Evaluation of Nature Based Materials for the Remediation of AMD Water

A Laboratory Based Case Study with the focus on Aluminium and Heavy Metals

Florian Blum

Evaluation of Nature Based Materials for the Remediation of AMD Water. A Laboratory Based Case Study with the focus on Aluminium and Heavy Metals

Florian Blum

Abstract

Abandoned mines often face the problem of Acid mine drainage (AMD). AMD is characterized by high acidity, elevated metal concentrations, and often significant salinization making a treatment of the water necessary to prevent environmental damage and secure water availability. Especially in South Africa, where mining has a big history, solutions to treat AMD are needed.

This study evaluates the effectiveness of various nature-based materials, including limestone, zeolite, unactivated and activated bentonite, and recycling concrete, in treating synthetic AMD with the focus on heavy metals and aluminium. A batch experiment was conducted, using solid to liquid ratio of 2 and 10 g/L and a synthetic AMD based on the water analysis of Brugspruit. The research examines their impact on pH levels and their ability to reduce mineral and metal concentrations. The two main mechanisms to decrease concentration in solution are adsorption and precipitation. Adsorption is mainly attributed to zeolite and the bentonites and precipitation to limestone and concrete due to their chemical and physical properties.

Results indicate that limestone and recycling concrete are particularly effective, increasing pH to 7.3 and 8.4 respectively at a dosage of 10 g/L. Recycling concrete demonstrated superior metal removal capabilities, achieving reductions of 99.7% for aluminium, 100% for iron, 98% for nickel, 100% for zinc, and 88% for manganese. At a lower dosage of 2 g/L, only limestone significantly increased pH and effectively removed metals from the solution. Modelling the process showed, that the removal for limestone and concrete batches might not only be according to precipitation but also adsorption. This means that forming precipitates can also act as adsorbents. Adsorptive materials did not reduce elements in solution in a significant manner.

The pH value was found to be important for metal removal. Adsorptive materials that were not able to increase pH were not able to adsorb metals at low pH values. On the other hand, pH increasing materials such as limestone and concrete showed promise regarding their ability to treat AMD.

However, further investigation is needed to fully understand the exact removal mechanisms and to evaluate applicability of adsorption materials when pH is increased in a first step in a multi stage treatment.

Keywords: Acid mine drainage, water treatment, adsorption, precipitation, natural-based materials

Table of contents

List of tables

List of figures

Abbreviations

Abbreviation	Description
AAS	Atom Adsorption Spectroscopy
ALC	Anoxic Lime Drain
AMD	Acid Mine Drainage
CEC	Cation Exchange Capacity
PRB	Permeable Reactive Barrier
IAP	Ion Activity Product
IC	Ion Chromatography
MIW	Mining Influenced Water
OLC	Oxic Lime Channel
S/L	Solid/Liquid
T&DB	Transvaal & Delago Bay

1. Introduction

1.1 General Scope

The history of coal mining in South Africa goes back until 1857 and has played a vital role in the economic growth of the country (Lebepe 2022). This is not only due to the export of coal but also for the power supply within South Africa, as it is one of the most coal-dependent economies in the world (Republic of South Africa 2021; Hobbs et al. 2008). The impacts of active mining, waste rock piles and abandoned mines are considered as one of the biggest environmental hazards concerning global water pollution (Mashamba 2012). Loss of land and biodiversity on the one hand and the release of toxic elements on the other hand cause the degradation of land and pollution of surface and groundwater (Limpitlaw et al. 2005). Coal mining and the subsequent generation of energy from coal requires large quantities of water. In combination with the pollution of water resources this aggravates the challenging water situation in South Africa and poses a threat to 60 percent of river ecosystems in the country (Ncube 2022). Most of the coal mines and coal-fired power plants are located in the province of Mpumalanga which is considered the hub of coal development. Within this province the town eMalahleni (translates to "place of coal") is located and next to it the river Brugspruit. The Brugspruit river is also subject to contamination due to acid main drainages (AMD) and the contaminants are transported via the Brugspruit River into the Olifants River and ending up in the Loskop Dam north of Emalahleni (Greenpeace). In 2021 there were 6100 so called "derelict and ownerless" mines additionally to the still active ones (5906 more than 2009).

AMD and the release of toxic elements is mainly caused by oxidation of pyrite and other sulphide bearing minerals due to exposure to the atmosphere and water according to Eq. (1)

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{1}$$
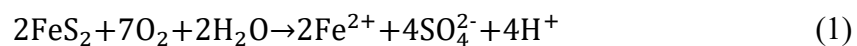
The release of hydrogen ions lowers the pH and fosters the dissolution of metals and minerals (Masindi et al. 2022). In the case of Brugspruit the main contaminants are Na^+, SO_4^{2-}, NH_4^+, Al, Mn, Fe, Ni and Zn accompanied by a low pH-value (Mine Water Network 2023). Those contaminants pose a risk to the adjacent water bodies and endanger the water supply. To protect water bodies and water utilization, it is necessary to treat the AMD and remove acidity and contaminants.

In this study, limestone, bentonite, zeolite and recycling concrete will be tested and evaluated as possible treatment materials to decrease acidity and remove heavy metals from AMD. Those nature-based materials are available in South

Africa and represent a promising alternative to highly technical solutions and can be applied in drains or barriers. The experiments will be carried out with synthetic lab water that was prepared according to the water analysis of the Brugspruit mine. These experiments are the first step in the planning of a site-specific treatment method.

1.2 Site Description Brugspruit

The mine responsible for the contamination of the Brugspruit river is the abandoned Transvaal and Delago Bay colliery (T&DB), which was an underground coal mine. Officially the mine was operating from 1896 until closure in 1953. Thus, it was closed before the legal obligation for mine closure practices was established in 1956 and lies now within the hands of the government. Apart from environmental risks, such as the formation of AMD, the abandoned mine also brings safety hazards with it. Spontaneous combustion, surface collapses and reopened shaft sealings can be a risk for people living close by and passing through the area or people looking for coal reminders for cooking purposes (Limpitlaw et al. 2005; US EPA 2014). According to Munnik et al. (2010) the risk coming from T&DB is the greatest of all abandoned mines in South Africa. Figure 1 shows the decanting AMD from the abandoned mine on the left and a stream of AMD on the right.

Figure 1. Decanting AMD from abandoned Brugspruit mine (left) and AMD stream (right)

To treat the contaminated water of the Brugspruit river, the eMalahleni Water Reclamation Plant was built and started operating in 2007 (Anglo Operations (PTY) LTD). It treats the water in a multistage principle using oxidation, precipitation, ultrafiltration, and reverse osmosis (Hutton et al. 2009). 30 m³/d of water are produced that way (Sergienko). However, the production is still three times more expensive than simply using distributed water and does not solve the ecological problem (Baloyi et al. 2023).

1.3 AMD Formation and Treatment

There are different approaches to treat AMD water. However, all of them can be categorized into two ways of treatment, active and passive. The differences between those two treatment methods are the input of energy, treatment materials and labor. Whereas the active treatment requires higher input the passive treatment aims to minimize them. Different handbooks have been released in the past where the differences in treatment methods are described and specific technologies within them explained (US EPA 2000; Wolkersdorfer 2022; Skousen et al. 1998). Also the chemical analysis and the constituents of the AMD play a vital role for the decision-making process. Gusek (2009) gives a comprehensive overview of all elements that are treatable via passive systems and a provides a decision-making tree to find the most suitable system according to the AMD characterization.

Not all water that drains mines is considered as acid mine drainage. The more general term is mining influenced water (MIW) (Wolkersdorfer 2022). MIW can be classified in different ways depending on the pH value and acidity, dissolved iron species and aluminium and sulphate concentration according to the modified Hill Framework (Thisani et al. 2021).

Table 1. Classification of Mining Influenced Water adapted and modified from the Hill Framework

Class	Class Description	Thresholds		
Class 0 **	Highly concentrated and acidic mine drainage **	pH = 0.5–3 ** Acidity = 5–45 g/L **	Total Fe = 1000–12,000 mg/L **	SO_4 = 10–60 g/L ** Al = 1000–18,000 mg/L **
Class I	Acid Mine Drainage	pH = 2.0–4.5 Acidity = 0 **–15 g/L	Fe^{2+} = 0 **–10,000 mg/L Fe^{3+} = 0 mg/L	SO_4 = 0 **–20 g/L Al = 0–2000 mg/L
Class II	Partially oxidised and/or neutralised	pH = 3.5–6.6 Acidity = 0–1 g/L	Fe^{2+} = 0–500 mg/L Fe^{3+} = 0–1.000 mg/L	SO_4 = 500–10,000 mg/L Al = 0–20 mg/L
Class III	Neutral and not oxidised	pH = 6.5–8.5 Acidity = 0 mg/L	Fe^{2+} = 0–500 mg/L Fe^{3+} = 0 mg/L	SO_4 = 500–10,000 mg/L Al = 0–2000 mg/L
Class IV	Oxidised and neutralised/alkaline	pH = 6.5–8.5 Acidity = 0 mg/L	Fe^{2+} = 0 mg/L Fe^{3+} = 0 mg/L	SO_4 = 500–10,000 mg/L Al = 0 mg/L
Cytotoxic metals indicator **		Low = Zinc $\leq$ 1 mg/L **	Mid = Zinc $\leq$ 25 mg/L **	High = Zinc > 25 mg/L **

Asterisks (**) indicate the revisions made to the original Hill (1968) framework.

Table 1 shows the different classes according to the thresholds of those water parameters. For a MIW to be classified as AMD a pH between 2.0 and 4.5 is required, an acidity of 0 – 15 g/L, ferrous iron concentration Fe^{2+} of 0 – 10,000 mg/L and a ferric iron concentration Fe^{3+} of 0 mg/L, as well as a sulphate concentration SO_4^{2-} of 0 – 20000 mg/L and an aluminium concentration Al of 0 – 2000 mg/L. The selection of those indicator parameters has different backgrounds. The initial work of Hill focused on the characterisation of AMD along the streamflow. This should help to determine age and origin of AMDs. Thisani et al. (2020) used this framework and validated/modified it by analysing 72 mines from 18 countries in 6 continents. Iron and its ratio of ferrous and ferric form and Aluminium can help determining the state of oxidation. Further, the

origin of AMD can be determined by the acidity and sulfate concentration and zinc indicates the toxicity (Thisani et al. 2020; Opitz and Timms 2016). The dominant oxidation state of iron is Fe^{2+} due to the higher stability at the prevailing redox conditions and pH conditions. The formation of AMD occurs if sulfide bearing rock material gets to the surface and thus in contact with the atmosphere during mining activities. This is the case during mining operations, when material is excavated and processed. Deposits of material like tailing dams and spoil heaps can then become oxidized on the surface and weathering products mobilized by rainwater. A mobilization and formation of AMD also occurs from the mine itself. When operation stops, the pumps for lowering the groundwater do not run anymore and the groundwater table starts increasing again.

Microorganisms can accelerate the weathering kinetics and act as catalysts for the process according to Eq. (2)

$$2FeS_2 + 7O_2 + H_2O \xrightarrow{Microorganisms} Fe(OH)_3 + H_2SO_4 \tag{2}$$
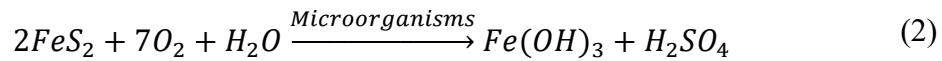
Depending on the available oxygen the forming ferrous iron (Fe^{2+}) (see Eq. 1) can be oxidized to ferric iron (Fe^{3+}) according to Eq. (3)

$$4Fe^{2+} + O_2 + 2H^+ \rightarrow 4Fe^{3+} + H_2O \tag{3}$$
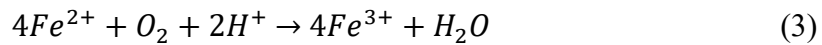
This process consumes acidity in the first step but increases it in a follow-up reaction by either precipitating as iron hydroxide after Eq. (4)

$$2Fe^{3+} + 6H_2O \rightleftharpoons 2Fe(OH)_3(s) + 6H^+ \tag{4}$$
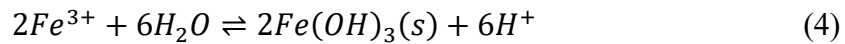
or by further reactions of sulfide minerals after Eq. (5)

$$14Fe^{3+} + FeS_2(s) + 8H_2O \rightarrow 2SO_4^{2-} + 15Fe^{2+} + 16H^+ \tag{5}$$
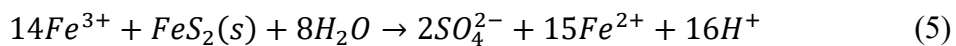
There are different ways to treat AMD. The mechanism behind applied treatment methods are precipitation, adsorption, filtration, bioremediation, and crystallization (Masindi et al. 2022). As mentioned before, there are active and passive methods which make use of those mechanisms. For the active method, a combination of oxidation, dosage of alkalinity and sedimentation is most applied. For most metals, oxidation will turn reduced soluble metal species into a less soluble oxidized form – this is often achieved by aeration. Dosage of alkalinity increases the pH and decreases the solubility of metals leading to metal precipitation. and sedimentation serves to separate the metal precipitates from the water (Alloway et al. 2002). For the improvement of sludge quality and flocculation, flocculants such as aluminium- or iron-sulphates are added before sedimentation (Wolkersdorfer 2022). Another active treatment is membrane treatment as a filtration process. Micro-, ultra- and nanofiltration as well as

reverse osmosis are used to separate contaminants from the water. This is rather used as a secondary treatment as membranes tend to get clogged due to the high loads and are not resistant towards strong acidity. Furthermore, they are costly (Thisani et al. 2021).

Passive treatment is cheaper compared to active treatment and does not require a constant input of chemicals (Skousen et al. 1998). The aim is rather to look at and learn from natural occurring chemical and biological processes like the release of alkalinity from minerals for example (Alloway et al. 2002). However, this is not the same as natural attenuation, as the passive treatment still requires some intervention and input (Wolkersdorfer 2022). Within the passive systems the treatment methods can be further divided into abiotic and biotic methods.

Abiotic methods comprise anoxic limestone drains (ALD), open limestone channels (OLC), limestone leach beds, reducing and alkalinity producing systems or permeable reactive barriers and biotic systems for example in wetlands (constructed or natural) (Wolkersdorfer 2022; Baloyi et al. 2023). Limestone drains and channels differ from each other with respect to residence time and exposure to the atmosphere. Drains are not in contact with the atmosphere and have long residence times as they are built under the surface. Channels are constructed aboveground and thus exposed to the atmosphere and have short residence times. In anaerobic wetlands microbial activity is utilized to fix metals as sulfides. The water flows through an organic substrate where the microorganisms are treating it. Reducing and alkalinity producing systems bring anoxic drains and anerobic wetlands together and consist of a limestone and a compost layer (Wolkersdorfer 2022; Alloway et al. 2002). Another way to passively treat AMD is via permeable reactive barriers (PRB). Therefore, a permeable barrier is placed into the ground in the pathway of the groundwater flow, which interacts with the contaminated water. The barrier contains materials which mediate microbial activities and precipitation of metals (Shabalala et al. 2014).

Materials used in the aforementioned treatments have the aim to either increase pH and/or to adsorb contaminants. For pH neutralization, there's a range of possible materials. The most commonly used material is limestone (calcium carbonate, $CaCO_3$), but there are also other calcium-based materials like hydrated lime (calcium hydroxide, $Ca(OH)_2$) or pebble quicklime (calcium oxide, CaO). The differences regarding AMD treatment are efficiency and costs. Limestone, being the cheapest, has the lowest efficiency (up to 50%) whereas hydrated lime and pebble quicklime have higher efficiencies (up to 95% and up to 90% respectively) but are also more cost intensive (Skousen et al. 1998). Another group of alkaline materials are sodium based like soda ash (sodium carbonate, Na_2CO_3) or liquid or solid caustic soda (sodium hydroxide, $NaOH$) which have a higher efficiency (Skousen et al. 1998; Wolkersdorfer 2022). Materials used in the

treatment with PRB are mainly organic to feed the sulphate-reducing microorganisms, but also iron, limestone or carbon are being used to promote the removal of dissolved metals (Shabalala et al. 2014; Costello 2003). For adsorption the materials are not as clearly defined, as the method is emerging rather than well established. However, there has been a lot of research done on possible materials (Wolkersdorfer 2022). The studied materials range from waste products like fly ash or walnut shells to natural based materials like zeolite or clay minerals to engineered ones like modified silica gel or carbon nano tubes. Each of them has a selectivity for different contaminants (Wibowo et al. 2023).

1.4 Mechanisms for Metal Removal

Two mechanisms are well known for the removal of metals and the decrease of concentration in solution, adsorption and precipitation. Depending on the material being used, either one of those mechanisms or sometimes also both can be identified as the responsible mechanisms (Prepilková et al. 2022). Following, the mechanisms will be explained.

1.4.1 Adsorption

Adsorption is a process which occurs on the liquid-solid interface (also other interfaces but they don't play a role here). The crystal structure and central atoms within the lattice, as well as functional groups on the surface of the solids cause electrostatic charges which can attract and repulse other charged particles and ions. In general adsorption can be classified in electrostatic attraction, ion exchange, surface complexation and physical adsorption (Stumm and Morgan 1996).

Electrostatic attraction appears due to opposite charges. This means that the negatively charged surface of the adsorbate can attract positively charged ions. Ion exchange works similarly, but in this case the negatively charged site is occupied by another positively charged ion, which is then replaced by the adsorbed ion. Surface complexation occurs via hydrolysis and the formation of coordinative bonds. Physical adsorption is the detention of ions in pores. (Stumm and Morgan 1996)

Bentonite and Zeolite

Bentonite is mainly composed of montmorillonite (clay mineral). It has two tetrahedral layers (SiO_4) separated by an octahedral ($Al(OH)_6$) layer. The negative surface charge is due to isomorphic substitution. Ions of lower charge (like Al^{3+}, Mg^{2+} and Fe^{2+}) replace ions with higher charge (Si^{4+}, Al^{3+}) thus the net charge becomes negative. Those negative charges are neutralized by compensating cations, which then can be replaced. (Marouf et al. 2021)

Zeolite is a crystalline, microporous aluminosilicate and consists of corner sharing SiO_4/ AlO_4 tetrahedra. Also, in zeolite there are Na^+, K^+ or Ca^{2+} that can be exchanged by metal cations and thus be immobilized. Zeolite can be quite selective based on the size, charge and hydration energy of metal ions. (Pérez-Botella et al. 2022)

1.4.2 Precipitation

Precipitation occurs when a solution becomes oversaturated. This is the case when the free energy is negative, which is true when the ion activity product (IAP) is bigger than the solubility constant. A shift in pH can cause an oversaturation of minerals, as the IAP increases with a decreasing concentration of H^+. The following equation shows the equilibrium reaction on an example of a divalent metal hydroxide with protons.

$$Me(OH)_{2(s)} + 2H^+ = Me^{2+} + H_2O \tag{6}$$
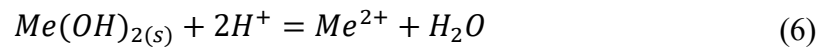
If the solubility product is calculated according to Stumm and Morgan (1996)

$$^{c*}K_{s0} = \frac{[Me^{2+}]}{[H^+]^2} \tag{7}$$

when there is a low pH, hence a high proton concentration, the product gets smaller, thus the concentration of $Me(OH)_2(s)$ gets smaller. On the other hand, when the pH increases, the constant gets bigger and the concentration of $Me(OH)_2(s)$ increases.

So, with neutralizing acidity, not only protons are reduced but also dissolved metal contamination. Figure 2 shows a schematic example of the solubility for metal hydroxides. This figure indicates that metals turn to insoluble forms when the solution becomes oversaturated (Stumm and Morgan 1996).
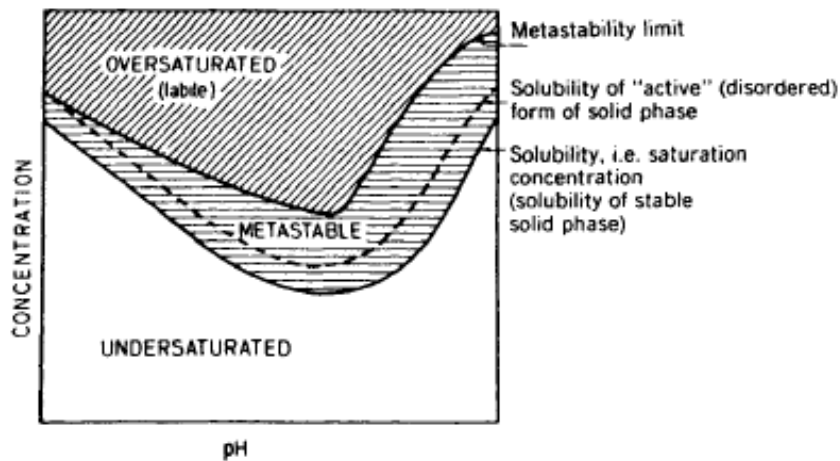
Figure 2. Schematic display of relation between concentration and pH for saturated and undersaturated solutions (Stumm and Morgan 1996)

The solubility changes with every metal and is also depending on the general hydrochemistry of the solution. Therefore, the target pH value depends on the metal to be removed and a staged treatment might be necessary (Wolkersdorfer 2022).

Juragrain and Concrete

Juragrain and concrete are both able to increase the pH value of an acidic solution. Juragrain consists of calcite ($CaCO_3$) and magnesite ($MgCO_3$). Concrete consists mainly of quicklime (CaO). The dissolution of these compounds neutralizes acidity after the following equations

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \qquad (7)$$

$$MgCO_3 + 2H^+ \rightarrow Mg^{2+} + CO_2 + H_2O \qquad (8)$$

$$CaO + 2H^+ \rightarrow Ca^{2+} + H_2O \qquad (9)$$
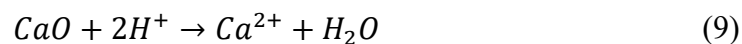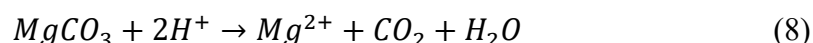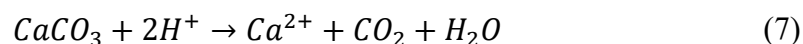
1.4.3 Influences

Main influencing factor for both processes are pH and ionic strength. The influence of pH for precipitation could already be seen in Figure 2. But also, for adsorption it plays a vital role, as positively charged protons can screen the negatively charged surface of adsorbents.

Ionic strength can influence available binding sites, activity coefficients and electrostatic attraction. An increasing ionic strength might reduce available binding sites due to a reduction of electrostatic repulsion, reduce the activity for

example of Zn, Al or Mg and a high salt concentration can screen the surface of the adsorbate which hinders an electrostatic attraction with metal ions. But it is important to say that not all metals are affected in the same way (Stumm and Morgan 1996). Table 2 shows a list of ions and their activity coefficients at different ionic strengths. This visualizes the differences in the effect. But an increase in ionic does not necessarily has to have negative effects. It can also cause a compression of the electric double layer, thus increases adsorption and vice versa (He et al. 2009). The effect of ionic strength also depends on the prevailing pH. If the pH is above the point of zero salt effect, adsorption is not dependent on the ionic strength anymore (Li et al. 2009). A higher ionic strength and variability of present ions can also lead to the complexation of metal ions in solution leading to a higher solubility and lower adsorption (He et al. 2009).

Another influencing factor is initial concentration. A higher concentration in solutions means a bigger gradient, which is the driving force for diffusion, meaning that diffusion is not the limiting factor in highly concentrated solutions. At a certain point the repulsion forces become the limiting factor. (Xu et al. 2022)

However, the aqueous complexation of divalent metal cations with SO_4^{2-}, CO_3^{2-}, HCO_3^- or Cl^- can increase the solubility of dissolved metal hydroxides (Millero and Hawke 1992). Therefore, the actual solubility is dependent on the general hydrochemistry.

Table 2. Activity coefficients for different solutes and different ionic strengths

Ion Size Parameter a ($\mathring{A}$)[a]	Ion	Activity Coefficients Calculated with Equation 2 of Table 3.3 for Ionic Strength				
		10^{-4}	10^{-3}	10^{-2}	0.05	10^{-1}
9	H^+	0.99	0.97	0.91	0.86	0.83
	Al^{3+}, Fe^{3+}, La^{3+}, Ce^{3+}	0.90	0.74	0.44	0.24	0.18
8	Mg^{2+}, Be^{2+}	0.96	0.87	0.69	0.52	0.45
6	Ca^{2+}, Zn^{2+}, Cu^{2+}, Sn^{2+}, Mn^{2+} Fe^{2+}	0.96	0.87	0.68	0.48	0.40
5	Ba^{2+}, Sr^{2+}, Pb^{2+}, CO_3^{2-}	0.96	0.87	0.67	0.46	0.39
4	Na^+, HCO_3^-, $H_2PO_4^-$, CH_3COO^-	0.99	0.96	0.90	0.81	0.77
	SO_4^{2-}, HPO_4^{2-}	0.96	0.87	0.66	0.44	0.36
	PO_4^{3-}	0.90	0.72	0.40	0.16	0.10
3	K^+, Ag^+, NH_4^+, OH^-, Cl^- ClO_4^-, NO_3^-, I^-, HS^-	0.99	0.96	0.90	0.80	0.76

1.5 Purpose and Strategy

As mentioned in chapter 1.3, there are some technologies for the treatment of AMD that have been established. However, they can not or will not applied be in southern Africa. This is due to various reasons. Often technologies are too costly to be applied, and responsibilities might be unknown due to illegal activities and

abandonments of mine sites. Further, the complexity of the issue is too high and the technical expertise not sufficient to make use of the technologies. This also leads to a wrong application of treatment technologies regarding dimension and operation and maintenance for example. Therefore, it is necessary to investigate and establish methods that are low in cost, locally available and easy to operate and maintain while being site specific, sufficient and sustainable in the treatment of contaminated water. The materials investigated within this study are locally available (local mines and concrete factory) and do not need a constant input of electrical energy.

This study aims to evaluate the applicability for removing metals from AMD of limestone, zeolite, bentonite and concrete and further investigate the mechanisms leading to the removal from solution. This will be done by using a synthetic AMD prepared in the laboratory and with materials obtained from contacted companies for research purposes. With those materials and the synthetic AMD, a batch experiment is conducted. After the experiment samples are taken and analyzed for metals and ions used to prepare the AMD. The results will then be discussed regarding changes in concentrations and underlying mechanisms. Further, the results are compared to other studies investigating the same materials for the treatment of AMD. To further distinguish possible occurring processes, a calculation of saturation indexes is done using Visual MINTEQ.

2.   Materials

2.1   Synthetic AMD

For the laboratory experiments, two synthetic AMD waters (*SynAMD1*, *SynAMD2*) have been used. Full analysis of the Brugspruit mine water is shown in Appendix 1. The analysis synthetic AMDs and of the comparison to the original AMD water (Brugspruit mine) are shown in Table 3. *SynAMD1* was used for bentonites, recycling concrete and zeolite. *SynAMD2* was used for the experiment with limestone, as limestone was delivered at a later date.

Table 3. Analysis of synthetic AMD and the original AMD

		Brugspruit mine	SynAMD1	SynAMD2
Sampling Date		16.02.2023	22.03.2024	26.03.2024
spec. el. conductivity (25°C) Lab	µS/cm	8250	12020	9890
pH value Lab		3.15	2.3	2.3
Temperature Lab	°C	21.8	21.5	18.5
Sodium (Na$^+$)	mg/L	890	1600	900
Potassium (K$^+$)	mg/L	14.5	34	18
Calcium (Ca^{2+})	mg/L	454	370	410
Magnesium (Mg^{2+})	mg/L	298	270	290
Ammonium (NH$_4^+$)	mg/L	52	48	83
Chloride (Cl$^-$)	mg/L	88	86	92
Sulphate (SO$_4^{2-}$)	mg/L	5700	7500	5300
Aluminium (Al)	mg/L	81	219	96
Iron total (Fe)	mg/L	5.22	183	206
Manganese total (Mn)	mg/L	27	25	27
Nickel (Ni)	mg/L	1.41	1.59	1.11
Zinc (Zn)	mg/L	3.53	2.64	2.77
Ionic strength (calculated)	mol/L	0.1297	0.1615	0.1239

2.2 Tested Materials

For the experiment, five different materials, limestone, zeolite, bentonite, activated bentonite and recycled concrete, have been investigated. In the case of bentonite three different kinds and in case of activated bentonite two different kinds have been used, as all contacted companies sent samples.

(a)　　　　　　　　(b)　　　　　　　　(c)

(d)　　　　　　　　(e)　　　　　　　　(f)

(g)　　　　　　　　(h)
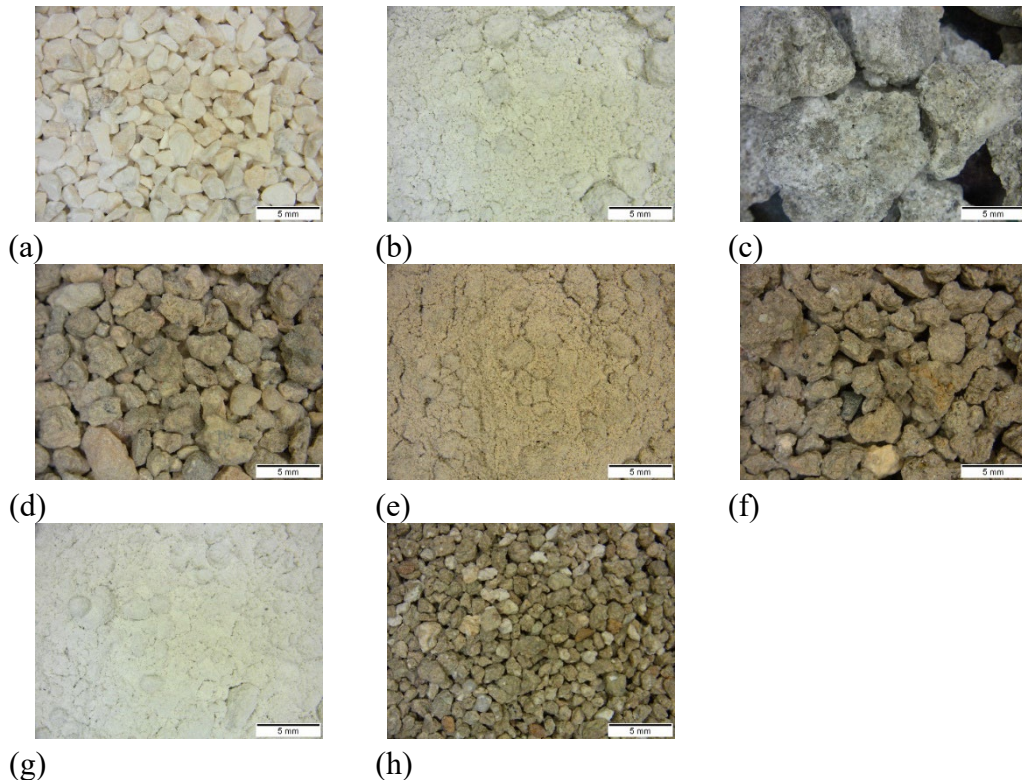
Figure 3. Microscopic picture in 7 - fold enlargement of (a) lime, (b) zeolite, (c) recycling concrete, (d) Florisol B-extra, (e) B316, (f) not activated bentonite, (g) B337 and (h) activated bentonite

The used jura grain (CWG Watertechnology GmbH) consists of 99 % of calcium carbonate (54.5 %) and magnesium carbonate (45.3 %) and is used to filtrate particles and remove acidity. It has a grain size of 1.0 – 2.5 mm. (see Figure 3 (a))

Zeolite (ZeoCem) is an aluminium silicate. It has a porous structure and a good cation exchange capacity (cec) and can adsorb heavy metals. It is used as building material, in agriculture and for water treatment. It has the grain size 0 – 0.2 mm. (see Figure 3 (b))

Recycled concrete (Hechinger GmbH) was picked up at the recycling yard as boulders. (see Figure 3 (c))

Ca-bentonite was provided by three different companies (Florisol B-extra by Stephan Schmidt Group (see Figure 3 (d)), not activated bentonite by Keramost (Figure 3 (e)), B316 by Theodor Stephan KG (Figure 3 (f))). Bentonites, like

zeolites, also have a good cec (Florisol = 80 mmol/ 100 g; unactivated bentonite = not specified; B316 = 76 mmol / 100 g) and are used in building materials, soil additives in agriculture and for water treatment. The fractions of the Ca-bentonite were < 0.7 mm for Florisol B-extra, < 2 mm for the one from Keramost and < 0.063 mm for B316.

Na-bentonite (provided by Keramost (Figure 3 (g)) and Theodor Stephan KG (Figure 3 (h))) is activated Ca-bentonite. Soluble soda is added to the Ca-bentonite and Na replaces Ca. This increases the swelling ability and exchange capacity (activated Bentonite = not specified; B337 = 105 mmol / 100 g) and has a positive effect on rising the pH. Keramost Na-bentonit was provided granulated in a grain size of < 2 mm and the one from Theodor Stephan KG in a grain size of < 0.25 mm. Table 3 shows an overview of the used materials and their properties.

Table 4. Materials used in this study with corresponding mineralogy, grain size and CEC

Material	Mineralogy	Grain size	CEC
Jura Grain	54.5 % CaCO3 45.3 % MgCO3	1.0 – 2.5 mm	-
Zeolite	Al-silicate	< 0.2 mm	
Recycled Concrete	CaO	Boulders	
Florisol-B	Clay mineral (Ca-Bentonite)	< 0.7 mm	80 mmol / 100 g
Not activated bentonite	Clay mineral (Ca-Bentonite)	< 2 mm	-
B316	Clay mineral (Ca-Bentonite)	< 0.063 mm	76 mmol / 100 g
Activated bentonite	Clay mineral (Na-Bentonite)	< 2 mm	-
B336	Clay mineral (Na-Bentonite)	< 0.25 mm	105 mmol / 100 g

3. Methods

3.1 Preparation of Synthetic AMD

The laboratory experiments will be conducted with a synthetic AMD water according to the water analysis of the Brugspruit mine. The synthetic water is slightly simplified, and not all of the elements analysed from the original water sample were added. Although this study only focuses on metal removal, other critical elements are added as well to achieve a water chemistry close to reality. Therefore, Zn, Ni, Al, Fe, Mn, Mg^{2+}, Ca^{2+}, Na^+, K^+ NH_4^+, Cl^- and SO_4^{2-} were used for the preparation of the synthetic AMD water. Results of the effect on the ion concentrations are displayed in the Results section (Chapter 4) but not discussed separately. The addition of Fe is done using Fe^{2+} salts as this is the predominant form of iron in AMD (see chapter 1.3).

The salts and acids used, and the masses added to prepare a 5 L solution are listed in Table 5. Based on the analysis of the Brugspruit water and the available salts for the preparation, the weightings needed to achieve the necessary concentrations were calculated using the molecular weight of the hydrated salts.

Table 5. Added salts and acids for the preparation of synthetic AMD

	Synthetic AMD 1	Synthetic AMD 2
Salt	**Dosage [mg]**	**Dosage [mg]**
$ZnSO_4 * 7 H_2O$	0.0824	0.0794
$NiSO_4 * 6 H_2O$	0.0317	0.0296
$Al_2(SO4)_3 * 18 H_2O$	9.9	5.019
$FeSO_4 * 7 H_2O$	0.1314	0.1293
$MnCl_2 * 4 H_2O$	0.4946	0.4844
$MgSO_4 * 7 H_2O$	15.137	15.024
$CaSO_4 * 2 H_2O$	9.645	9.807
$Na_2SO_4 * 10 H_2O$	61.954	31.162
K_2SO_4	0.3597	0.1639
$(NH_4)_2[Fe(SO_4)_2] * 6 H_2O$	5.799	5.686
Acid	**Dosage [mL]**	**Dosage [mL]**
H_2SO_4 62%	2.98	2.98
HCl 25%	0.96	0.96

For practical reasons, the 5 L solution was prepared stepwise using a 1 L graduated cylinder. In five steps the cylinder was first filled with 1 L of deionized water and then some of the salts were added. For mixing in the salts, the cylinder was placed on a stirring plate and stirred using a magnetic stirrer. This was repeated five times and the final solution was given in a 5 L can. Hydrochloric acid and sulfuric acid were added in the fourth step and iron salt is added last, so the pH of the solution is as low as possible, and the immediate precipitation of iron prevented.

3.2 Experimental Procedure

To evaluate and compare the different materials, a batch experiment was carried out. Therefore, 150 mL of the prepared synthetic AMD solution was given into 250 mL bottles. Two different Solid/Liquid (S/L) -ratios were examined, 2 and 10 g/L. This helps to make first assumptions for adsorbent usage in further studies and to understand adsorption capacities and kinetics. For the S/L-ratio of 2 mg/L, 0.3 mg of material were added to the bottle and for the S/L-ratio of 10 mg/L, 1.5 mg were added. For each material a duplicate set was prepared as well as a blank reference without any material. The bottles were then placed on a plate shaker at 160 rpm for 24 h. After shaking, the samples were centrifuged at 4000 rpm for 5 minutes using a Phoenix Instruments DC0412-50. After centrifuging the sample was filtered using a 0.45 µm polyamide syringe filter to remove the last remaining particles.

Due to a delivery delay, the experiments with limestone were carried out later and a new synthetic AMD was prepared. The second prepared AMD differed slightly from the first as the analysis showed differences from the original AMD sample.

The samples were named according to the used material and the S/L-ratio as displayed in Table 6.

Table 6. Used materials with according sample names

Material	Company	Brand Name	2 g/L	10 g/L
Limestone	CWG Watertechnology GmbH	Filtermaterial CC (Jurakorn)	Jurakalk 2	Jurakalk 10
Zeolite	ZeoCem	ZeoAqua	Zeo 2	Zeo 10
Recycling concrete	Hechinger GmbH		recBet 2	recBet 10
Ca-bentonite	Stephan Schmidt Group	Florisol B-extra	Florisol 2	Florisol 10
	Theodor Stephan KG	B316	B316 2	B316 10
	Keramost	Nicht aktivierter Bentonit	noBen 2	noBen 10
Na-bentonite	Theodor Stephan KG	B337	B337 2	B337 10
	Keramost	aktivierter Bentonit	actiBen 2	actiBen 10

For a better comparison of the materials, they were prepared to have the same grain size. The recycling concrete was first crushed using a hammer and chisel. Jura grain, Florisol B-extra, the bentonites from Keramost, B337 and the crushed recycling concrete were milled using the Retsch PM 200 ball mill. All materials were then sieved with the Retsch AS 450 Basic vibratory sieve shaker. Between milling and sieving the beaker and sieves were cleaned to avoid contamination. For all experiments, the fraction < 63 μm was used.

Further, the pH values of the used materials in deionized water were determined. The comparison of the pH in deionized water and in AMD can give an idea about the buffer capacity and the potential for acidity removal for the materials. To determine the pH in deionized water, a 400 mL beaker was placed on a stirring plate with a magnetic stirrer and a pH probe was placed in it. 200 mL of deionized water was then added to the beaker followed by 2 g of material, to get a S/L-ratio of 10 g/L. The pH was measured throughout the whole time and recorded every 10 seconds. This was repeated for every material used for the batch experiment.

Metal concentrations (Al, Fe, Mn, Ni and Zn) were measured using atom absorption spectroscopy (AAS, Analytic Jena ContraAA 800) and ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^- and SO_4^{2-}) were measured using ion chromatography (IC,

Dionex ICS-2100). For the pH measurements, a WTW MultiLine 3620 IDS with the Sentix 940 probe was used.

All applied materials were examined under the microscope (Olympus SZX16) unprepared (not milled and sieved) and prepared before and after the batch experiments.

4. Results

In case of the laboratory preparation of the Brugspruit AMD, most elements had similar concentrations in the synthetic AMD compared to the original Brugspruit mine sample. Especially for the *SynAMD2* sample, only iron and ammonium with 206 and 83 mg/L compared to 5.22 and 52 mg/L showed bigger differences. For the *SynAMD1* sample iron (183.7 mg/L) but also aluminum, sodium, potassium, and sulphate had higher concentrations (219, 1600, 34 and 7500 mg/L) compared to the original AMD (81, 890, 14 and 5700 g/L). The resulting ionic strength was calculated using Visual MINTEQ and is displayed in Table 3. Especially for *SynAMD1* the ionic strength exhibited a higher value (0.1615 mol/L) compared to the original AMD (0.1297 mol/L). The pH values of the synthetic AMDs (both 2.3) are lower compared to the original one (3.15). For the IS *SynAMD2* has a similar value (0.1239 mol/L) compared to the original (0.1297 mol/L), but *SynAMD2* has a higher value (0.1615 mol/L).

The results of the pH measurement in deionized water are displayed in Figure 4. *B316* and *Florisol* had the least effect on pH (7.5 and 7.8), followed by *Zeo* and *noBen* (8.8 and 9.1). The greatest impact had *Jurakalk* and the activated bentonites *B337* and *actiBen* (9.7, 10.3 and 10.5) and *recBet* (10.7).
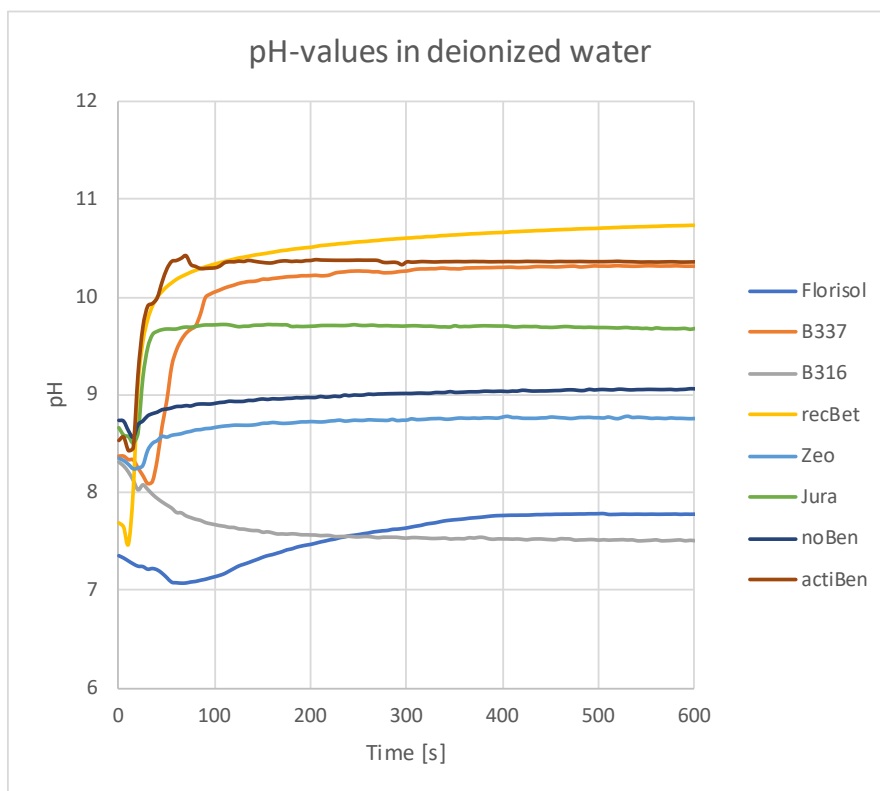

Figure 4. pH values of tested materials in deionized water

The effect on the pH of the AMD in relation to the S/L ratio is shown in Figure 5. For *B316*, *noBen*, *B337* and *Zeo* the higher dosage of material did not result in a stronger increase in pH and pH remained almost the same. But *Florisol*, *actiBen*, *recBet* and *Jurakalk* did cause a bigger increase in the experiments with a dosage of 10 g/L. For *recBet* and *Jurakalk* there was the biggest increase in pH (8.4 and 7.3). But also, for *actiBen* and *Florisol* there was a slight increase in pH (4.3 and 3.4). In case of *B316*, *B337*, *Zeo* and the *blank* sample the pH showed nearly no differences (2.4, 2.4, 2.4 and 2.3) to the *SynAMD1* initial pH (2.3).
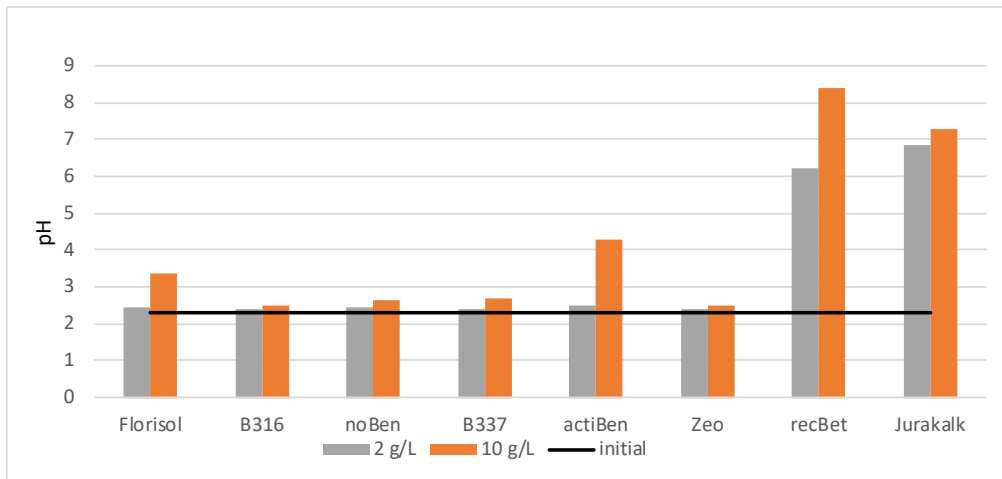
Figure 5. Comparison of pH- values of experiments with S/L-ratios of 2 and 10 g/L to the initial pH of the synthetic AMD

Comparing the pH in deionized water and AMD for the dosage of it stands out that the activated bentonites did not have the same effect in AMD as in deionized water, where the effect was bigger than for *Jurakalk*, although *actiBen* was able to increase the pH to some extent. Otherwise (apart from *Jurakalk* and *recBet*) the effect was similar (little to no effect).

The concentrations of cations and anions are shown in Figure 6 a - g. The concentrations of the untreated synthetic AMD and the *blank* sample are displayed in black bars and the batches containing material are in grey (2 g/L) and orange (10 g/L). For Na^+, K^+, Mg^{2+} and Cl^- the concentrations remained almost the same for all materials and S/L-ratios. Only *actiBen* showed a clear increase of Na^+ for 10 g/L (2000 mg/L). For K^+ *Zeo* had higher concentrations in both S/L-ratios (48.5 mg/L for 2 g/L and 73.5 mg/L for 10 g/L) and *Florisol* and *B337* a slightly higher in the 10 g/L batch with 42.5 and 45 mg/L. *recBet* had a strong rise for Cl^- for 10 g/L (130 mg/L). For Ca^{2+} all materials had higher concentrations in the 10 g/L batches and higher values compared to the untreated AMD. NH_4^+ and SO_4^{2-} showed higher concentrations in the *blank* sample compared to the untreated sample. For NH_4^+ especially *Florisol* (93 mg/L for 2 g/L and 71 mg/L for 10 g/L), *noBen* (84 mg/L for 2 g/L and 75 mg/L for 10 g/L), *actiBen* (81 mg/L for 2 g/L and 85 mg/L for 10 g/L) and *recBet* (84 mg/L for 2 g/L and 86 mg/L for

10 g/L) had higher concentrations compared to the untreated AMD (45 mg/L) and the *blank* sample (59 mg/L). Only *Zeo* in the 10 g/L batch was able to decrease NH_4^+ concentrations (38 mg/L). In case of SO_4^{2-}, all batches exhibited values between *SynAMD1* (7500 mg/L) and the *blank* sample (9000 mg/L). Only *Florisol* (9900 mg/L in 2 g/L and 9550 mg/L in 10 g/L) and *B316* (9650 mg/L in 2 g/L and 9150 mg/L in 10 g/L) had higher concentrations. It also stands out that NH_4^+ exhibits a higher standard deviation compared to the other ions.
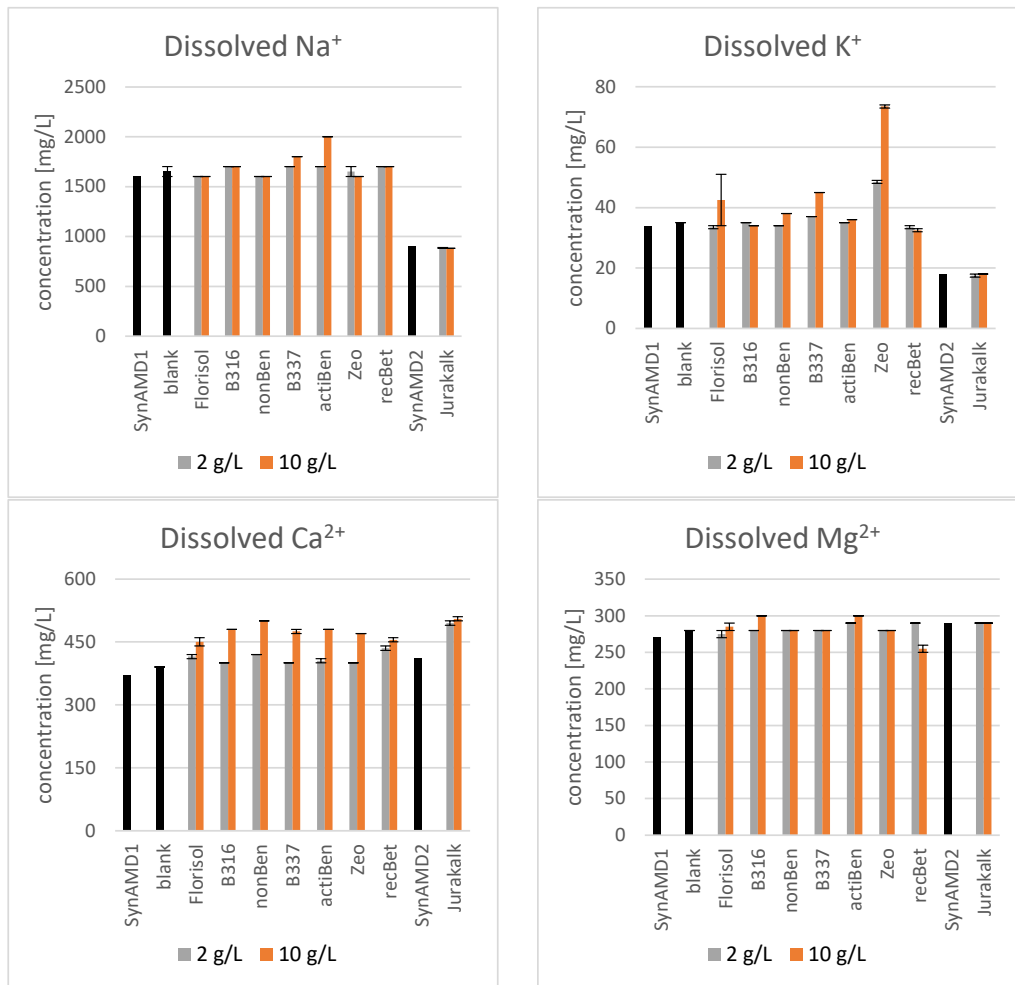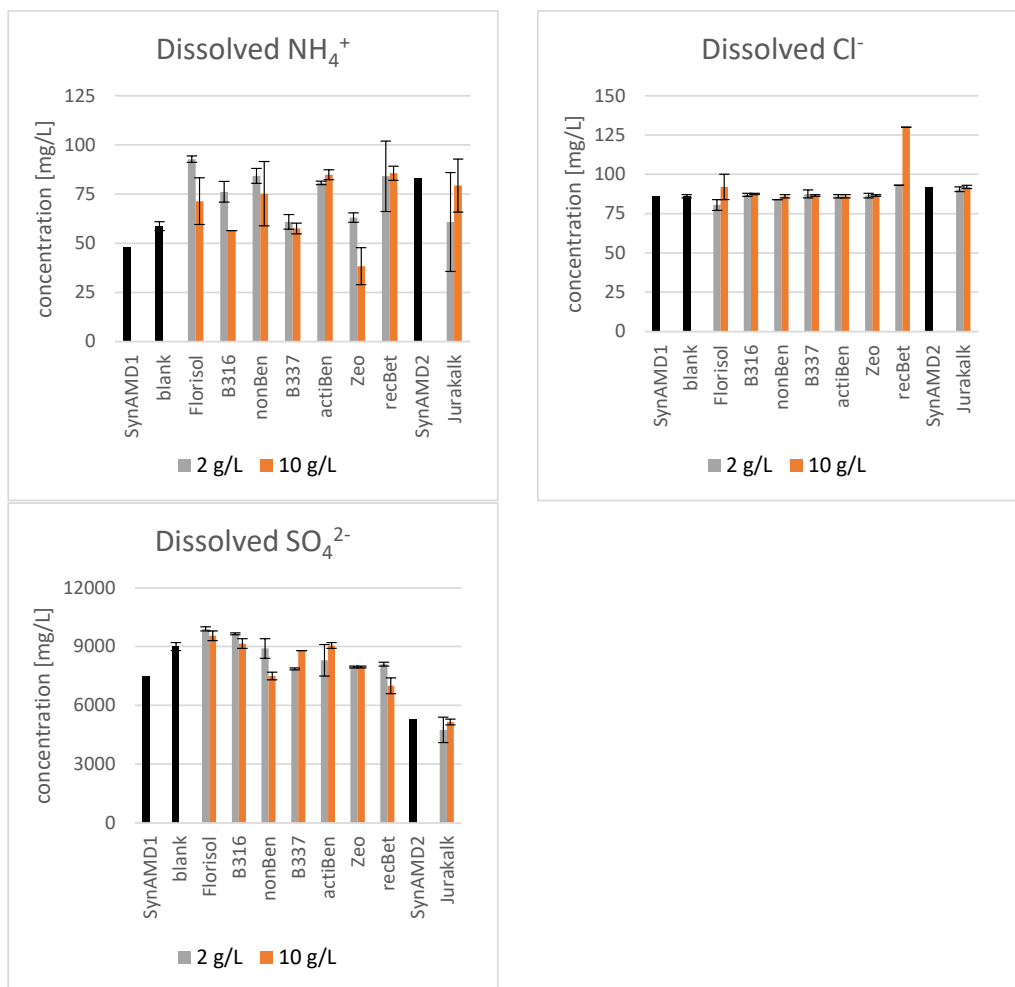
Figure 6. Comparison of ion concentrations of the batch experiments and "SynAMD1", "SynAMD2" and "blank" sample for Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^- and SO_4^{2-}

Figure 7 shows the concentrations of metals. The concentrations of the untreated synthetic AMD and the blank sample are again displayed in black bars and the batches containing material are in grey (2 g/L) and orange (10 g/L). For 2 g/L the concentrations of metals remained almost the same for all materials except of *Jurakalk*. *Jurakalk* was able to decrease concentrations of Al (0.003 mg/L), Fe (13 mg/L) and Zn (1.3 mg/L) compared to the *SynAMD2* sample (96.8, 206 and 1.8 mg/L). In case of 10 g/L the differences to the untreated AMD are more visible. For Al, it can be perceived that the samples with higher increases in pH (*Jurakalk*, *recBet* and *actiBen*) have lower concentrations (0.7, < 0.02 and 114 mg/L). For Fe this is only true for *Jurakalk* (< 0.2 mg/L) and *recBet* (< 0.2 mg/L). *actiBen* (163 mg/L) did not have such a strong effect on metal concentrations despite an increased pH (4.3) compared to the untreated sample (173 mg/L). When it comes to Mn, Zn and Ni, despite the strong increase in pH of *Jurakalk*, the elements were not completely removed from solution (22.9, 0.56 and 0.74 mg/L compared to 27, 2.77 and 1.1 mg/L). However, it did remove most

of Zn, around half of Ni but almost no Mn. For some materials there was an increase of elements in solution. *Florisol, noBen* and *Zeo* showed an increase in Al-concentration and *B316, Florisol* and *noBen* samples showed a significant increase in Mn-concentration (35.1, 35.3 and 36.6 mg/L).
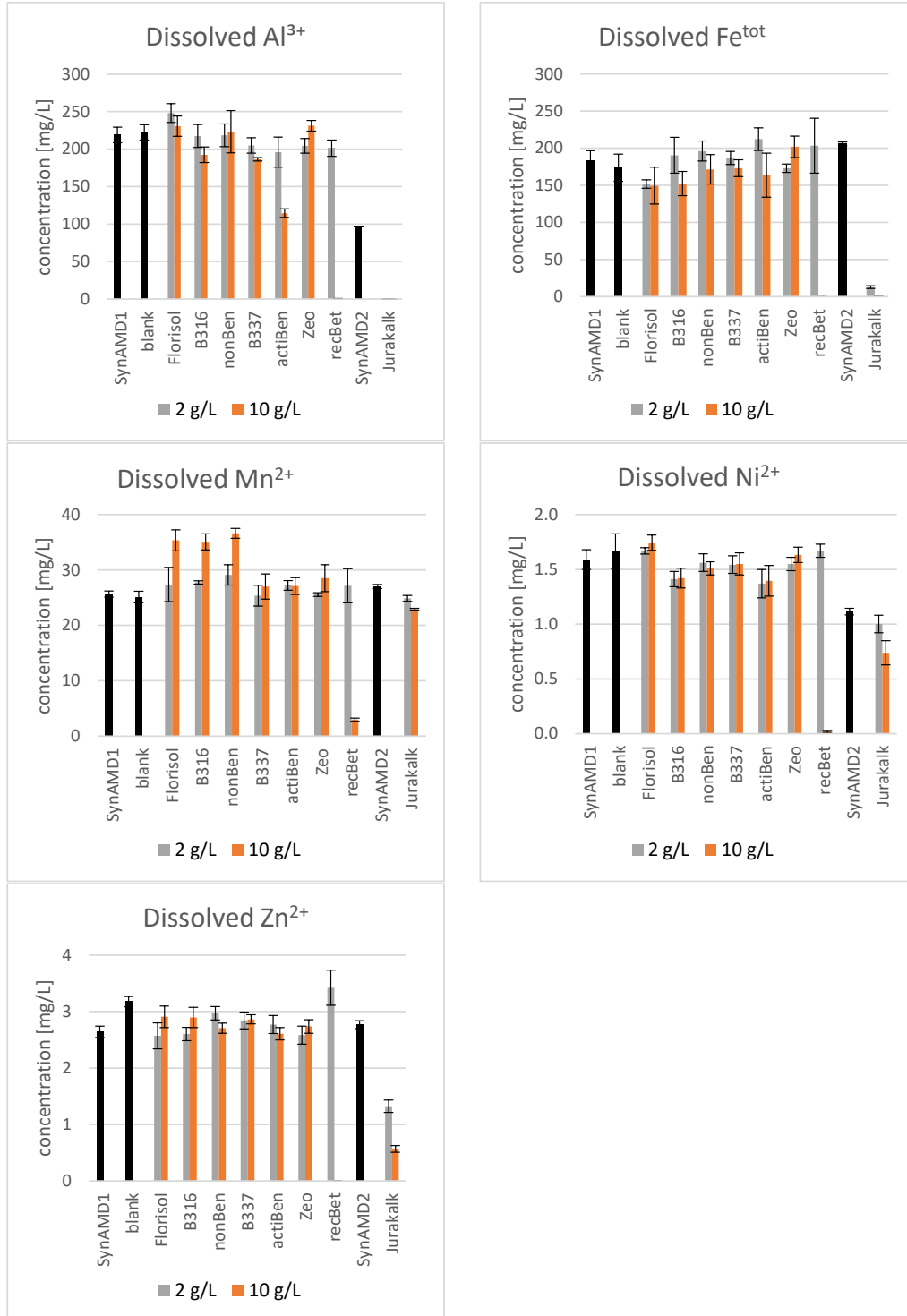
Figure 7. Comparison of metal concentrations of the batch experiments and "SynAMD1" "SynAMD2" and "blank" sample for Al^{3+}, Fe^{tot}, Mn^{2+}, Ni^{2+} and Zn^{2+}

Visual MINTEQ was used to investigate if the process of precipitation can be a reason for the reduction of elements in solution. Therefore, the initial concentrations before the experiment of *SynAMD1* and *SynAMD2* have been put in as components and the pH fixed to the pH after the experiment. After running the program, the saturation indexes have been used to see which minerals possibly precipitated (indicated by a positive index and green cell, see Appendix 3). Afterwards, those minerals have been set as "possibly solid phase". After running the program again, the theoretical amount of precipitated element was displayed by "Equilibrated mass distribution". Table 7 and Table 8 show the precipitation on the example of *Jurakalk* and *recBet* with an S/L-ration of 10 g/L

Table 7.Output-file "Equilibrated mass distribution" form Visual MINTEQ for Jurakalk 10 g/L

Component	Total dissolved [mol/L]	% dissolved	Total precipitated [mol/L]	% precipitated
Al^{+3}	1,88E-07	0,002	8,11E-03	99,998
Ca^{+2}	1,88E-01	100	0,00E+00	0
Cl^{-1}	2,43E-03	100	0,00E+00	0
CO_3^{-2}	1,00E-16	100	0,00E+00	0
Fe^{+2}	2,03E-09	0	3,29E-03	100
H^{+1}	-2,92E-04	100	0,00E+00	0
K^{+1}	8,70E-04	100	0,00E+00	0
Mg^{+2}	1,11E-02	100	0,00E+00	0
Mn^{+2}	4,67E-04	100	0,00E+00	0
Na^{+1}	6,96E-02	100	0,00E+00	0
NH_4^{+1}	2,66E-03	100	0,00E+00	0
Ni^{+2}	5,18E-06	19,11	2,19E-05	80,89
SO_4^{-2}	7,81E-02	100	0,00E+00	0
Zn^{+2}	4,04E-05	100	0,00E+00	0

Table 8. Output-file "Equilibrated mass distribution" from Visual MINTEQ for recBet 10 g/L

Component	Total dissolved [mol/L]	% dissolved	Total precipitated [mol/L]	% precipitated
Al^{+3}	2,24E-10	0	3,59E-03	100
Ca^{+2}	3,11E-03	2,828	1,07E-01	97,172
Cl^{-1}	2,60E-03	100	0,00E+00	0
CO_3^{-2}	1,03E-02	4,7	2,08E-01	95,3
Fe^{+2}	1,90E-03	51,392	1,79E-03	48,608
H^{+1}	1,09E-02	100	0,00E+00	0
K^{+1}	4,60E-04	100	0,00E+00	0
Mg^{+2}	2,93E-02	22,457	1,01E-01	77,543
Mn^{+2}	4,92E-04	100	0,00E+00	0
Na^{+1}	3,91E-02	100	0,00E+00	0
NH_4^{+1}	4,60E-03	100	0,00E+00	0
Ni^{+2}	1,89E-05	100	0,00E+00	0
SO_4^{-2}	5,52E-02	100	0,00E+00	0
Zn^{+2}	4,24E-05	100	0,00E+00	0

In both cases, all Al (100 and 100 % for *Jurakalk* and *recBet*) precipitates. Fe shows a higher percentage of precipitation for *recBet* than for *Jurakalk* (48.6 and 100 % for *Jurakalk* and *recBet*). In case of *recBet* also Ni (80.9%) shows a high percentage for precipitation.

Figure 8 shows the percentage removal for the 10 g/L batches. *recBet* removed almost all metals in solution (100 % Fe, 99.7 %, 88.3 % Mn, 98.7 % Ni, and 100 % Zn). For Al, Fe and Zn *Jurakalk* also showed a high removal (100 %, 100 % and 79.5 % respectively). However, the removal of Mn and Ni was significantly lower than with *recBet* (15.2 % and 33.7 %). The other tested materials had either a very low removal of metals or even increased concentrations. Especially for Mn, a higher concentration of about 40 % at the end of the experiment can be observed for *B316*, *Florisol* and *nonBen*
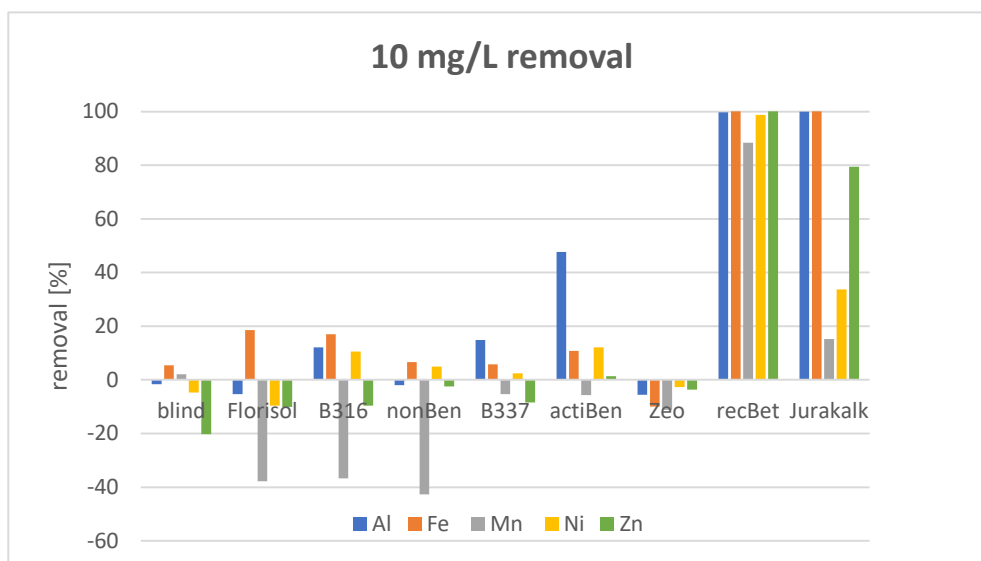
Figure 8. Metal removal in % for the S/L-ration of 10 g/L

Table 9. Comparison of total removal and theoretical (modelled) precipitation of metals in %

	recBet			Jurakalk		
	total removal	theo. Precip.	theo. Adsorption	total removal	theo. Precip.	theo. Adsorption
Al	99.7	100	-0.3	100.0	100	0.0
Fe	100.0	100	0.0	100.0	48.6	51.4
Mn	88.3	0	88.3	15.2	0	15.2
Ni	98.7	80.9	17.8	33.7	0	33.7
Zn	100.0	0	100.0	79.5	0	79.5

In Table 9 the theoretical percentage of adsorbed metal ions is shown. It is calculated by the subtraction of the modelled precipitation from the total experimental removal. For *Jurakalk* there is a high adsorption for Fe (51.4%) and especially Zn (79.5%) but also for Ni (33.7%). For *recBet* the values for adsorption for Mn (88.3%) and Zn (100%) are very high.

For *recBet*, *actiBen* and *B337* there was also a clear change visible when looking at the materials before and after the experiment. Whereas *B337* had a more whitish color before the experiment, the color changed to brown and yellow (see Figure 9 (a)). *actiBen* exhibited a change in color the other way around from being yellow/brown before the experiment to being white after the experiment (see Figure 9 (b)). *recBet* changed the color from white to brown/orange, this is also true for *Jurakalk*. For *recBet* and *Jurakalk* there was also a formation of

spiky crystals visible (see Figure 9 (c) and (d)). The microscopic pictures of all materials before and after the experiment are shown in Appendix 2.

(a)

(b)

(c)

(d)
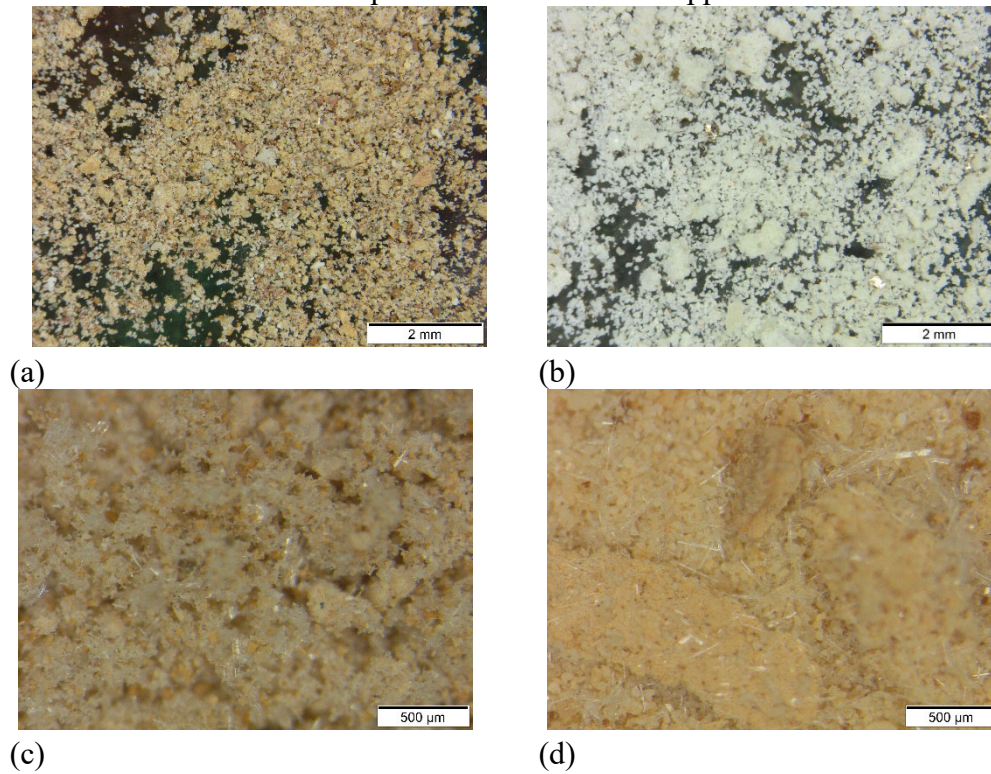
Figure 9. Microscopy after the 10 g/L batch experiments in 7-fold enlargement of (a) B337 and (b) actiBen and in 63-fold enlargement of (c) recBet and (d) Jurakalk

5. Discussion

Both synthetic AMD waters have higher Fe concentrations than the actual AMD of Brugspruit (183 and 206 mg/L compared to 5.2 mg/L) due to a calculation error in the preparation. Fe is comparably easy to precipitate and can act as an adsorbent when precipitated as iron hydroxide. Therefore, the lower concentrations of other metals in the batch experiments can be due to the precipitation of iron hydroxide and the adsorption onto the created surface. However, the concentration of only about 5 mg/L is rather low compared to other mines with iron concentrations up to 10000 mg/L. Therefore, the results might not demonstrate the exact situation for Brugspruit but can be transferred to other sites with higher iron concentrations.

The differences between the synthetic AMD and the original AMD in pH and IS can also influence the processes of adsorption and precipitation as described in chapter 1.4. The lower initial pH values in the synthetic AMDs also result in a lower pH value after the experiment. Therefore, a precipitation could have occurred when the pH value would have been higher. Further the adsorption is reduced as more positive charged protons are in solution at a lower pH, which occupy negative surface sites. The differences in IS for *SynAMD1* can have different influences. A higher IS could cause a screening of the surface of the adsorbents, as Na^+ and K^+ are mainly responsible for the higher IS. As seen in Table 3 the activity coefficient for the elements in solution might be lower in *SynAMD1* compared to the original AMD. Those effects lead to reduced adsorption and precipitation, hence a worse performance of the tested materials. If *SynAMD1* had been more similar to the original AMD the removal probably would have been better.

When comparing the 2 g/L and 10 g/L batches it is interesting to see, that limestone was able to remove most dissolved metals already in the lower dosage, whereas concrete barely removed any metals in the lower dosage but almost all of them in the higher dosage. The difference between low and high dosage for limestone was only minor. A reason therefore could be the different buffer capacities of the individual materials. But, as described in chapter 1, the efficiency for the removal of acidity of CaO is supposed to be higher compared to $CaCO_3$ and $MgCO_3$ and thus a lower increase in pH is rather unlikely. This could indicate the inhomogeneity of concrete, which is a mixture of gravel and cement and not pure CaO. In general, the differences between low and high dosage show that a dosage of 2 g/L is not sufficient for adsorption and also for precipitation with limestone a higher dosage is beneficial for a better result.

The increase in pH for activated bentonite clays can be explained by release of hydroxide ions from the surface (Wieland et al. 1994). However, the pH-values that could be reached in deionized water could not be reached in the synthetic

AMD, especially for the activated bentonites which had a higher pH value in deionized water compared to limestone but not in the batches. This is due to differences in the buffer capacity, which is higher for limestone and concrete as it reacts with the acid and has a higher ability to neutralize acidity as bentonite by releasing hydroxides.

In the case of *actiBen* Al is removed more efficiently than Fe. This is in accordance with the modelled saturation indexes, which show positive values for Alunite, Diaspore and aluminum hydroxide sulphate for example (see Appendix 3). This also explains the change to a more whiteish color.
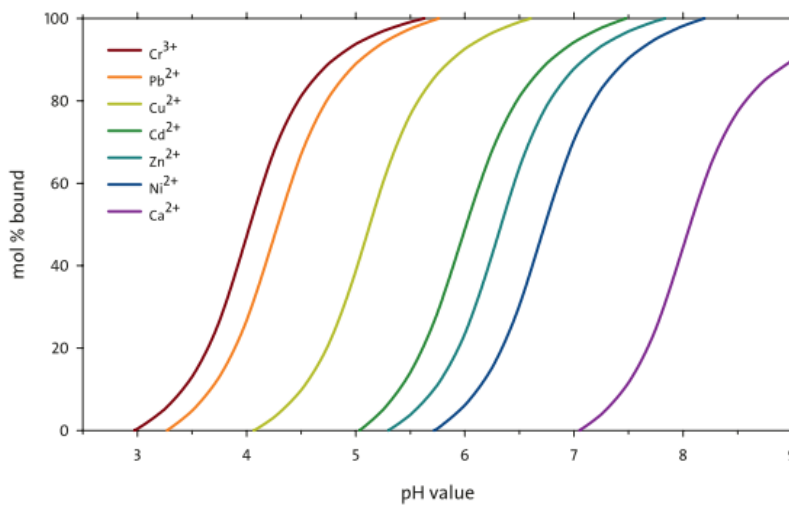
Figure 10. pH-dependent sorption of metals onto iron hydroxide (Wolkersdorfer 2022)

The removal of metals that are not turning into their insoluble form might be due to the sorption onto the surface of precipitating iron hydroxides. Figure 10 shows an example for a total iron concentration of 10^{-3} mol, total metal concentration of $5*10^{-7}$ mol and an ionic strength of 0.1mol $NaNO_3$. Although the system differs, having a lower total metal concentration and a lower ionic strength, it indicates the possibility of removing dissolved metals by sorption onto iron hydroxides. Thus, the removal of Ni and Zn could also be due to this effect. According to Figure 10, sorption of Zn starts already at lower pH values. Also, in this study, Zn had a higher percentage removal compared to Ni which is in accordance to the Figure 10.

The increase of Mn for *B316*, *Florisol* and *noBen* is due to leaching Mn from the materials into the solution. According to the product data sheet, *noBen* contains 0.1-0.3 % of MnO, *B316* 0.5 %; for *Florisol* there is no information about the chemical composition available. For a mass of about 1.5 g that means a maximum of 7.75 to 23.24 g/L for *noBen* and 38.73 mg/L for *B316* can be leached and brought into the solution. With an increase of 9.69, 9.42 and 10.95 mg/L for *B316*, *Florisol* and *noBen* in Mn-concentration, these values are reasonable.

Miller et al. (2013) investigated the influence of iron content in solution on the removal of zinc and nickel with limestone in iron rich and iron poor solutions. They added 0.1 g of $CaCO_3$ to 50 ml solution, what led to a pH increase from 2.1 to 6.44-7.03. For Zn they found out that most of it was removed carbonate related in low Fe concentration, but iron related in high iron concentrations. For nickel on the other hand the removal was mainly iron associated in both cases. That shows that the iron content in the solution does influence the removal processes. Calcium increased from 0 to 530 mg/L in low and to 751 mg/L in high iron solution, indicating that a higher iron content also influences the dissolved limestone. This means the higher iron content in the synthetic AMD compared to the original changes the outcome of the experiment and thus the applicability of the tested materials. Therefore, limestone might be a good material for the general treatment of AMD but might not be suitable for the removal of all metals by itself in case of the Brugspruit mine. Silva et al. (2021) conducted a column test and compared a single and a double stage treatment with limestone alone and in combination with zeolite. Here also the aluminum and iron concentration could be reduced with limestone itself but no manganese. And as they used actual AMD samples the role of ionic strength was considered (chemical analysis and IS of AMD sample was not shown). In combination with zeolite, it was possible to also remove manganese. This implements, that the combination of the tested materials would also be suitable for the AMD used in this study and the application for the AMD treatment given. Their study showed that dolomitic limestone turned from white to brown and calcitic limestone to grey. This observation was also made within this study and indicates the precipitation of iron hydroxides, whereas the grey color indicates aluminum hydroxides.

In a study conducted by Masindi et al. (2015), they investigated the use of natural Ca-bentonite for the removal of Fe, Mn, Al and SO_4^{2-}. For a dosage of 100 g/L material they were able to increase the pH from <3 to 5.5. The removal of the contaminants in scope were 65% of iron (initial c=2000mg/L), 40% of Mn (initial c=100 mg/L) 70% of Al (initial c=200 mg/L) and 35% of sulfate (initial c=6000 mg/L). The removal was higher compared to the Ca-bentonites within this study, which can be attributed to the ten times higher dosage of material. This might also be the reason for the higher increase in pH which fosters the removal of contaminants. Further, the number of different contaminants in the study of Masindi et al. (2015) was lower, which means less competing ions on the one hand and lower ionic strength on the other hand. Both increase the ability for the adsorption of single elements explaining the better performance of bentonite compared to this study. The removal of Zn was investigated by Kubilay et al. (2007). They also found that for the removal of Zn the pH plays an important role, and the amount of adsorbed elements can be increased from 6 mg Zn per g bentonite to 12 mg when the pH increases from 3 to 10. This means, that an

increase in pH would also be beneficial within this study to increase the possibility for adsorption of Zn. However, one must also consider competing ions and ionic strength, and the adsorption might not increase to the same extend. The effect of activated bentonite on the removal of Ni and Cu was studied by Liu and Zhou (2010). They showed that the load per element was lower in a binary mix compared to a single element solution. At a pH of about 4 (*actiBen*) and 3 (*B337*), which was achieved in the batch experiment in this study, Liu and Zhou (2010) were able to remove around 40 and 35 % Ni, which is way higher compared to 12 and 2 %. This proves, that if you go from a binary system to a more complex system, processes get more complicated and the competition for adsorption sites is not only between two elements. Therefore, the application of bentonite might be possible in a lab based simplified experiment but not under the circumstances on site. (Nkonyane et al. 2012) compared the dosage of bentonite alone to a bentonite limestone mix for the removal a range of different heavy metals. Within this study they used real AMD and not a synthetic one. For a S/L-ratio of 10 mg/L of unactivated bentonite, they were able to remove 30 % of iron but no manganese. Also, the pH remained stable at around 2 for this S/L-ratio. Therefore, the removal of iron was higher compared to the ones in this study, but they did not mention initial concentrations and general chemical composition of the AMD which makes it hard to discuss influencing factors in this case.

Erdem et al. (2004) used zeolite in their experiments to remove Zn and Mn. They were able to reduce concentrations of Mn by 20 % and Zn by 50 % with an initial concentration of 50 mg/L at a pH of 6-7 with a S/L ratio of 1 g/L. But again, they tested the performance of the material in single element solution. However, the study by Erdem et al. (2004) showed that adsorption of Mn and Zn is possible at neutral pH (even at low dosage), supporting that an excess of protons screens the negative surface. Hence, the tested materials could be applicable if the pH is increased in a first step. The possibility of metal removal in acidic conditions was demonstrated by Motsi et al. (2009). At a pH of 3.5 they were able to adsorb 100 % of Mn with a S/L ration of 37 g/L and a grain size of 1-3 mm and the Mn adsorption was even higher than that of Fe and Zn (in a single element solution). However, they also experienced better adsorption at higher pH values which was highest for Mn (increase of 49% by a change of pH from 2.5 to 3.5). They even looked at differences of single element solution to mixed solution. Whereas the differences for adsorption did not change for iron the adsorption for Zn and Mn decreased noticeably especially for higher concentrations. This also indicates, that the low removal for adsorption seen in this study are reasonable as there are even more ions in solution. Markovic et al. (2015) conducted column experiments using zeolite to remove heavy metals at a pH of 6.8. Zeolite showed a good removal for Mn and Zn (85 % and 100 %) but only low removal for Ni (25 %). Like the study by Erdem et al. (2004) they also had a higher pH value

compared to this study, again underpinning that a higher pH value is necessary for the application of zeolite. They also showed, when removing the fine fraction, the removal capacity of metals decreased drastically. In a set up with different grain sizes, they looked at the effect of removing the fine fraction. One containing a fraction < 0.3 mm and one without, the adsorption for Mn reduced from 85 to 20 %, for Zn from 100 to 50 % and for Ni from 25 to 10 %. That means that not only the pH plays a role but also the fractions being used. That means, that also an experiment with the original grain size is necessary before applying the zeolite in a pilot on site.

In case of concrete, Shabalala and Ekolu (2019) made an experiment where they used concrete in a reactive barrier which shows similar results to the one in this study, where concrete had positive effect on pH and was able to rise it above 8 and thus a good performance in removing metals like Al, Fe, Mn, Zn and Ni but also could not remove sulphate properly. Also Ho et al. (2023) proved that concrete has a positive effect on pH, they further showed the influence of particle size and that there is a shift of reactivity towards slower pH increase for bigger particles. This is important for the application of concrete as the particles used might not be in the same small fractions as in the laboratory test.

The investigation for possible materials to treat AMD or generally remove metals from solution is not standardized and all scientists use different approaches and set-ups. This makes it hard to compare studies and their outcomes. In most studies, the materials are tested only for single element solutions which is far from application in the field and excludes many important influencing factors as pH-buffering, competing ions, common ions and ionic strength. This problem is also underlined by Tien (2019). There it is stated that processes for adsorption might differ comparing single to multi element solutions. Also grain size and S/L-ratio differ in most studies. A different grain size means different surface are thus different active sites. The same is true for S/L-ratio. Further, important values like ionic strength (probably because it is unnecessary in single element solutions) are not mentioned. Sometimes not even the initial concentrations. Therefore, the comparison mostly only helps to give an idea but not a clear prediction for what's possible.

6. Conclusion

The batch experiments showed the importance of the pH value for the removal of critical elements like metals in contaminated water. No matter if it is for the precipitation or the adsorption of metals. However, it also proved the applicability of limestone and recycling concrete to increase pH and remove metals from solution. Limestone was able to increase pH already at a low dosage, recycling concrete on the other hand needed a higher dosage to do so. Except of Al on actiBen, a removal of metals in lower pH values was not possible.

The comparison with other studies highlights the importance of this study as many others only consider "simple" laboratory conditions and the transfer to the application on site is not possible.

7. Perspective

For activated bentonite the effect of a higher S/L-ratio needs to be examined to see if bentonite in a single stage treatment can increase the pH further and therefore have a higher removal. An elemental analysis of the concrete used in this study should be done, to see the composition and further assess the suitability of other concrete materials. For materials which are not able to increase the pH the next step is going to be a multistage experiment where the effect of a pH increasing material in the first stage and an adsorptive material at the second stage are applied. Also, a repetition of the 10 g/L batch experiment with the actual iron concentration should be done to investigate the role of iron for the co-precipitation. Higher iron concentrations might be useful to remove other metals and thus a material which is able to leach iron into the solution could be applied for low iron AMD. For the scale up and set-up of a pilot system, the original fraction should be tested as ball milled material can only be provided in lab experiments but in a large scale readily available material should be preferred

References

Alloway, Brian J.; Trevors, Jack T.; Younger, Paul L.; Banwart, Steven A.; Hedin, Robert S. (2002): Mine Water. Hydrology, Pollution, Remediation. Dordrecht: Springer Netherlands (5).

Anglo Operations (PTY) LTD: eMalahleni Water Reclemation Plant. Consolidated Environmental Management Programme 2021.

Baloyi, Jeffrey; Ramdhani, Nishani; Mbhele, Ryneth; Ramutshatsha-Makhwedzha, Denga (2023): Recent Progress on Acid Mine Drainage Technological Trends in South Africa: Prevention, Treatment, and Resource Recovery. In *Water*.

Costello, Christine (2003): Acid Mine Drainage: Innovative Treatment Technologies.

Erdem, E.; Karapinar, N.; Donat, R. (2004): The removal of heavy metal cations by natural zeolites. In *Journal of colloid and interface science*.

Greenpeace: AMD Polluted Water in Witbank. Available online at https://media.greenpeace.org/archive/AMD-Polluted-Water-in-Witbank-27MZIFLWFOSI.html.

Gusek, James J. (2009): A Periodic Table of Passive Treatment for Mining Influenced Water. In *JASMR* 2009.

He, Jiang; Xue, Hong-Xi; Lü, Chang-Wei; Fan, Qing-Yun; Liang, Ying; Sun, Ying et al. (2009): The impacts of common ions on the adsorption of heavy metal. In *Environ Geol*, 2009.

Ho, Hsing-Jung; Iizuka, Atsushi; Vadapalli, Viswanath Ravi Kumar; Coetzee, Henk; Petrik, Leslie; Petersen, Jochen; Ojumu, Tunde (2023): Potential investigation of concrete fines as an alternative material: A novel neutralizer for acid mine drainage treatment. In *Environmental Technology & Innovation*.

Hobbs, P.; Oelofse, S. H. H.; Rascher, J. (2008): Management of Environmental Impacts from Coal Mining in the Upper Olifants River Catchment as a Function of Age and Scale. In *International Journal of Water Resources Development*.

Hutton, B.; Kahan, I.; Naidu, T.; Gunther, P. (2009): Operating and Maintenance Experience at the Emalahleni Water Reclamation Plant.

Kubilay, Ş.; Gürkan, R.; Savran, A.; Şahan, T. (2007): Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite. In *Adsorption*.

Lebepe, C. (2022): Investigation of Environmental Impacts of Disposing Coal Slurry and Discard in Mined Out Pits with the Focus on Groundwater Pollution. University of South Africa.

Li, Jiaxing; Hu, Jun; Sheng, Guodong; Zhao, Guixia; Huang, Qing (2009): Effect of pH, ionic strength, foreign ions and temperature on the adsorption of Cu(II) from aqueous solution to GMZ bentonite. In *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2009.

Limpitlaw, D.; Aken, M.; Lodewijks, H.; Viljoen, J. (2005): Post-Mining Rehabilitation, Land Use and Pillution at Collieries in South Africa.

Liu, Zhi-rong; Zhou, Shao-qi (2010): Adsorption of copper and nickel on Na-bentonite. In *Process Safety and Environmental Protection*.

Markovic, Radmila; Gardic, Vojka; Obradovic, Ljubisa; Djordjievski, Stefan; Stevanovic, Zoran; Stevanovic, Jasmina; Gvozdenovic, Milica (2015): The Application of a Natural Zeolite for Acid Mine Drainage Purification. In *Mater. Trans.*

Marouf, Reda; Dali, Nacer; Boudouara, Nadia; Ouadjenia, Fatima; Zahaf, Faiza (2021): Study of Adsorption Properties of Bentonite Clay.

Mashamba, M. L. (2012): Geochemical stdueis of the Brugspruit Stream water and acid mine drainage (AMD) contaminant source in the Brugspruit catchment area, eMalahleni (Witbank) voalsfield, Mpumalanga. Dissertation, Johannesburg, South Africa. University of Johannesburg.

Masindi, V.; Foteinis, S.; Renforth, P.; Ndiritu, J.; Maree, J. P.; Tekere, M.; Chatzisymeon, E. (2022): Challenges and avenues for acid mine drainage treatment, beneficiation, and valorisation in circular economy: A review. In *Ecological Engineering*.

Masindi, Vhahangwele; Gitari, Mugera W.; Tutu, Hlanganani; DeBeer, Marinda (2015): Efficiency of ball milled South African bentonite clay for remediation of acid mine drainage. In *Journal of Water Process Engineering*.

Miller, Andrew; Wildeman, Thomas; Figueroa, Linda (2013): Zinc and nickel removal in limestone based treatment of acid mine drainage: The relative role of adsorption and co-precipitation. In *Applied Geochemistry*.

Millero, F. J.; Hawke, D. J. (1992): Ionic interactions of divalent metals in natural waters.

Mine Water Network (2023): Research Proposal - Water Security in Africa.

Motsi, T.; Rowson, N. A.; Simmons, M.J.H. (2009): Adsorption of heavy metals from acid mine drainage by natural zeolite. In *International Journal of Mineral Processing*.

Munnik, V.; Hochmann, G.; Hlabane, M.; Law, S. (2010): The Social and Environmental Consequences of Coal Mining in South Africa - A CASE STUDY.

Ncube, Vuyisile (2022): The Forever Mines. Perpetual rights risks form unrehabilitated coal mines in Mpumalanga, South Africa. New York, NY: Human Rights Watch.

Nkonyane, T.; Ntuli, F.; Muzenda, E. (2012): Treatment of Acid Mine Drainage Using Un-Activated Bentonite and Limestone. In *International Journal of Chemical, Molecular, Materials and Metallugical Engineering*.

Opitz, Joscha; Timms, Wendy (2016): Mine water discharge quality – a review of classification frameworks, 2016.

Pérez-Botella, Eduardo; Valencia, Susana; Rey, Fernando (2022): Zeolites in Adsorption Processes: State of the Art and Future Prospects. In *Chemical reviews*.

Prepilková, Veronika; Poništ, Juraj; Schwarz, Marián; Samešová, Dagmar (2022): Possibilities of remediation of neutral mine drainage - Removal and recovery of potentially hazardous elements. In *Soil Water Res.*

Republic of South Africa (2021): South Africa - First Nationally Determined Contribution Under The Paris Agreement.

Sergienko, N.: The eMalahleni Water Reclamation Plan in South Africa.

Shabalala, A. N.; Ekolu, S. O. (2019): Quality of water recovered by treating acid mine drainage using pervious concrete adsorbent. In *WSA*.

Shabalala, A. N.; Ekolu, S. O.; Diop, S. (2014): Permeable reactive barriers for acid mine drainage treatment: a review: IOS Press.

Silva, Daniela; Weber, Cristiano; Oliveira, Cristiane (2021): Neutralization and uptake of pollutant cations from acid mine drainage (amd) using limestones and zeolites in a pilot-scale passive treatment system. In *Minerals Engineering* 170.

Skousen, J.; A. Rose, m. A.; Geidel, G.; Foreman, J.; Evans, R.; Hellier W. (1998): A Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage.

Stumm, W.; Morgan, J. J. (1996): Aquatic Chemistry : Chemical Equilibria and Rates in Natural Waters (3rd Edition). Environmental Science and Technology : A Wiley-Interscience Series of Texts and Monographs :

Thisani, Sandisiwe Khanyisa; Kallon, Daramy Vandi von; Byrne, Patrick (2021): Review of Remediation Solutions for Acid Mine Drainage Using the Modified Hill Framework. In *Sustainability* 13.

Thisani, Sandisiwe Khanyisa; Kallon, Daramy Vondi von; Byrne, Patrick (2020): Geochemical Classification of Global Mine Water Drainage. In *Sustainability* 12, 2020.

Tien, C. (2019): Introfuction to Adsorption. Basics, Analysis, and Applications.

US EPA (2000): Abandoned Mine Site Characterization and Cleanup Handbook. Seattle, Washington.

US EPA (2014): Public Participation Guide: Transvaal and Delogoa Bay Colliery - Witbank, Mpumalanga, South Africa | US EPA. Available online at https://www.epa.gov/international-cooperation/public-participation-guide-transvaal-and-delogoa-bay-colliery-witbank.

Wibowo, Yudha Gusti; Imron, Muhammad Fauzul; Kurniawan, Setyo Budi; Ramadan, Bimastyaji Surya; Taher, Tarmizi; Sudibya, Alvian Hayu et al. (2023): Emerging Strategies for Mitigating Acid Mine Drainage Formation and Environmental Impacts: A Comprehensive Review of Recent Advances. In *Sci. Technol. Indones* (4).

Wieland, E.; Wanner, H.; Albinsson, Y.; Wersin, P.; Karnland, O. (1994): A surface chemical model of the bentonite-water interface and its implications for modelling the near field chemistry in a repository for spent fuel.

Wolkersdorfer, Christian (2022): Mine Water Treatment – Active and Passive Methods. Berlin, Heidelberg: Springer Berlin Heidelberg.

Xu, Chenglong; Feng, Yali; Li, Haoran; Wu, Ruifeng; Ju, Jinrong; Liu, Shunliang et al. (2022): Adsorption of heavy metal ions by iron tailings: Behavior, mechanism, evaluation and new perspectives. In *Journal of Cleaner Production* 344, 2022.

Popular science summary

When coal is being extracted from the ground (no matter if it is an open pit or an underground extraction) sulfide bearing minerals become exposed to the atmosphere. This leads to the oxidation of those minerals and the following release of acidity, sulphate and metals. This fosters the weathering of other minerals which then dissolve. A water solution which is characterized by low pH and high concentrations in heavy metals, sulphate and often other ions, is formed which is called acid mine drainage (AMD). Due to its characteristics AMD poses a great hazard to the environment and needs to be treated.

This study investigates different natural-based materials on their ability to treat AMD. The materials in scope are limestone, zeolite, bentonite and recycling concrete. It is designed as a laboratory case study using a batch experiment. Therefore, the analysis of the Brugspruit mine (South Africa) is used to create a synthetic AMD. For each material two different dosages have been used and put together with the synthetic AMD into a bottle. After shaking for 24 hours samples have been taken and analyzed for pH, metal and ion concentration, to see which materials were able to increase pH and/or decrease concentrations.

The results showed that limestone and recycled concrete were able to increase the pH value and decrease metal concentrations, especially for aluminum and iron. Limestone achieved this already in a lower dosage. Activated bentonite did increase the pH a bit in higher dosage but could only decrease the concentration of aluminum. The other tested materials could not increase pH and did not decrease metal concentrations. Due to remaining low pH values, Ca-bentonites even leached manganese and increased concentrations.
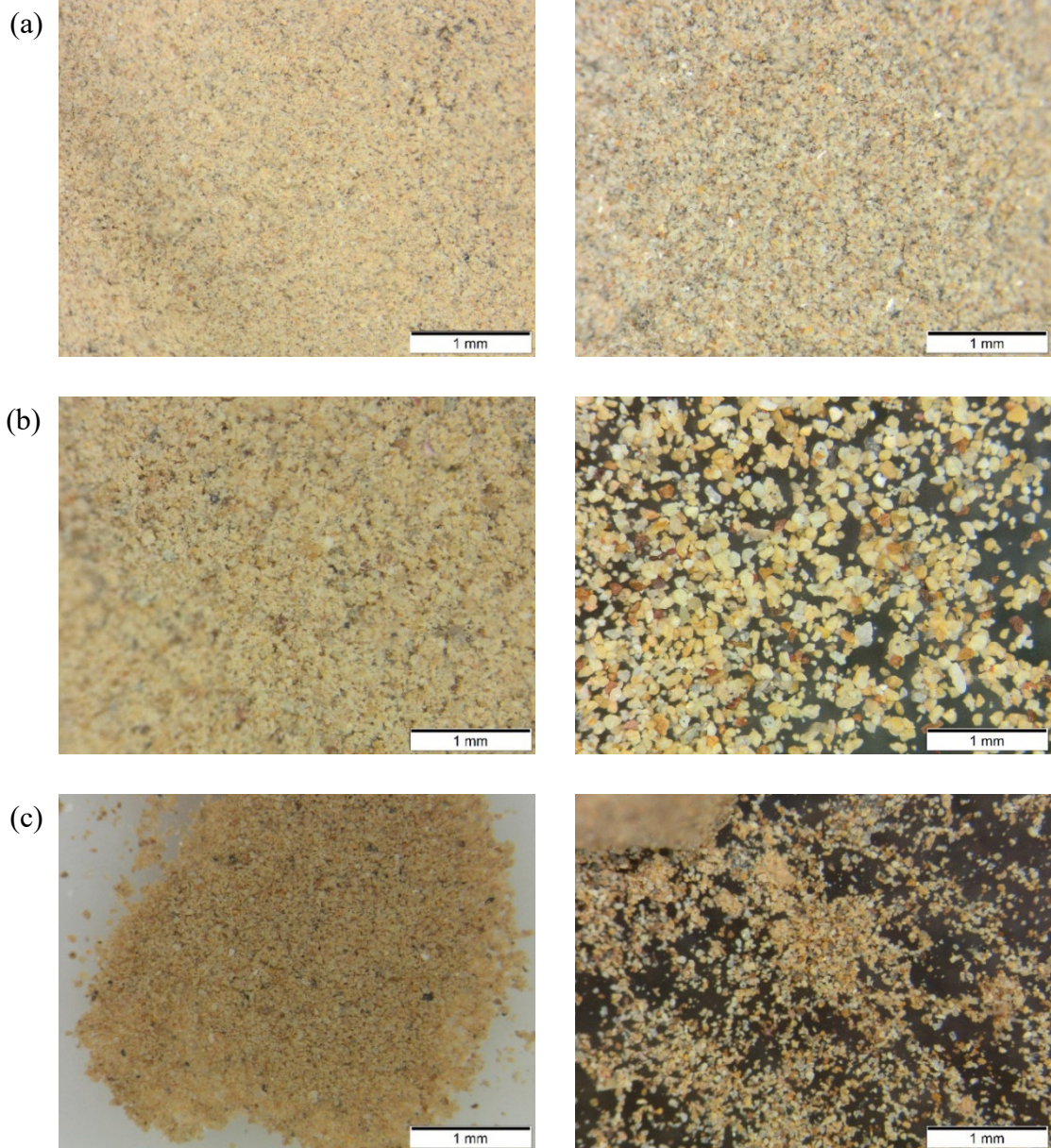
Appendix 1

*Appendix 1. Full analysis of AMD at mine-site and Brugspruit lake*

| Labor-Nr.		396241	396242	396243
		Brugspruit Lake	Brugspruit Mine	Brugspruit Mine filt.
		16.02.2023	16.02.2023	16.02.2023
Latitude		25; 49; 31,205 S	25; 51; 51,752 S	
Longitude		29; 8; 19,935 E	29; 8; 38,476 E	
Lab parameter				
Spec. electr. conductivity (25 °C) Lab.	µS/cm	2430	8250	
pH value Lab.		3,28	3,15	
Temperature Lab.	°C	21,7	21,8	
Sodium (Na+)	mg/l	121	890	
Potassium (K+)	mg/l	4,3	14,5	
Calcium (Ca2+)	mg/l	157	454	
Magnesium (Mg2+)	mg/l	90,5	298	
Ammonium (NH4+)	mg/l	< 0,05	52,4	
Chloride (Cl-)	mg/l	12,1	88,0	
Sulphate (SO42-)	mg/l	1430	5700	
Nitrate (NO3-)	mg/l	17,1	3,9	
Antimony	mg/l	0,02		0,071
Fluoride (F-)	mg/l	2,6	7,3	
Ortho-phosphate (PO43-)	mg/l	< 0,03	< 0,03	
Aluminium	mg/l	46,6		81,4
Arsenic	mg/l	< 0,005		< 0,005
Lead	mg/l	0,0037		< 0,002
Iron total	mg/l	1,1		5,22
Copper	mg/l	0,086		0,143
Manganese total	mg/l	15,6		27,4
Nickel	mg/l	0,461		1,41
Uranium	mg/l	0,0064		0,014
Zinc	mg/l	1,49		3,53
DOC	mg/l		1,1	
Oxygen-18 (*18O) CRDS	‰	-1,61	-1,91	
Deuterium (*2H) CRDS	‰	-7,7	-9,4	
Deuterium-excess	‰	5,18	5,88	

Appendix 2

Appendix 2. Microscopy of used materials before (left) and after the experiment (right) for (a) Florisol B-extra, (b) B316, (c) unactivated bentonite, (d) B337, (e) activated bentonite, (f) ZeoAqua, (g) recycling concrete and (h) Jurakalk
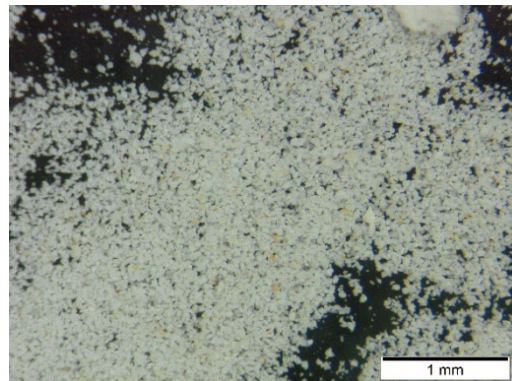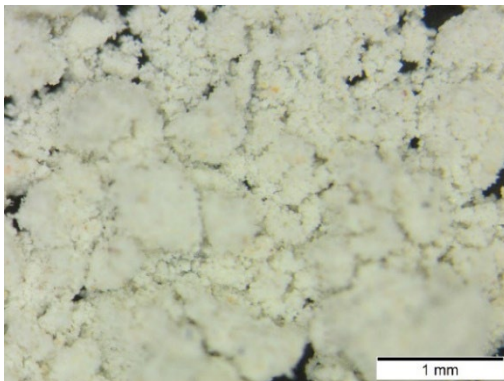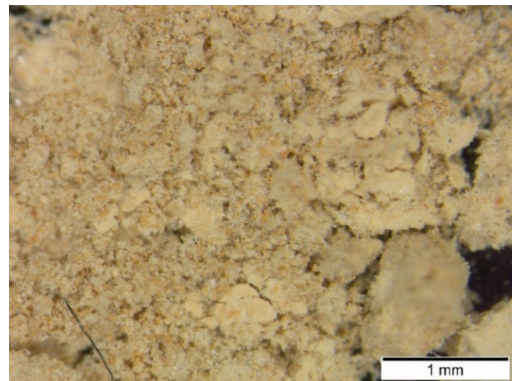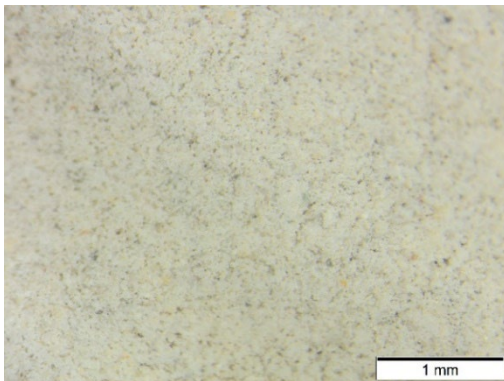
(a)

(b)

(c)

(d)
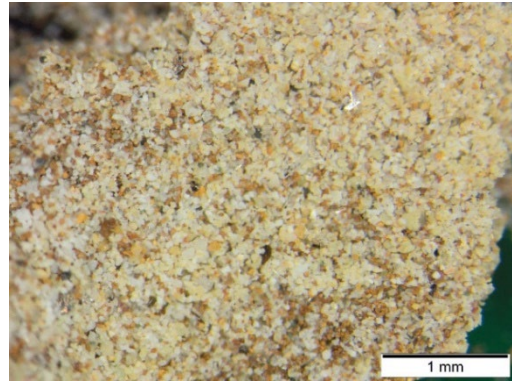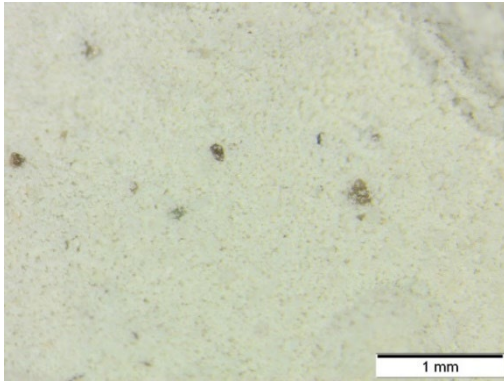
(e)
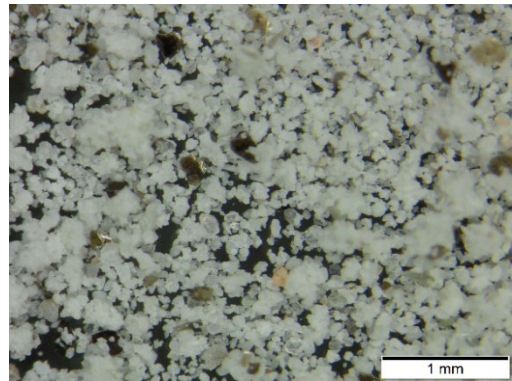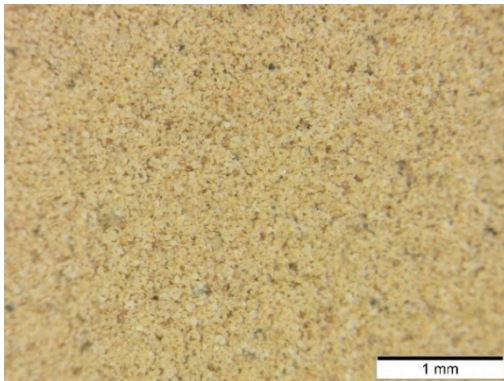
(f)

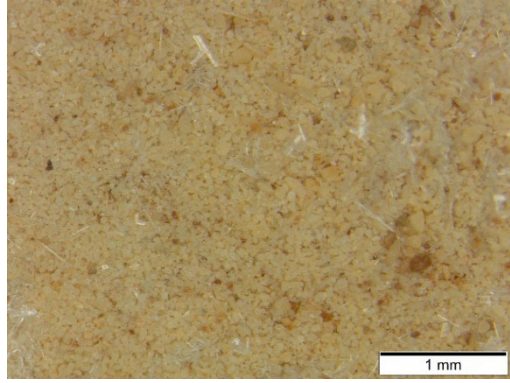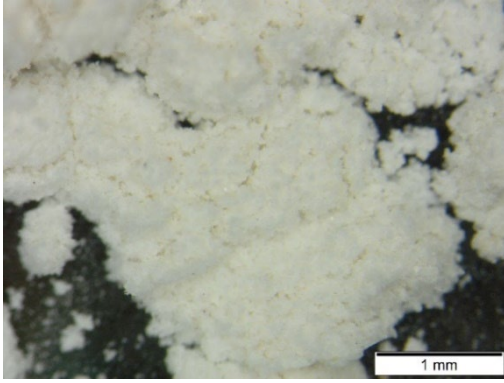(g)

(h)

Appendix 3

Appendix 3. Saturation indexes at end pH of the experiments

Mineral	pH 2.4	pH 2.5	pH 2.7	pH 3.4	pH 4.3	pH 6.2	pH 6.9	pH 7.2	pH 8.4
Al(OH)3 (am	-8.284	-7.997	-7.415	-5.342	-2.649	2.072	3.032	2.793	1.73
Al(OH)3 (Soi	-5.762	-5.474	-4.893	-2.819	-0.126	4.595	5.554	5.316	4.252
Al2O3(s)	-14.69	-14.115	-12.952	-8.805	-3.419	6.025	7.944	7.466	5.339
Al4(OH)10SC	-18.353	-17.394	-15.454	-8.542	0.435	15.571	18.024	16.272	9.818
AlOHSO4(s)	-0.663	-0.567	-0.372	0.321	1.218	2.191	1.765	0.729	-2.534
Alunite	-4.901	-4.321	-3.151	1.006	6.393	14.949	15.758	13.847	7.357
Anhydrite	-0.32	-0.316	-0.309	-0.3	-0.298	-0.283	-0.273	-0.271	-0.271
Bianchite	-5.345	-5.343	-5.34	-5.336	-5.335	-5.341	-5.333	-5.332	-5.382
Boehmite	-6.074	-5.786	-5.205	-3.131	-0.438	4.283	5.243	5.004	3.941
Brucite	-15.237	-15.041	-14.647	-13.257	-11.459	-7.693	-6.296	-5.496	-3.297
Diaspore	-4.338	-4.051	-3.469	-1.396	1.297	6.019	6.978	6.739	5.676
Epsomite	-2.406	-2.401	-2.394	-2.384	-2.382	-2.369	-2.355	-2.352	-2.352
Ettringite	-60.291	-59.117	-56.756	-48.414	-37.63	-16.863	-10.72	-8.791	-4.318
Fe(OH)2 (am	-12.168	-11.973	-11.58	-10.191	-8.393	-4.63	-3.235	-2.436	-0.242
Fe(OH)2 (c)	-11.377	-11.182	-10.79	-9.4	-7.603	-3.839	-2.444	-1.645	0.549
Gibbsite (C)	-5.212	-4.924	-4.343	-2.269	0.424	5.145	6.104	5.866	4.802
Goslarite	-5.07	-5.068	-5.065	-5.061	-5.061	-5.067	-5.059	-5.058	-5.107
Gypsum	-0.058	-0.054	-0.047	-0.038	-0.036	-0.022	-0.011	-0.009	-0.009
Halite	-5.603	-5.604	-5.605	-5.607	-5.607	-5.622	-5.618	-5.617	-5.617
Hercynite	-16.53	-15.76	-14.205	-8.669	-1.485	11.723	15.037	15.358	15.425
K-Alum	-6.153	-6.148	-6.141	-6.132	-6.13	-7.024	-8.131	-9.564	-13.927
KCl(s)	-6.871	-6.872	-6.873	-6.875	-6.876	-6.891	-6.888	-6.887	-6.887
Lime	-31.126	-30.93	-30.537	-29.148	-27.35	-23.586	-22.19	-21.391	-19.191
Melanterite	-2.893	-2.888	-2.882	-2.874	-2.872	-2.861	-2.849	-2.847	-2.853
Mg(OH)2 (ac	-16.693	-16.498	-16.104	-14.713	-12.916	-9.15	-7.753	-6.953	-4.753
Mg2(OH)3Cl:	-26.955	-26.664	-26.077	-23.995	-21.3	-15.675	-13.578	-12.377	-9.078
Mirabilite	-3.213	-3.205	-3.194	-3.178	-3.175	-3.149	-3.13	-3.125	-3.125
MnCl2:4H2O	-12.309	-12.313	-12.32	-12.329	-12.331	-12.376	-12.374	-12.372	-12.374
MnSO4(s)	-8.626	-8.621	-8.614	-8.604	-8.601	-8.584	-8.573	-8.57	-8.571
Morenosite	-5.017	-5.012	-5.005	-4.996	-4.994	-4.982	-4.97	-4.968	-4.989
Ni(OH)2 (am	-13.62	-13.424	-13.031	-11.641	-9.843	-6.078	-4.683	-3.884	-1.705
Ni(OH)2 (c)	-11.32	-11.125	-10.731	-9.341	-7.543	-3.779	-2.383	-1.584	0.595
Ni4(OH)6SO4	-40.76	-40.169	-38.982	-34.802	-29.407	-18.097	-13.899	-11.502	-4.987
Periclase	-19.796	-19.6	-19.206	-17.816	-16.018	-12.252	-10.855	-10.055	-7.855
Portlandite	-20.997	-20.802	-20.409	-19.019	-17.222	-13.457	-12.062	-11.262	-9.063
Pyrochroite	-14.664	-14.468	-14.074	-12.683	-10.886	-7.12	-5.723	-4.923	-2.724
Retgersite	-5.135	-5.13	-5.124	-5.124	-5.112	-5.099	-5.088	-5.086	-5.107
Spinel	-30.051	-29.281	-27.724	-22.187	-15.003	-1.792	1.523	1.845	1.918
Thenardite	-4.809	-4.801	-4.79	-4.774	-4.77	-4.739	-4.722	-4.719	-4.718
Zincite	-11.868	-11.675	-11.286	-9.901	-8.105	-4.358	-2.966	-2.168	-0.018
Zincosite	-11.196	-11.193	-11.19	-11.187	-11.186	-11.188	-11.182	-11.181	-11.231
Zn(OH)2 (am	-13.106	-12.913	-12.524	-11.139	-9.343	-5.597	-4.205	-3.407	-1.256
Zn(OH)2 (bet	-12.381	-12.188	-11.799	-10.414	-8.618	-4.871	-3.48	-2.682	-0.531
Zn(OH)2 (del	-12.298	-12.105	-11.716	-10.331	-8.535	-4.788	-3.397	-2.599	-0.448
Zn(OH)2 (eps	-12.152	-11.959	-11.569	-10.185	-8.388	-4.642	-3.25	-2.452	-0.302
Zn(OH)2 (gar	-12.358	-12.165	-11.776	-10.391	-8.595	-4.849	-3.457	-2.659	-0.509
Zn2(OH)2SO4	-15.048	-14.853	-14.46	-13.072	-11.275	-7.531	-6.133	-5.334	-3.234
Zn2(OH)3Cl(:	-21.246	-20.96	-20.381	-18.312	-15.62	-10.031	-7.946	-6.749	-3.548
Zn3O(SO4)2(	-34.09	-33.893	-33.498	-32.105	-30.307	-26.565	-25.161	-24.362	-22.311
Zn4(OH)6SO4(s)		-36.275	-35.104	-30.946	-25.556	-14.32	-10.138	-7.743	-1.342
Zn5(OH)8Cl2(s)		-50.299	-48.752	-43.23	-36.048	-21.125	-15.562	-12.37	-3.819
ZnCl2(s)		-17.956	-17.967	-17.982	-17.986	-18.048	-18.052	-18.053	-18.102
ZnSO4:1H2O(s)		-6.548	-6.545	-6.541	-6.54	-6.543	-6.537	-6.536	-6.586

Publishing and archiving

Approved students' theses at SLU are published electronically. As a student, you have the copyright to your own work and need to approve the electronic publishing. If you check the box for **YES**, the full text (pdf file) and metadata will be visible and searchable online. If you check the box for **NO**, only the metadata and the abstract will be visible and searchable online. Nevertheless, when the document is uploaded it will still be archived as a digital file. If you are more than one author, the checked box will be applied to all authors. You will find a link to SLU's publishing agreement here:

- https://libanswers.slu.se/en/faq/228318.

☒ YES, I/we hereby give permission to publish the present thesis in accordance with the SLU agreement regarding the transfer of the right to publish a work.

☐ NO, I/we do not give permission to publish the present work. The work will still be archived and its metadata and abstract will be visible and searchable.