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# Utilization of by-products from mine industry as sorbents in water treatment

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**Abstract** Ammonium removal from explosive agent residues containing mining effluents represents a challenge, especially in cold climate. As environmental agencies are demanding ammonium removal at mine sites in e.g. Finland and Sweden, new methods are required. Natural zeolites are the most studied sorbents for ammonium removal and one promising material is a mining industry by-product, analcime. In this study, the ammonium removal capacity of analcime was improved by using geopolymerization. Four types of geopolymers were prepared and tested as an ammonium sorbent by using model solutions at different temperatures. Finally, the material could be regenerated or utilized e.g. as a fertilizer.

**Key words** ammonium removal, analcime, geopolymer, sorbent

## Introduction

Zeolites are crystalline-hydrated aluminosilicate minerals with a three-dimensional framework, which consists of $SiO_4$ and $AlO_4$ tetrahedra linked with shared oxygen atoms. Zeolites possess large surface area and high cation exchange capacity. Zeolites are as cation exchangers and consequently they have been frequently applied as sorbents in water and wastewater treatment (Wang and Peng 2012). The most common types of zeolites are clinoptilolite, mordenite, dachiardite, analcime, phillipsite and heulandite. Zeolites have been reported to be effective in removing cations with widely variable size, such as dyes (Karadag et al. 2007; Wang and Zhu 2006), organics (Bowman 2003; Huttenloch et al. 2001), ammonium (Lei et al. 2008; Luukkonen et al. 2016) and metal ions (Cincotti et al. 2006; Oter and Akcay 2007) from wastewaters. Zeolite mineral, analcime [$Na_{16}(Al_{16}Si_{32}O_{96})\cdot16H_2O$], is formed as a by-product when lithium carbonate is produced from spodumene ($LiAlSi_2O_6$) using sodium pressure leaching process (Chen et al. 2011). Analcime has also been reported to be a sorbent in the wastewater treatment (Atta et al. 2012; Mallah et al. 2012; Montalvo et al. 2012).

Ammonium ($NH_4^+$) in mining effluents originates mainly from explosive agents such as ammonium nitrate-fuel oil explosives (ANFO) which contains 33% (w/w) of nitrogen (Forsyth et al. 1995). Ammonium is a major contributor to the eutrophication of water bodies in those cases when nitrogen is the nutrient in shortest supply. In fact, ammonium is more severe in term of eutrophication than the other common nitrogen species nitrate ($NO_3^-$) (Wetzel 2001). Therefore, several countries have set limit values to the nitrogen removal from wastewaters, also in small-scale wastewaters, and more commonly also from mining effluents. Typically, mines have a maximum annual nitrogen release amount. Currently sorption-based technologies are not widely applied for mining effluents but they have potential since the process is generally little affected by temperature or variations on concentration. Metakaolin geopolymer (Luukkonen et al. 2016) and natural zeolites (of which clinoptilolite is the most widely studied) or wollastonite (Hedström 2006a; Hedström 2006b), for example, have been developed earlier to ammonium removal.

Geopolymers consist of an anionic framework of corner-sharing $SiO_4$ and $AlO_4$, and the exchangeable cations are located in the voids in the same way as in zeolites (Davidovits 2015). However, geopolymers are x-ray amorphous unlike zeolites. Geopolymers are most commonly prepared by a synthesis method in which aluminosilicate raw material (such as metakaolin) and alkaline activator (typically sodium hydroxide and/or silicate) react at room temperature and pressure (Luukkonen et al. 2016).

In the present study, the industrial waste material, analcime, was applied as a sorbent in the ammonium removal. Based on the literature, analcime removes ammonium at elevated temperature but water treatment should occur at ambient temperature which is, for example in Finland, typically low. Therefore, analcime was geopolymerized by four types of processes. Sorbent was studied for ammonium removal in batch experiments with synthetic wastewater with a high ammonium concentration. Sorption was studied at room (22 ˚C) temperature and elevated (80 ˚C ) temperatures and the effect of ammonium solution concentration was assessed. In addition, experiments with analcime without geopolymerization were performed for comparison.

## Materials and methods

### Preparation of geopolymers

Analcime was provided by Keliber Oy, Finland (Keliber Oy 2016). Two geopolymer precursors were prepared. In the first, analcime was first acid-washed with 2 M HCl for 24 h and dried at 105 °C for 24 h. Acid washing causes dealumination and renders the mineral into more reactive form (Jozefaciuk and Bowanko 2002). Calcination was performed at 400 °C or 700 °C for 2 h. The second precursor was prepared by mixing analcime and metakaolin (3:1 w/w) and drying at 105 °C for 24 h. Geopolymers were synthesized by mixing precursors (analcime or analcime and metakaolin mixture) with 10 M sodium hydroxide (NaOH) and sodium silicate (VWR International, $SiO_2$:$Na_2O$=3.1-3.4) 1:1 (w/w) mixture. The formed pastes were mixed for 5 min and poured into molds and they were allowed to consolidate at 22 °C for 2–4 weeks to ensure complete reaction. Before sorption experiments, the geopolymers were crushed and sieved to a particle size <500 µm and washed with deionized water. The compositions and sample names of the analcime geopolymers synthesized in this study are presented in Table 1. The example of the synthesized geopolymers is presented in Fig 1. Dried and sieved analcime was used as a reference material to analcime-geopolymers.

***Table 1** Analcime geopolymers preparation conditions.*

| Sample | Precursor | Pre-treatment | Calcination temperature | Alkali activator | Precursor-alkali activator ratio (w/w) |
|---|---|---|---|---|---|
| GP1 | Analcime | Washed with 2 M HCl, 10 g/200 mL, 24 h. | - | 10 M NaOH + sodium silicate | 0.9:1 |
| | | Dried at 105°C for 24 h. | | (1:1 w/w) | |
| GP2 | Analcime | Washed with 2 M HCl, 10 g/200 mL, 24 h. | 400°C, 2 h | 10 M NaOH + sodium silicate | 0.9:1 |
| | | Dried at 105°C for 24 h. | | (1:1 w/w) | |
| GP3 | Analcime | Washed with 2 M HCl, 10 g/200 mL, 24 h. | 700°C, 2 h | 10 M NaOH + sodium silicate | 0.9:1 |
| | | Dried at 105°C for 24 h. | | (1:1 w/w) | |
| GP4 | Analcime + metakaolin (3:1 w/w) | Dried at 105°C for 24 h | - | 10 M NaOH + sodium silicate | 1.36:1 |
| | | | | (1:1 w/w) | |

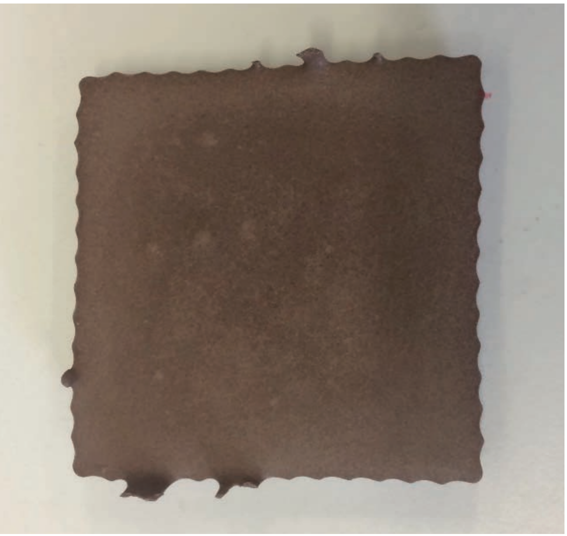

***Figure 1** Analcime-metakaolin geopolymer GP4.*

## Ammonium sorption experiments

The effect of temperature on the ammonium removal efficiency of four analcime geopolymers and unreacted analcime was studied. Experiments were conducted in batch mode with synthetic wastewater. Sorbent dosage was 20 g/L, concentration of ammonium solution was 1000 mg/L, volume of solution 50 mL and initial pH 2 (adjusted with HCl). Sorption temperatures were 22 °C at 80 ˚C in water bath. Samples were shaken during contact time with laboratory shaker at 300 rpm. All sorption experiments were performed as duplicate. Solids were separated from ammonium solution by sentrifuging before measurement of ammonium concentration with a Hach Lange IntelliCal ammonium ISE- electrode.

## Results and discussion

Yuan et al. (2016) found that ammonium removal with analcime was increased at elevated temperatures and therefore, experiments were conducted at 80 ˚C in addition to the room temperature (22 °C): the results are shown in Tables 2 and 3, respectively. Sorption efficiencies of materials at different temperatures are compared in Figure 2. At the room temperature, GP2 is the most efficient material with a removal efficiency of 15 % and a sorption capacity of 5 mg/g. Results indicate that the ammonium removal efficiencies are much higher at elevated temperatures than at the room temperature. At 80 °C the removal efficiencies are at the same level approx. 50-60% (q = 10-13 mg/g) with all sorbent materials except GP3 (removal approx. 15 % and q = 1 mg/g). Analcime without geopolymerization removes ammonium ions at elevated temperature as well as analcime-geopolymers but at room temperature ammonium removal efficiency is much higher for analcime-geopolymers (except GP3) compared to with analcime. In literature has been reported that analcime has two types of ion exchange: at room temperature and at elevated temperatures. Since, ion exchange occurs easier at elevated temperature because of small pores of analcime (Barrer and Hinds 1953; Sakizci 2016).

Before sorption experiments, initial pH was adjusted to value 2 to ensure that ammonium was present as $NH_4^+$ and not as $NH_3$. During experiments, pH increased due to alkalinity of analcime (pH approx. 11).

***Table 2*** *Results of ammonium sorption experiments at elevated temperature (80 ˚C)*

| Sample | Sorbent dosage [g/L] | Temperature [˚C] | Concentration of $NH_4^+$ [mg/L] | pH. Initial | pH. Final | Removal [%] | Sorption capacity [mg/g] |
|---|---|---|---|---|---|---|---|
| Blank | - | 80 | 507 | - | - | - | - |
| Analcime | 20 | 80 | 261 | 2.4 | 7.7 | 50.2 | 12.4 |
| GP1 | 20 | 80 | 298 | 2.3 | 8.4 | 56.8 | 11.0 |
| GP2 | 20 | 80 | 234 | 2.3 | 8.5 | 54.0 | 10.1 |
| GP3 | 20 | 80 | 419 | 2.3 | 2.9 | 20.1 | 1.65 |
| GP4 | 20 | 80 | 258 | 2.5 | 7.2 | 52.7 | 9.9 |

***Table 3*** *Results of ammonium sorption experiments at room temperature (22 ˚C)*

| Sample | Sorbent dosage [g/L] | Temperature [˚C] | Concentration of $NH_4^+$ [mg/L] | pH, Initial | pH, Final | Removal [%] | Sorption capacity [mg/g] |
|---|---|---|---|---|---|---|---|
| Blank | - | 22 | 705 | 2.4 | 2.5 | - | - |
| Analcime | 20 | 22 | 679 | 2.5 | 7.8 | 3.8 | 1.3 |
| GP1 | 20 | 22 | 614 | 2.2 | 8.4 | 13.0 | 4.6 |
| GP2 | 20 | 22 | 595 | 2.2 | 8.0 | 15.6 | 5.5 |
| GP3 | 20 | 22 | 754 | 2.1 | 2.3 | 0.5 | 0.2 |
| GP4 | 20 | 22 | 636 | 2.9 | 5.4 | 9.8 | 3.4 |

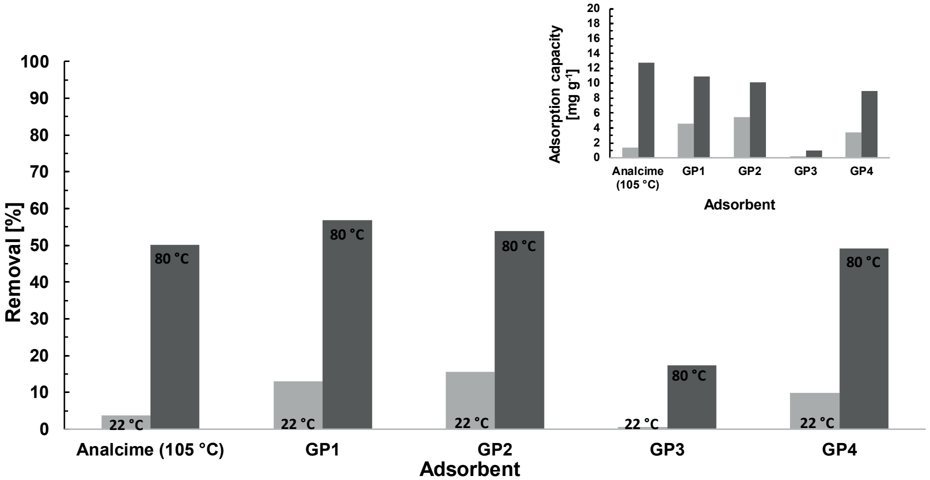

***Figure 2*** *Comparison of removal efficiencies for analcime and analcime-geopolymers at room temperature and at 80 °C. The small figure presents sorption capacity (mg/g) for studied samples at room temperature and at 80 °C.*

## Conclusions

Different types of analcime-based geopolymers were prepared and tested as a sorbent in ammonium removal. Ammonium removal efficiencies were clearly higher at elevated temperature comparing with room temperature. Results from batch experiments with powdered analcime-geopolymer indicated that the maximum ammonium sorption capacity was 11 mg/g at 80 ˚C and 5.5 mg/g at room temperature. For analcime these results were

12.4 mg/g and 1.3 mg/g, respectively. Therefore, the analcime seems to have higher affinity to ammonium at elevated temperatures. Wastewater purification materials should act at wide temperature range and therefore, geopolymerization with 10 M NaOH and sodium silicate solution is a suitable treatment method to increase ammonium adsorption capacity at room temperature.

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# Potential strategies for sustainable control of acid generation from pyrite oxidation

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**Abstract** Kinetic leach column (KLC) tests were conducted to define the conditions required to control acid and metalliferous drainage (AMD) from a highly reactive, potentially acid forming (PAF) waste. 0.1 wt.% lime addition plus either blending of silicates (25 wt.% K-feldspar and 25 wt.% chlorite), or addition of a non-acid forming (NAF) cover , when watered/flushed with lime-saturated water, greatly reduced acid generation as compared to the control KLC (PAF alone, watered/flushed with Milli-Q), but did not result in circum-neutral pH as required for effective AMD mitigation. In contrast, the combined use of these treatments resulted in leachate pH of >12.

**Keywords** At-source acid and metalliferous drainage control, Kinetic leach column, NAF cover, Pyrite surface passivation, Reactive silicates

## Introduction

Acid and metalliferous drainage (AMD) from both operating and inactive/abandoned mines (Sheoran et al. 2006) is a global environmental problem. In most cases AMD is triggered naturally by the oxidation of sulfide minerals, in particular pyrite—the most abundant sulfide mineral on the earth—through chemical and microbially-mediated reactions with both surface water and oxygen (Erguler et al. 2014). Acidic leachates containing toxic metals/metalloids, such as Fe, Mn, Cd, Pb, As and Se can be released. AMD is a complex and costly environmental issue, due to both the severity and long-lasting nature of the impacts. For the mining industry and governments AMD remediation is expensive with costs in the US and Canada alone estimated to be in the tens of billions of dollars (RoyChowdhury et al. 2015).

Accordingly, cost-effective and sustainable strategies for AMD prevention and remediation are highly desired. Pyrite surface passivating layers, incorporating silicates from the natural dissolution of reactive silicates in real sulfide waste rocks, can be preserved in a continuous, coherent and stable form at pH ≥6, and have been found to reduce the pyrite oxidation rate by 50-95% (Zeng et al. 2013). However, in some cases the establishment of these stable surface layers requires initial short-term treatment with greater concentrations of alkalinity than can be obtained from limestone covers. After passivation layers are established, the acid generation rate (AGR) can be reduced significantly so that some carbonates and reactive silicates such as limestone, anorthite feldspar, and hornblende, all commonly found in waste rocks, provide the required matching acid neutralising rate (ANR)(Smart

2015). This forms the fundamental hypothesis of our experimental approach for treatment of a highly reactive potentially-acid forming (PAF) iron ore waste (Mt McRae shale) from the Pilbara region of Western Australia.

The aims of this study were whether in conjunction with lime-saturated watering/flushing the following treatments could maintain circum-neutral pH as required for the establishment and maintenance of pyrite passivation: (1) lime blending; (2) combined use of silicates (chlorite + K-feldspar) and lime blending; and (3) application of a dolomitic NAF cover in conjunction with lime blending or with both lime and silicate blending.

## Materials and methodology

### KLC tests setup

Kinetic leach column (KLC) tests were run with lime addition and/or the application of silicate minerals and locally-sourced non-acid forming (NAF) covers, to explore the conditions required to control AMD from the natural PAF waste. All KLC tests other than the control were watered/flushed with lime-saturated water.

Quartz, K-feldspar and chlorite (Geo Discoveries, New South Wales, Australia) were crushed, pulverised and dry sieved to -4 mm size. Setup and daily operation for the KLC (tab. 1) were based on Smart et al. (2002), except that different solutions were used for weekly watering (200 mL) and four-weekly flushing (800 mL). 0.1 wt.% lime was added to all KLC tests, except the control column, to establish a condition favourable for the formation of surface passivation layers on pyrite.

### Sample characterisation

All mineral samples (dry-ground to -38 µm) were examined using powder X-ray diffraction analysis as per Qian et al. (2017). The concentration (± 10% error) of major ions from four-weekly KLC leachates was analysed via inductively coupled plasma optical emission spectroscopy (ICP-OES; Perkin Elmer Optima 5300 V). Calculations of mineral saturation indices were performed using the PHREEQC computer program, with the Lawrence Livermore National Laboratory database ('llnl.dat'), using $E_h$, pH, and solution chemistry of the leachates.

## Results and Discussion

### Sample characterisation

The results of net acid generation (NAG) and acid base accounting (ABA) tests of the two waste rock samples are provided in Tab. 2. The net acid producing potential (NAPP) results demonstrate the correct assignment of PAF and NAF for these two waste types. Quantitative XRD analysis indicated the following compositions (wt.%) for the PAF material - 42 quartz, 22 muscovite, 5 pyrite, 4 K-feldspar, 3 lizardite, and 24 amorphous phase(s), and for the NAF material - 54 quartz, 13 chlorite, 11 dolomite, 10 K-feldspar, 8 siderite, and 4 amorphous phase(s).

***Table 1** The composition (wt.%) of the KLC tests.*

| KLC (−4 mm) | Contents | Watering and flushing protocol |
|---|---|---|
| control | 50% PAF[1] (4.1 wt.% pyrite) + 50% quartz | Milli-Q for all watering/flushing |
| (1) lime | 50% PAF + 50% quartz + 0.1 % lime | Milli-Q watering/flushing prior to flush 1 and lime-saturated water for watering/flushing from flush 1 |
| (2) lime+cover | (1) + 400 g NAF cover[2] | |
| (3) lime+silicate | 50% PAF +25% chlorite +25% K-feldspar + 0.1 % lime | |
| (4) lime+silicate+cover | (3) + 400 g NAF cover | |

[1]Mt. McRae Shale (Undifferentiated); [2]Wittenoom Formation Paraburdoo Member

***Table 2** ABA and NAG test result of PAF and NAF wastes (in kg $H_2SO_4$ $t^{-1}$).*

| | ANC | $NAG_7$ | MPA | MPA* | NAPP | NAPP* |
|---|---|---|---|---|---|---|
| **PAF** | 2.4 | 125.0 | 123.3 | 117.8 | 120.9 | 115.4 |
| **NAF** | 109.3 | – | 19.3 | 18.4 | -90.9 | -90.0 |

MPA = maximum potential acidity = total S ´ 30.6;
MPA* = CRS ´ 30.6 (CRS from tab. 3);
NAPP = net acid producing potential = MPA–ANC;
NAPP* = MPA*–ANC.

## Leachate properties

The pH of the KLC leachates indicate that blending with 0.1 wt.% lime alone or with silicates (KLCs lime and lime+silicate, fig. 1A) provided insufficient neutralisation to maintain circum-neutral pH as required for the formation and maintenance of a pyrite surface passivating layer. The greater leachate pH for lime+silicate as compared to lime, especially over weeks 8–12, suggests that the added silicates may have neutralised a minor amount of acidity from the PAF waste during the 24 weeks.

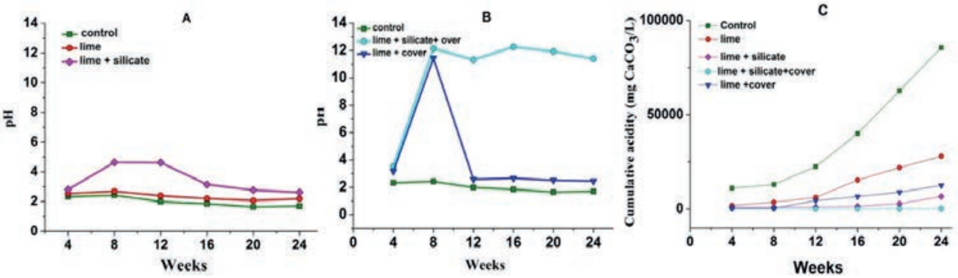

***Figure 1** KLC leachate pH and cumulative acidity profiles during 24 weeks of operation.*

The blending of silicates into the PAF waste in addition to a NAF top cover (lime+silicate+-cover) resulted in basic pH, but the application of the same NAF cover to the lime-blended KLC (lime+cover) gave rise to acidic pH (around 2.5) after 12 weeks (fig. 1B).This again demonstrates the positive role of silicates through neutralisation of acid generated from pyrite oxidation.

Figure 1c shows that the cumulative acidity is greater from the lime and lime+cover KLCs over 24 weeks than from lime+silicate and lime+silicate+cover. This also demonstrates that the blended silicates play a significant role in decreasing the acidity released from the KLCs. In addition, a NAF cover (lime+cover and lime+silicate+cover) decreased the total leachate acidity during the 24 weeks, as compared to the absence of a NAF cover - lime and lime+silicate, respectively - despite the acidic pH for lime+cover after 12 weeks. Only the combined use of blended lime and silicate and a NAF cover with lime-saturated watering/flushing completely inhibited acidity generation across the 24 weeks (fig. 1C).

The results clearly indicate that both silicates and NAF play positive roles in reducing acidity generation from PAF. It is possible that a combined use of lime addition, NAF covers and silicates blending (with saturated lime watering/flushing) may maintain circum-neutral/basic pH enabling establishment and maintenance of pyrite surface passivation, although longer-term testing would be required.

## Calculation of acid neutralization rate (ANR) and acid generation rate (AGR)

ANR and AGR were calculated based on the concentration of metals and S (sulfate) released(Miller et al. 2010). For the KLC tests without a NAF cover (fig. 1A) for the periods 8–12 and 12–24 the pH variations were small for these three columns and thus their ANR and AGR were relatively constant and are reported in Tab. 3. For the KLC tests with a NAF cover (fig. 1B) the period 12–24 week maintained almost constant pH (stable ANR and AGR) for ANR and AGR calculations.

***Table 3*** *ANR and AGR (mmol H2SO4 week*$^{-1}$*) calculated using the concentration of cations and S in leachates during different periods.*

| | Weeks | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 8–12 | | | 12–24 | | | | |
| | control | lime | lime+ silicate | control | lime | lime+ silicate | lime+ cover | lime+ silicate+ cover |
| AGR | 9.53 | 8.78 | 7.32 | 21.12 | 11.86 | 8.03 | 10.47 | 1.01 |
| ANR (with $Ca^{2+}$) | 1.55 | 7.68 | 7.13 | 1.40 | 6.36 | 7.39 | 9.79 | 6.25 |
| AGR/ANR(with $Ca^{2+}$) | 6.15 | 1.14 | 1.03 | 15.08 | 1.86 | 1.09 | 1.07 | 0.16 |
| ANR (no $Ca^{2+}$) | 1.44 | 1.03 | 0.36 | 1.25 | 1.21 | 2.18 | 3.60 | 0.09 |

Between weeks 8-12, the AGR of control, lime and lime+silicate was greater than the ANR, consistent with the acidic leachates. The total added $Ca^{2+}$ (31.4 mmol) added to lime+silicate from combined watering and flushing (i.e. 1.4 L per month) with lime-saturated water, assuming a lime solubility of ≈1.66 g $L^{-1}$, was much greater than that released (13.5 mmol) in the leachate, suggesting that the $Ca^{2+}$ retained (17.9 mmol) in the KLC may have precipitated. PHREEQC calculations suggested that leachates were saturated with respect to gypsum (tab. 4).

***Table 4*** *Gypsum saturation indices calculated for lime+silicate and lime+cover using PHREEQC.*

| Column | Weeks | pH | $E_h$(SHE) | Gypsum (SI) |
|---|---|---|---|---|
| lime+ silicate | 8 | 4.6 | 418 | 0.08 |
| | 12 | 4.6 | 380 | 0.14 |
| lime+ cover | 12 | 2.6 | 617 | 0.03 |
| | 16 | 2.7 | 647 | 0.12 |
| | 20 | 2.5 | 661 | 0.10 |
| | 24 | 2.5 | 702 | 0.03 |

SEM-EDS analysis of samples taken from lime+silicate within this time period clearly showed rod-like euhedral crystals containing Ca, O and S, providing further evidence that gypsum precipitation occurred. The precipitation of gypsum can result in inaccurate estimations of AGR based on S concentrations and ANR based on Ca concentrations, but it does not affect the rate difference between ANR and AGR.

During the period of weeks 12–24, lime+silicate+cover gave rise to the lowest AGR and was the only KLC with alkaline effluent. Assuming a lime solubility of 1.66 g $L^{-1}$, nearly 94.2 mmol $Ca^{2+}$ was applied to lime+cover and lime+silicate+cover KLCs through watering and flushing with lime-saturated water (9 watering and 3 flushing, totalling 4.2 L; tab. 5).The total amount of $Ca^{2+}$ in the leachates from lime+silicate+cover was 37.0 mmol, indicating that 57.2 mmol $Ca^{2+}$, possibly in the form of calcite (SEM-EDS analysis found Ca carbonate; data not shown) and/or other Ca-containing phases, were retained in this KLC. Note that the sample from lime+silicate+cover was not coated by carbon prior to the environmental SEM-EDS analysis, and thus the detection of Ca, C and O suggests the presence of calcium carbonate, possibly calcite.

For lime+cover (pH <3 during weeks 12–24), 63.0 mmol $Ca^{2+}$ was retained in the KLC, suggesting the possible formation of Ca-containing secondary minerals. It was found that gypsum was the only Ca-containing mineral phase with positive saturation indices (tab. 4). Similar to lime+silicate, rod-like euhedral crystals containing Ca, O and S were also found in lime+cover by SEM-EDS analysis.

***Table 5*** *Mass balance calculations of Ca2+ for lime+cover and lime+silicate+cover between weeks 12–24.*

| | **lime+cover** | **lime+silicate+cover** |
|---|---|---|
| $Ca^{2+}_{influent\text{-}lime}$ 1 | 94.2 | 94.2 |
| $Ca^{2+}_{leachate}$ 2 | 31.2 | 37.0 |
| $Ca^{2+}_{alkalinity}$ 3 | – | 9.4 |
| $Ca^{2+}_{neutralised}$ 4 | 31.2 | 27.6 |

1: $Ca^{2+}$ from watering/flushing with lime-saturated solution;
2: $Ca^{2+}$ in leachate;
3: Leachate $Ca^{2+}$ calculated from alkalinity measured, assuming the alkalinity is in the form of $Ca(OH)_2$;
4: Leachate $Ca^{2+}$ minus alkalinity $Ca^{2+}$.

## Conclusions

Using laboratory-scale KLC tests, combinations of PAF waste blended with lime and silicates, application of natural NAF materials (readily available on-site) as top covers, in conjunction with saturated lime-water watering/flushing have been employed to determine the conditions required to control acid generation from a highly reactive PAF waste material. It was found that an initial 0.1 wt.% lime addition to the PAF waste, even with addition of silicates or a NAF top cover, was not able to maintain leachate pH near or above neutral during 24 weeks of operation. In contrast, the application of both silicates and a NAF cover, together with 0.1 wt.% initial lime addition and flushing/watering with lime-saturated water, maintained a pH of around 12 up to 24 weeks.

The blending of lime combined with a NAF cover substantially reduced the cumulative leachate acidity from the KLC by approximately 65%, as compared to lime addition alone. Similarly, the addition of both lime and silicates in conjunction with a NAF cover significantly reduced cumulative leachate acidity by >90%, relative to the acidity of the same treatment but without silicates addition, demonstrating the positive role of blended silicates in reducing acid generation.

This study suggests that treatment of highly reactive PAF wastes via blending of lime (over 0.1 wt.%), silicates and addition of a NAF cover, when combined with other control measures (e.g. construction of waste rock emplacements using layered and compacted methods), could substantially reduce or eliminate acidity and metal loads in mine drainage. These results highlight to industry the potential for beneficial use of on-site neutralising waste materials and/or lithologies for cost-effective AMD control and mitigation strategies.

### Acknowledgements

This project was financially supported by BHP Billiton (Australia), Teck (Canada) and the Australian Research Council (ARC) via ARC Linkage projects LP140100399 and LP130100568. AMIRA International and staff members Gray Bailey (ex-Program Director) and Chris Ward are also acknowledged for support of the P933B project.

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# Technical and Economic Aspects of Recent Achievements in Mine Water Management in the Mines of Quang Ninh Coal Basin, Vietnam

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**Abstract** Vietnam National Coal and Mineral Industry Holding Corporation Limited (VINACOMIN) had to overcome two main challenges in order to achieve an efficient mine water treatment in the mines of the Quang Ninh Coal Basin, Vietnam: (i) low investment capacity for mine water treatment, and (ii) variation in mine water quantity and quality due to climate conditions. Solutions included equalizing reservoirs for a stable quality of the mine water inflow and parallel treatment lines for treatment capacities varying with seasonal changes. Furthermore, VINACOMIN established a joint environmental fund in order to mobilize financial resources for investment into mine water treatment plants.

**Keywords** coal mine, mine water treatment, Vinacomin Central Environmental Fund, changing weather conditions, equalizing reservoir

## Introduction

The Quang Ninh Coal Basin is situated in the North East of Vietnam, near the coast of Halong Bay, which has been recognized as World Natural Heritage by UNESCO. Almost all coal mining activities in this area are controlled by Vietnam National Coal and Mineral Industries Holding Corporation Limited (VINACOMIN).

The main sources of mine water are surface water and groundwater running into the mines. Additionally, there are other waters contaminated by mine related processes, such as wastewater from workshops or coal screening stations.The average quantity of mine water discharged from coal mines is from 1.9 to 2.1 $m^3$ per ton of raw coal (VITE 2014). The two primary types of water pollution are physical and chemical (inorganic). The mine water isacidic and contains coal sludge (SS), iron (Fe) and manganese (Mn) which are considered to bemajor pollutants (Kurtz 2009; Bilek et al.; 2011) andusually exceed permitted limits. The concentration of metals such as As, Pb, Hg, Cd is below the permitted limits as shown in Tab. 1.

***Table 1*** *Averagevalue ranges and limits of the main pollution parameters in mine waters in Quang Ninh according to the National Technical Regulation on Industrial Wastewater No.40 (QCVN 40:2011/BTNMT)*

| | pH | SS (mg/L) | Fe (mg/L) | Mn (mg/L) | Hg (mg/L) | As (mg/L) | Pb (mg/L) | Cd (mg/L) |
|---|---|---|---|---|---|---|---|---|
| Range of measured values | 2.6-6.8 | 70-1,714 | 2.3-247.4 | 0.85-24.6 | 0.0005 | 0.0005 | 0.0019 | 0.0033 |
| QCVN40* | 5.5-9 | 100 | 5 | 1 | 0.01 | 0.1 | 0.5 | 0.1 |

* basic values which have to be adjusted further in case of wastewater discharge into a water body used for water supply purposes and depending on volume parameters of the receiving water body and the wastewater flow

The climate of Northern Vietnam has 4 seasons but one year can be divided into 2 main seasons regarding the rainfall: the rainy season that lasts from April / May to October / November and the dry season that lasts from November / December to the following April / May. The annual rainfall in Quang Ninhvaries from 2,200 mm to 2,400 mm and mainly concentrates in July, August and September. These seasonal changes affect both mine water quantity as well as mine water quality.

The quantity of mine water reaches the highest values in the 3rd quarter of the year with up to 2 – 2.5 times for underground and 4 – 5 times for open pit mines in comparison with the 1st and the 2nd quarters. The mine water volume in the 3rd quarter is also higher than in the 4th quarter, up to 1.2 – 1.3 times for underground and 1.1 – 2 times for open pit mines. The average quantity of mine water in the rainy season is 1.33 – 2.05 times higher than in the dry season (VITE 2014).

The mine water quality in the rainy season is characterized by less acidity (pH) but higher contents of suspended solids (SS) and metals (Fe and Mn) as shown in Tab. 2.

***Table 2*** *Variations in raw mine water quality due to seasonal changes at VangDanh underground coal mine*

| Items | pH | SS (mg/L) | Fe (mg/L) | Mn (mg/L) |
|---|---|---|---|---|
| Monitoring results from February to October 2015 | 5.2 - 7.4 | 39 - 210 | 4.07 - 13.33 | 0.71 - 2.42 |
| Monitoring results after a big rain in August 2015 | 6.74 | 633 | 96.4 | 6.71 |

Aside from interdependent factors (Marcus 1997), the mine water quality in Quang Ninh is also influenced by the depth of mining and the geological conditions including endosmosis of surface water into galleries through fissures on the surface.

Mine water is discharged into rivers and small streams as well as directly into coastal waters of Ha Long Bay.

During a very long period (1955 – 1994) the mine water was discharged untreated into the environment and has impacted the receiving water courses seriously. In the period 1994–2009, mine water was treated using a very simple technique for mine water neutralization and sludge settling (Fig. 1). Other parameters were not treated at all.

As for many years, the domestic coal selling price in Vietnam was fixed below the actual coal production costs in order to prevent cost increases in some key industrial branches such as power supply, cement, paper and fertilizer production, the coal mines were left without any profit. Therefore, internal financing for an improved mine water treatment in the coal mines was not available.

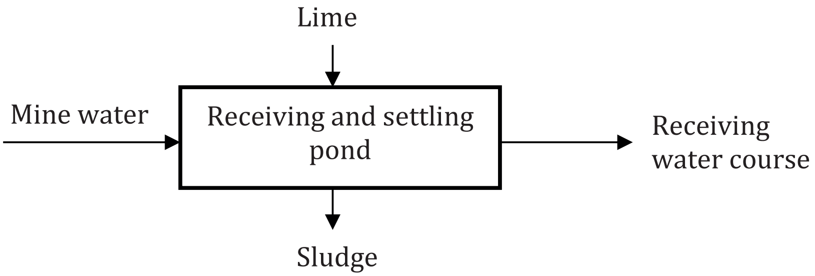

***Figure 1*** *Outline of mine water treatment before 2009*

## Methods

A good combination of economic and technical solutions was necessary in order to achieve an effective solution for mine water treatment in Quang Ninh.

### Setting up a financial source for mine water treatment

In 2009, the VINACOMIN Central Coal – Mineral Environmental Fund (VCEF) for investment into environmental measures including mine water treatment was established. The fund receives an annual financial contribution from all coal mining companies as a proportion of the coal production costs. Currently the rate is fixed at 1.5%. It is annually defined by the Members Board of VINACOMIN. The payment of contribution to VCEF is recognized under the coal production costs of every coal mining company. With regards to mine water treatment, VCEF is used for mine water treatment plants (MWTP) investment as well as the costs for maintenance of MWTP. Through the fund large as well as small mining companies get the chance to invest into environmental measures and especially mine water treatment solutions.

Furthermore, VINACOMIN set up a company specialized in environmental measures named Vinacomin - Environmental Company Limited (VEC) in order to enhance step-by-step the capacity through experiences made in the projects and to centralize the operation of mine water treatment plants in one unit. The company is responsible for the construction of MWTP as well as managing, operating and maintaining MWTP as a non-profit enterprise. The relation between the stakeholders in VCEF and their responsibilities are shown in Fig.2.

### Adaptation of mine water treatment technology to seasonal variations

With the establishment of VCEF the first MWTP were implemented. The treatment steps consisted of neutralization and reaction, flocculation, sedimentation and manganese filtration (Fig. 3).

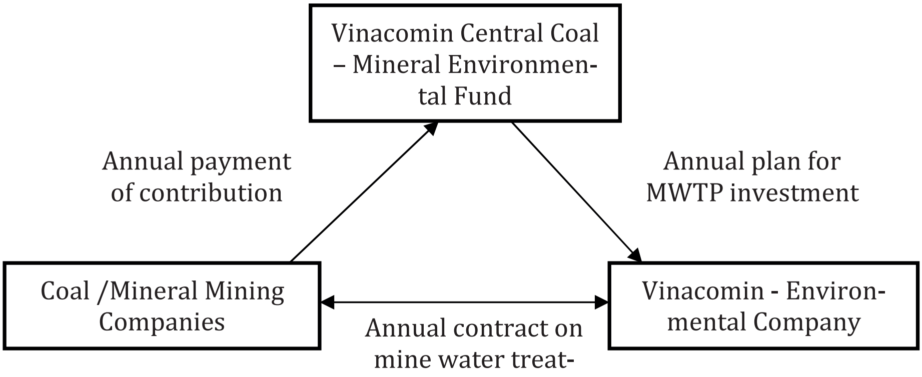

***Figure 2*** *Relationbetween the stakeholders in VCEF and their responsibilities*

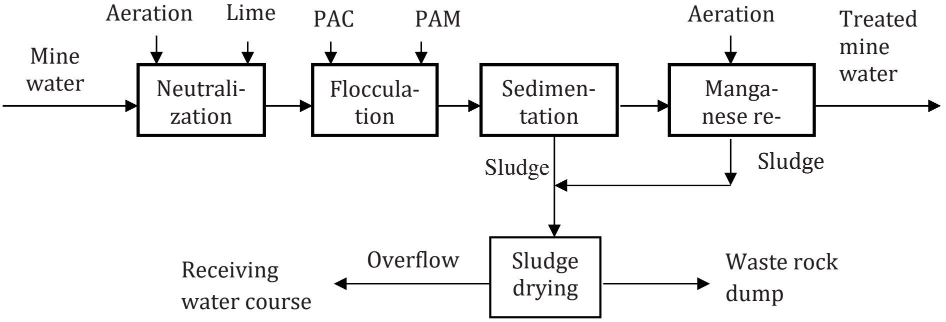

***Figure 3*** *Outline of mine water treatment applied for the first MWTP in the period 2009 – 2010 (Abbreviations: PAC –Poly Aluminium Chloride, PAM - Polyacrylamide)*

When taking the MWTP into operation, it was found that the seasonal variation of mine water quantity and quality leads to a very unstable operation of MWTP. The following factors are affected: (i) in the dry season the treatment capacity of the MWTP reached only 40 – 50% compared with its design capacity. In the rainy seasonthe MWTP were usually overloaded due to the large volumes of mine water which led to partial discharges of untreated mine water into receiving water courses. In some cases the MWTP were operated with 120 –160% of the design capacity during rainy season, which led to reduced treatment qualities. The treated water often did not fulfil the environmental standards. (ii) The design parameters of the technological process failed due to constantly changing mine water characteristics, which led to additional demand for treatment chemicals, such as lime, PAC, PAM. (iii) Increased sludge amounts and demand for equipment repairs due to overload led to increased operation costs.

One solution approach for quantity variation was the design of multiple treatment lines. While the first generation of MWTP (11 MWTP put in operation in the period of 2009 – 2010) was only designed with one treatment line the following MWTP had 2 – 4 parallel treatment lines (Fig. 4) which can be operated independently. The number of treatment lines operated at the same time depends on the mine water volume. The operation of treatment lines in accordance with the seasonal volume of mine water led to a reduced consumption of energy and treatment chemicals. Furthermore, during dry season the treatment lines can be maintained easily without stopping operation (VITE 2014).

***Figure 4*** *VangDanh MWTP:capacity of 3,000 m³/h, designed with 3 treatment lines*

In an attempt to further homogenize the inflow to the MWTP with regards to quality and quantity equalizing reservoirs have been studied and applied. An equalizing reservoir is a reservoir constructed by reinforced concrete or natural stone masonry (Fig. 5). In some cases abandoned settling ponds of coal preparation plants were reused. The reservoir is located outside the boundaries of the MWTP near the points of mine water drainage. The main tasks of equalizing reservoirs are: (i) homogenization of different mine water sources before flowing to the MWTP, (ii) prevention of overflow of untreated mine water into receiving water courses during intense rainfall events, (iii) partial sedimentation of coal particles contained in raw mine water for a general reduction and homogenization of the suspended solids concentration in the input to the MWTP.

***Figure 5*** *Equalizing reservoir in Nui Nhen MWTP, Quang Ninh*

Equalizing reservoirs were designed and constructed based on the analysis of the mine water volume and the available area at the mine site. The minimum required volume of the reservoir is defined as the total volume of mine water discharged within 4 hours. If possible, the retention time should be increased to 8 or to the maximum of 12 hours in order to ensure that no untreated mine water is discharged into receiving water sources.

Through laboratory experiments it was found that the raw mine water from open pit mines reaches a suspended solids concentration in the reservoir outflow of 100 mg/L (allowed limit according to QCVN40, see Tab. 1) after a settling time of 1.5 to 2 hours. For raw mine water from underground mines the corresponding settling time with 2 to 3 hours is slightly longer. The settling of coal dust also affects the concentrations of Fe and Mn. For open pit mine water the concentration of Fe is decreased by ⅔ and for Mn by ½. For mine water originating from underground mines nearly no reduction in Fe and Mn concentrations was found (VITE 2014).

## Results

The setup of the VCEF as source for investment into mine water treatment led to the construction of 41 mine water treatment plants in the Quang Ninh coal mining area between 2009 and 2015 where currently a total amount of 565,000 m$^3$/day istreated. The total investment amounts to 47 million USD. In a period of only 6 years a mine water treatment ratio of 75% was achieved for the Quang Ninh coal mining area.

Based on the experiences made the general design for any new MWTP under the control of VINACOMIN includes an equalizing reservoir and 2 or more parallel treatment lines. The design follows the structure as shown in Fig. 6.

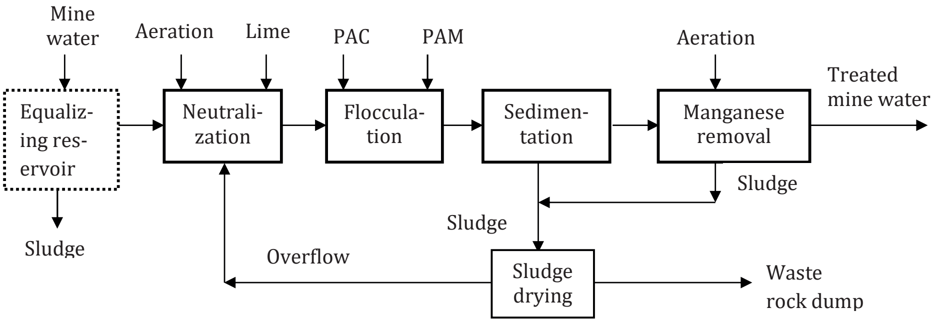

***Figure 6** Outline of mine water treatment with equalizing reservoir*

The 11 MWTP which were equipped with an equalizing reservoir showed an improved operation efficiency. Tab. 3 shows the example of Mao Khe MWTP (VITE 2014, 2015).

***Table 3*** *Operational efficiency of Mao Khe MWTP designed with a capacity of 1,200 m³/h, 2 treatment lines and an equalizing reservoir of 3,700 m³ which was added in 2012*

| Items | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 |
|---|---|---|---|---|---|---|
| Achieved max. monthly output [$m^3/h$] | 594 | 769 | 1,025 | 1,054 | 997 | 980 |
| Achieved max. monthly output compared with the design capacity [%] | 49,5 | 64,0 | 85,4 | 87,8 | 83,1* | 81,7* |
| Consumption of Lime [$g/m^3$] | no data | no data | 200 | 200 | 190 | 170 |
| Consumption of PAC [$g/m^3$] | no data | no data | 6 | 6 | 6 | 6 |
| Consumption of PAM [$g/m^3$] | no data | no data | 1 | 1 | 1 | 1 |

* The operational efficiency decreased due to an extraordinary heavy rain event in Quang Ninh (1,600 mm within 10 days, July/August 2015) that flooded the whole MWTP. The repair works lasted until 2016.

## Conclusions

Mine water and mine water discharge in the Quang Ninh coal mining areas were not controlled during a very long period. Although legal regulations for mine water treatment and quality standards for mine water discharge were in place, the mine operators did not comply with the regulations due to financial and technical constraints. Finally, the mining industry defined the target of 100% mine water treatment before discharge into water bodies and the issue became the top priority with regards to environmental measures.

The VINACOMIN Central Environmental Fund as a form of "joint responsibility" was an appropriate solution which has helped the coal mining companies in the Quang Ninh Coal Basin to overcome their lack of investment capacity. Nowadays, almost all coal mining companies in theQuang Ninh Coal Basin have been equipped with at least one MWTP, some mines even with two, such as the Mao Khe and the Nam Mau Underground Coal Companies. Seasonal changes of weather conditions and especially tropical rain events require special solutions in mine water treatment. If this is not taken into account, the treatment results cannot fulfil the environmental standards during operation. The combination of several parallel treatment lines with an additional upstream equalizing reservoir seems to be an appropriate solution for mine water management in Vietnamese coal mines.

The example on mine water management in Quang Ninh has shown that only the combination of suitable economic and technical solutions lead to a successful implementation of mine water treatment for all mines. Under the new regulations of the Law on Water Resources of Vietnam, the use of surface and underground water sources is controlled even more strictly. With an annual amount of tens of millions of cubic meters the treated mine water is an important potential reserve for the surface water resources in Quang Ninh.

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# Sulfate Removal from Water Streams Down to ppm Level by Using Recyclable Biopolymer

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**Abstract** Sulfate in not highly toxic to life, but nowadays sulfate concentrations in water are under increasing inspection from regulatory authorities. Typical sulfate drinking water limit in Finland is 250 mg/L, but places like Minnesota future waste water sulfate discharge limit is expected to be as low as 10 mg/L. Several methods to remove sulfate from aqueous solutions have been developed, but most of these methods do not fulfill the criteria of circular economy. This study focuses on sulfate removal by using chitosan as adsorbent in the laboratory and pilot scale.

**Key words** sulfate removal, biopolymer, recycling, ion exchange material

## Introduction

One of the main problems in industrial waste waters are sulfur compounds. Sulfur has several oxidation states between -2 and +6 and most commons in the nature are the pure elementary sulfur ($S_n$), sulfide ($S^{-2}$) and sulfate ($SO_4^{2-}$). The sulfate or sulphate ion is a polyatomic anion with the formula $SO_4^{2-}$. Sulfates occur widely in everyday life, like in see water (ca. 2.5 g/L) and sulfate salts and sulfuric acid are also widely used in industry. Many examples of ionic sulfates are known, and most of these are highly soluble in water, like $FeSO_4$. Poorly soluble compounds are only $CaSO_4$, $SrSO_4$, $PbSO_4$ and $BaSO_4$, while radium sulfate is the most insoluble sulfate known.

As such sulfate in not highly toxic to life, but sulfate increases salinity in receiving waters and may cause secondary toxic effect when sulfate is biologically reduced to toxic hydrogen sulfide ($H_2S$). Nowadays, sulfate concentrations in water are under increasing inspection from regulatory authorities based mainly on public demands. Compared to other contaminants like nitrate, arsenic, and metals, sulfate has no strict standard for drinking water or aquatic life. Typical drinking water limit in Finland and many other countries is 250 mg/L, for livestock drinking water sulfate limits are higher e.g. in Canada, Australia and EU 1000 mg/L, while concentrations above 600 mg/L may create laxative effects. However, in some places like Minnesota, future sulfate discharges may be limited to as low as 10 mg/L.
Several methods, like lime precipitation ($CaSO_4$), barium precipitation ($BaSO_4$), membrane techniques (e.g. reverse osmosis), ion-exchange and biological processes have been developed. The simplest method for sulfate removal is precipitation as gypsum, which is used widely as fertilizer or plaster. The main problem is gypsums moderate solubility (~2.0–2.5 g/L at 25 °C) to water. Solubility is increased if sodium cations are present in the same solution, but in contrast to most other salts, it exhibits retrograde solubility, becoming less soluble at higher temperatures. $BaSO_4$ has lower solubility to water, but the problem is that water-soluble barium compounds are poisonous.

Outotec has develop ettringite ($3CaO\cdot3CaSO_4\cdot Al_2O_3\cdot31H_2O$) precipitation process, in which lime and $Al(OH)_3$) can be used to remove sulphate and metals. Ettringite has very low water solubility (200-1000 mg/L) and therefore the resulting sulphate concentrations are low. Disadvantages are the large amount of sludge generated, highly basic solutions and the fact that high sodium concentrations inhibit the process.

Also several other processes have been developed like reverse osmosis (RO) and biological processes. RO is a water purification technology that uses a semipermeable membrane to remove ions (e.g. sulfate), molecules, and larger particles from water. RO is effective but a costly method to purify waste waters and results significant amount of reject water needing additional treatment. Biological process under anaerobic conditions convert sulfates into sulfides. Biological processes are cost effective but rather slow, difficult to control and formation of highly toxic $H_2S$ cause additional problems.

Most of these methods mentioned above do not fulfill the criteria of circular economy. Recently, we have developed environmentally friendly method for the removal of inorganic sulfur compounds based on a generally available biopolymers, like chitosan which is prepared from shrimp shells as shown in Fig. 1. Here, preliminary results from our laboratory and pilot experiments are shown.

***Figure 1**. Chitosan used in this study is prepared from shrimp shells.*

## General methods

Most of our sulfate containing solutions were taken from mining sites and paper mills in Finland. We also studied samples from Huelva area (Rio Tinto) in southwest Spain and drinking water from Kuopio town. Sulfur concentrations from samples were measured before and after treatment with different adsorbents by using either PANalytical Epsilon $3^{XLE}$

energy dispersive X-ray fluorescence (EDXRF) spectrometer or S2 Picofox Total Reflection X-ray Fluorescence spectrometer (TXRF, Bruker). Also, ion chromatography methods was tested to determine sulfate concentrations during one pilot session. Reagents here were commercial p.a. quality.

In a typical laboratory scale experiment weighted amount (1-20 g/L) adsorbent was added with stirring to sulfur containing water (800-8000 mL). Reaction pH was controlled during mixing and contact time varied depending on experiments being typically from minutes to an hour. After reaction was completed adsorbent was filtered off and sulfur concentration was measured from the treated solutions and the filtered adsorbent.

### Pilot scale experiments

Sulfate removal has been demonstrated also in pilot scale (ca. 0.25-1.0 $m^3/h$) on field using two different water source: 1) metal ore mine dewatering water and 2) non-metal mineral mine infiltration water. Typical flow chart of our pilot experiments are shown in Fig. 2 and typical experimental condition with additional supervisors in Fig. 3.

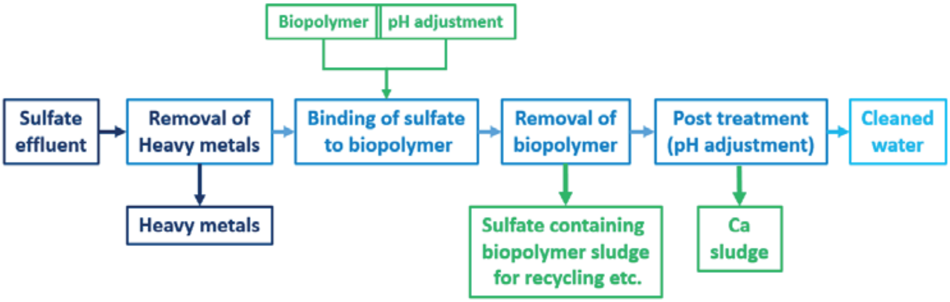

***Figure 2****. Flow chart of biopolymer based sulphate removal process. The sulphate binding step lasts typically 5 to 30 min.*

### Result and discussion

Our sulfate removal method (FI and PTC patents pending) is based on the reaction between positively charged functionalities in solid material containing modified sugar units and dissolved negatively charged sulfur substances in acidic waters and subsequent separation of the $SO_4^{2-}$ containing solid material from the aqueous medium.

In the beginning of the project we tested in laboratory scale different types of waters containing variable amount sulfur starting from Kuopio town drinking water (40 mg/L) and ending up to RO water (40 000 mg/L). However, mostly we concentrated on water samples 1) obtained from lime precipitation processes and 2) water samples from which sulfate cannot be removed with lime. The results of some of these tests are shown in fig. 4.

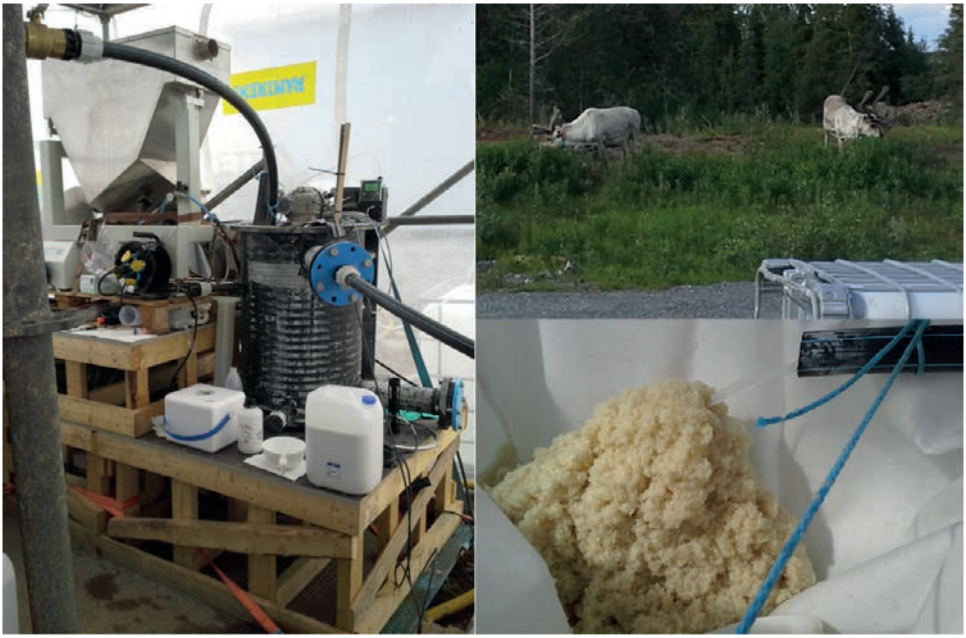

***Figure 3****. Pilot testing of biopolymer based sulfate removal system: part of used pilot equipment (left), pilot supervisors (top right) and sulfate containing biopolymer sludge (bottom right).*

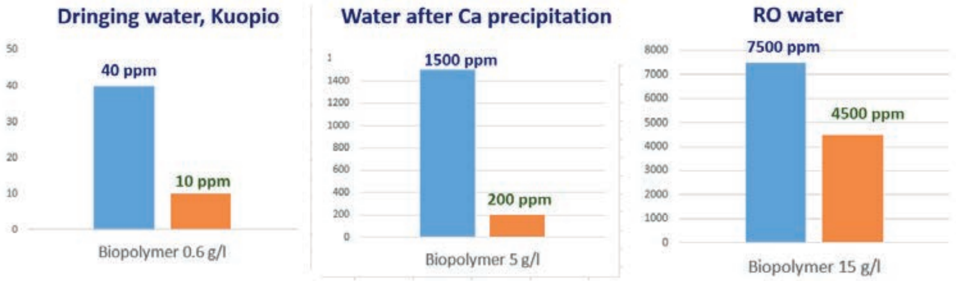

***Figure 4****. Chitosan is effective adsorbent to purify different type of real water and waste water samples regardless of sulfate concentration.*

As expected, adsorption is quite directly dose dependent and binding capacity for sulfate compared to adsorbent weight is typically ca. 20%. The tests in Fig. 5 were carried out using Kemwater Flocculator 2000 JAR equipment at 10°C - 14°C with 15 min mixing time.

The pilot tests results shown here were done at a metal mine site using two different dewatering waters (five separate tests). Each test was continuous and lasted 5 to 8 hours. Water flow was varied between 0.25 - 0.4 $m^3/h$ and retention time in mixing from 22 to 36 min between tests. Under normal adsorption conditions, when pH and adsorbent amount is well controlled there is no problem to reduce sulfate concentration under drinking water limit (see fig. 6 case II, IIIA and V). If pH is not controlled results are poor (see fig. 6 case IV A and IVB).

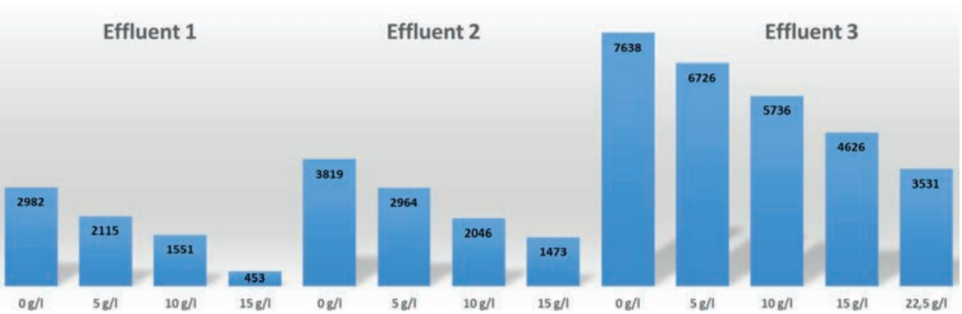

***Figure 5***. *Effect of biopolymer dosing on sulfate removal in three different mining industry effluents.*

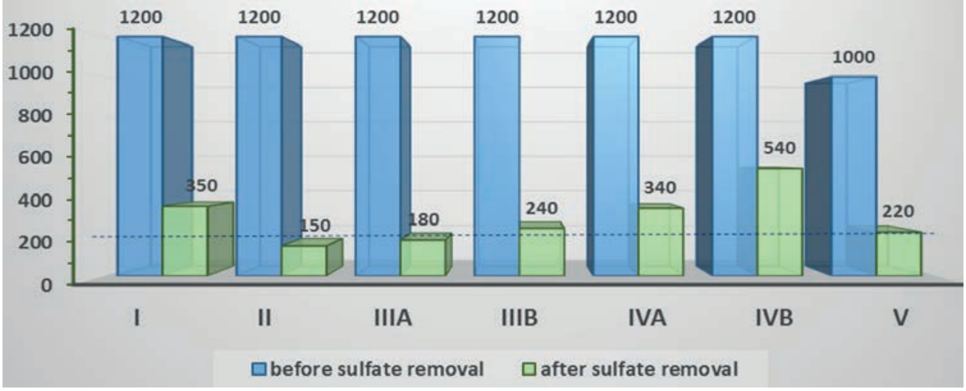

***Figure 6***. *Results of sulfate removal pilot tests. Target SO42- level was 200 mg/L (dotted line).*

Based on our laboratory and pilot scale testing, our method has following advances compared to many traditional methods: 1) effective under large sulfate concentration range, 40 – 36 000 mg/L; 2) effective also under low temperatures +4...+50°C; 3) removal of sulfur species is not inhibited by high sodium, potassium, magnesium or calcium concentrations; 4) process is fast and robust; 5) sulfate binding biopolymer can be recycled (>10 times); 6) method is safe for humans and environment, all materials are non-toxic; 7) binding capacity compared to adsorbent weight is high, typically ca. 20%; and 8) cast-off polymer is possible to use as fertilizer.

## Conclusions

The method efficiently removes sulfate from cold and diluted water streams from which sulfate cannot be removed by using gypsum precipitation (sulfate <1500 mg/L) method or from water streams containing high concentrations of sodium. Exceptionally low residual sulfate levels can be reached (sulfate <250 mg/L). Removed sulfate can be recycled: sulfate biopolymer sludge from pilot tests fulfilled the requirements set for harmful substances on the decree of the Ministry of Agriculture and Forestry on fertilizer products 24/11.

**Acknowledgements**

This study is part of Green mining program project called "SO4" funded by the Finnish Funding Agency for Innovation (TEKES). The authors would like to thank Helena Vepsäläinen and Sonja Holopainen from UEF for assistance and Lasse Moilanen from Chemec Oy for helpful discussions. This work was supported also by the Regional Council of Pohjois-Savo (Kaivos VV and Keveys projects).

# Sources of groundwater inflows into the “Czatkowice” limestone quarry in southern Poland

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**Abstract** Lower Carboniferous limestone has been extracted in the “Czatkowice” open-pit hill-slope quarry in southern Poland since 1948, for the needs of metallurgical and building industries, as well as farming. We can distinguish two aquifers in the Czatkowice area: the Quaternary porous aquifer and the Carboniferous fissure-porous one. Two vertical zones representing different hydrodynamic characteristics can be indentified in the Carboniferous formations. One is a weathering zone and the other one the zone of fissures and interbedding planes. Groundwater inflows into the quarry workings have been observed at the lowest mining level (+315 m above the sea level (asl)) for over 30 years. This study concerns two hypotheses of the sources of such inflows originating either from (a) the aeration zone or from (b) the saturation zone.

**Key words** limestone quarry, groundwater, monitoring

## Introduction

Lower Carboniferous limestone has been extracted in the “Czatkowice” quarry since 1947. Initially, limestone was used as building material and later delivered to the ironworks. “Czatkowice” is a hill-slope quarry, situated on the slope of the Krzeszówka stream valley. Limestone mining operations are conducted close to several high-capacity water springs, called the Czatkowice Water Springs (Fig. 1) from which water is supplied to the nearby town of Krzeszowice and neighbouring locations. For that reason, the attention of hydrogeologists has been concentrating for over 40 years on the establishment of the lowest possible mining level at which limestone extraction does not threaten with the degradation of water-source capacity.

It was found during the stage of documenting the Czatkowice limestone resources that the groundwater tables were situated at the levels from +315 to +323 m asl and those in the east section of the quarry from +330 to +350 m (asl). It was established in the mid-1970’s that the +315 m asl level, being on the boundary of the lowest ordinate of the groundwater table, within the concession, was a safe mining level which would not affect the capacity of the Czatkowice Water Springs. In 1974, a groundwater-table monitoring system was implemented upon installation of piezometers in the “Czatkowice” quarry. Limestones started to be mined on the level in question in 1976. Small outflows appeared at the +315 m asl level in the east section of the quarry in the mid-1980’s. Their total output was increasing with time. Outflow water penetrated limestones at that level and that is why it was not necessary to drain the quarry. The present study discusses the issue of the origin of water appearing in the outflows of the “Czatkowice” quarry and how the outflows affect the Czatkowice Water Springs.

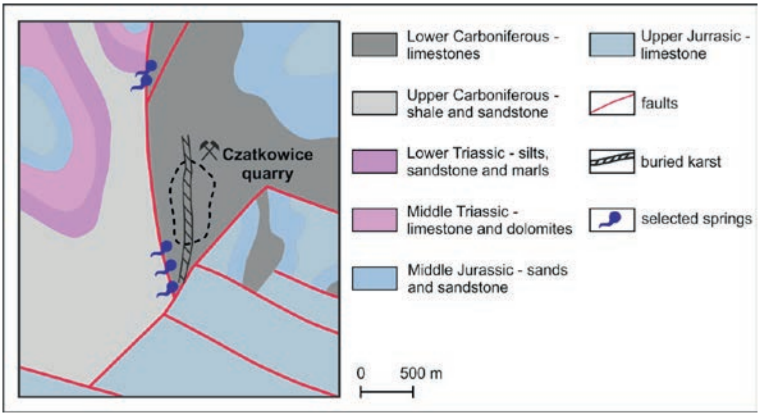

***Figure 1**. Geological map of the Czatkowice area (after Leśniak, Motyka 1991).*

## Geological and hydrogeological setting

The oldest indentified formations of Czatkowice belong to the Carboniferous rocks and they are of two types in lithological terms. The Lower Carboniferous formations consist of limestones and the Upper Carboniferous ones of coal-bearing clastic rocks. The Krzeszówka stream fault, running along the stream's valley, is the boundary of the outcrops of the Lower and Upper Carboniferous formations (Fig. 1).

Locally, the Triassic clastic and carbonate rocks and single sand shoals and sandstones of the Middle and Upper Jurassic limestones are situated on the Upper Carboniferous formations in the west wing of the Krzeszówka stream fault. The elevated west wing of that dislocation is formed by the Lower Carboniferous Czatkowice limestones, locally covered by the Middle Jurassic sands and sandstones and the Upper Jurassic limestones. The limestones mined in the "Czatkowice" quarry create a shear displacement structure, adjacent to the slope of the Krzeszówka stream fault (Fig. 2). They also constitute the main aquifer level in the quarry surroundings.

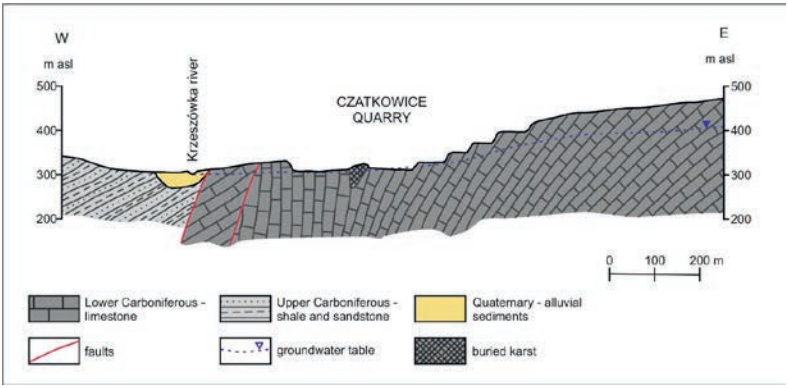

***Figure 2**. Geological cross-section of the limestone deposit area in Czatkowice (after Leśniak, Motyka 1991).*

The Czatkowice limestones contain an aquifer of the fissure-porous type (Leśniak, Motyka 1991). The porosity matrix is not essential for groundwater conductivity and storage. Hydraulic conductivity coefficients usually amount to $10^{-11}$ m/s (Borczak et al. 1994). Fractures in interbedding planes are the main groundwater conductivity and storage systems. They are characterised by a small hydraulic capacity of the fraction of a percentage point and fairly large conductivity. The fissure space filtration coefficients range from $6.7\times10^{-7}$ to $1.1\times10^{-3}$ m/s (Leśniak 1991).

The system of karst voids is very important for the development of water relationships in the "Czatkowice" quarry area. The drilling results indicated that the main system of karst channels that deliver water to the Czatkowice Water Springs is located about 45 m below the current water table in the quarry, i.e. at the level of ca. +260 m asl ordinate.

Two distinct vertical hydrodynamic zones can be identified in the quarry. In the upper one, reaching more or less the third mining level, i.e. ca. +370 m asl ordinate, numerous karst formations occur, developed mainly along the bedding planes, next to a thick network of fissures of various origins. Those are usually caverns with secondary karst clay filling (Fig. 3a). The other zone whose lower boundary is not known as it is located below the lowest mining level (+315 m asl) is primarily dominated by fissures and interbedding planes (Fig. 3b). Those are the main groundwater-flow channels. Small karst voids, partly filled with residual clays, developed along some of those fissures and interbedding planes. The previously mentioned karst channel systems are located in that zone. The Czatkowice source waters are flowing out of them.

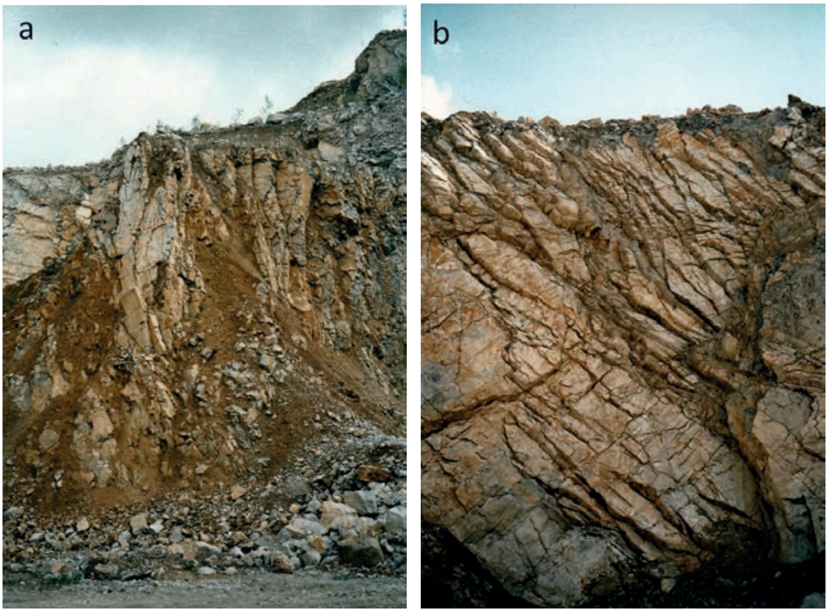

***Figure 3**. Vertical arrangements of the Czatkowice limestone layers in the "Czatkowice" quarry.*

## Water in the "Czatkowice" quarry

Several years after limestone mining had started at the +315 m asl level, small water outflows appeared under the east slope (Fig. 4a). Water sank into the ground after covering a short distance (Fig 4b). The total output of those outflows was insignificant and it was not measured because water quickly disappeared in the floor of the open-pit quarry. Monitoring of the output was implemented in 1991 and established at 4-5 L/s. That rate was maintained more or less until mid-1992. The outflow output strongly depended on precipitation and it ranged from 0.5 to 4.5 L/s in 2011. In 2012-15, however, despite such fluctuations, the total output ranged from 4 to 20.5 L/s (Fig. 5).

***Figure 4**. Water outflow in the "Czatkowice" quarry.*

Two different views have been expressed on the origin of the above-described outflows: (a) water is coming either from the saturation zone, i.e. due to the fact that an underground aquifer was cut through by a mine working; or (b) infiltrating water is flowing out. The first hypothesis was formulated on the basis that the groundwater table was indentified on the area. It was subjected to monitoring activities at various mining levels. The other hypothesis was formulated on the basis of the measurements of changing water-table levels at the piezometers distributed at various mining levels, the chemical composition of the water samples collected from those piezometers, and the essential geological factor: nearly vertical arrangement of rock layers (Fig. 3) that facilitates infiltrating water penetration along the interbedding planes into the open pit.

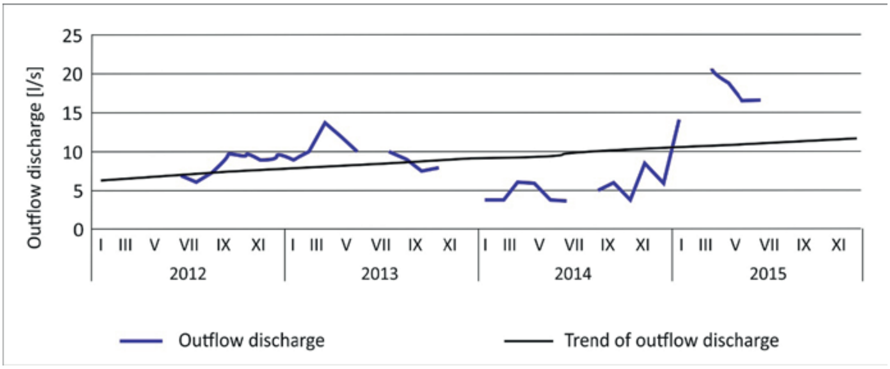

***Figure 5***. *Fluctuations of the capacity of water inflow (l/s) into the working at Sub-Level 310 in 2012-15.*

The amplitudes of water-table fluctuations in the piezometers placed in the first hydrodynamic zone reached 16 m. At the same time, large hydraulic gradients were recorded between the water levels at various piezometers distributed in that zone, reaching up to 16‰, which could indicate the presence of micro-reservoirs, with limited mutual hydraulic contact between them. In the second hydrodynamic zone, the amplitudes of water-table fluctuations were reaching only 6 m (Fig. 6).

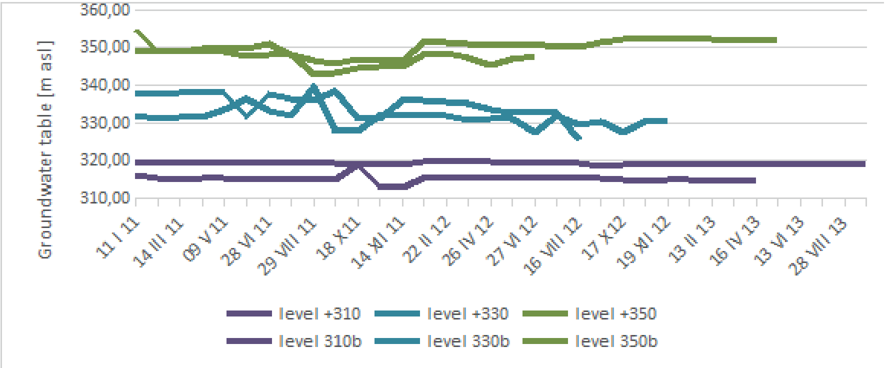

***Figure 6***. *Fluctuations of the water-table levels on the piezometers of the "Czatkowice" quarry.*

General mineralisation of two water samples collected from the piezometers at the level of 350 amounted to 212 mg/L and 259 mg/L, respectively. The type of less mineralised water was $CaHCO_3$, and that with higher mineralisation: $Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$. Water samples collected from five piezometers installed at the level of 330 represented higher mineralisation than those collected from the higher level of +350 m asl. The values ranged from 221 to 391 mg/L, and the water types were the following: $Ca\text{-}HCO_3$, $Ca\text{-}HCO_3\text{-}SO_4$, $Ca\text{-}Mg\text{-}HCO_3$, and $Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$. The last water group, collected from three piezometers located at the level of +310 m asl, represented the highest mineralisation, ranging from 426 to 453 mg/L. Waters belonged to the types of $Ca\text{-}HCO_3\text{-}SO_4$ and $CaHCO_3$. Mineralisation of quarry outflows ranged from 373 to 436 mg/L, while the hydrochemical types of water samples collected from those outflows were the following: $Ca\text{-}HCO_3$ and $CaHCO_3SO_4$. The chemical composition of water outflows in the quarry indicated a similarity to that of the second hydrodynamic zone samples.

It seems that the tendency of increasing outflow output at the level of +310 m asl, identified in recent years, supports the conception claiming that water is arriving from the aeration zone. The increasing outflow output was associated with the shift of the mining face, with the subsequent enlargement of the depression near the quarry. Since the floor of the mining level cuts through the groundwater table only in the east section, with its west section located above the water table, water originating from the outflows penetrates the pit bed and thus it is not required to pump it out of the quarry (Fig. 7).

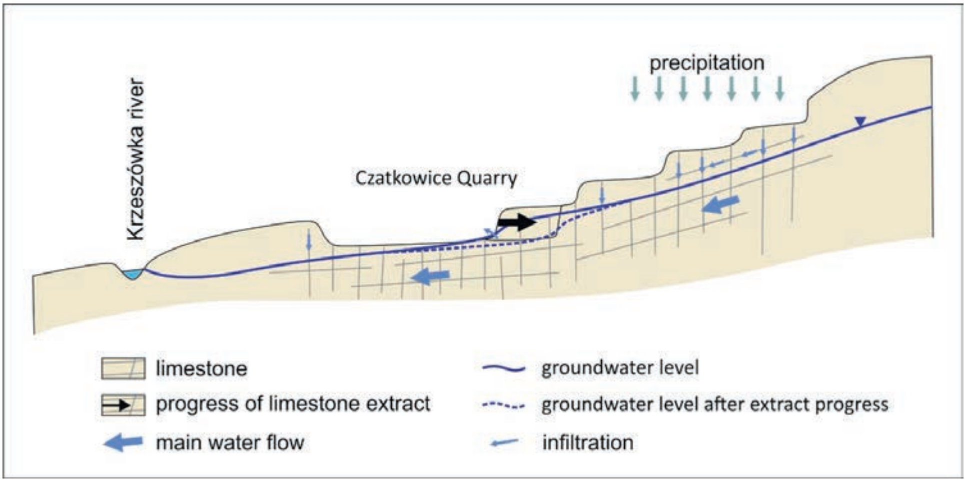

***Figure** 7. Water flows within the "Czatkowice" quarry.*

## Conclusions

The Lower Carboniferous limestones are mined in the "Czatkowice" quarry. They belong to the shear displacement structure and their layers are arranged vertically. The limestones create a fissure-porous reservoir of groundwater in which we can distinguish two vertical hydrodynamic zones. In the first one, located next to a thick network of fractures, numerous karst formations occur, usually in the form of caverns filled in with karst clays. In the other zone, the hydraulic network is composed mainly of the interbedding planes and fissures, with small and rare karst formations along.

In the east section of the lowest mining level, water is flowing out at several places. The outflows are integrated in one stream which penetrates the floor of the mining level at which the outflows occur. Consequently, no water removal from the open-pit quarry is required. The trend of the increasing total output of outflows, indentified in 2012-15, makes the authors of this study accept the hypothesis that the outflows originate from the saturation zone rather. The increasing outflow outputs are caused by the relocation of the mining face at that level in the eastern direction, with the enlargement of the depression located in that area (Fig. 7).

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# A Thallium-Contaminated Drinking Water Supply in an Abandoned Mining Area: an Environmental Health Hazard

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**Abstract** Sulphide ores in abandoned mine sites from the southern Apuan Alps (Italy) are known to carry significant thallium levels. In September 2014, thallium contamination was found in the tap water distributed in Valdicastello Carducci Village (southern Apuan Alps) (from 2 to 10 μg/L). The thallium-contaminated water that fed the aqueduct of this area originates from a spring located very close to the abandoned mining sites. In the present study, to assess the impact of thallium exposure in the inhabitants who used the contaminated tap water, thallium was quantified in hair, urine and saliva samples.

**Key words** Thallium, Human Contamination, Biomonitoring, Water Pollution, Abandoned Mines

## Introduction

Thallium (Tl) is a non-essential, highly toxic element. Its poisonousness to mammals is considered comparable to that of mercury, cadmium or lead (Rodriguez-Mercado et al. 2013).

The ingestion of Tl-contaminated drinking water represents the most likely pathway of exposure for humans. The U.S. Environmental Protection Agency (EPA) poses a maximum concentration level (MCL) of 2 μg/L for drinkable water. Hence, contamination processes of waters and soils by Tl may have serious consequences for human health.

A recent geological study (Biagioni et al. 2017) showed the presence of Tl at high concentrations (up to 37 μg/L) in a groundwater spring that fed the aqueduct of Valdicastello Carducci village and part of the aqueduct of Pietrasanta town (southern Apuan Alps). The source of Tl has been identified in the Tl-bearing pyrite ores occurring in the area. The spring is indeed located between two abandoned mines, in an area characterized by the widespread occurrence of baryte, pyrite, magnetite, hematite, and iron hydroxide mineralizations (Biagioni et al. 2017). Recent geological studies show Tl concentration levels up to ≈600 μg/g in the pyrite ores of the study area (D'Orazio et al. 2017). Pyrite ores are subjected to both biotic and abiotic oxidation processes releasing Tl and other metals (e.g. Fe, As, Sb, Pb, Zn, Cd etc.) into the aquatic environment. Acid drainages from the abandoned mining tunnels typically contain 200-1000 μg/L of Tl, while some very acidic (pH = 1.5-2.0) water ponds inside the tunnels can reach even more extreme Tl levels, up to 9000 μg/L.

In September 2014 a substantial Tl contamination was also found in tap water distributed in Valdicastello Carducci village and in part of Pietrasanta town and in October 2014 local authorities replaced the contaminated spring with a Tl-free source. A geochemical survey of the contaminated spring is currently in progress in order to assess the origin of Tl contamination in the spring.

The goal of our work was to assess the impact of Tl exposure as a result of tap water contamination in Valdicastello Carducci and Pietrasanta. For this purpose, we quantified Tl levels in 45 saliva, 150 urine and 318 hair samples from the population living in the contaminated area and thallium values found in biological samples were correlated with Tl concentrations found in tap water. Thallium concentrations in the different matrices was measured by inductively coupled plasma—mass spectrometry (ICP-MS). Urine and hair represent convenient matrices due to their straightforward sample collection, sufficient quantities for analysis and ethical approval for sampling. The exposure to metals and metalloids is reflected in elevated concentrations in the hair, which provides informations about long-term exposure, while urine was chosen as model matrix indicative of short-term exposure (Gil et al. 2015).

## Methods

### Sampling

In the studied area the drinking water was supplied by a spring (Molini di Sant'Anna) located very close to an abandoned mining site (Fig. 1). Water samples were collected from six public tap fountains (Fig. 1), which are representative of the water distributed in each single house in the area considered.

Water samples were collected without filtering and acidified with 1% $HNO_3$.

A total number of 150 subjects provided a urine sample. Urine samples were frozen at –20 °C. Before the analysis, the samples were defrosted, centrifuged (5000 rpm for 10 min) and diluted 1: 10 with 2% $HNO_3$.

A total number of 318 subjects provided a hair sample. Hair samples with a length ranging between 3-15 cm were collected, cut in pieces and mixed. Considering that the hair growth is about 1-1.5 cm/month, Tl quantitation in hair evidenced an average exposure of 2-7 months. About 200–300 mg of hair from each sample were weighed into Teflon vessels, washed three times with 1:1 acetone/ultrapure water and pre-digested for 1 h at room temperature with $HNO_3$ (6 mL, 69 % w/w) and $H_2O_2$ (2 mL, 30 % w/w). Then, the vessels were placed in the microwave oven for the digestion (up to 200°C). After cooling at room temperature, samples were quantitatively transferred into 50-mL flasks and diluted with ultrapure water up to 50 mL. Samples were stored at room temperature.

### Instrumentation and method

A quadrupole ICP-MS Agilent model 7700 (Agilent Technologies) equipped with a collision cell system was used for water and biological sample analysis. A solution of 10 µg/L iridium in 2% $HNO_3$ was used as internal standard.

Samples and standards were analyzed in triplicate. The limit of detection (LOD), based on the mean of the blank samples from all runs plus three times its standard deviation, was 2 ng/L for aqueous samples. To evaluate the accuracy a water sample certified for Tl (NIST1640A) was analyzed. The certified concentration of Tl reported for was 1.619 ± 0.016

μg/L, and the concentration that we found was 1.61 ± 0.08 μg/L. In addition, for the urine samples, the method was validated analyzing a certificate sample of lyophilized urine (NIST 2670, certificate Tl concentration = 5.417 ± 0.064 μg/L). The Tl concentration value found was 5.34 ± 0.11 μg/L (n=6, RSD% 2.06). The LOD for urine was 20 ng/L. Currently, hair reference materials certified for Tl are not commercially available. Thus, the commercially available hair European Reference Material ERM-DB001 certified for seven metals and metalloids (As, Cd, Cu, Hg, Pb, Se, Zn) was spiked with Tl in order to evaluate the matrix effect. We spiked the certified material before the digestion procedure with 250 μL of Tl standard solution (final concentration 81.0 ng/g). We found a Tl concentration of 79.6 ± 4 ng/g, corresponding to a recovery of 98.3% (6 replicates, RSD% 5.5%). The LOD for hair was 0.6 ng/g. Hair washing, digestion, and ICP-MS analysis were repeated three times for 7 samples, to estimate the reproducibility of the entire procedure. The maximum relative standard deviation obtained was 11%.

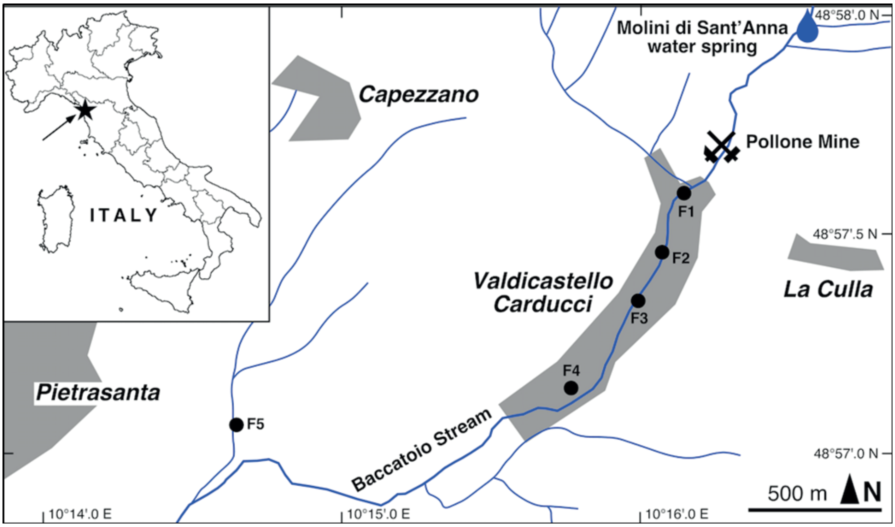

***Figure 1*** *Sketch map showing the localities cited in this work. F1 to F5 are the public fountains whose water was analyzed for this study (fountain F6 is located close to the Pietrasanta cemetery, outside the map); Molini di St'Anna is the contaminated spring that fed the aqueduct.*

## Results

Figure 2 shows thallium concentrations measured in tap water from Valdicastello and Pietrasanta in September 2014. Water analysis revealed Tl concentrations ranging from 1.77 to 10.1 μg/L. The Tl contamination level in tap water was higher in upper Valdicastello > medium> lower ≈ Pietrasanta.

Until September 2014, the drinkable-water distribution system of Valdicastello Carducci (and, thus, also the public fountains F1 – F5) was fed by a single water spring which lies within the abandoned mining area (Molini di Sant'Anna, see Fig. 1). The same spring also fed about 10% of the drinkable water distribution system of Pietrasanta (public fountain

F6). This spring was found heavily contaminated by Tl (from 5 to 37 µg/L). On October 3rd, 2014 local authorities excluded the contaminated spring from the distribution system.

Fig. 3 shows the frequency distribution relative to thallium concentrations measured in urine samples sampled in October 2014. The 36% of the examined population (N=150) had Tl urine concentrations below 0.4 µg/L, the 49% between 0.4–1 µg/L and in the 15% of the population Tl exceeds 1 µg/L. Tl concentration ranged from 0.046 to 5.44 µg/L, with a mean value of 0.74 µg/L ± 0.67 µg/L. The maximum Tl concentration (5.14 µg/L) is 600 times higher than the Tl urinary mean value reports for European Union.

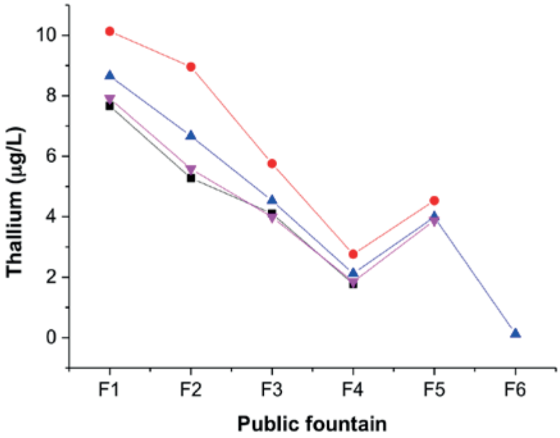

***Figure 2*** *Levels of Tl measured in tap water collected during four sampling in September 2014 from public fountains in Valdicastello and Pietrasanta (F1-F2: up part of the village; F3-F4: middle part of the village; F5: down part of the village; F6 located in Pietrasanta)*

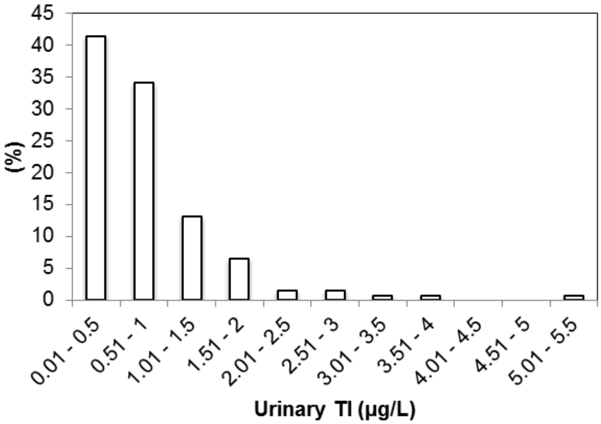

***Figure 3*** *Frequency histograms of the raw data set of Tl concentration (µg/L) found in the urine of 150 subjects.*

Thallium concentration found in saliva sample was between 0.03 to 3.48 µg/L, while salivary Tl level found in unexposed subject was below 0.04 µg/L. To the present day, there are not reference values for Tl in saliva.

Fig. 4 shows the frequency distribution relative to thallium concentrations measured in hair samples sampled in October 2014. Thallium levels in hair (N = 318) ranged from 1 to 498 ng/g, with a mean value of 41 ng/g ± 68 ng/g.

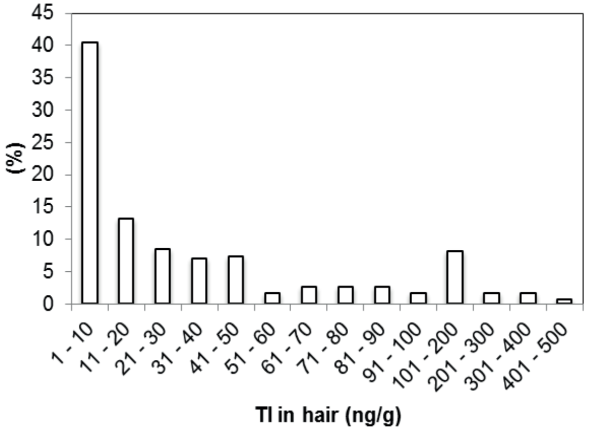

***Figure 4*** *Frequency histograms of the raw data set of Tl concentration (ng/g) found in the hair of 318 subjects.*

By providing the data of Tl concentration found in hair and urine samples according to the residence of the subjects, the upper area of Valdicastello emerged as the major area of exposure (data not shown). This trend is analogous to that found in the tap water, where the fountains in the upper area of Valdicastello were the most contaminated by thallium (Fig. 2). This suggests a correlation between Tl levels found in hair and urine and Tl concentration in tap water.

## Conclusions

Thallium is an emerging pollutant. The widespread use of Tl, and its subsequent release into the environment, has led to an increase in Tl levels in several ecosystems and trophic chains, increasing its exposure to humans and other living organisms. Moreover, its presence, with other potentially toxic metals, close to mines, has been demonstrated. As no regulation exists from EU Authorities, this issue has to be carefully considered.

The present study investigates the accumulation of Tl in a population living in the southern Apuan Alps (Italy) where drinking water was contaminated by thallium. Hair, saliva and urine are suitable matrices for non-invasive exposure assessments in human population. Our findings indicate that people resident in the contaminated area of Valdicastello Carducci and Pietrasanta significantly accumulated Tl in their hair, urine and saliva compared to the reference values of Italian population and to the values of unexposed people. About 50% of urine samples had a thallium concentration value above 0.5 mg/L; about 70% of hair samples had a thallium concentration > 10 ng/g. The high values of thallium found in hair samples suggest a long-term exposure.

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# Uranium Removal via Sorption Using Peat and Waste Digested Activated Sludge

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**Abstract** Uranium is a toxic metal used in atomic energy production. Uranium contamination within, or emanating from mine sites can pose a threat to the environment and exposure to uranium is hazardous to health. Although several methods are already available for uranium removal from aqueous solutions, there is still a need for developing alternative, cost-effective and recoverable techniques to deal with the continuing problem of environment contamination. This study focuses on uranium removal by adsorption using widely available, natural sorbents, namely peat and waste digested activated sludge (WDAS) from municipal wastewater treatment.

**Key words** Waste digested activated sludge, peat, adsorption, fed-batch reactor, hydraulic retention time

## Introduction

The global exploration and mining industry currently faces the challenge of discovering and extracting metals from increasingly complex and low grade ores, while still meeting increasing expectations for community acceptance and compliance with principles of ecologically sustainable development. Uranium is an important metal for nuclear energy security. However, the mining of uranium lead to the generation of mine tailing that has low concentration of uranium. On the other hands, the presence of uranium at low concentrations in polymetallic ore deposits is a challenge, as uranium poses threats to humans and the environment due to its chemical and radiological toxicity. Thus, the removal and recovery of uranium from such wastewater will not only prevent the environmental damage but also provide secondary source of uranium.

In 2008, the U.S. Environmental Protection Agency (EPA) set the standard for maximum contaminant levels for uranium in drinking water as 30 µg/L. The World Health Organization (WHO) subsequently revised the recommended limit upwards from 15 µg/L to 30 µg/L in 2011, since according to human studies no clear evidence was found of adverse health effects below that concentration. However, the evaluation of maximum contaminant levels is based on the chemical toxicity of uranium to the kidney instead of its radiological toxicity.

The uranium present in the wastewater is removed by methods such as adsorption, coagulations, precipitation, membrane exchange and chemical or biological reduction (Li et al. 2012). However, some techniques such as coagulation suffers from lower removal rates, chemical reduction methods are not at mature stage on implementation while adsorption in some cases suffers from high cost. In general, adsorption is an efficient method for the removal of contaminants at low concentration from large volume wastewaters (Hua et al. 2012), which would fit perfectly for removal of uranium from mining wastewaters. The cost-effectiveness of the method can be improved by the use of adsorbents which are produced in large volumes and at low cost.

The activated sludge treatment plants produces large quantity of sludge, where the waste sludge is generally digested under anaerobic process for energy production (Guo et al. 2013). The waste digested activated sludge (WDAS), remaining after the anaerobic digestion process, is generally discarded on land as fertilizer. This WDAS, a waste by-product and present in large quantity, has potential to be a good adsorbent for removal of uranium (Al-Qodah 2006), however, there are no studies that explored this possibility.

As conclusion, adsorption and desorption is a fast and cost-effective process for the removal and recovery of uranium from low concentration, high volume waste streams such as mining wastewaters. This study focuses on uranium removal by adsorption using widely available, natural sorbents, namely peat and WDAS from municipal wastewater treatment.

## Peat as an adsorption material

Peat is typically an acidic and heterogeneous organic substance and the quality will vary depending on the physical, chemical and biological properties. These properties include plant origin, elemental content, decomposition degree, pH, cation exchange capacity, hydraulic conductivity, porosity and surface area (Heikkinen et al. 1995, Vymazal 1998). Generally, peat is a complex material with cellulose, hemicellulose and lignin as major constituents. Lignin and humic acid in particular have polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides and ethers that can be involved in chemical bonding (Chaney and Hundemann 1979).

In Finland, well-decomposed Carex-Sphagnum peat types with high caloric values are mostly used for energy production. On average, peat has accounted for 5-7% of the total energy consumed in Finland. Also, Sphagnum peat of different decomposition rates are used in agriculture, cultivation, as a growing media in seedling production, tree nurseries, gardening, landscaping and largely in environmental impact management. The important properties of weakly decomposed Sphagnum peat include the porous structure with high water retention capacity, low pH and nutrient content, allowing plant-specific fertilization, no sources of plant diseases, pests or weeds. Weakly decomposed peat has a large specific surface, up to 26.5 $m^2/g$ using the nitrogen adsorption method, and a pore volume of more than 90% (Poots and McKay 1979). These properties alone create a high liquid-retention capacity and thus peat has been used in agriculture for manure handling and soil improvement material, composting and as soil litter in different types of farming (Iivonen 2008).

Peat has also been used for the purification of municipal and industrial wastewaters contaminated with dissolved metals. Also, thermally treated peat has been used in the prevention of oil spill related damages because the thermally treated peat absorbs oil but not water.

Peat can also be used in mechanical filters to remove solid particles from the air. Generally, the large surface area of peat removes metal ions, for example, by ion exchange and adsoption. Because of the specific structure and character of the peat, the adsorption potential is high. Peat can provide an effective medium for retention of nitrogen, phosphorus and suspended solids (Kieckbusch and Schrautzer 2007), dissolved metals such as aluminium, iron and nickel (Brown 2000, Räisänen et al. 2001), metals such as Cu, Cd, Zn, Pb, Fe and U(VI) ions (Couillard 1994 and references within that paper, Zhirong and Shaoqi 2010), metalloids such as arsenic (Palmer et al. 2015), pesticides (Roseth and Haarstad 2010), oils and odours (Iivonen 2008).

## WDAS adsorption methods

The activated sludge treatment plants used widely for treatment of municipal and some industrial wastewaters produce large quantity of excess waste sludge, which is often anaerobically digested to produce biogas (Appels et al. 2008). The WDAS, remaining after the anaerobic digestion process contains nutrients (e.g. nitrogen and phosphorus) removed from the wastewaters and could be used as agricultural fertilizer. However, municipal wastewater sludges and their digestates can contain trace levels of metals and organic pollutants as well as pharmaceutical residues (Suominen et al. 2014, Mininni et al. 2015) and therefore their land use is restricted in some countries. Because of this WDAS disposal can be a significant cost factor for wastewater treatment plants due to the high quantity of WDAS generation. However, as WDAS consists largely of residues of microbial cells, which have large variety of functional sites such as carboxyl, amino, phosphate and hydroxyl moieties on their surfaces, this waste by-product is a potential adsorbent for metals such as uranium. The use of activated sludge and digested sludge as a biosorbent for removal of metals such as cadmium, copper, lead, nickel and zinc has been studied widely (Bux et al. 1999, Lister and Line 2001, Al-Qodah 2006), but to our knowledge the use of WDAS for biosorption of uranium has not been previously reported.

### General methods

Uranium reference standard solution (1000 mg/L) purchased from AccuTrace™ was used as uranium stock solution. All standard solutions were prepared in Milli-Q water and stored at 4-8 °C until use, as were the stock solutions. All other reagents were of commercial p.a. quality. Uranium and other element concentrations in synthetic water samples and solid peat samples were analyzed by S2 Picofox Total Reflection X-ray Fluorescence spectrometer (TXRF, Bruker).

In the case of peat, two-meter-long (diameter ca. 10 cm) sample column was collected from a drained Varkaansuo peatland in Kurkimäki nearby Kuopio. Peat samples for adsorption studies were selected from the top (Peat1), bottom (Peat 5) and three in the middle (Peats 2-4, depth: 0.5, 1.0 and 1.5 m) of the peat column representing different peat types and decomposition degrees of organic material. Typically, ca. 0.4 g of peat was mixed into 100 ml of water containing 10 mg $L^{-1}$ of uranium for 60 min.

WDAS used in this study was obtained from Viinikanlahti municipal wastewater treatment plant in Tampere. WDAS adsorption experiments were conducted in batch-type shake flaks with ca. 0.2 g (as volatile suspended solids) of WDAS varying initial solution pH (2.2-4.5), uranium concentration (3.3-119 mg $L^{-1}$) and reaction time (0-960 min), and in 900 mL fed-batch reactor operated with 3.1 mg $L^{-1}$ of uranium at initial uranium solution pH of 3.2 and varying hydraulic retention times (15-60 min). The experiments were conducted at room temperature (20±2 °C).

## Result and discussion

In the case of peat, metal concentration of peat samples 1-5 were measured by using TXRF instrument. As shown in figure 1, amounts of metals are increased from top to bottom. Especially calcium, iron, strontium and lanthanum concentrations are increased dramatically (note that scale in figure 1 is logarithmic).

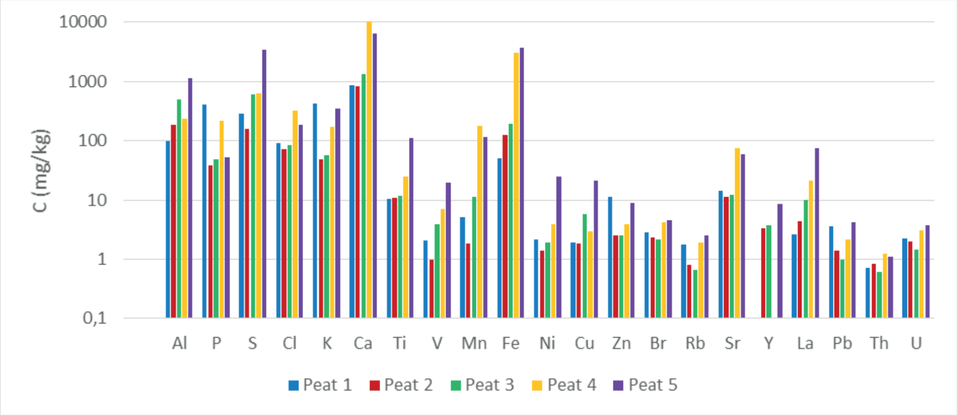

***Figure 1**. Element concentrations in peat samples.*

In batch experiments with peat 96-100% of uranium was removed from the artificial sample solutions. All peat samples removed uranium effectively (Table 1), but the best removal was achieved with peat sample taken from 0.5 m depth. Removal of uranium took place slightly better at pH 7, but functioned well also at lower pH's (e.g. pH 3 in Figure 2).

The equilibrium adsorption capacity (Qe) of WDAS was 100 mg of uranium adsorbed per g of WDAS. The adsorption edge was found at pH 3.0 suggesting the applicability of the WDAS for the mining wastewaters which are generally acidic. Moreover, the fed-batch reactor with WDAS enabled more than 90% uranium removal efficiency even at a very short hydraulic retention time of 15 minutes.

## Conclusions

This study indicates that both peat and WDAS are promising options for uranium removal from acidic mining wastewaters and provides a proof-of-concept for the development of a fed-batch system for WDAS based uranium removal.

***Table 1**. Removal of uranium by using peat.*

| | | Removal-% | |
|---|---|---|---|
| **Adsorbent** | **Depth (m)** | **pH 3** | **pH 7** |
| Peat 1 | 0 | 97,6 | 99,3 |
| Peat 2 | 0,5 | 97,8 | 99,9 |
| Peat 3 | 1 | 92,4 | 99,4 |
| Peat 4 | 1,5 | 97,4 | 99,2 |
| Peat 5 | 2 | 96,5 98,9 | |

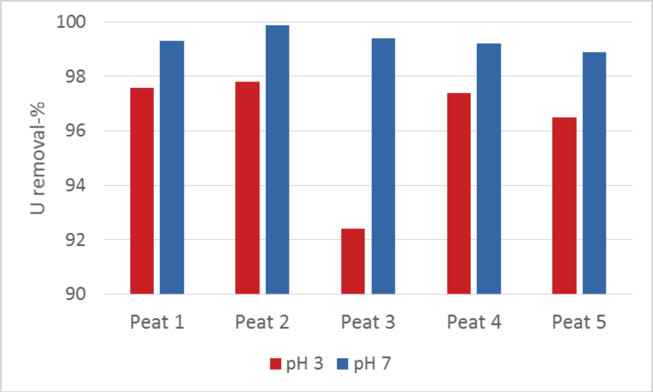

***Figure 2**. Removal of uranium by using peat.*

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# Geochemical and Mineralogical Characterization of Gold mine tailings for the potential of acid mine drainage in the Sabie-Pilgrim’s Rest Goldfields, South Africa

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**Abstract** The environmental hazards arising from active and abandoned mine tailings are a cause for concern. We report on the presence of mineral-related environmental hazards in both Glynn Lydenburg and Nestor mine tailings, approximately 6 km apart and located in the Mpumalanga Province of South Africa. Based on XRD, shows a wide range of minerals: pyritic sulphide, quartz and mica. The XRF results showed that quartz was the dominant oxide in both the mine tailings; followed by $Fe_2O_3$ and $Al_2O_3$. Furthermore, trace elements, such as As, Cr, Cu, Pb, V and Zn, were also found which are hazardous to the environment.

**Key words** Acid Mine Drainage, Mine Residues Deposits, environmental hazards

## Introduction

Mining is one of the most important economic activities in South Africa. The country receives huge economic benefits from the mining industry. However, different kinds of mine residue deposits (herein referred to as mine tailings) associated with the extraction and processing of metals which have accumulated stand out as sources of potential environmental pollution in specific mining areas and the country at large (McCarthy 2011). For coal and gold mining operations, these mine tailings are a continuous source of acid mine drainage (AMD) generation (Kleinman et al. 1981; Oberholster et al. 2013) and an environmental hazards (Rosner et al. 1998; Nelushi et al. 2013).

The Sabie-Pilgrim’s Rest goldfield, Mpumalanga is one such area where gold mining activities occurred in the past. The area has various mine tailings of different ages and sizes. What is key here is that a few or no environmental studies had been carried out on mine tailings; hence this study focused on the Nestor and Glynn Lydenburg Gold mine tailings. The main objective of this study was to determine the mineralogy and the geochemistry of mine tailings.

## Methods

### Location of the study area

The Nestor (NS) and Glynn Lydenburg (GL) mine tailings, are located in the Sabie area of the Mpumalanga Province of South Africa (Fig. 1).

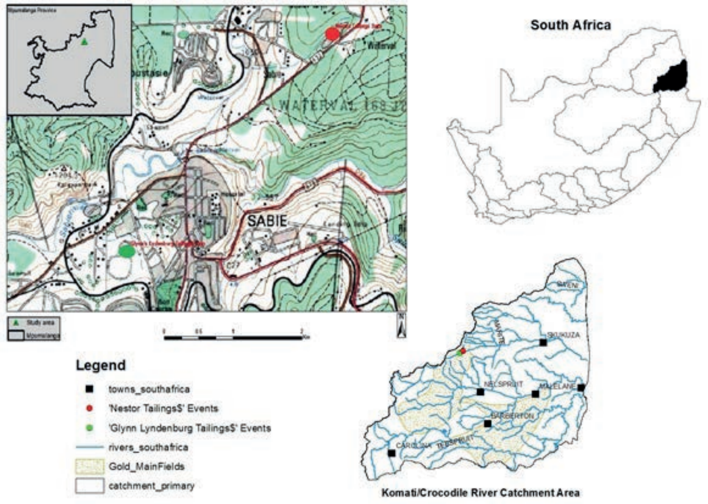

***Figure 1*** *Location of the Study Area*

## Sampling

Thirty tailings profile samples and five grab samples were collected at mine tailings from 20 to 23 February 2015. A truck-mounted and a hand auger were used at GL (drilling to 10 m) and NS (drilling to 3 m) respectfully. The collected samples were sent to the Council for Geoscience's laboratory in Pretoria, South Africa, for analysis.

## Sample preparation and quality control

The samples were then ground using milling pots made of carbon steel to minimize the level of contamination on a single swing mill (TM-SPR003 ) method which involved air drying, crushing and milling of samples to a size reduction of <75 µm. In between milling, the equipment was washed using distilled water and wiped with the disposable paper towels wetted with ethanol and then allowed to dry to avoid the contamination of samples.

## Geochemical and mineralogical analysis

The samples were analysed by X-ray florescence spectrometry (XRF) and X-ray diffraction spectrometry (XRD) according to procedures of USEPA (1986). The glass disks and wax pallets were analyzed using a PANalytical wavelength dispersive AXIOS X-ray fluorescence spectrometer that was equipped with a 4kW Rh tube. Both major and minor elements have been determined and reported as oxides and trace elements.Quality control/Quality assurance (QC/QA) was done using the in-house amphibolite reference material (sample 12/76). Furthermore, one in every ten samples was duplicated during sample preparation. The X-ray diffraction (XRD) technique employed scanning from 2 to 70° $2\theta$ $Cu_{K\alpha}$ radiation at a speed of 0.02° $2\theta$ steps size/0.5 sec, with a LYNXEYE detector and generator settings of 40 kV and 40mA. Semi-quantitative approximations of the minerals present were based on the relative peak heights to area proportion according to Brime (1985).

### ICP MS analysis

The milled samples were weighed and transferred to a 100 ml glass beaker, where acids HCl and $HNO_3$ (mixture) were then added and heated on hotplate in fume hood. The mixture was cooled and then was transferred to a 100 ml volumetric flask and then this was topped to the mark with deionised water. The acid digests samples were analysed using the ICP-MS (Perkin Elmer Elan 9000, Weltham, USA) in triplicates.

## Results and discussion

### Geochemistry of mine tailings

The three dominant oxides in both tailings materials are $SiO_2$, $Fe_2O_3$ and $Al_2O_3$. CaO (average ≈5.4%) is the fourth abundant oxide in Glynn Lydenburg tailings whereas $TiO_2$ and $K_2O$ are the fourth abundant oxides in the Nestor tailings materials (Fig. 2A). It is important to note herein that the concentration of CaO in most samples of the Nestor tailings is <0.05 % with a few samples showing higher concentration ranging from 0.3 to as high as 3.2% which brings the overall average concentration of CaO in the Nestor tailings to 0.45% which still is significantly lower than that of the Glynn Lydenburg tailings which contains an average concentration of 5.4 % CaO. MgO is also high in Glynn Lydenburg tailings with an average concentration of 3.6% compared to that which is in Nestor tailings (average ≈0.33%). The chemical composition therefore shows that the Glynn Lydenburg mine tailings material shows high acid neutralizing capacity due to its high calcite percentage compared to the Nestor mine tailings material (Figure 2B).

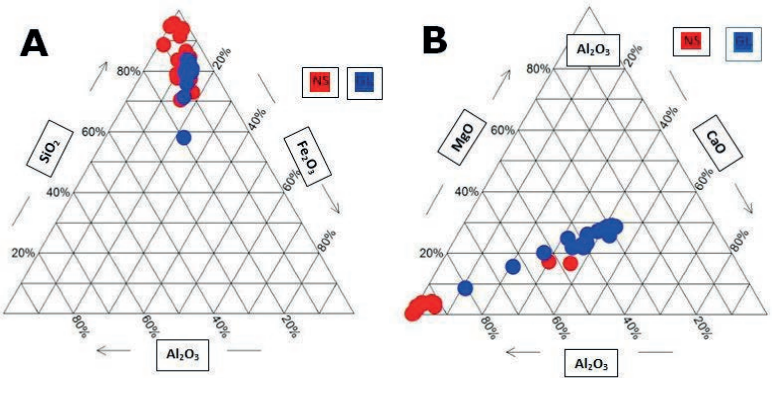

***Figure 2*** *Distribution of (A) dominant oxides (B) dominant neutralizing oxides and acid-forming oxide in Nestor (NS) and Glynn Lydenburg (GL) mine tailings*

The concentration of aluminum oxide ($Al_2O_3$) and ferric oxide ($Fe_2O_3$) increases with depth indicating the progressive decrease of oxidation with depth which in turn indicates the decrease in availability of oxygen with depth.

Trace metals such as Cu, As, Cr, Ni, Pb, V and Zn occur within the mine tailings (Tab. 1) in excess of South African guidelines soil screening levels, National Norms and Standards for

Remediation of Contaminated Land and Soil Quality in the Republic of South Africa (DEA, 2013).

***Table 1*** *The distribution of metals and As at the mine tailings (range, ppm), average values are shown in brackets*

| Metal | Nestor | Glynn Lydenburg | All land uses, protective of water sources | Informal residential | Standard residential |
|---|---|---|---|---|---|
| As | 137-1599 (599) | 807-2502 (1471) | 5.8 | 23 | 48 |
| Cu | 34-571 (154) | 10-104 (30) | 16 | 1100 | 2300 |
| Cr | 43-273 (172) | 117-238 (140) | 6.5 | 6.5 | 13 |
| Pb | 12-276 (54) | 13-63 (37) | 20 | 110 | 230 |
| Ni | 16-157(53) | 45-132 (66) | 91 | 620 | 1200 |
| V | 29-255 (140) | 56-235(82) | 150 | 150 | 320 |
| Zn | 7-485 (73) | 90-240 (150) | 240 | 920 | 19000 |

This is likely to result in As poisoning through water pollution, dust inhalation and contamination of the food chain as especially evident in the Nestor tailings storage facility, which is highly weathered and exposed to erosion yet lying adjacent to Sabie River. According to Harada (1996), a concentration of 100 mg/kg As in soil can reduce crop yield by 90% and lead to As poisoning, which results in diseases such as skin and lung cancer. Other possible effects associated with As poisoning are cardiovascular disease and diabetes (Centeno and Finkelman 2007). Copper provides essential micronutrients to plants, animals and humans. Nevertheless a Cu concentration in water over 30 ppm may result in liver, kidney and blood cell damage (DWAF 1996), hence the likely environmental disaster. The total Cr levels including $Cr^{6+}$ were high and may have a negative impact on the environment. $Cr^{6+}$ is more toxic than $Cr^{3+}$, with a $Cr^{6+}$ concentration of more than 0.5 g/mL being considered as having a negative effect (Alloway and Ayres 1998). In addition the excessive ingestion of $Cr^{6+}$ is carcinogenic. The concentration of Cr was in the range of 10-19 mg/kg which is in suitable range for plant growth (Alloway and Ayres 1998). The Zn levels may have a negative impact on the aquatic environment. The Pb levels though lower in Glynn Lydenburg mine tailings than Nestor are still able to contaminate the aquatic environment (Ngole-Jeme et al. 2017). The high V levels are likely to impact negatively on the environment (Luo et. al. 2017). Generally, a Zn content of over 15 ppm of water is considered toxic and can result in renal damage. Furthermore, a deposition of Zn salts into fish gills can lead to their death (USEPA, 2009).

## Mineralogical analysis of mine tailings

The mineralogical composition (primary and secondary minerals) based on X-ray diffraction as expressed in weight percent (wt %) of bulk samples show variation among the Nestor and Glynn Lydenburg mine tailings (Fig. 4). The primary minerals for tailings are defined by Jambor (1994) as the ore and gangue minerals processed and deposited in an impoundment without any changes other than reduction in grain size by comminution. Alpers et al.

(1994), define secondary minerals as those minerals formed by processes that lead to precipitation, such as evaporation, oxidation, reduction, dilution, mixing and neutralisation.

Quartz is the dominant mineral here and showed an almost constant trend throughout the mine tailings. This can be attributed to its dominance in the original tailings as well as to its high resistance to physical and chemical weathering and dissolution. The important primary minerals to consider for the purpose of this study (for acid generating potential vs. neutralization potential of the materials) are pyrite, calcite, and dolomite. The Glynn Lydenburg samples show low pyrite (0.73%), high calcite (4.4%)and very high dolomite (19%) compared to the Nestor tailings materials which are composed of high pyrite (4.2%), very low calcite (0.01 %), and 0.96 % of dolomite. The associated secondary minerals are gypsum, Jarosite and goethite all of which are higher in concentration in Nestor tailings materials than that of which are in GL. This mineralogical data shows the high net acid generating capacity of the Nestor tailings compared to the Glynn Lydenburg ones.

Jarosite and Gypsum are the dominant secondary minerals on top layers (first top 5 samples) of the tailings at Nestor Mine. Furthermore, Goethite, a secondary oxide mineral, is absent from the grab samples collected from Nestor tailings but observed in high concentrations in the samples from the deeper part of the auger hole. Gibbsite is also not present in all Nestor mine tailings samples except for the one recorded at un-oxidized part of the tailings at about 2 m depth in one of the auger hole samples. Minerals such as quartz have no potential to neutralize acid due to their physical property (hardness) and their low relative reactivity rate of 0.004 that is twice slower than the relative reactivity rate of kaolinite (Sverdrup 1990; Kwong 1993).

Pyrite ($FeS_2$) and hematite are the major acid producing minerals. Mica is also common in high concentrations in both samples collected using handheld auger and grab samples. There is irregular trend in handheld auger drilled samples with some showing a decrease with depth which might be due to original mineralogical variation of the tailings deposits. Jarosite is a secondary mineral from oxidation of sulphides and it precipitates during evaporation of acidic, iron, and sulfate-rich water within mine waste material and store acid generated by oxidation process. The dissolution of soluble and less soluble iron sulfate minerals also contribute to the acid mine drainage; however, most of the AMD from sulphide-bearing geological formations are from oxidation of sulphide minerals (Lapakko 2002).

Calcite is very low or absent in the Nestor Mine tailings with dolomite only found in two oxidized grab samples thus indicating that these tailings have high acid generating potential which has the potential to generate acidic discharge which may result in adverse conditions for the growth of plants and grass. The tailings from Glynn Lydenburg are comprised of quartz and dolomite [$CaMg(CO_3)$] as major mineral assemblages (Fig. 4B). Other primary minerals that are acid neutralizing include mica and plagioclase. Gypsum and goethite are also present as secondary and neutralizing minerals, while the absence of jarosite in Glynn Lydenburg mine tailings could be attributed to the high neutralizing capacity of the materials due to the high concentrations of carbonates within the Malmani dolomite host rocks.

Plagioclase is mainly found in truck-mounted auger samples and showed a constant trend of decreasing with depth. Mica being common in all three drilled holes including handheld auger samples also showed a decrease with depth trend.

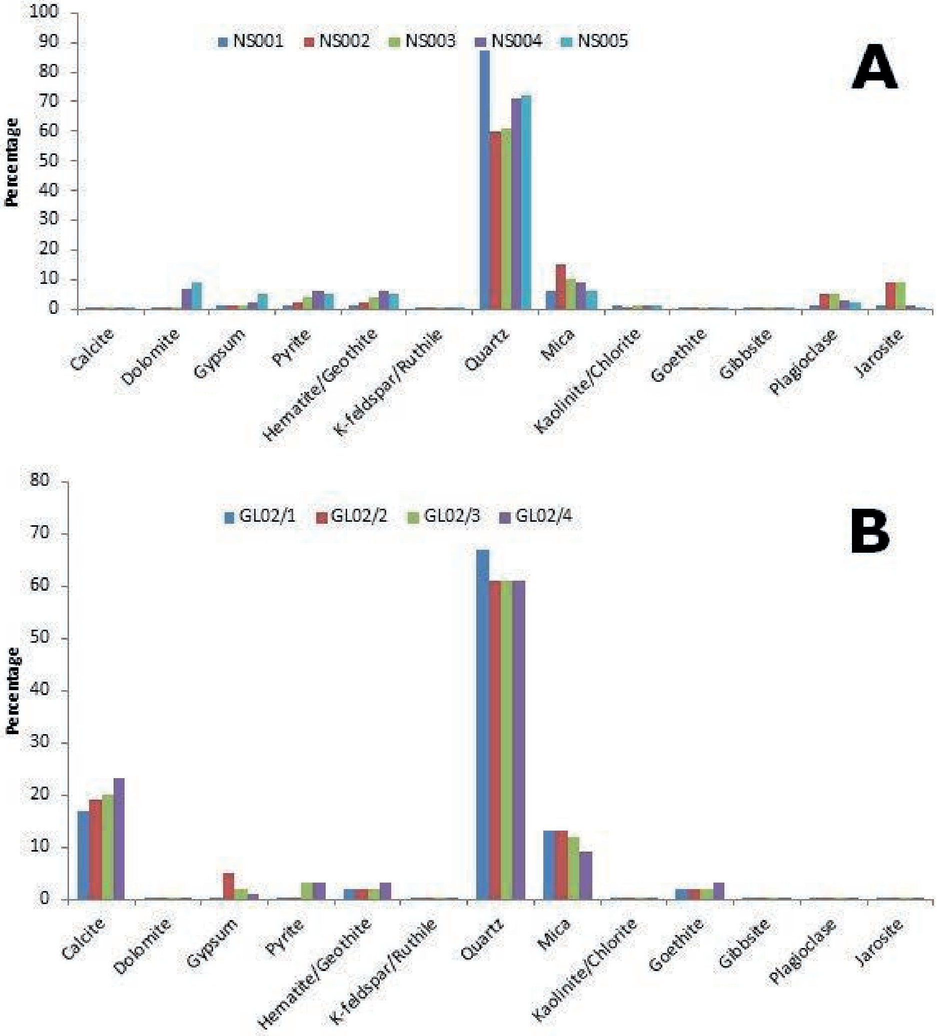

***Figure 4*** *The mineralogical analysis of (A) Nestor and (B) Glynn Lydenburg mine tailings*

## Conclusions

The study showed that the metal mobility was enhanced by the net acid generating capacity of the Nestor mine tailings. Whereas the alkaline conditions of the Glynn Lydenburg mine tailings lead to a non-acidic discharge. The presence of metals, metal oxides, neutralizing oxides and acid-forming oxides in the mine tailings are likely to have negative impact on the environment.

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# Water resources degradation by acid mine drainage: the Sancho Reservoir (Odiel River Basin, SW Spain)

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**Abstract** The Sancho reservoir (58 $hm^3$ of storage capacity) in the Odiel River Basin is an extreme case of AMD pollution. The reservoir receives acid leachates from the Tharsis mines, provoking low pH values and high dissolved metal concentrations. Although mining ended in 2001, a progressive worsening of the reservoir water quality has been detected since 2007. This seems to be linked to the uncontrolled dumping of milled pyrite wastes from nearby industrial facilities. Changes in AMD pollution levels in the main river feeding the reservoir were not apparent due to its high hydrological and hydrochemical variability, typical of the Mediterranean rivers. The monitoring of receiving water bodies, such as reservoirs, allows a more reliable detection of trends in water quality.

**Key words** Iberian Pyrite Belt, sulphides, water pollution, metals

## Introduction

The Sancho reservoir is fed by the Meca River, a tributary of the Odiel River (Fig. 1). Both rivers are located in the Iberian Pyrite Belt (IPB), which hosts one of the largest concentrations of massive sulfide deposits in the world. The intense mining of these resources has left an immense amount of abandoned mine wastes in the area. The oxidation of sulphides contained in these wastes releases high loads of sulfate, acidity and metals, generating acid mine drainage (AMD) which provokes a strong deterioration of the water courses in the region (Sarmiento et al. 2009). Until now, this reservoir is the biggest of the Odiel basin, with a storage capacity of 58 $hm^3$ and presents acidic conditions ($pH<5$) and significant dissolved metal concentrations (up to 4.4 mg/L of Al), which makes this reservoir an extreme case of surface water pollution worldwide. A new large reservoir with a capacity of 246 $hm^3$ is currently under construction in the Odiel basin, although there is great concern about its final stored water quality (Olías et al. 2011). Although mining in the zone ended in 2001, a progressive worsening of the Sancho reservoir water quality has been detected in the last years (Cánovas et al., 2016). Here, we present the evolution of the water quality in the reservoir from 1994 to 2016, the latest data available.

## Site description

The Sancho Reservoir was built in 1962 to supply water to a paper mill factory. The Meca River watershed has a surface of 315 $km^2$ with a maximum height of 394 m. The region has a Mediterranean climate, with mean rainfall close to 600 mm, but with high intra- and inter-annual variability (Galván et al. 2009). The average river flow is 0.84 $m^3/s$ and usually dries up during the dry season (from June to September). The river watershed is mainly underlain by IPB materials, with rocks belonging to the Phyllitic-Quartzitic (PQ) and Vulcano-Sedimentary Complex (CVS) groups. This latter outcrops at the northern area of the watershed and contains massive sulfide deposits forming the mining district of Tharsis, one of the largest of the IPB. The deposits are mainly composed by pyrite (more than 90%), followed by chalcopyrite, sphalerite, galena, chalcocite and covellite (Tornos et al., 1997).

These deposits were exploited by Tartessians and Romans but it is from 1853 when the mining underwent a great impulse for Cu extraction and, later, to obtain sulfuric acid. Also, the gossan has been exploited to obtain Au and Ag by cyanidation. Mining activity in Tharsis ceased completely in 2001 but there is an extensive area of flooded open-pits, galleries, shafts and mining wastes which release metal and acidity to the rivers. Therefore, the Meca River is currently deeply contaminated by AMD, transporting huge amounts of contaminants to the Sancho Reservoir (Galván et al. 2009; 2012). Most of these pollutants precipitate and are transferred to the bottom sediments (Sarmiento et al. 2009, Torres et al., 2014).

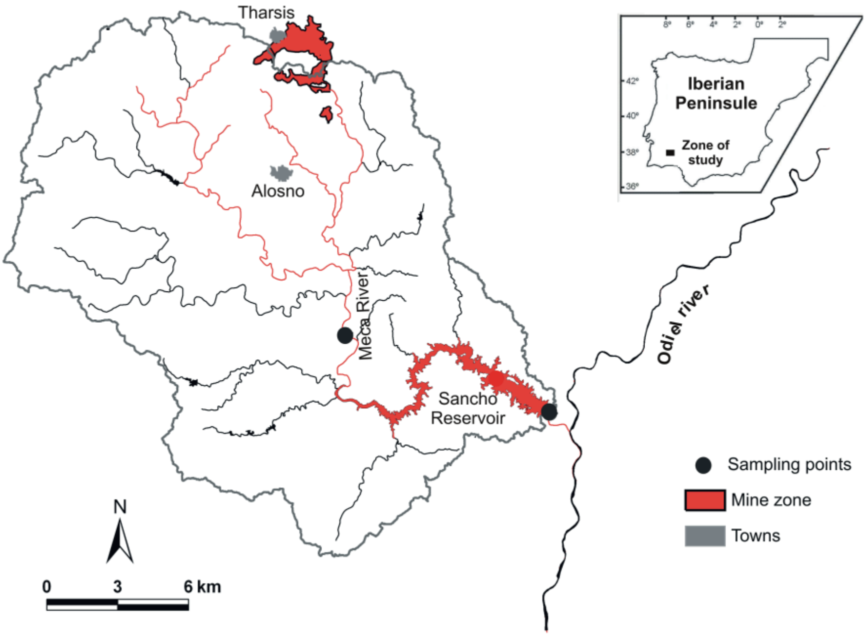

***Figure 1*** *Location map showing the streams affected by AMD.*

## Methods

The Meca River hydrochemical information was obtained in a sampling point upstream the reservoir by several studies conducted since 2003 (189 samples). This includes analytical information from 2004 to 2006, 2009 to 2010 and 2012 to 2014 with a variable frequency (from monthly to daily). Most of the samples (114) correspond to a high-resolution sampling performed during the hydrologic year 2012/13. Hydrochemical data of the Sancho Reservoir was obtained from the Regional Water Authority, collected since 1994 to 2016 with around a quarterly sampling frequency, although there are years with one only sample. This dataset was completed with our own data from 2003/04 and 2008–2014 with a variable frequency. The samples were taken in the water surface from the top of the reservoir dam. Up to 103 measurements of electrical conductivity (EC) and pH are available for the reservoir data set (Table 1), with a lower number for sulfate (101), Zn (98), Cu (94), Mn (98), Fe (77) and al. (15). There are few analyses of the latter because it was not determined in the Water Authority controls.

The protocol for sample collection, handling and data quality assurance at laboratories was similar for both datasets. Samples were filtrated through 0.45 µm Millipore Teflon filters and acidified with $HNO_3$ suprapur to pH<2, and finally kept in the dark at around 4°C until analysis. Temperature, EC, and pH were determined in the field with portable meters. The instruments were calibrated against certified standards. Analyses were performed using ICP-OES. Different elements were determined but here only Al, Cu, Fe, Mn, Zn and sulfate will be used. Both laboratories have quality assurance and quality control protocols (Cánovas et al., 2016).

## Results

During the study period reservoir waters showed pH values between 3.4 and 5.2, with an average of 4.3 (Table 1). The average EC was 0.42 mS/cm, with values ranging from 0.19 to 0.68 mS/cm. The highest mean concentrations of AMD-related metals were found for al. (4.4 mg/L), although the number of available samples for this element is low, followed by Mn (2.2 mg/L) and Zn (2.1 mg/L).

There are some oscillations in the evolution of pH values (Fig. 2). Nevertheless, it can be seen that pH values remained around 4.5 from 1994 to 2006, but a progressive decrease is observed since 2007, with values below 3.5 from 2014 onwards. In relation to EC, a slight upward trend seems to occur from 2000, which is more clearly defined since 2007. This tendency was interrupted at the beginning of 2010, coinciding with huge river inputs and a large rise of the water level in the reservoir (Cánovas et al., 2016). Other oscillations of EC values were subsequently observed related to rainfalls, remaining between 0.30 and 0.70 mS/cm.

***Table 1*** *Results obtained for the Sancho Reservoir (1994-2016).*

| | pH | E.C. mS/cm | Al mg/L | Cu mg/L | Fe mg/L | Mn mg/L | Zn mg/L | $SO_4$ mg/L |
|---|---|---|---|---|---|---|---|---|
| Data no. | 103 | 103 | 15 | 94 | 77 | 98 | 98 | 101 |
| Mean | 4.3 | 0.42 | 4.4 | 0.65 | 0.45 | 2.19 | 2.05 | 147 |
| Min. | 3.4 | 0.19 | 1.6 | 0.31 | 0.01 | 0.21 | 1.01 | 61 |
| Max. | 5.2 | 0.68 | 14.3 | 1.83 | 5.25 | 3.86 | 4.22 | 305 |
| Stand. Dev. | 0.5 | 0.12 | 2.9 | 0.26 | 0.71 | 0.80 | 0.75 | 51 |

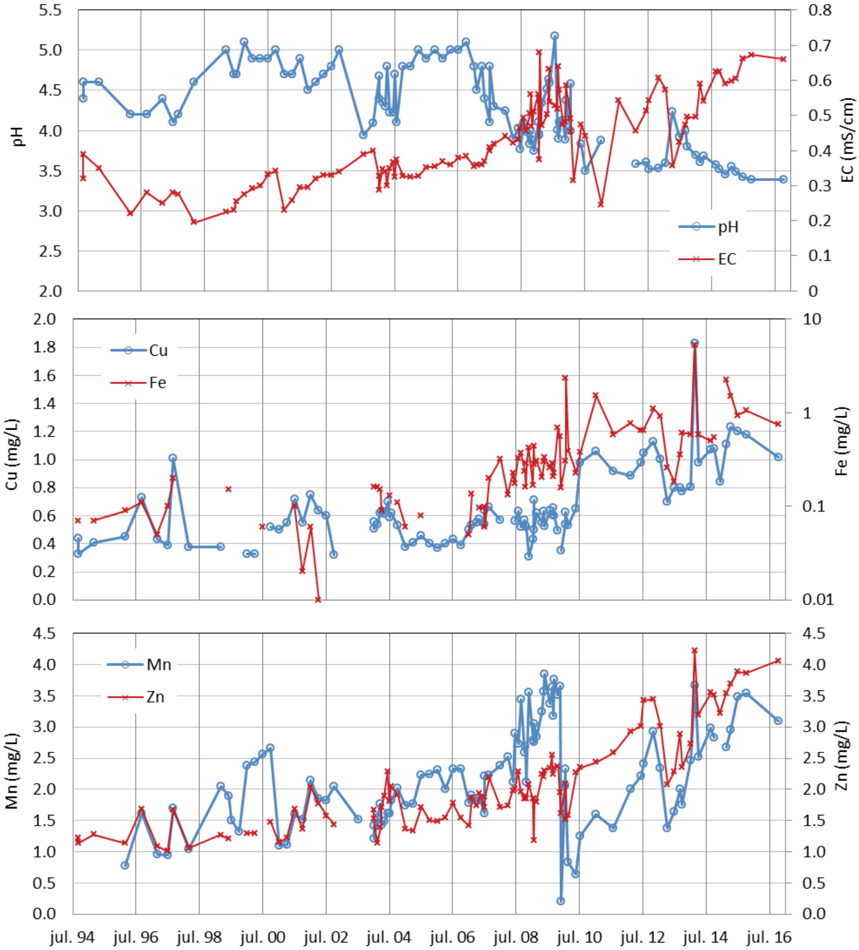

***Figure 2*** *Evolution of pH, EC and concentrations of some elements in the Sancho reservoir*

Sulfate concentration (not shown in Fig. 2) follows a similar evolution as EC, from 1994 to 2006 ranged from 70 to 150 mg/L while since 2007 values varied between 100 and 300 mg/L. The concentration of Fe in reservoir waters did not exceed 0.2 mg/L until 2007, being frequently even below the analytical detection limit. However, from this year onwards, a significant increase in concentration was observed, ranging usually between 0.2 and 1 mg/L and reaching up to 5.2 mg/L (Fig. 2). The concentration of Mn and Zn also began an upward tendency from 2007. Between 2007 and 2009 higher concentrations of Mn were found than for Zn, but from 2010 this tendency reverses. Manganese concentrations are affected by sharp decreases during the flood periods (Fig. 2). The concentration of Cu also shows a clear increase from 2010, later than the others, when pH values decrease below 4. With regards of the Meca River data upstream the reservoir, the mean pH and CE values are 3.1 and 1.57 mS/cm, respectively (Table 2). The most abundant toxic metal is al. (mean of 55 mg/L) followed by Fe, Zn, Mn and Cu (Table 1).

***Table 2** Results obtained for the Meca River (2003-2014).*

| | pH | E.C. mS/cm | Al mg/L | Cu mg/L | Fe mg/L | Mn mg/L | Zn mg/L | $SO_4$ mg/L |
|---|---|---|---|---|---|---|---|---|
| Data no. | 189 | 189 | 188 | 189 | 189 | 189 | 189 | 188 |
| Mean | 3.1 | 1.57 | 55 | 6.4 | 24 | 8.8 | 16 | 817 |
| Min. | 1.7 | 0.25 | 0.02 | 0.05 | 0.01 | 0.4 | 0.51 | 53 |
| Max. | 6.1 | 5.39 | 305 | 43 | 311 | 41 | 108 | 5440 |
| Stand. Dev. | 0.6 | 0.85 | 49 | 5.3 | 36 | 7.4 | 15 | 683 |

The available data show a high variability (Fig. 3). The evolution of pH and EC does not show a clear pattern or trend for the controlled period. Regarding concentrations, the higher values occurred in 2010 (the same that EC), just after a period of strong floods. The concentrations of Cu, Mn, Zn, al. and sulfates (the last two not shown in the figure) neither show a clear trend. On the contrary, Fe concentrations exhibited noticeably higher concentrations after 2007 (Fig. 3).

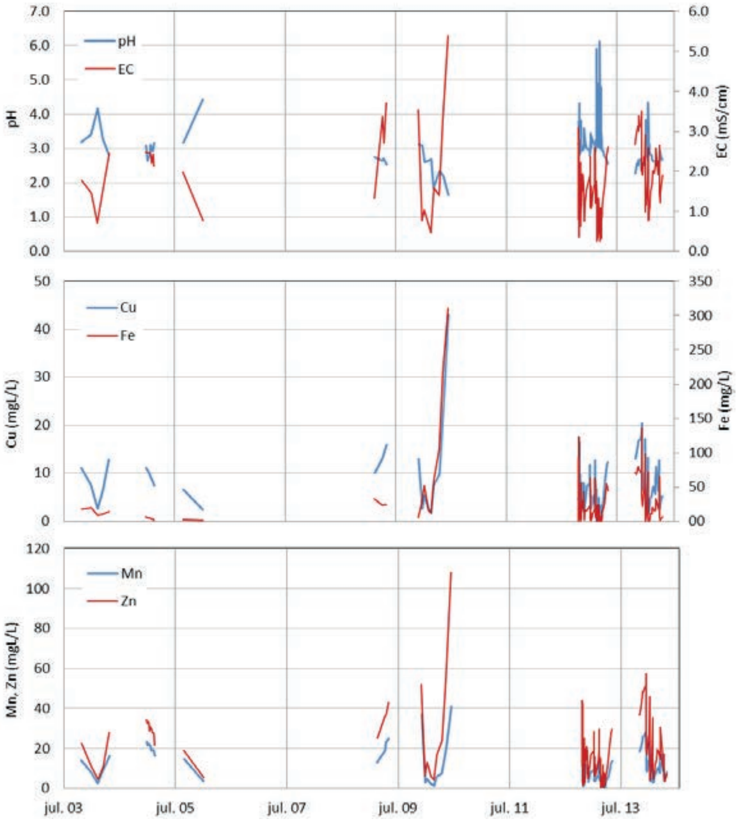

***Figure 3** Evolution of pH, EC and concentrations of some elements in the Meca River*

## Discussion

The recurrence of dry and rainy periods causes oscillations of pH, EC and element concentrations in the river and, at to a lesser extent, in the reservoir (Figs. 2 and 3). In the IPB, the first rainfalls recorded in autumn provoke the wash-out of evaporitic soluble salts formed in the mining zones during summer, reaching the highest concentrations of sulfate and metals of the year (Cánovas et al., 2010). The opposite effect is observed during winter high floods, because of the dilution effect of runoff waters after all evaporitic salts have been washed.
The occurrence of winter floods causes a decrease in EC values and metal concentrations in the reservoir by the dilution effect exerted by the high inputs of less mineralized waters, causing intra- and inter-annual hydrochemical variations in the reservoir. These variations are less noticeable in the Sancho Reservoir (Figs 2 and 3) because the effects are buffered when the river water mix with the reservoir stored water.

The reservoir is classified as holomictic with a turnover period lasting three months in winter. Seasonal hydrochemical variations occur in the hypolimnion related to the turnover and stratification periods. During stratification periods, when the conditions in the hypolimnion are anoxic, intense sulfate and Fe(III) reduction occurs in the first centimeters of sediment (Torres et al. 2013) increasing pH and Fe(II) concentration. During turnover, dissolved oxygen reaches the sediment surface and FeS previously formed in the shallower sediments is oxidized. However, Fe(II) is immediately oxidized and precipitated as schwertmannite. Consequently, pH and Fe(II) concentrations in the hypolimnion decrease in winter (Cánovas et al., 2016). Aluminum and other trace metals are also precipitated during stratification and are partially redissolved in winter. On the whole, there is a net flux of acidity and metals from the water column to the sediment (Torres et al, 2014). However, these changes barely affect the epilimnion, where samples were taken. On the other hand, during the summer evaporation at the epilimnion cause an increase in EC, sulfate and metal concentrations.

All these fluctuations are overlapped by a decreasing trend in pH values and an increase in EC and dissolved concentrations of AMD-related elements (Fig. 2), more clearly identifiable from 2007. This tendency must be linked to an increase of the pollutant load transported by the Meca River into the reservoir. The reason of the increase is not clear. These hydrochemical variations are not linked to shifts in the precipitation regime in the watershed but to the higher input of metals and acidity due to the rebound effect after the Tharsis mine closure in 2001 (Cánovas et al., 2016). Another cause that may have contributed to the increase of contaminants in the reservoir is the uncontrolled dumping of milled pyrite wastes from nearby industrial facilities in the Tharsis spoil heaps area. Remedial measures need to be adopted in AMD sources of the Tharsis mine in order to reduce the pressure on the water reservoir
Apart from the change of Fe concentration before and after 2007 (Fig. 3), which could be easily unnoticed, the pollutant increment is not evident from the Meca River analyses. The high hydrologic and hydrochemical variability typical of the Mediterranean rivers can mask important changes in the pollutant load. The monitoring of receiving water bodies, such as reservoirs, where this variability is attenuated, allows a more reliable detection of long-term trends in water quality.

The differences in the evolution of the toxic metals elements in the reservoir are also influenced by their hydrochemical behavior. Thus, before 2007, Fe displayed very low concentrations, while al. was the predominant AMD-related metal buffering the water pH values between 4 and 5 (Fig. 2). At this pH range, Fe was removed from the solution by the precipitation of amorphous oxyhydroxisulfates. When the pH decreased below 4, the solubility of Fe increased. The increase of Cu concentration, which occurred in 2010 later that the Fe concentration rise, also seems controlled by some solubility control (Fig. 2). The observed decrease of pH values could change the transfer rates of pollutant between bottom sediments and water in the reservoir.

## Conclusions

This work shows that the end of the environmental controls by the closure of Tharsis mine, together with the inadequate use of already polluted mining zones as industrial landfills, must be the main causes of the worsening of the Sancho reservoir water quality. Because of the high variability typical of Mediterranean rivers the increase of metal load transported by the Meca River is not evident while the monitoring of the reservoir clearly shows this trend. Thus, receiving water bodies such as reservoirs or lakes allows a more reliable detection of long-term trends in water quality. The evolution of toxic metal concentrations in the reservoir water shows some differences due to their different hydrochemical behavior. Remediation measures should be taken to reverse this trend and gradually improve the conditions of the Meca River and the Sancho reservoir.

### Acknowledgements

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# Nitrogen removal efficiency and wintertime hydraulics in mine peatlands

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**Abstract** Increased N load on recipient water bodies often deteriorate water quality and highlight the importance of efficient N removal. In this study, constructed wetlands as an N removal step in mine wastewater were studied with the focus of winter purification efficiencies and hydraulic wetland designing. The results showed lower N removal efficiency during winters than in frost-free periods although some N removal happened also at low temperatures. Temperature was not the only factor controlling N removal but also oxygen availability were important while snow/ice cover restrict oxygen transportation. The results increase the understanding of N removal processes in winter condition.

**Key words** Passive treatment, peatland, nitrogen, snow, frost

## Introduction

Management and mitigation of harmful substances such as nickel, antimony, lead and sulphate contained in mine waters have received considerable attention in the last few decades (Nordstrom 2011, Kauppila et al. 2011, Räisänen 2009), but less attention has been paid to nitrogen (N) loads from mining activities (Chlot 2011). However, use of explosive, certain mineral processing activities, including pH regulation, use of cyanide in gold extraction and use of ammonia as lixiviant, generate nitrogenous load to the environment. The effect of increased N load on recipient water bodies can be remarkable, especially if N is the limiting nutrient in an aquatic ecosystem such as in many oceanic and coastal waters, but also some rivers in Finland. The high N concentration can also be toxic to ecosystems. A sustainable mining industry requires efficient N removal methods, but this has not been achieved yet.

At mines, N removal is mainly based on passive water treatment by recycling water via tailings ponds, or in constructed wetlands, where the water flow is delayed and a large filtration network is available with many adsorptive surfaces on plant roots or soil particles (Younger et al. 2002). Due to the high and temporally variable amount of mine water produced and variable mine water quality, efficient N removal is difficult in Nordic climate. It is well-known that winter conditions are extremely challenging to N removal processes, and wetland hydraulics is one of the crucial factors determining N removal efficiency.

The aim of this study was to understand changes in N removal efficiency that occur throughout the year and the role of winter conditions in the performance of treatment peatlands at a mine site.

## Material and Methods

Winter conditions (soil and air temperature, snow depth, snow water equivalent, precipitation, frost depth) were studied in two constructed wetlands treating mine waters from October 2015 to the beginning of 2017. From September 2016 onwards, soil gas measurements have been conducted at different depths and at different points to demonstrate possible accumulation of $N_2O$ in the soil during the winter time. Water quality monitoring data required in the environmental permit were used to study purification efficiencies of the wetlands. The inflow and outflow of the wetlands were sampled at least once or twice a month, but the number of inflow samples collected exceeded 30 in some months. Purification efficiencies of the wetlands were calculated based on inflow and outflow concentrations. The wintertime performance of the wetlands was compared to their performance during frost-free period.

## Preliminary results

First results showed that N removal is clearly lower during winter time than during frost-free period although N removal processes still occurred at low temperatures in the wetlands (Fig. 1). Ammonium ($NH_4$-N) was removed clearly better than $NO_3$-N. The part of low $NO_3$-N removal could due to efficient anaerobic ammonia oxidation but uncompleted denitrification process resulting increase in $NO_3^-$ concentration. It seems that temperature is not the only factor controlling N removal processes, but that also oxygen availability is important, as snow and ice cover restrict oxygen transport into the wetland soil. The results of this study increase our understanding of N removal processes in winter conditions and can be used in the design of constructed wetlands for mine waters.

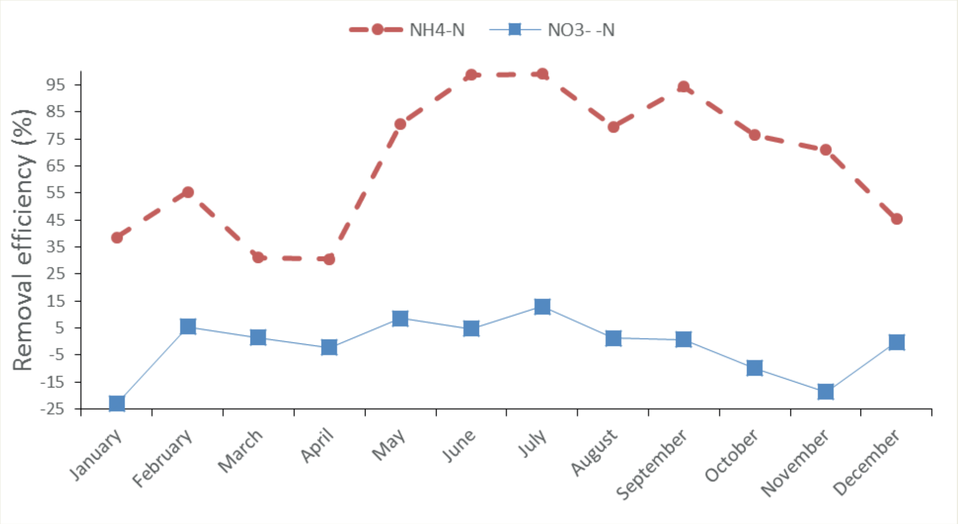

***Figure 1*** *The mean removal efficiencies of Ammonium ($NH_4^+$) and nitrate ($NO_3^-$) nitrogen in different months at a constructed wetland treating mine waters.*

## Acknowledgements

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# Application of the Ground Penetrating Radar (GPR) Technique for Characterizing the Internal Structure of Tailings Impoundments

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## Abstract

Tailings impoundments generated in the old mining district of Linares (Spain) constitute at present a severe environmental problem. Especially alarming is the case of those abandoned ponds located on the banks of the main stream of the area, the Guadiel River. Concerned by this situation, the regional government has proceeded during the last five years to restore some of the biggest impoundments to ensure both their geotechnical stability as to reduce the pollution processes affecting the surface waters.

We report the efficiency of the ground penetrating radar (GPR) as a geophysical tool to analyze the effectiveness of the process of isolation in restored tailings impoundments, and to characterize the internal structure of abandoned tailings ponds.

In the first case, the nature of the sludge and the level of sealing causes a rapid attenuation of the GPR signal, so the depth of research is scarce (less than 10 m) with any of the frequency antennas used (30, 100 and 250 MHz). Despite this, the technique presents a great utility since it allowed to obtain a great detail in the surface zone. Using the 250 MHz antenna, it has been possible to differentiate the continuity and thickness of insulation levels in the restored impoundment.

In the second case, in an unrestored dam, the GPR technique gave equivalent results for the penetration capacity, reaching no more than 10-12 m in depth with the three frequency antennas. Results obtained with the 250 MHz antenna provide detail of the internal structures of the tailings up to 2.5 m deep. In addition, relationship between moisture content and variations in the wave amplitude or signal attenuation can be used to detect the water table and areas with relatively high saturation.

In summary, application of GPR to tailings can be used to identify discontinuities in the top seal layers and analyze the internal structure of these tailings ponds.

**Key words** Tailings pond, restoration, ground penetrating radar

# Occurrence and Distribution of Metal(oid)s in Soils near an Abandoned Lead Smelter

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## Abstract

The slags of the abandoned smelter of La Cruz (Linares mining district, Spain) present very high concentrations of As (300 mg/kg), Cu (4200 mg/kg), Pb (22900 mg/kg), and Zn (51300 mg/kg). The smelting dump lacks of any restoration process, it is affected by erosion, and generates alkaline leachates (pH 8-9) of sodium-sulphate type, with dissolved As ranging from 40 to 100 mg/L.

Due to the pollution risk of this smelting site, we have studied the occurrence and distribution of metal(oid)s in the vicinity of the smelter, analyzing the total contents in 50 soil samples uniformly distributed over a 3 km$^2$ area. Nine of the 33 analyzed elements presented a high to very high enrichment factor (Ag, As, Bi, Cd, Cu, Pb, Sb, Tl and Zn), and they reached average contents that largely exceed the environmental quality standards for soils. In the case of Pb and Tl values, all the collected samples have contents higher than the maximum allowable concentrations established by the regional government.

In general, there is a preferential distribution of the metal(oid)s coincident with the direction of the prevailing winds to NE of the smelter, and with a maximum range of 500 meters. However, the maximum As contents (up to 1920 mg/kg) have been detected at the south of the slag dump, in a sector receiving its leachates. The highest values for Cd (180 m/kg) and Tl (65 mg/kg) also appeared in soils very close to the smelting slag, near a drainage channel at the foot of the dump.

These polluted soils affect both a residential zone and an olive grove located in the study area. These activities are incompatible with the current state of the soils, taking into account the elevated metal contents that still persist in this zone.

**Key words** Arsenic, soil contamination, lead smelter

# Quantifying the Impact of Oxygen, Nitrate and Ferric Iron on Sulfate Reducing Bioreactor Design

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**Abstract** The efficiency of anaerobic bioreactors targeting sulfate reducing conditions is negatively impacted by the presence oxygen, nitrate and ferric iron (electron acceptors) in the influent water. The impact of the competing electron acceptors can be accounted for using by using redox stoichiometries derived from bacterial energetics. The effect of competing electron acceptors can be expressed as a function of the influent concentration, flow and reactor volume. The impact of oxygen can be mitigated by increasing the reactor volume. Nitrate has the highest potential for complete inhibition of sulfate reduction. The stoichiometric approach presented demonstrates the importance of explicitly including competing electron acceptors on the sizing of sulfate reducing bioreactors.

**Key words** metal removal, passive treatment, denitrification, iron reduction

## Introduction

Sulfate reducing bioreactors have the potential to provide treatment of mining influenced water (MIW) with low operation and maintenance requirements. However, sulfate reducing bacteria are out competed by aerobic, denitrifying and iron reducing bacteria in the presence of oxygen, nitrate ferric iron in MIW. Empirical concentration thresholds have been proposed (e.g., Bratcova et al. 2002) but the expected impact does not always hold true in operating systems. Johnson and Hallberg (2005) attributed poor performance of sulfate reducing bioreactor in part to the high oxygen saturation of the influent MIW. However, Willow and Cohen (2003) did not see any decrease in performance for sulfate reducing bioreactors with influent oxygen concentration. The method presented in this paper will demonstrate that the extent of sulfate reducing activity is impacted by the coupled effect of the competing electron acceptor concentration and the reactor volume to flow ratio.

## Methods

Thermodynamic fundamentals of bacterial energetics and growth (Rittmann and McCarty 2001) were used to develop stoichiometric relationships which are subsequently used to calculate the impact of competing electron acceptors (e.g., oxygen and) on the required volume of organic substrate. I use the derived stoichiometries to show how to relate the concentrations of oxygen and nitrate along with reactor volume to flow ratio (V/Q) to a decrease in the design volumetric sulfate reduction rate (sulfide production rate).

### Glossary

| | |
|---|---|
| V | Reactor volume, $m^3$ |
| CCR | Carbohydrate Consumption Rate, mol $CH_2O$/d |
| V/Q | Reactor volume to flow ration (Empty bed contact time), d |
| VSPR | Volumetric sulphide production rate, mol S/$m^3$/d |

VCCR Volumetric carbohydrate consumption rate, mol $CH_2O/m^3/d$
SRR Sulfate reduction rate, mol $S/m^3/d$

## Results and Discussion

### Loading rate

Metal loading rate is a key design parameter. The goal is for the metal loading to be equal to or less than the rate of reagent production. Reagent production rate must be equal to or greater than the metal loading (of potential metal precipitates). This is based on the assumption that only a stoichiometric amount of reagent will be required to achieve the desired extent of precipitation. The required units of metal loading are mol per time. Influent metal concentration of the targeted metals must be converted from grams (g) to mol. Typical target metals for sulfide precipitation with the molecular weight conversion factor are presented in the Table below.

Metal, mol/L = $Cd/MW_{Cd} + Cu/MW_{Cu} + Fe/MW_{Fe} + Ni/MW_{Ni} + Pb/MW_{Pb} + Zn/MW_{Zn}$
where metal concentration is in g/L and $MW_{Me}$ is the molecular weight of the respective metal (e.g., Cd).

Once the metal concentration in mol per liter (Me) is determined. The volume of the bioreactor based on the metal loading criteria can be estimated if the flow rate (Q) is known. To determine the reactor volume, we must balance the volumetric rate of reagent production with the target metal loading.

### Metal sulfide precipitation

For the initial examination of how this applies to metals, we will look at the case of metal sulfide precipitation. For any volumetric sulfide production rate (VSPR), the reactor volume would be:

$$V_{Me}, m^3 = \frac{Q\,Me}{VSPR}$$

A typical VSPR value used for design is 0.3 mol $S/m^3/d$ (Williow and Cohen 2003). However, VSPR rates will vary with influent water composition, specific bioreactor substrate mix, temperature and age. Competing electron acceptors are currently not included in the analysis and can reduce the volumetric sulfide production rate.

Competing electron acceptors of concern are oxygen, nitrate and iron. Oxygen and iron are commonly measured in MIW yet not included in the current analysis protocol. One way to approach the impact of competing electron acceptors is to increase the required volume of the substrate to account for the other electron acceptors.

$$V_{design}, m^3 = V_{Me} + V_{O_2} + V_{Fe^{3+}} + V_{NO_3^-}$$

Stoichiometries for the potentially competing electron acceptors oxygen, nitrate and ferric iron are shown below with the sulfate stoichiometry for reference.

$SO_4^{2-} + 2CH_2O \Rightarrow H_2S + 2HCO_3^{-}$

$O_2 + CH_2O \Rightarrow H_2O + CO_2$

$NO_3^{-} + 5/4CH_2O \Rightarrow 1/2N_2 + HCO_3^{-} + CO_2 + 3/4H_2O$

$Fe^{3+} + 1/4CH_2O + 1/4H_2O \Rightarrow Fe^{2+} + 1/4CO_2 + H^+$

The sulfide production rate is associated with a carbohydrate ($CH_2O$) consumption rate. The impact of the consumption of available carbohydrate by the other electron acceptor can be estimated using the relationships shown in the table below.

***Table 1*** *Mol of carbohydrate consumption per mole of electron acceptor*

| Electron acceptor | Mol | Mol $CH_2O$ required per mole acceptor |
|---|---|---|
| $SO_4^{2-}$ | 1 | 2.2 |
| $O_2$ | 1 | 2.5 |
| $NO_3^-$ | 1 | 2.5 |
| $Fe^{3+}$ | 1 | 0.5 |

The potential impact of any of the three more energetically favorable electron acceptors can be estimated using the above stoichiometries. These stoichiometries include cell synthesis. Cell synthesis demands will increase the effect of the competing electron acceptors.

Example:
An example MIW is used to demonstrate the analysis method (shown in Table 1) for treatment in a sulfate reducing bioreactor. For this example, pH considerations are not included. The design flow is 30,000 L/d.

***Table 2*** *Major water constituents for example system analysis*

| Constituent | Conc., mg/L |
|---|---|
| $Zn^{2+}$ | 6.5 |
| $SO_4^{2-}$ | 960 |
| $O_2$ | 8 |
| $Fe^{3+}$ | 55 |
| $NO_3^-$ | 50 |

The approach is to calculate the volume required for metals and competing electron acceptor. The method to calculate the volume for metal removal was shown above. The volume for the competing electron acceptors can be calculated if we relate the design sulfide production rate to a carbohydrate consumption rate. For a value of 0.3 mol S/m$^3$/d the equivalent carbohydrate consumption rate (CCR), based on our stoichiometry, is 0.66 mol of $CH_2O$/m$^3$/d. We can then use the stoichiometries presented in Table 1 to determine the additional volume for each of the competing electron acceptors. For this example, we are using the 0.3 mol S/m$^3$/d as the design point. The values will be different for another volumetric sulfide production rate. The analysis presented below is developed on this basis and only includes the analysis for the impact of oxygen.

Influent metals for MeS Calculations

| Constituent | Conc., mg/L | MW | Conc., mM/L | Loading, M/d |
|---|---|---|---|---|
| $Zn^{2+}$ | 6.5 | 65 | 0.1 | 3 |

Influent sulfate load Calculations

| Constituent | Conc., mg/L | MW | Conc., mM/L | Loading, M/d |
|---|---|---|---|---|
| $SO_4^{2-}$ | 960 | 96 | 10 | 300 |

Required sulfate reduction Calculations

| Constituent | Metal load, M/d | Sulfate needed, M/d | M $CH_2O$ required/d (CCR) |
|---|---|---|---|
| $SO_4^{2-}$ | 3 | 3* | 6.6 |

* important to check that sulfate needed < sulfate influent

Influent competing electron acceptors Calculations

| Constituent | Conc., mg/L | MW | Conc., mM/L | Loading, M/d | M $CH_2O$ required/d |
|---|---|---|---|---|---|
| $O_2$ | 8 | 32 | 0.25 | 7.5 | 18.75 |

$$V_{Me}, m^3 = \frac{CCR_{Me}}{VCCR} = \frac{6.6\ moles\ CH_2O/d}{0.6\ moles\ CH_2O/m^3/d} = 11\ m^3$$

$$V_{O_2}, m^3 = \frac{CCR_{O_2}}{VCCR} = \frac{18.75\ moles\ CH_2O/d}{0.6\ moles\ CH_2O/m^3/d} = 31.25\ m^3$$

Total volume required is 42.25 m$^3$/d.

This example illustrates an important point on sizing of sulfate reducing bioreactors. The reactor size based on metal removal only would have resulted in a volume of 11 m$^3$ relative to the size needed to accommodate the oxygen impact. Thus, the reactor volume would have been undersized by a factor of 4. The above analysis was completed for a range of electron acceptor concentrations and reactor volume to flow ratios.

Competing electron acceptors impacts can be presented in units of equivalent mol of sulfate reduction/m³/d. This allows for a visual comparison of the potential reduction in sulfate reduction rate as a function of competing electron acceptors concentration, reactor volume and flow. Figures 1, 2 and 3 present the results for three different concentrations of the three competing electron accepts for reactor volume to flow ratios of 1 to 20 days.

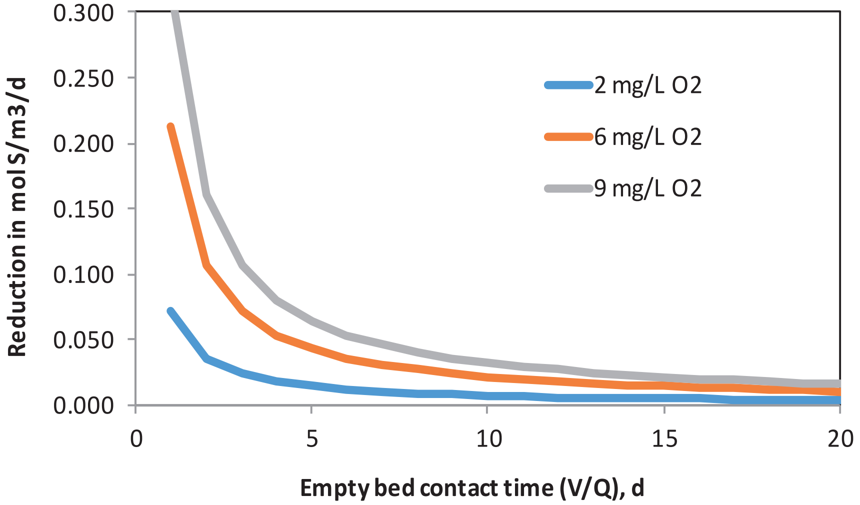

***Figure 1*** *Calculated reduction in volumetric sulphate reduction rate (SRR) by oxygen (O2) as a function of the reactor volume to flow ratio (V/Q).*

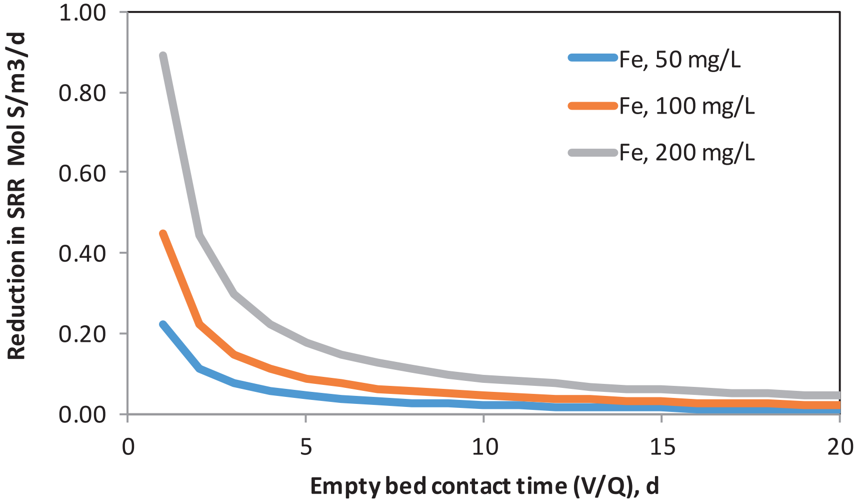

***Figure 2*** *Calculated reduction in volumetric sulphate reduction rate (SRR) by ferric iron (Fe) as a function of the reactor volume to flow ratio (V/Q).*

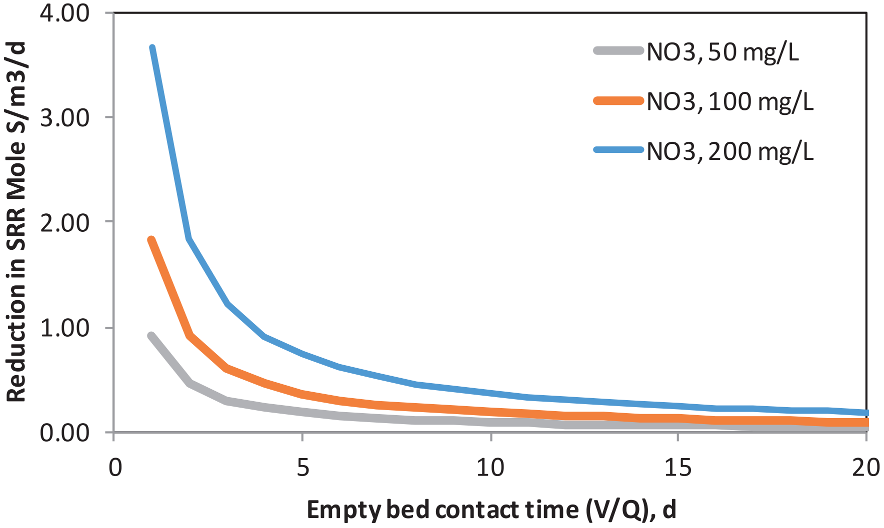

***Figure 3*** *Calculated reduction in volumetric sulphate reduction rate (SRR) by nitrate (NO3) as a function of the reactor volume to flow ratio (V/Q).*

Implications of the dissolved oxygen concentration and EBCT on inhibition of sulfate reduction rate (SRR):

- Low DO (2 mg/L) coupled with low V/Q (1 to 5 days) will reduce effective SRR by 5 to 50%
- High DO (9 mg/L) coupled with low V/Q (1 to 5 days) will reduce effective SRR by 20 to 100%.
- Low DO (2 mg/L) with high V/Q (> 15d) will have a very low impact on effective SRR (reduction ≤ 2 to 3%)
- High DO (9 mg/L) with high V/Q (> 15d) will have a low impact on effective SRR (reduction ≤ 7 to 14%)

Implications of the ferric iron concentration and V/Q on inhibition of sulfate reduction rate (SRR):

- Moderate Fe (50 mg/L) coupled with low V/Q (1 to 5 days) can reduce effective SRR by 15 to 100 %
- High Fe (200 mg/L) coupled with low V/Q (1 to 5 days) can reduce effective SRR by ≤ 60 to 100 %.
- Moderate Fe (50 mg/L) with high V/Q (> 15d) will have a low impact on effective SRR, reduction ≤ 5 to 10 %)
- High Fe (200 mg/L) with high V/Q (> 15d) will have a a moderate impact on effective SRR, reduction ≤ 20 to 40 %)

Implications of the nitrate concentration and EBCT on inhibition of sulfate reduction rate (SRR):

- Moderate NO3 (50 mg/L) coupled with low V/Q (1 to 5 days) can reduce effective SRR by 60 to 100 %
- Moderate NO3 (50 mg/L) with high V/Q (> 15d) will have a low impact on effective SRR, reduction ≤ 20 %
- High NO3 (200 mg/L) with high V/Q (> 15d) will have a high impact on effective SRR (reduction of 80 to 100 %)

## Conclusions

The analysis supports that it is possible to achieve good sulfate reducing activity in the presence of oxygen saturated MIW if the volume is increased proportionately. If only metal loading coupled with sulfide production had been considered for a model MIW, the reactor volume would be undersized by a factor of 4 for a volume to flow ratio of 2 d. This is equivalent to an apparent volumetric sulfate reduction rate of 0.075 $mol/m^3/d$ compared to the typical proposed value of 0.3 $mol/m^3/d$. The analysis tool developed herein illustrates the importance of explicitly including competing electron acceptors on the sizing of sulfate reducing bioreactors.

### Acknowledgements

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# Efficiencies of different alkaline generating agents for the treatment of acid mine drainage: A comparative study and techno-economic appraisals

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**Abstract** This comparative study aims at evaluating the efficiencies of different alkaline generating agents for neutralising acid mine drainage. Batch laboratory experiments (at 1:10 S/L ratio) were used to achieve the goal of this study. Neutralisation studies revealed that: hydrated lime, Periclase, magnesite and caustic soda achieved pH ≥ 9, and ≥ 99%, metals removal respectively whereas the use of soda ash, limestone, lime and brucite yielded pH ≥ 6, al. and Fe ≥ 99%, and Mn ≥ 60%. Techno-economic evaluations revealed that hydrated lime is the cheapest and most effective material for mine water neutralisation.

**Key words** Acid mine drainage, Alkaline generating agents, precipitation

## Introduction

Depending on the sources and the host rocks, mine drainages are categorised under different types and they include: acid, neutral and basic mine drainage (Nordstrom et al. 2015). Of prime concern is acid mine drainage which results from the weathering of pyrite ($FeS_2$) and other reactive sulphide-bearing minerals when exposed to oxidising conditions as shown by equation 1 – 4 (Masindi 2016):

$$2FeS_{2(s)} + 7O_{2(g)} + 2H_2O \xrightarrow{\text{bacteria}} 2Fe^{2+}_{(aq)} + 4H^+_{(aq)} + 4SO^{2-}_{4(aq)} \quad (1)$$

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_l \quad (2)$$

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO^{2-}_{4(l)} + 16H^+ \quad (3)$$

$$Fe^{3+}_{(aq)} + 3H_2O_l \rightarrow Fe(OH)_{3(s)} + 3H^+_{(aq)} \quad (4)$$

The reactions are also mediated by micro-organisms (Nordstrom et al. 2015). The most visual legacy of AMD is undoubtedly the precipitation of ferric ($Fe^{3+}$) hydroxide and oxy-hydroxide and oxy-hydrosulphates complexes as a yellow or orange coating in stream channels. These precipitates lead to a reduction in dissolved oxygen concentrations in affected water bodies during their formation, and have abrasive effects on biota and clog streambeds. Acid mine drainage is mainly characterised of pH < 3 and elevated levels of Al, Fe, Mn and sulphate in addition trace of other components (Masindi et al. 2015).

Worldwide, a number of treatment methods, both passive and active, have been proposed and used for abating AMD (Zipper and Skousen 2010) and they include ion-exchange (Torres and Auleda 2013), adsorption (Falayi and Ntuli 2014), bio-sorption (Çabuk et al. 2013), neutralisation (Alakangas et al. 2013), coagulation and precipitation (Zhao et al. 2012). The extent of application of most of these methods has largely been limited by factors such as cost and generation of excessive secondary sludge that is toxic and expensive to dispose (Simate and Ndlovu 2014). Effectiveness and efficiency of a given material also affect its industrial deployment. This pioneer and ground breaking comparative study was, therefore, developed and designed with the aim of appraising the efficiency and effectiveness of different alkaline generating agents for mine water pre-treatment and develops a guide for mine houses and respective industries.

## Materials and methods

### Materials and Characterization

Raw magnesite rock was collected from the Folovhodwe Magnesite Mine in Limpopo Province, South Africa. Field AMD samples were collected from a coal mine in Mpumalanga province, South Africa. The samples were stored in closed High Density Polyethylene (HDPE) bottles to prevent further oxidation and precipitation of metals, and kept in 4°C until utilisation in neutralisation experiments. Prior utilisation, the AMD samples were filtered through 0.4μm perforated filter. The chemical compositions of the Eight (8) neutralizing agents and they include: lime, limestone, hydrated lime, soda ash, caustic soda, periclase, brucite and magnesite. All other chemicals were of analytical grade quality. Water samples were analysed using inductively coupled plasma mass spectrometer (ICP-MS) (7500ce, Agilent, Alpharetta, GA, USA). Elemental composition was determined using X-ray fluorescence (XRF).

### Quality control/quality assurance

A QA/QC programme was established and implemented to ensure the production of trustworthy results. The QA/QC process entailed conducting the experiments in triplicate and reporting the data as mean value. Data was considered acceptable when percentage difference within triplicate samples and percent error were below 10%. The analytical values below detection limit (BDL) were managed in according to EPA guideline. The accuracy of the analysis was monitored by analysis of National Institute of Standards and Technology (NIST) water standards. Inter-laboratory analysis was also done to further verify the validity of the results.

### Neutralisation experiments

Aliquots of 1L, each of AMD, were pipetted into 1L beaker flasks and 1 g of each alkaline reagent was added into each flask. The mixtures were mixed using an overhead stirrer for 60 min at >250 rpm. The shaking speed and optimum time were obtained from a study conducted by Masindi et al. (2015). After mixing, the mixtures were filtered through a 0.45 μm pore nitrate cellulose filter membrane. After filtration, the filtrates were preserved by adding two drops of concentrated $HNO_3$ acid to prevent aging and immediate precipitation of Al, Fe and Mn, and refrigerated at 4 °C prior to analysis. The pH, before and after agitation, was measured using the CRISON multimeter probe (model MM40).

## Results and discussions

### Reaction of AMD with different neutralizing agents

The chemical profiles of raw AMD and AMD after contacting different alkaline generating agents at optimized conditions are shown in tab. 1.

***Table 1*** *Chemical profiles of AMD after contacting different alkaline generating agents at optimized conditions*

| **Parameters** | **AMD** | **Caustic soda** | **Soda ash** | **Periclase** | **Brucite** | **Magnesite** | **Lime** | **Hydrated lime** | **Lime-stone** |
|---|---|---|---|---|---|---|---|---|---|
| pH | <2 | 13 | 7 | 10 | 6 | 9 | 6 | 11 | 6 |
| Acidity (mg/L $CaCO_3$) | 8133 | <5,0 | 473 | <5,0 | 1564 | <5,0 | 29 | <5,0 | 117 |
| Alkalinity (mg/L $CaCO_3$) | <5,0 | 3565 | 1398 | 71 | <5,0 | 56 | <5,0 | 57 | 354 |
| Aluminium (mg/L Al) | 300 | 95 | BDL | BDL | BDL | BDL | BDL | 5 | BDL |
| Calcium (mg/L Ca) | 337 | <50 | 232 | 316 | 320 | 683 | 549 | 630 | 594 |
| Electrical Conductivity (mS/m [25°C]) | 547 | 1635 | 959 | 599 | 646 | 619 | 441 | 218 | 433 |
| Iron (mg/L Fe) | 1800 | 5 | 45 | BDL | 450 | BDL | BDL | BDL | BDL |
| Magnesium (mg/L Mg) | 273 | <40 | 278 | 1693 | 1590 | 1565 | 621 | <40 | 652 |
| Manganese (mg/L Mn) | 75 | 0.4 | 50 | BDL | 75 | BDL | 55 | BDL | 65 |
| Potassium (mg/L K) | <60 | <60 | <60 | <60 | <60 | <60 | <60 | <60 | <60 |
| Sodium (mg/L Na) | <30 | 5836 | 4035 | <30 | <30 | <30 | <30 | 54 | 40 |
| Sulphate (mg/L $SO_4$) | 33705 | 33700 | 33700 | 30705 | 32705 | 20705 | 3705 | 3005 | 9000 |
| Total Dissolved Solids | 3556 | 10628 | 6234 | 3894 | 4199 | 4024 | 2867 | 1417 | 2815 |
| Total Hardness (mg/L) | 1965 | <290 | 1724 | 7759 | 7345 | 8149 | 3928 | 1738 | 4168 |

As shown in tab. 1, AMD had the pH of < 2 which is suitable for dissolution of metals. It had high content of Fe and sulphate, hence showing that it might have been formed from the oxidation of pyrite. Caustic soda managed to increase the pH to > 13 and remove all the metals except al. and sulphate. Soda ash managed to increase the pH to > 7 and remove Al, with partial removal of Fe and Mn. Periclase removed all the metals from the aqueous system, except the sulphate. It also increased the pH to > 10. Brucite managed to increase the pH to > 6 and partially removed the metals from the mine water. It managed to achieve > 90% removal for al. and partial removal of Fe and Mn. Magnesite raised the pH to > 9 which is suitable for all the metals to precipitate. It removed > 99% of Al, Mn and Fe and 40% sulphate. Ca-based reagents managed to removed > 80 sulphate from acid mine drainage. Lime managed to remove 99% of Fe and al. from mine water and 70% Mn. Hydrated lime managed to remove > 99% of all the metals from acid mine drainage. Limestone managed to remove > 99% of al. and Fe but failed to remove Mn which was only 20% removal.

## Elemental composition of different alkaline agents after contacting AMD

The Elemental compositions of different alkaline generating agents after contacting AMD are shown in tab. 2.

***Table 2*** *Elemental compositions of different alkaline generating agents after contacting acid mine drainage*

| Element | Caustic soda | | Soda ash | | Periclase | | Brucite | | Magnesite | | Lime | | Hydrated lime | | Limestone | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Before | After | Before | After | Before | After | Before | After | Before | After | Before | After | Before | After | Before | After |
| $SiO_2$ | <0,01 | 9.33 | <0,01 | 4 | <0,01 | 0.33 | <0,01 | 0.57 | 5 | 3.4 | <0,01 | 1.25 | <0,01 | 0.56 | <0,01 | 0.19 |
| $TiO_2$ | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 |
| $Al_2O_3$ | <0,01 | 4.84 | <0,01 | 7.56 | <0,01 | 2.52 | <0,01 | 2.71 | <0,01 | 3.08 | <0,01 | 3.23 | <0,01 | 2.84 | <0,01 | 4.18 |
| $Fe_2O_3$ | <0,01 | 38.5 | <0,01 | 33 | <0,01 | 11.1 | <0,01 | 12.5 | <0,01 | 14.2 | <0,01 | 7.08 | <0,01 | 6.15 | <0,01 | 10.9 |
| MnO | <0,01 | 1.24 | <0,01 | 1.03 | <0,01 | 0.38 | <0,01 | 0.16 | <0,01 | 0.47 | <0,01 | 0.34 | <0,01 | 0.22 | <0,01 | 0.16 |
| MgO | <0,01 | 6.12 | <0,01 | 3.04 | 98 | 51.5 | 70 | 52.4 | 80 | 46.5 | <0,01 | 3.18 | 2 | 2.94 | 8 | 0.42 |
| CaO | <0,01 | 6.36 | <0,01 | 5.36 | 0.5 | 0.46 | 4 | 0.28 | 9 | 2.98 | 95 | 39.7 | 77 | 29.8 | 80 | 43.5 |
| $Na_2O$ | 90 | 7.2 | 96 | 10.1 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 |
| $K_2O$ | 2 | 0.1 | <0,01 | 0.42 | 0.5 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 |
| $P_2O_5$ | <0,01 | <0,01 | 1 | 0.01 | <0,01 | <0,01 | <0,01 | <0,01 | 1 | <0,01 | 1 | 0.01 | 1 | <0,01 | <0,01 | 0.01 |
| $Cr_2O_3$ | <0,01 | 0.02 | <0,01 | 0.01 | <0,01 | 0.02 | <0,01 | 0.05 | <0,01 | 0.05 | <0,01 | 0.04 | <0,01 | 0.04 | <0,01 | 0.05 |
| NiO | <0,01 | 0.03 | <0,01 | 0.02 | <0,01 | 0.02 | <0,01 | 0.02 | <0,01 | 0.04 | <0,01 | 0.02 | <0,01 | 0.02 | <0,01 | 0.02 |
| $V_2O_5$ | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | 1 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | 1 | <0,01 | 2 | <0,01 |
| $SO_3$ | <0,01 | 2.79 | <0,01 | 7.34 | <0,01 | 0.08 | <0,01 | 0.11 | <0,01 | 2.79 | <0,01 | 22.8 | <0,01 | 22.3 | <0,01 | 16.5 |
| BaO | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 |
| CuO | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | 0.02 | <0,01 | 0.02 | <0,01 | 0.04 |
| ZnO | <0,01 | 0.08 | <0,01 | 0.09 | <0,01 | 0.03 | <0,01 | 0.03 | <0,01 | 0.03 | <0,01 | 0.02 | <0,01 | 0.02 | <0,01 | 0.03 |
| LOI | 7 | 23.2 | 3 | 27.9 | 1 | 33.6 | 15 | 31.2 | 5 | 26.5 | 4 | 22.3 | 20 | 35.1 | 10 | 23.8 |
| Total | 99 | 99.93 | 100 | 100.02 | 100 | 100.04 | 90 | 100.03 | 100 | 100.06 | 100 | 99.99 | 101 | 100.02 | 100 | 99.81 |

As shown in tab. 2, there was high content of Si, Al, Fe, Mn, Ca, Mg, Na and S in the secondary sludge. These are the main components in acid mine drainage. These results complement the ICP-MS results. Similar results were obtained for soda ash except the levels of those inorganic contaminants. Results also revealed that Na-based salts are the best candidates for Mg and Ca removal. They are also suitable for the recovery of Fe from acid mine drainage. Magnesium based salts removed Al, Fe, Mn from acid mine drainage since they are the major constituents. High content of Ca was also observed in magnesite. This might have contributed to the reduction of sulphate in the product water after contacting the acid mine drainage with magnesite. The Ca-based reagents removed Al, Fe, Mn and elevated levels of sulphate from acid mine drainage. Ca was present because it is part of the seeding material that is being used for neutralization. From this XRF results, one could conclude that an integrated approach can be derived from this treatment process. Mg-based salts can be used for neutralization of acid mine drainage and leave the residual sulphate in solution. Ca-based reagents can be used to remove the residual sulphate to form gypsum.

## Techno-economic appraisals

Economic and technical efficiency of different alkaline generating materials as pre-treatment of acid mine drainage are shown in tab. 3.

***Table 3** Economic and technical efficiency of different alkaline generating materials*

| Material | Caustic soda | Soda ash | Periclase | Brucite | Magnesite | Lime | Hydrated lime | Limestone |
|---|---|---|---|---|---|---|---|---|
| Price (R gram$^{-1}$) | 0.26 | 0.3 | 0.41 | 0.5 | 0.64 | 0.34 | 0.12 | 0.24 |
| Dosages | 10 g | 10 g | 10 g | 10 g | 10 g | 10 g | 10 g | 10 g |
| Liquid | 1 L | 1 L | 1 L | 1 L | 1 L | 1 L | 1 L | 1 L |
| S/L ratio | 1:100 | 1:100 | 1:100 | 1:100 | 1:100 | 1:100 | 1:100 | 1:100 |
| Cost (RL$^{-1}$) | 2.6 | 3 | 4.1 | 5 | 6.4 | 3.4 | 1.2 | 2.4 |
| Particle size | <100 μm | <100 μm | <100 μm | <100 μm | <100 μm | <100 μm | <100 μm | <100 μm |
| Contact time | 60 mins | 60 mins | 60 mins | 60 mins | 60 mins | 60 mins | 60 mins | 60 mins |
| Final pH | 13 | 7 | 10 | 6 | 9 | 6 | 11 | 6 |
| Fe (mgL$^{-1}$) | 3.5 | 45 | 0.9 | 461 | 0.9 | 0.9 | 0.9 | 0.9 |
| Al (mgL$^{-1}$) | 94 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 4.5 | 0.7 |
| Mn (mgL$^{-1}$) | 0.4 | 50 | 0.25 | 75 | 0.25 | 55.6 | 0.25 | 65.7 |
| Sulphate (mgL$^{-1}$) | 33700 | 33700 | 30705 | 32705 | 20705 | 3705 | 3005 | 9000 |
| Host metal (mgL$^{-1}$) | 5836 | 4035 | 1693 | 1590 | 1565 | 549 | 630 | 594 |

As shown in tab. 3, the results obtained from the treatment of acid mine drainage with Caustic soda, Soda ash, Periclase, Brucite, Magnesite, Lime, Hydrated lime and Limestone when contacted with them for 60 min and their respective costs. Magnesium-based agents are more expensive that Na-based and Ca-based agents. Caustic soda, periclase, magnesite and hydrated lime were efficient in the removal of Mn from AMD. Magnesite and periclase were effective for all the chemical species in AMD except the sulphate. This can be removed by a polishing step. Hydrated lime was the most effective, efficient and economic viable way for the treatment of acid mine drainage. It is also much cheaper than all the other neutralizing agents. Lime and limestone could remove Fe and al. complete and partially remove sulphate except Mn. This may be attributed to pH of the secondary solution.

## Conclusions

From this comparative study, it can be concluded that acid mine drainage was successfully treated using different alkaline agents and the techno-economic appraisals were successfully executed. At 60 mins of equilibration, 10 g/L solid/Liquid ratio, >250 agitation speed and ≤ 100 µm particle sizes, the following results were obtained: pH ≥ 13, metal species removal ≥ 90% and sulphate ≥ 10% for caustic soda. pH ≥ 7, al. ≥ 99%, Fe ≥ 60, Mn≥ 30% and sulphate ≥ 30% for soda ash. pH ≥ 10, metal removal efficiency ≥ 99% and ≥ 10% sulphate removal for periclase. pH ≥ 6, al. ≥ 99%, Fe ≥ 60%, Mn ≥ 40% and sulphate ≥ 10% for brucite. pH ≥ 9, al. ≥ 99%, Fe ≥ 99%, Mn ≥ 99% and sulphate ≥ 40% for magnesite. pH ≥ 6, al. ≥ 99%, Fe ≥ 60%, Mn ≥ 30% and sulphate ≥ 60% for lime. pH ≥ 11, al. ≥ 60%, Fe ≥ 99%, Mn ≥ 99% and sulphate ≥ 90% for hydrated lime. pH ≥ 6, al. ≥ 99%, Fe ≥ 99%, Mn ≥ 60% and sulphate ≥ 80% for limestone. Regarding cost, Caustic soda, Soda ash, Periclase, Brucite, Magnesite, Lime, Hydrated lime and Limestone are valued at R 2.6 $L^{-1}$, R 3 $L^{-1}$, R 4.1 $L^{-1}$, R 5 $L^{-1}$, R 6.4 $L^{-1}$, R 3.4 $L^{-1}$, R 1.2 $L^{-1}$, R 2.4 $L^{-1}$ respectively.

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