mg/L	67
	Magnesium plate Weight	kg	20
	Plates per year	No	402
Solids generation	Solids generation	mg/L	120
	Waste sludge off clarifier	%ds	2
	Dewatered sludge	%ds	30
	Volume of dewatered sludge	m^3/week	6.5
Required Power	Sono- EC power	kW	77
	Total Power	kW	107

Conclusions

1. This final pilot trial has repeated the excellent removal rates shown in previous trials and confirmed that the Soneco© treatment process is a viable alternative treatment process for AMD.
2. The costed CapEx (excluding groundworks and power supply) for a sono-electrochemistry process is favourable when compared to a traditional HDS process with a ratio of 1:3.
3. Due to existing costs of magnesium electrodes the OpEx of a sono-electrochemistry is less favourable with an HDS plant. Working with the supply chain will, however, reduce electrode costs and make the OpEx applied at Cwm Rheidol more competitive.
4. Further planned process enhancements will halve the required number of units, lowering CapEx, whilst also halving the power demand, hence OpEx. This will make the whole life cost over forty years more favourable for a sono-electrochemistry system enabling consideration during optioneering.
5. Due to the compact design the process is suitable for applications where land availability or access is constrained and landscape, habitat or heritage are sensitive.

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