Removal of Iron from Dyffryn Adda, Parys Mountain, N. Wales, UK using Sono-electrochemistry (Electrolysis with assisted Power Ultrasound)

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Abstract The Dyffryn Adda from Parys Mountain, N. Wales is one of the most polluting mine waters in the UK releasing c. 10 tonnes of copper per annum and 24 tonnes of zinc per annum into the Irish Sea. The Metal Mines Strategy for Wales has ranked it first. An acid, iron rich mine water visible by its ochreous staining along 3 km of the Afon Goch Amlwch to its coastal discharge at Porth Offeiriad (Priest Port) has a negative impact on both river and coastal water quality and local businesses and communities. Several investigations using Active, Passive and Hybrid treatment processes employing conventional treatment technologies as well as Pump to sea have been considered, however successful treatment has not proven to be cost beneficial to date. This study shows that sono-electrochemical treatment (combined electrolysis and power ultrasound) to produce magnesium hydroxide can raise the pH of the water, precipitate iron as insoluble iron hydroxide [$Fe(OH)^2$] and has the potential to preferentially precipitate other metals in their stable hydroxide forms. Extrapolating the laboratory results and methods to full scale treatment (12 l sec-1 flow rate) indicates that it is a viable Active treatment process compared to other treatment options being considered and can aid failing water bodies achieve compliance with the EU Water Framework Directive.

Introduction

Parys Mountain, N. Wales is one of the most polluting mine waters in the UK, discharging more metals into the Irish Sea than the River Mersey despite having less than 0.3% of the flow of the River Mersey. Parys has a number of discrete discharges of which Dyffryn Adda is considered the most challenging water chemistry being more acidic and metal rich than most surface water discharges in the UK. The Dyffryn Adda pollutes 3 km of the Afon Goch Amlwch before discharging into the sea at Port Offeiriad causing ochreous staining and depositing copper ($\approx$ 10 t a-1), zinc ($\approx$ 24 t a-1) and cadmium (~45 kg annum-1) into the Irish Sea. The discharge chemistry also includes other contaminants (Table 1).

A 'Parys Mountain Treatment Options Report' was commissioned in 2012 by Natural Resources Wales (formerly Environment Agency Wales) (URS 2012) to review treatment options to ameliorate the environmental impact of Parys Mountain on the economic and well being benefits to local and national communities. In further discussions it was considered that the first stage of amelioration would be to reduce the total iron discharged from Dyffryn Adda to <1.0 mgl-1 and to reduce the ochreous visual impact discharge in the Afon Goch Amlwch and into the sea, now the North Anglesey Marine possible Special Area of Conservation.

Table 1. *Dyffryn Adda – Flow Concentrations (12 L s-1 [1040 m3 day-1])*

Total (μgl^{-1})	Minimum	Mean	Maximum
Acidity (as $CaCO_3$)	1,194	1,743	2,210
pH	2	3	3
Iron	453,000	599,000	708,000
Copper	30,600	38,130	52,600
Zinc	55,900	65,311	92,900
Manganese	14,300	20,470	30,400
Aluminium	4	63,571	87,800
Sulphate	1,940,000	2,534,000	3,020,000
Cadmium	153	175	196
Arsenic	129	360	662
Nickel	154	189	240
Lead	19	28	46

The releases of iron, sulphate and high levels of acidity are primarily a result of pyrite oxidation catalyzed by sulphur oxidizing bacteria (Barbes *et al.*, 1968):

$$4FeS_2 + 15O_2 + 14H_2O = 4Fe(OH)_3 + 8H_2SO_4 \text{ (Sulphuric acid)}$$

Traditional treatment methods for Mine water can generally be divided into 2 techniques:-

1. Active treatment which require ongoing mechanical / electrical operations and manual maintenance e.g. aeration, liquid chemical pH neutralization, chemical cationic coagulants and precipitation; membrane processes; ion exchange and chemical and / or biological sulphate removal;

2. Passive treatment typically refers to processes that do not require human intervention, operation, or maintenance, use gravity flow for water movement and promote the growth of natural vegetation e.g. reed bed systems.

Given the high concentrations of metals and low pH passive treatment at Parys Mountain is broadly accepted as being impractical and technically unfeasible. Active treatment comprising of High Density Sludge (HDS) with pH adjustment using lime is however widely used for treating acid mine drainage (AMD) water. In addition some success has been achieved using sulphide reduction (addition of sodium sulphide) after pH adjustment (caustic soda dosing) as a potential treatment option. In some circumstances hybrid active/passive systems may be employed e.g. semi-passive iron removal with targeted removal of other metals by sul-

phide precipitation or biological removal of iron as schwertmannite and removal of targeted metals by sulphide reduction along with part treatment and part pumped sea dispersal options. Budget costs for these various options are presented (Table 2).

Table 2. Cost Estimates for Iron removal / reduction from Dyffryn Adda adit

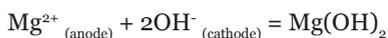| Element / Description	Cost Estimate
Pumped sea dispersal of partially treated mine water	£ 0.6 to £ 0.7 M
High Density Sludge (HDS) Plant	£ 1.8 to £ 2.0 M Capex / £ 0.5 to £ 0.7 M Opex
Hybrid Active / Passive Treatment (incl. Sulphide treatment)	£ 1.8 to £ 2.5 M Capex / £ 0.25 M Opex

The presence of metal species either in their ionic form or in equilibrium as their stable oxide, hydroxide forms, in a water phase such as mine water, are determined by their respective Pourbaix solubility diagrams (Pourbaix 1964). For example, the Pourbaix diagram for Iron in Water (Fig. 1) indicates the predominance of iron as aqueous ions (Fe^{2+}, Fe^{3+}) or as stable insoluble oxide or hydroxide forms [$Fe(OH)_2$, $Fe(OH)_3$] based on the pH of the water (horizontal axis) and its E_H (voltage potential) i.e. oxidizing or reducing potential (vertical axis).

For example in Dyffryn Adda (pH = 3.13 and E_H = 0.287) iron will be present as soluble Fe^{2+} aqueous ions. If the mine water is aerated (E_H > 0.0) and pH corrected to < pH 6.5 iron will precipitate as insoluble orange/brown ferric hydroxide [$Fe(OH)_3$]. Under an oxygen reduced state (E_H < 0.0) the iron will precipitate as green ferrous hydroxide [$Fe(OH)_2$]. Similar reactions can be achieved within an electrochemical treatment process by selecting appropriate electrode materials and applying a voltage across the anode and cathode electrodes to control current density (Amps/Electrode area [Am^{-2}]) (Fig. 2). Increasing – decreasing current density can be regarded as way of speeding up or slowing down reactions and depending upon the electrode material making reactions more oxidizing or more reducing.

By applying a voltage to an oxidizing over-potential anode electrode (e.g. MMO – mixed metal oxide) the water in the electrochemical reactor can be oxidized and made acidic.

$$2H_2O = H_2O_2 \text{ (oxidized)} + 2H^+ \text{ (acid)} + 2e^-$$

Similarly by employing a voltage to an alkaline earth metal anode in water, the water becomes reduced and alkaline due to the formation of the hydroxide $Mg(OH)_2$.

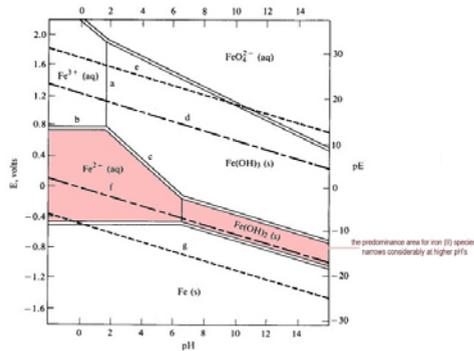$$Mg^{2+}_{(anode)} + 2OH^-_{(cathode)} = Mg(OH)_2$$
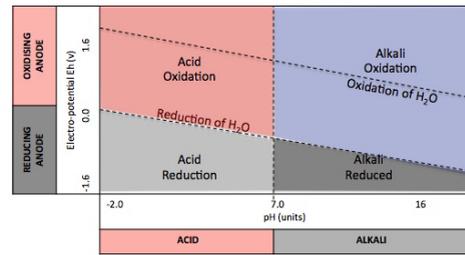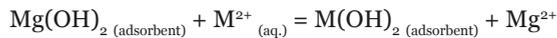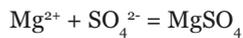
Fig 1. *Iron – Water Pourbaix diagram*

Fig 2. *pH and EH variations within an electrochemical reactor*

Once magnesium hydroxide is generated it operates by the principal of ion exchange, where a magnesium ion (Mg^{2+}) exchanges with a metal ion (M^{2+}) as shown by the following equation:

$$Mg(OH)_{2\ (adsorbent)} + M^{2+}_{\ (aq.)} = M(OH)_{2\ (adsorbent)} + Mg^{2+}$$

Although the metal is shown to be divalent ($^{2+}$) in this equation for simplicity, it may be of any valency provided that ion exists as a cation in solution. The magnesium ions (Mg^{2+}) may further react with sulphate ions (SO_4^{2-}) to produce insoluble magnesium sulphate.

$$Mg^{2+} + SO_4^{2-} = MgSO_4$$

In general, the tendency is for the solubility of the hydroxides of other treated metals to be lower than that of magnesium hydroxide as shown in Table 3 and to precipitate in preference to magnesium hydroxide.

Table 3. *Solubility Data for Metals*

Metal Hydroxide	KsP	Solubility (molel^{-1})
Copper – $Cu(OH)_2$	2.2×10^{-20}	2.8×10^{-7}
Cadmium -$Cd(OH)_2$	1.7×10^{-15}	1.2×10^{-5}
Chromium -$Cr(OH)_3$	1.7×10^{-24}	1.2×10^{-8}
Nickel – $Ni(OH)_2$	6.5×10^{-18}	1.9×10^{-6}
Zinc – $Zn(OH)_2$	1.7×10^{-16}	5.5×10^{-6}
Lead – $Pb(OH)_2$	1.1×10^{-20}	2.2×10^{-7}
Iron – $Fe(OH)_2$	8.8×10^{-16}	6.0×10^{-6}
Magnesium – $Mg(OH)_2$	1.1×10^{-11}	2.2×10^{-4}

Traditional chemical methods of treating AMD using magnesium hydroxide are already described (Bologo *et al.*, 2009, 2012) and report good removal rates for metals from similar AMD waters in Witwatersrand Basin in S. Africa and other surface finishing and wastewater streams (Walter *et al.,* 2015). The sacrificial dissolution of a magnesium electrode by electrolysis to electro-generate magnesium hydroxide in-situ in a treatment process however has not been reported. The use of electrolysis, which encompasses electro-coagulation, -flocculation and –flotation, have previously been trialled and reported for treatment of AMD waters (Florence 2013) using iron, aluminium sacrificial electrodes and oxygen over-potential electrodes such as MMO and Ebonex (Hayfield 2001).

One major draw back with electrolysis (electro-coagulation) is passivation of the anode and cathode electrode surfaces during operation. Such fouling can lead to deterioration of treatment performance and excessive electrical voltages being used to achieve acceptable treatment current densities in the treatment process. Passivation is partially overcome in some electrochemical equipment by using high shear velocities across the electrode surfaces, polarity reversal and off-line electrode acid washing. This paper reports the novel use of sono-electrochemistry, electro-coagulation with combined power ultrasound (Morgan 2014) for treatment of 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.

Materials and Methods

Water samples were collected from the sampling flume at Dyffryn Adda (GIS SH4380791223). Two litre aliquot samples were treated using a Soneco® (Power & Water) sono-electrochemical reactor consisting of stainless steel cathode, four sets of 28 kHz ultrasonic transducers, magnesium anode, two litre B-Ker square flocculator jar and Watson Marlow peristaltic re-circulation pump. Water samples were re-circulated between the B-Ker and Soneco® reactor using the peristaltic pump. Following sonication and electro-coagulation, samples were flocculated on a Phipps & Bird bench flocculator for one minute at 250 rpm with addition of 5g of dried micro-sand ballast (<150 um diameter, stirred at 150 rpm with addition of 0.2ml polymer for three minutes and settled for 3 minutes at 0 rpm. 50ml aliquot samples were then filtered through a Whatman No. 10 filter before being tested for iron on a Hach-Lange DR 3900 spectrophotometer using the Hach Lange Iron Test kit (LCK 320). Due to limited time constraints and test methods the only other metal tested was copper using Quantofix Copper (0 – 100 mgl^{-1}) dip-test.

Reaction time, pH (Hanna Instruments), E_H (mV) (Hanna Instruments) and amperages were noted during the treatment procedure and photographs of the treatment reactions were taken. 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
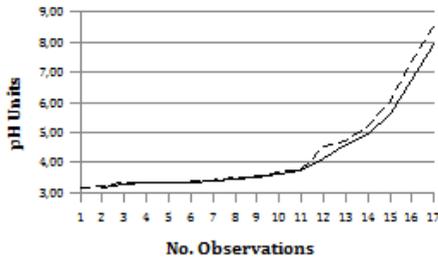
Table 4. *pH change over reaction period (13 mins.)*

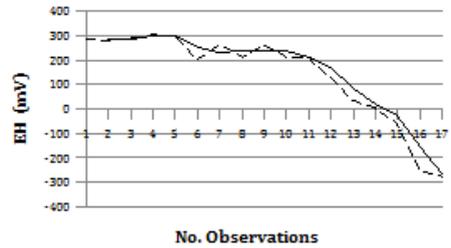**Table 5**. *EH (mV) change over treatment period (13 mins.)*

Table 6. *Changes in sample through treatment process*

T_0 min	T_3 min	T_{10} min	T_{12} min	T_{12} min	T_{13} min
Untreated sample	Precipitation at pH c. 3.5-3.7	Precipitation at pH c. 7.5	Addition of micro-sand and polymer	Rapid settlement	Clarified sample

Table 7. *Iron reduction*

Test	Amperage	Time	$[Fe]_{Start}$ (mg L^{-1})	$[Fe]_{End}$ (mg L^{-1})
Run 1	2	13	800	0.069
Run 2	1.5	17	800	0.007

Table 8. *Copper reduction*

Test	[Cu] Before mg L^{-1}	[Cu] after mg L^{-1}
Run 1	40	<1.0
Run 2	40	<1.0

Based on the above tests its is estimated that the magnesium (Mg^{2+}) dissolution required to both pH neutralize and precipitate iron to <1 mg L^{-1} is 325 mg L^{-1}. Based on this ratio the predictive scale-up costs (capital and operating) based on a flow of 12 L s^{-1} will:

1. Capex – £840,000 GBP – Soneco® Reactor & Power Supply excl. solid-liquid separation tank

2. Opex – £220,000 GBP per annum – Sono-electrochemical plant excl. replacement anodes

Discussion

The results confirm that electrical dissolution of a magnesium electrode produces magnesium hydroxide which exhibits the same characteristics as $Mg(OH)_2$ powders and granules currently employed in AMD treatment but overcomes the potential Health Safety and Environmental impacts of having liquid chemicals and pH correcting chemicals on site. The reaction raises the pH of acid waters, precipitates iron as ferrous hydroxide and other metal hydroxides. In common with Bologo et al. 2012 ferric hydroxide is first precipitated as a result of raising the pH from c. 3.0 to 3.5-3.7 to the insolubility product of $Fe(OH)_3$. As the pH further rises and the water becomes reduced iron is finally precipitated as $Fe(OH)_2$. The removal of copper during the reaction supports the findings that magnesium hydroxide will precipitate other metals before itself. The Bologo et. al., 2009 paper purports that these metal hydroxides precipitate at 1 pH unit below their normal insolubility product. Accordingly it is likely that this treatment method should provide a 'sweep' removal of most alkaline mine water metals dissolved in Dyffryn Adda adit including cadmium.

Extrapolating the bench scale operating parameters and results to a full-scale treatment plant (12 L s^{-1} flow rate) indicates that the Capex and Opex will be £840,000 GBP and £220,000 GBP respectively. These costs are slightly lower than the budget costs already presented (Table 2, above).
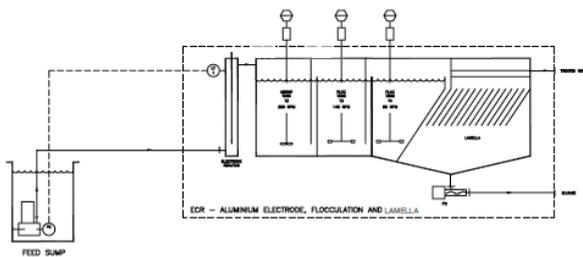

Fig. 3 *P&ID Sono-electrochemical treatment plant for AMD*

Fig. 4 *Soneco® Sono-electrochemical water treatment for removal of Phosphorus from wastewater*

For future consideration, the Capex and Opex costs could be off-set by the recovery of metal from the sludge after treatment, and as reported by Bologo *et al.,* 2009, even the soluble magnesium in the treated water could be recovered by precipitating with carbon dioxide

gas and recycled as magnesium hydroxide back to the head of works within the treatment process.

Further, the potential use of renewable energy sources at site could be used as an electrical power source for a sono-electrochemical treatment process.

For illustration purposes, a P&ID Sono-electrochemical treatment to treat Dyffryn Adda adit water is shown in (Fig. 3), together with a typical Soneco® (sono-electrochemical treatment plant) for removal of Phosphorus from municipal wastewater (Fig. 4).

Conclusion

1.   Electro-generation of magnesium hydroxide by electrolysis of a magnesium electrode has been successfully demonstrated and that its properties for water treatment are similar to proprietary powders and granular media. These properties include:

>   a. Raising the pH of an acid water and use on AMD schemes;
>   b. Electro-generated magnesium hydroxide successfully precipitates Fe^{2+} aqueous as insoluble ferrous hydroxide; the residual iron concentrations of the treated water being <1.0 mg L^{-1};
>   c. Magnesium hydroxide will simultaneously precipitate other metals as their insoluble hydroxide forms.

2.   The predicted Capex and Opex of a sono-electrochemical treatment plant is broadly attractive to other treatment / disposal options being considered for Dyffryn Adda adit water. These costs could be off-set by the revenue earned form metals recovered from the treated sludge. Electrical energy for a sono-electrochemical plant could be sourced from a renewable energy supplies.

3.   This present study was undertaken under a time constraint and as 'proof of concept' to quickly assess the viability of sono-electrochemistry (electro-generation of magnesium hydroxide) for water treatment for AMD. Having achieved favourable results and conclusions, further bench trials, extensive sampling testing and site pilot study would be recommended.

4.   This technique is transferable and can be accordingly scales for metal mine water treatment projects at other mines challenged by steep terrain and exhibiting acid or ochreous mine discharges, like those at Cwm Rheidol and Cwmystwyth mines also being considered by Natural Resources Wales.

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9 Case Studies

Improving Resource Efficiency and Minimize

Environmental Footprint – a case study preliminary results

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Abstract Panasqueira Mine (Portugal) has been mainly exploited for wolframite, cassiterite and chalcopyrite (W, Sn, Cu). Through the detailed and careful characterization of tailings with different mineralogy, new invaluable insights into the weathering characteristics of many different minerals will be received, making possible proper risk assessments, and predict which type of tailings might pose severe future environmental risk namely to the Zêzere river. The Zêzere River is an important river and is under the Cabeço do Pião tailings influence. The knowledge and methods acquired will lead to a conceptual model working as guidance to a more sustainable mining in the hereafter.

Key words Panasqueira mine; Cabeço do Pião; Risk assessment; guidance

Introduction

The worldwide demand for metals and minerals is rapidly rising, driven by economic growth. Europe delivers a huge trade deficit for metallic minerals, and thus needs to evoke more of its own resources to reduce this dependence. Mining is still the primary method of metals extraction so it is of crucial importance to identify new processing methods and process design, as well as risk assessment for the remaining residuals.

Since 1898, Panasqueira Mine in Portugal was exploited for wolframite, cassiterite and chalcopyrite (W, Sn Cu), the latter two as by-products. Until 1912 the mining scale was minor, but increased by 1928 and ultimately got a large development. One, of seven areas is the Cabeço do Pião (Fig.1) where tailings have been displaced from 1927 and 90 years ahead. The tailings deposit has an average height between 30 and 40 m and slopes around 35º. The estimated volume of the tailings is 731 034 m3. An ore processing plant was constructed at that site using gravity, electromagnetic separations, and flotation. The grain size of the material is variable. The tailings have average grades around 4000 ppm of W, 6800 ppm of Zn, 2494 ppm of Cu, but also contain 76350 ppm of As. The geochemistry and mineralogy of the tailings have been thoroughly studied as well as the acid mine drainage impact. The tailings are nowadays property of the municipality of Fundão and they are not included in the National Program for Mine Rehabilitation.

Material and Methods

Sampling of the tailings was performed in two different dates: in December 2016 and January 2017. It was used an excavator (Fig.2) to gather 33 superficial (50 to 60 cm of depth) mineral waste samples. The sampling was performed on a rectangular grid of 40 x 20 m and a Global Position System (GPS) allowed to georeferenced all with UTM system.
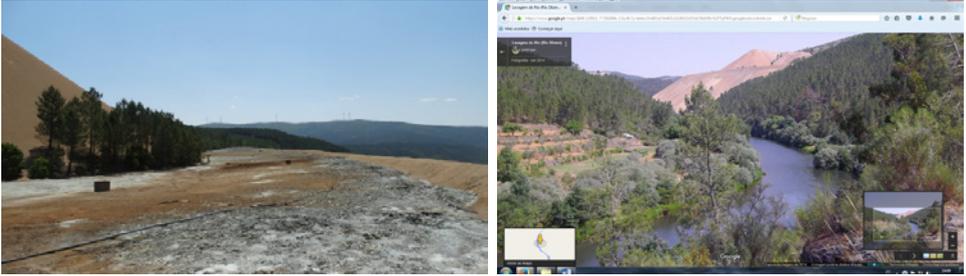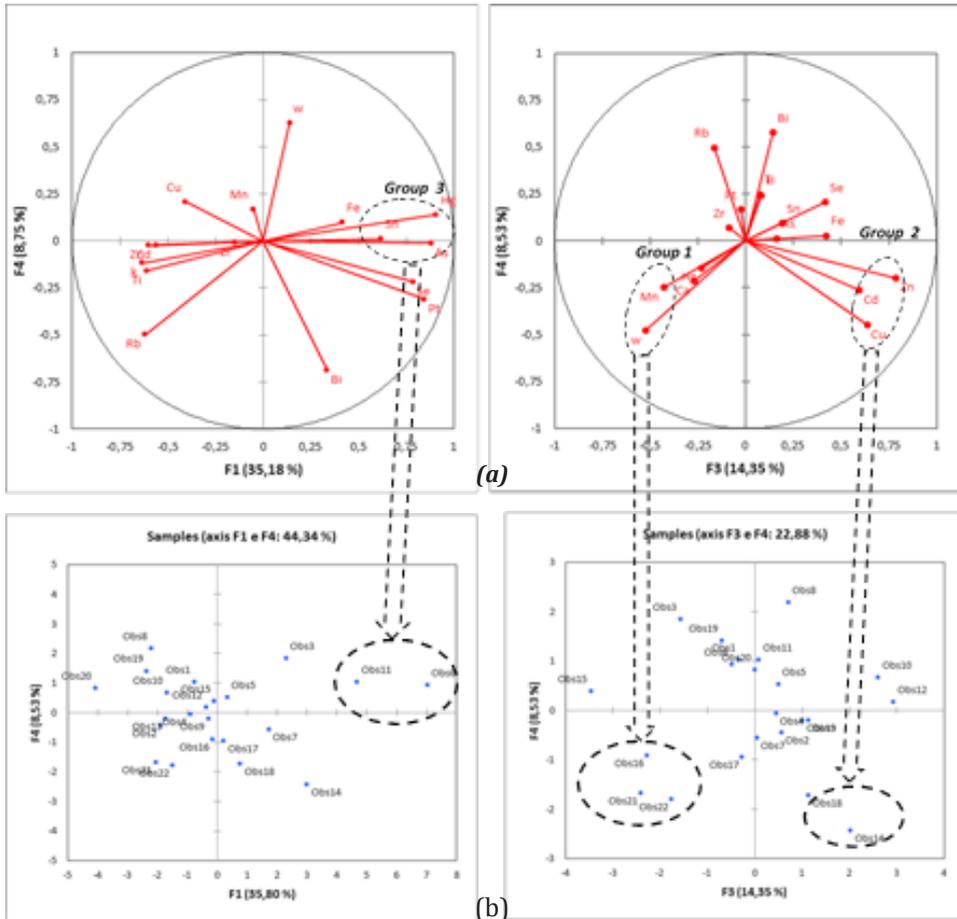
Figure 1 Cabeço do Pião tailings deposit (Joel Braga, Sept 2014)

Figure 2 Sampling procedure – Cabeço do Pião tailings deposit

The samples were then dried at a temperature of 50 ºC during 24 h. The potentially toxic metals and semi-metals were analyzed by Energy Dispersive X-Ray Fluorescence (XRF) method using an X-MET8000 instrument (Oxford Instrument). The equipment was used in Mining Mode, allowing fast and accurate analysis with low limits of detection. After, the geochemical dataset composed by 16 elements (Bi; Cu; Zn; Se; Hg; As; Pt; Rb; K; Mn; Sn; Ti; W; Zr; Fe and Cd only determined in 22 samples) went through a multivariate statistic analysis (Principal Components Analysis – PCA Spearman technique) to evaluate the relationships among the trace elements and the presence of outliers. The first four factors retain 78% of the total variability and hence providing an accurate image for the geochemical association s definition. Three important associations emerged: Group 1: W and Mn Group 2: Cd; Zn; Cu and Group 3: Sn; As; Hg (Fig. 3).

Figure 3 *Principal Component Analysis (PCA) – Factorial planes F1/F4 and F3/F4; a) Correlation circle and attributes' projection; b) individual's projection*

Thus, in a first step the missing Cd values were estimated using multi-linear regression where Cu and Zn were used as independent attributes for Cd prediction (Tab. 1; Fig. 4):

$$Cd = -2.53 \times 10^{-4} - 2.36 \times 10^{-3}Cu + 1.49 \times 10^{-2}Zn \qquad (1)$$

Table 1 *Correlation matrix and Multiple Correlation Index for Cu; Zn and Cd*

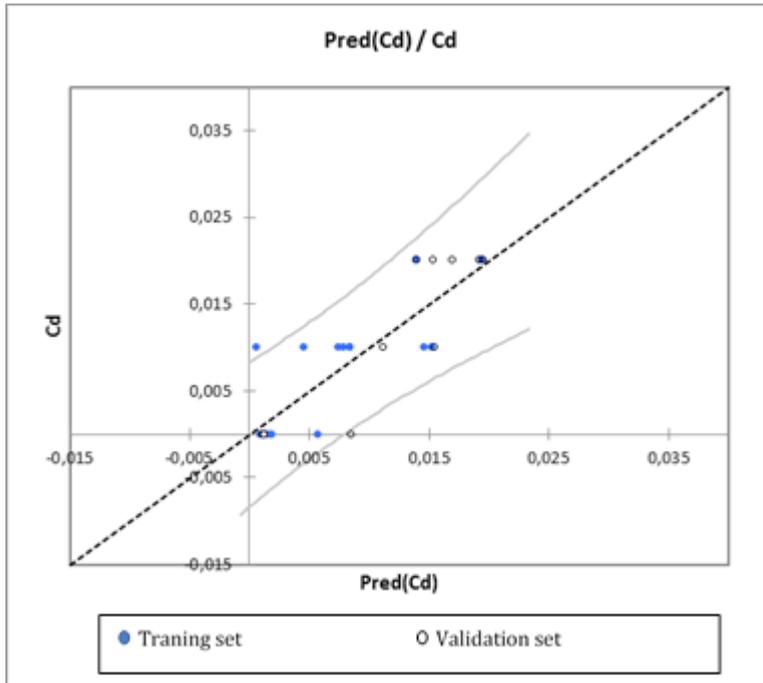|	**Cu**	**Zn**	**Cd**
Cu	**1**	0,839	0,699
Zn	0,839	**1**	0,871
Cd	0,699	0,871	**1**
Multiple Correlation index: Cd Cu Zn		0,84	

Figure 4 *Linear regression: training and validation sets*

In a second step a geostatistical approach was used to accomplish the construction of elements' concentration patterns.

Geostatistical techniques are founded along the theory of regionalized variables (Matheron, 1971) which says that variables within an area show both random and spatially structured properties (Journel and Huijbregts, 1978). Experimental variograms must be estimated and modelled to quantify the spatial variability of random variables as a function of their separation lag (Antunes et al. 2013). When forecasting the risk of contamination (e.g. months ahead), it is mandatory to stress the importance of the future estimated values to exceed the maximum admissible values. The delineation of enriched zones requires the interpolation of content values to the nodes of a regular grid where a prediction model will work as guidance to a more sustainable mining management.

The new variables (F1 and F3) obtained by PCA are defined as regionalized variables and are additive by construction. Therefore, a two-step geostatistical modelling methodology was used as follows:

1) Selected attributes (F1 and F3) went through structural analysis, and experimental variograms were computed (Fig. 5);