Sono-electrochemistry (Electrolysis with assisted Power Ultrasound) Treatment Trials of discharges from Cwm Rheidol – Ystumtuen mines, Ceredigion, Mid Wales, UK ◎

Sarah A. Rose[1], Zoe N. Matthews[1], Gareth Morgan[1], Chris Bullen[1] and Peter Stanley[2]

[1]*KP2M Ltd., C10 Ashmount Business Park, Swansea, SA6 8QR, UK. srose@powerandwater.com,*

[2]*Natural Resources Wales, Tŷ Cambria, 29 Newport Rd., Cardiff, CF24 0TP, UK. peter.stanley@cyfoethna-turiolcymru.gov.uk*

Abstract

The Cwm Rheidol-Ystumtuen metal mines discharge acidic waters adversely effecting 18 km of the River Rheidol to the sea. Collectively Adits 6 and 9 discharge c. 4.8 tonnes zinc, 160 kg lead, 11 kg cadmium and 4 tonnes iron into small ineffective limestone filter beds before reaching the river at the mouth of the Rheidol gorge. The Metal Mines Strategy for Wales has Cwm Rheidol ranked as the seventh most polluting. Previous Passive treatment trials confirm that such treatment would require a large area of unavailable flat land. Laboratory sono-electrochemistry trial success on Parys Mountain discharges indicated that magnesium electrodes could be trialled at Cwm Rheidol to produce magnesium hydroxide, raise the pH of the water and precipitating the metals as insoluble hydroxides. These highly successful electro-chemistry treatment trials (sono EC reactor, flocculator and lamella clarifier) identify that 99.5% of metals can be safely recovered using 1 kW/m³. Full scale treatment (32 m³/hr flow rate) is now a viable Active treatment process that can be applied in NRW's feasibility options for Cwm Rheidol at full scale, demonstrating an additional treatment tool to help failing water bodies achieve compliance with the EU Water Framework Directive (WFD).

Keywords: electrochemistry, WFD, AMD, sonification, treatment, zinc.

Introduction

The Central Wales Orefield has been exploited for it's mineral wealth since the Bronze Age through to the early 20th century. The country rock comprises Silurian and Ordovician marine basin sediments of thick mudstones and clastic conglomerates. These strata have experienced several periods of ore genesis from early Devonian to the Permian, when low temperature sulphurous brines penetrated along fractures and faults. Early events tend to be more mineralogically diverse with cobalt and nickel present, whereas later events typically bearing galena with lower silver content. The final hypogene mineralising event deposited abundant iron sulphide as marcasite and pyrite, which potentially was post Permian (Mason 2019). The mines in the complex are Ystumtuen in the west with the earliest recorded activity in 1698, Penrhiw, Bwlchgwyn and Llwynteifi in the east. They drain via two adits, Adit 6 (173.7 mOD) and Adit 9 (100.6 mOD), into Cwm Rheidol (Rheidol valley) immediately below the gorge. The deeper adit was driven in 1901 by the Cwm Rheidol Mine Company primarily for zinc. Collectively the mines raised a recorded 15,000 tons of galena and sphalerite, plus 4,000 tons of pyrite (Lord 2018). It is recognised that the lode has less marcasite eastwards, with abundance at Ystumtuen, rare in the open stopes of Bwlchgwyn and Llwynteifi, and less ochre in spoil at Penrhiw (SRK 2004).

Water Quality

The Rheidol catchment is affected by numerous abandoned metal mines on it's tributaries and fails WFD classification for zinc and cadmium upstream of Cwm Rheidol. The highly acidic combined discharge of Adits 6 and 9 at Cwm Rheidol contribute substantially to the Rheidol, by raising concentrations of zinc and cadmium by 144%

and 107% respectively, which continues to fail WFD for both metals to the tidal limit.

Results of ecological impact assessments have been equivocal with fish population studies showing salmon tolerance to zinc concentrations in the Rheidol, which average more than ten times WFD standards in places (NRW 2016).

Active Pilot Trial

The application of ©Soneco (Morgan 2014) sono-electrochemistry, with combined power ultrasound for treatment of acid mine drainage (AMD) using a magnesium anode to produce magnesium hydroxide in-situ. Using power ultrasound simultaneously with electrolysis removes the ionic boundary and passivation layers (Stern and Helmholtz layers) that can develop along the electrode surface during operation, making 'fresh' electrode material available for treatment. This reduces the electrical resistance of reactor circuit, reduces the power requirement and increases treatment efficiency and effectiveness. Other benefits include the cavitation and collapsing of oxygen formed at the anode, by removing the micro-bubble production. There is little or no chance of the contaminants binding to the oxygen bubble and rising to the surface, thus allowing for greater settlement characteristics.

The background and principles to the ©soneco process were detailed in an earlier paper on laboratory trials at Parys Mountain by the late Phil Morgan (Morgan 2017). The advantage of a pilot trial adopting electrochemistry and the successful adaption

of sonification and magnesium electrodes at Cwm Rheidol limits the need for the land area required for passive treatment which simply does not exist in the Rheidol gorge. This trial was progressed in late 2017.

Additional development has highlighted several, previously unknown, benefits to the the use of sonoelectrochemical generation of magnesium hydroxide to treat acidic mine water, for example, Magnesium has the capability of pH neutralisation, whereby the pH will increase as a result of the cathodic half-reaction (Rybalka 2014) shown by the following equation:

$$Mg(OH)_2(s) + 2e^- \rightarrow Mg(s) + 2OH^-$$
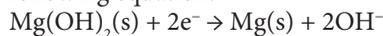
The rapid production and dissolution of hydroxide produced by the reaction results in an increase in the pH of the electrolyte (Martell 1974), in this case acidic mine water, in which the following reaction occurs:

$$Mg(OH)_{2(s)} \leftrightharpoons Mg^{2+}_{(aq)} + 2(OH)\text{-}_{(aq)} \; Ksp \approx 10^{-11}$$
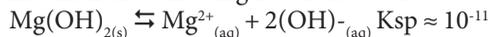
This increase of the pH enables the precipitation of metals and metalloids in their hydroxide form. It is further believed that the process by which the magnesium hydroxide reacts with sulphate ions found in mine water proceeds through a series of preferential leaching activities, this usually hinders contaminant removal rates but where magnesium is concerned, it benefits the treatment by a series of displacement reactions. "Sulfidic wastes commonly contain sulphides other than pyrite. If there is direct physical contact between at least two different sulphide minerals, electrons move between the sulphides and a galvanic cell is formed. During weathering the sulphide mineral with

Table 1 Average Results from 2010 to 2018 of sample points 81011 (Adit 6) and 35230 (Adit 9)

Monitoring Data	Adit 6	Adit 9	Σ
Flow L/s	7.6	0.7	8.3
pH	3.9	3.0	
Zn (mg/L)	12.1	83	
Pb (mg/L)	0.67	0.02	
Cd (mg/L)	0.03	0.12	
Fe (mg/L)	7.1	103	
Mn (mg/L)	0.57	3.8	
Zn (kg/yr)	2,916	1,842	4,758
Pb (kg/yr)	161	0.4	161
Cd (kg/yr)	8	3	11
Fe (kg/yr)	1,711	2,297	4,008
Mn (kg/yr)	137	83	220

the highest electrode potential is galvanically protected from oxidation, while the mineral with the lowest electrode potential is weathered more strongly. Selective oxidation of sulphide minerals occurs as one sulphide mineral is preferentially leached over another" (Nordstrom 1999).

A metal will always displace another based on its reactivity which, in this case, treatment utilising magnesium (which is higher in the reactivity series than all target species) will enable metals and metalloids to be forced out of its mineral compounds where it is then precipitated. The sonoelectrochemical process enhances this process as sonification modifies particle size, shape and surface morphology through high velocity interparticle collision which destabilises the contaminant, enabling enhanced rate of colloidal charge neutralisation and the formation of amorphous nanostructured adsorption sites resulting in a dense, dewatered sludge.

The reaction between magnesium hydroxide and the precipitation of metal and metalloid sulphides are known as a 'Displacement Reactions' occuring when one element is more reactive than another in solution e.g. the reaction between magnesium hydroxide and iron sulphate:

$MgHO + FeSO_4^2 \rightarrow MgSO_4^2 + FeOH.$
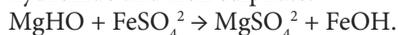
As displacement reactions are competing for non-metal anions such as sulphate, which is found in mineral complexes that make up the mine water, the atoms of the reactive metal (in this case magnesium) put their electrons on to ions of less reactive metal.

Metal and metalloids from the often acid-producing sulphide minerals such as pyrite (or marcasite as FeS2), galena (PbS) and sphalerite (ZnFeS) can be precipitated before they are galvanically protected, which results in either prolonged or unsuccessful treatment. The galvanic protection process is the same as that for galvanised iron. The more electroconductive sulphide mineral oxidises at a slower rate than it would when not in contact with another sulphide e.g. Among the three most common sulphide minerals, pyrite has the highest electrode potential followed by galena and then sphalerite. If these minerals are in contact with each other,

sphalerite will be preferentially weathered, and oxidation of pyrite is reduced. Hence, pyrite in direct contact with other sulphides does not react as vigorously as it does in isolation. Also, the oxidative dissolution of pyrite can be delayed, while other sulphides are preferentially oxidised (Lottermoser 2007).

Sulfidic wastes and AMD have been studied extensively and the chemical addition of MgOH has also been studied for its neutralising capabilities in the treatment of acidic mine water with successful results. The benefits of sonoelectrochemical treatment over chemical is its ability to produce an instantaneous, uniformed mass transport of highly mobile and active MgOH ions into solution, creating un-reversable REDOX reactions, precipitating metals as their hydroxide forms whilst substantially increasing the pH and preventing further acid producing oxidation reactions from occurring both during and after treatment.

Materials and Methods

During the three-month project at Cwm Rheidol, Power & Water segregated the project into two distinct sections. Both employing the ©Soneco process of electro generating Mg electrons for increased pH and removal of potentially toxic metals, but through two subtly different methods. Objectives were to confirm treatability in the field, generate data to demonstrate a full scale system could be sized, introduce flocculation, use recirculation to reduce magnesium take and increase precipitation, and identify optimum plate gap for energy demand.

Method 1 = Constant stirred tank electrode reactor (CSTER)

The CSTER is a shallow, cylindrical tank with externally mounted ultrasonic generators. The electrode plate is also cylindrical, but suspended internally via isolating guide rails within the tank itself. A stirrer motor is positioned centrally above the tank with variable speed drive (VSD) rotating an inert stirrer to keep the liquid and combined solids in suspension. This treatment method was employed for the first two months of the project.

Method 2 = Laminar flow fixed electrode reactor (DB1)

The DB1 reactor tank is a rectangular shaped tank, again with externally mounted ultrasonic generators, but this design includes a fixed, flat, electrode plate mounted internally via isolating guide rails. This design uses no moving parts, instead relying on the flow of liquid to promote laminar flow with both sides of the electrode plate utilised for proportional treatment without sacrificing efficiencies. This treatment method was employed for the last month of the project.

Process, Flow and Instrumentation

Liquid flowing from the inlet to the existing filter beds was captured within a small (above ground) sump and constantly pumped (via submersible pump) at a fixed flow rate (controlled via diaphragm valve and mechanical rotameter) through the Soneco reactor tanks. As the liquid passes through the Soneco reactor tank, the Power Supply Unit (PSU) comes into operation, gradually

increasing the amount of power (treatment) required until a separate, yet integrated pH probe (Partech Instruments) achieves a reading of 10.00. The PSU constantly monitors and adjusts the amount of power commanded by means of integrated feedback from the pH controller. As the pH of the liquid fluctuates, so too does the amount of power demand, which ensures optimum use of power and consistent precipitation downstream.

Once the liquid has been treated (via electrolysis and ultrasound) within the Soneco reactor tank, the coagulated liquid passes into the clarifier tank. The potentially toxic metals precipitate, flocculate and settle into a hopper at the bottom of the clarifier, condensing through the weight of metals falling from above. Periodically a timed actuator valve releases the settled solids into a sludge capture tank whilst the clear water flows through the clean water outlet, into the existing filter beds, before exiting through the cascade into the River Rheidol.
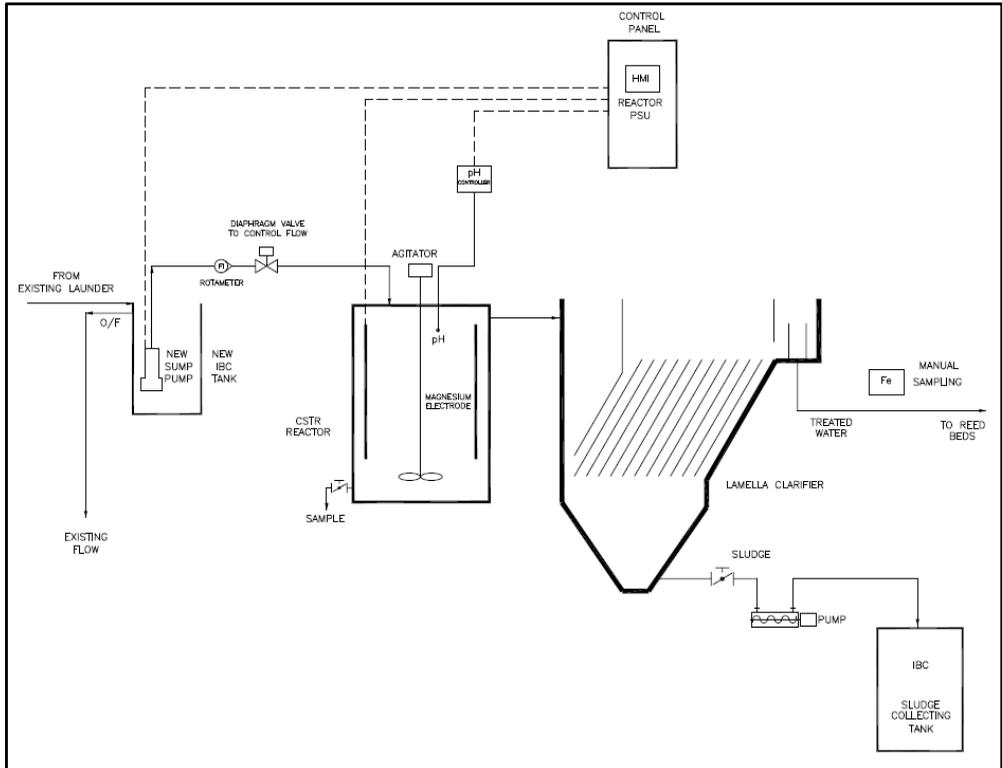
Figure 3 P&ID Method 1 – CSTER.

Reaction time, pH, E_H (mV) (both Hanna Instruments) and amperages were noted during the treatment procedure. These were used along with the mechanical and electrical specifications of the Soneco® reactor to calculate Capex and Opex for a full-scale treatment plant.

Results

The average power consumption for treating 4m³/hr was 5kW, therefore 1.25kW/m³.

Difference between treated water metals and dissolved metals due to metal hydroxid precipitates

TSS generated in system 126mg/L, the TSS in treated water was 11mg/L.

On site degassing and neutralization tests were conducted to establish if carbon dioxide was present in the mine water and ensure gypsum or calcium carbonate would not generate substantial unwelcome bi-products within the precipitates. Carbon dioxide was not present.

This method 2 system adopting the DB1 design had greater efficiency with more plate exposure and used an equivalent 1kW/m³/hr. Based on the above tests it is estimated that for 32m³/hr the magnesium (Mg^{2+}) dissolution required to both pH neutralize and precipitate iron to less than 1 mgl⁻¹ equates to is 26 mgl⁻¹ or 20kg/day. Scaling this up identifies a use of 0.6 plates per day based upon a 31kg plate. Conversely for a system to last one month it will require an equivalent twenty plates.

Using the solids generation rate of 126mg/L, it is estimated using the flow of 32m³/hr that 4kg/hr of dried solids would be produced or 97kg/day. This equates to 9.7m³ of clarifier settled sludge at 1% total solids. Initial cake pressing tests indicate the solid matter can be increased to 10%w/w. The consequence being that sludge generation would be 1m3/day with a composition of 17.4% iron, 10.4% zinc, 29.3% hydroxide and 9.3% carbonate.

To estimate the clarifier tank volume, tests using settlement velocities have been conducted. Assuming an upper value of

Figure 4 P&ID Method 2 – DB1.

Wolkersdorfer, Ch.; Khayrulina, E.; Polyakova, S.; Bogush, A. (Editors)
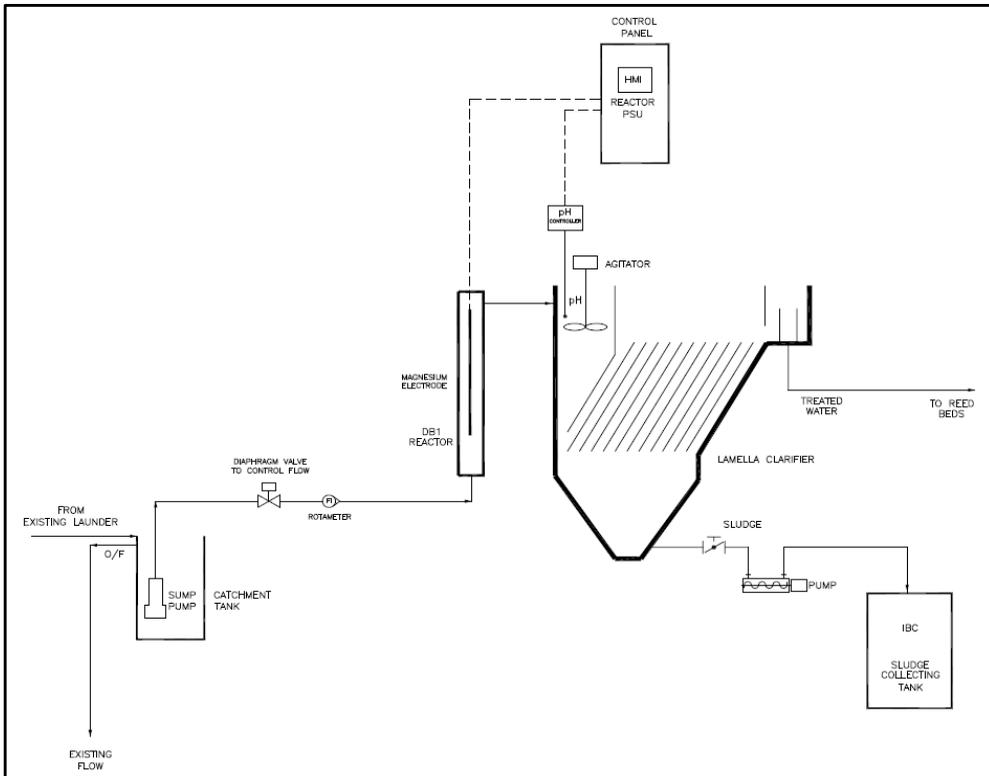
Table 2 Treatment Water Quality Method 1 (NRW filtered results. Metals in mg/L)

Test	Untreated	Treated	Removal %
pH	3.82	6.55	
Cd	0.036	0.002	99.46
Zn	17.08	0.016	99.90
Pb	0.499	0.002	99.59
Fe	7.98	0.040	99.48
Mg	11.45	29.32	-154.82

Table 3 Treatment Water Quality Method 2 Flow rate 1m³/hr (metals in mg/L)

Test	Mine Water Total	Soneco Dissolved Post Treatment	Treated Total Metals	Removal %
pH	3.3	8.3	8.5	
Cd	0.041	<0.001	0.004	90.2
Zn	17.77	0.01	1.65	90.7
Pb	0.79	<0.01	0.01	98.7
Fe	17.42	0.11	1.79	89.7
Ni	0.29	<0.01	0.03	89.7
Al	4.05	0.42	0.51	87.4
Mg	11.67	32.32	31.25	-167.8

Table 4 The Outline Concept Design following the Pilot Trial

	Stage	Unit	Value
Alkali Usage	Theoretical Hydroxide Dose	635	62.4
	Magnesium Use	680	600
	Magnesium plate weight	kg	31
	Plates per year	N°	20
	Plates per month	N°	1.6
System Design	Sono EC Reactor	Name	2 N° DB4
	Flash Mix	Retention min/Vol m³	1.5min/1m³
	Floc Mix	Retention min/Vol m³	3.0 min/2m³
	Rise rate	m/hr	0.6
	Clarification area	m²	54
	Lamella clarifiers	N°	2
	Clarrification area/clarifier	m²	30
Solids Generation	Solids generation	mg/L	126
	Waste Sludge off clarifier	%ds	1.0
	Dewatered sludge	%ds	10
	Volume of dewatered sludge	%ds	0.9m³
	Sludge dewatering	Type	Plate press

30mg/L for TSS a settlement velocity of 0.6m/hr is required, which equates to a total settlement area of 54m².

Conclusions

1. The predicted CapEx and OpEx of a sono-electrochemical treatment plant is attractive in comparison to other treatment / disposal options being considered for these adit discharges. Costs could be off-set by revenue earned by metals re-covery from treated sludge. Power for a sono-electrochemical plant could also be sourced from renewable energy supplies.

2. This pilot study has achieved excellent results and confirmed that the ©soneco treatment process is a viable alternative treatment tool for AMD that lends itself particularly where renewables offset energy demands. Natural Resources Wales are considering feasibility options for metal mine water treatment schemes at Cwm

Rheidol and three other sites.

3. Further research to enhance sediment harvesting to yield a cake with solids at 20%w/w and disposal/recovery options via resource recovery is required, as are communications with remote monitoring sensors to aid ongoing OpEx.

References

Mason JS (2019) The Genesis of the Central Wales Orefield. http://www.geologywales.co.uk/centralwales.htm#MENU

Lord I (2018) Rich Mountains of Lead. The metal mining history of Cwm Rheidol and Ystumtuen.

SRK (2004) Cwmrheidol Site Investigation. Report 2. Recommended Design and Management for Remediation of the Mine Complex

NRW (2016) Abandoned Mine Case Study: Cwm Rheidol Lead & Zinc Mine

Morgan PG (2014). British Patent No. GB 1503638.7 – Method and apparatus for decontamination of fluids (Soneco). International Patent PCT/GB2016/050692 – Method and apparatus for decontamination of fluids

Morgan SA, Matthews ZN, Morgan PG, Stanley P (2017) Removal of Iron from Dyffryn Adda, Parys Mountain, N. Wales, UK using Sono-electrochemistry (Electrolysis with assisted Power Ultrasound)

Rybalka KV (2014) Determination of metal corrosion rate using the pH-metry by the method of compensating additives. Russ J Electrochem, 50:500–2

Martell AE, Smith RM (1974) Critical stability constants. New York, London, Plenum Press

Nordstrom DK, Alpers CN (1999) Geochemistry of Acid Mine Waters

Lottermoser BG (2007) Mine Wastes