Lappeenranta University of Technology

Faculty of Technology

Double Degree in Chemical and Metallurgical Engineering

Maria Nikitenko

TREATMENT OF NI-CONTAINING ACIDIC MINE WATERS WITH CALCITE SIDE-STONES

Examiners: Professor Marjatta Louhi-Kultanen, DSc

Associate Professor Sergei Preis, DSc

ABSTRACT

Acid mine drainage (AMD) presents a serious problem for the environment for the massive formation of acidic leachates containing heavy metals. The present work deals with the AMD treatment using neutralizing limestone side-products. The conventional methods for prevention, mitigating and control of AMD formation are described. The experimental testing of Nordkalk Oy calcite-containing side-stones for acid neutralizing and removal of nickel from solutions presents the research objective. The batch experiments in acid neutralizing with subsequent metal content analysis were carried out. The results showed the dependence of pH on the dose of neutralizing material and the exposure time. The nickel removal, unlike iron, within the pH range from 1.2 to 6.0 appeared to be inadequate. The further research on nickel co-precipitation with iron and aluminium may appear to be necessary together with testing of alkalinity strengthening materials.

Acknowledgements

Cooperative personalities and hard work made this project possible even under limited time constraints.

I wish to thank Sergei Preis: for profound influence during the laboratory study, for attempts to clarify my topic with the project partners. Writing is a lonely process; revising is a social one. Many thanks for help in improving the quality of the manuscript.

I appreciate the valuable comments from Marjatta Louhi-Kultanen on the laboratory study design, for the smooth collaboration on administrative issues.

Thanks to LUT Laboratory of Filtration processes: Liisa Puro and Markku Maijanen, for lending the equipment, because I was in a hurry and had no time for waiting a new one. Thanks to Alexander Sokolov and Iris Panorel for the guidance around the laboratory. Thanks to Bing Han for the detailed instructions on laser diffraction analysis. Thanks to people, who explained me several times how to use the AAS equipment, especially to Jaana Ruokonen. Many thanks to Ritva Tuunila and guys from the 2nd floor for help with the heavy ball mill. Also, my acknowledgments go to my collaborators at 2357.

Finally, I acknowledge LUT and St-Petersburg Mining Institute double-degree programme coordinator, prof. Andrzej Kraslawski, for the possibility to study in Finland.

Table of contents

List of abbreviations:

AAS – Atomic Absorption Spectroscopy

ADTI – Acid Drainage Technology Initiative

ALD – Anoxic Limestone Drainage

AMD – Acid Mine Drainage

ARD – Acid Rock Drainage

INAP – International Network for Acid Prevention

MEND – Mine Environmental Neutral Drainage program

NOAMI – National Orphaned/Abandoned Mines Initiative

OLD – Oxic Limestone Drainage

SR – Store and Release cover

SRB – Sulphate-Reducing Bacteria

US EPA – United States Environmental Protection Agency

PREFACE

Managing acid mine drainage (AMD) for the reduced impact on the environment represents one of the key problems facing the mining industry. According to the problem description given by the Bioteq company web-site, AMD occurs at about 70% of the world's mine sites. Acid drainage affects the majority of sectors of the mining industry, including coal (e.g., Pennsylvania Coalfield, USA; Cravotta et al., 2010), precious metals (e.g., gold - Hillside Mine, Western Arizona, USA; Rampe and Runnels, 1989), base metals (e.g., nickel - Black Swan, Western Australia; Liang-qi et al., 2010), and uranium (e.g., Curilo, Bulgaria; Groudnev et al., 2008). Over the last 30 to 40 years, as mining have developed from low tonnage underground operations to large-tonnage open cut operations, the mass of sulphide material with the potential to generate acid drainage has increased dramatically (Australian Government Handbook, 2007).

As AMD enters groundwater and water bodies, the latters may contain sulphuric acid, high concentrations of toxic metals and low oxygen concentrations, which may present a huge risk to aquatic life and vegetation. Also, local communities dependent on waterways for their livelihood, may be posed to a great health risk. In addition, once a mining operation has ceased, poor water quality in the form of acid drainage may continue to affect the environment for decades or even centuries (Cáceres et al., 2013).

Today, poor practice cannot be tolerated in sustainable mining (Morrissey, 2003). Based on the widely accepted Brundtland Commission definition, sustainable development is "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (UNECE). Effective management of AMD is needed to meeting increasingly stringent environmental regulations and community expectations (Toit, 2013). Communities expect that all decisions concerning the management of AMD will be based on more than just economic costs and must therefore integrate social, economic and environmental aspects to achieve a strong sustainability.

The crucial step in benchmarking of AMD management is to quantify the risk as early as possible. Consistent evaluation of AMD risk during the whole life cycle of mining, from exploration till closure phase, provides the data necessary to assess potential impacts and management costs before the significant disturbance of sulphide material (Edelev, 2013). When projects proceed at sites where AMD is a potential risk, efforts should focus on prevention or minimisation, rather than control or treatment. At closed and older operating mine sites, where AMD management has been poor, high rehabilitation and treatment costs continue to impare the profitability of mining companies. The term 'treatment in

perpetuity' has entered the mining vocabulary as a result of drainage issues after the mine has been ceased.

Newmont Australia assessed closure costs for sites in which it has a financial interest is around US$150 million, of which greater than 65 per cent is for the waste management. Newmont's estimated closure liability is in the order of several hundred million dollars globally (Dowd, 2005). The most common cases are the prevention of acid drainage generation from exposed pit walls, waste rock piles, tailings storage facilities, and other disturbances. While the cost of AMD management during operations can be huge, it is usually small in comparison with the long-term costs that would otherwise be expended (USEPA, 2001). The conventional methods for prevention, mitigating and control of AMD formation are described below.

Currently, leading practice acid drainage risk management is not understood or practised widely, despite many examples of excellence that exist throughout the industry (Boonstra et al., 1999; Feng et al., 2000; Dowd, 2005). Leading practice companies also have targeted policies and procedures relevant to managing AMD in place. Additional engagement in environmental certification, involvement in initiatives such as Acid Drainage Technology Initiative (ADTI), the Mine Environmental Neutral Drainage (MEND) program, and the International Network for Acid Prevention (INAP), NOAMI (National Orphaned/Abandoned Mines Initiative), as well as regular participation of AMD experts in operational decision-making, all lead to improved business performance. (Australian Government Handbook, 2007)

1 BACKGROUND: ACIDIC MINE WATERS

1.1 Chemical characteristics of acid mine drainage (AMD)

Acid drainage in mining is traditionally called as acid mine drainage (AMD) or acid rock drainage (ARD). (Ibanez et al., 2008)

All AMD types have a number of common chemical characteristics: low pH values and high concentrations of sulphate and metal ions.

There are two components of acidity that need to be considered: acid (H^+) and mineral (latent) acidity. Acid is a measure of hydrogen ion (H^+) concentration which is generally expressed as pH, whereas acidity is a measure of both hydrogen ion concentration and mineral (or latent) acidity. Mineral or latent acidity considers the potential concentration of

hydrogen ions that could be generated by the precipitation of various metal hydroxides by oxidation, dilution or neutralisation.

Acid can be easily measured in the field using a calibrated pH probe. Estimates of acidity can be measured in a laboratory or estimated from water quality data using a formula such as equation 1, which is broadly used for coal mine drainage.

$$\text{Acidity (mg/L } CaCO_3) = 50 \times \{3 \times (\text{Total Solube Fe}) / 56 + 3 \times (Al^{3+}) / 27 + 2 \times (Mn^{2+}) / 55 + 1000 \times 10^{-[pH]}\}, \quad (1)$$

where ( ) denotes concentration, mg/L.

Among AMD high acidity values, such as 50 to15,000 ppm $CaCO_3$, are common. Typical values of pH are from 1.5 to 4; under these conditions metal ions (iron, aluminium, manganese, cadmium, copper, nickel, zinc, lead, arsenic and mercury) are in dissolved. Therefore, metal ions concentrations stay high in time, usually the amount of heavy metals contaminant noticeably exceed the US EPA limits for a drinking water: the allowed concentration of Ni^{2+} is 0.1 mg/l for long-term exposure on a human body (USEPA, Technical factsheet on nickel). However, AMD may contain up to 10 ppm of Ni or higher (Zhigang et al., 2009). Sulphate concentrations range from 500 to 10,000 ppm; typical conductivity range, which is corresponding with salinity level, from 1,000-20,000 µS/cm. (Nordstrom et al., 2000; Australian Government Handbook, 2007)

1.2. Formation of AMD

A common point of view on AMD formation (Montgait et al.,1978; Sullivan et al., 1988; Stumm and Morgan, 1996) the following: AMD is generated through sulphide minerals transformed to sulphates and iron oxyhydroxides via chemical and biological oxidation in water and air. Marcasite (FeS_2), pyrrhotite (FeS), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$) and other sulphide minerals containing iron can be a source of acid mine solutions, although pyrite (FeS_2), the most common sulphide in the earth's crust, is proved to be the major source of AMD (Nordstrom and Dagenhart, 1978; Alpers and Blowes, 1994; Tabaksblat, 2002; Korneeva, 2009).

The AMD can be formed within such mine site components as waste rock, tailings, open pit walls and underground workings (Morin and Hutt, 1997); classification of AMD sources is shown in the Table 1. Previously, AMD was associated mainly with the underground mining. More recently, AMD formation from open pit workings became more widespread. In this method of mining, large volumes of rock have a contact with an oxidizing

environment, which may lead to sufficient growth of acid generation rate (Akcil and Koldas, 2006).

Table 1. Sources of Acid Mine Drainage (Akcil and Koldas, 2006)

Primary sources	Secondary sources
Mine rock dumps	Treatment sludge pounds
Tailings impoundment	Rock cuts
Underground and open pit mine workings	Concentrated load-out
Pumped/nature discharged underground water	Stockpiles
Diffuse seeps from replaced overburden in rehabilitated areas	Concentrate spilos along roads
	Emergency ponds
Construction rock used in roads, dams, etc.	

The overall oxidative dissolution of pyrite is described with the equation 2.

$$FeS_2 + 15/4 O_2 + 7/2 H_2O \rightarrow Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+ \tag{2}$$
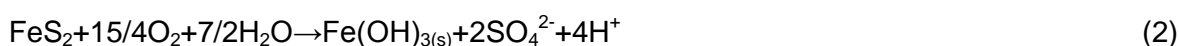
This reaction gradually increases water acidity, resulting in the mobilization of metals from mine wastes (Table 2).

Table 2. Major minerals relevant to AMD formation (Jennings et al., 2000; Montero et al., 2005; Lottermoser, 2007)

Mineral	Composition	Reaction
Arsenopyrite	$FeS_2.7FeAs$	$FeAsS + 2O_2(aq) + 3H_2O = Fe^{2+} + 2H_3AsO_3 + SO_4^{2-}$
Bornite	$CuFeS_4$	$CuFeS_4(s) + 8O_2(aq) = Cu^{2+} + Fe^{2+} + 4SO_4^{2-}$
Chalcocite	Cu_2S	$CuS_2(s) + 2O_2(aq) = Cu^{2+} + SO_4^{2-}$
Chalcopyrite	$CuFeS_2$	$CuFeS_2(s) + 4O_2(aq) = Cu^{2+} + Fe^{2+} + 2SO_4^{2-}$
Covellite	CuS	$CuS(s) + 2O_2(aq) = Cu^{2+} + SO_4^{2-}$
Galena	PbS	$PbS(s) + 2O_2(aq) = Pb^{2+} + SO_4^{2-}$
Greenockite	CdS	$CdS(s) + 2O_2(aq) = Cd^{2+} + SO_4^{2-}$
Millerite	NiS	$NiS(s) + 2O_2(aq) = Ni^{2+} + SO_4^{2-}$
Mobybdenite	MoS_2	$MoS_2(s) + 2O_2(aq) = Mo^{2+} + SO_4^{2-}$
Pyrite	FeS_2	$FeS_2(s) + O_2(aq) = Fe^{2+} + SO_4^{2-}$
Pyrrhotite	$Fe_{11}S_{12}$	$Fe_{11}S_{12}(s) + 24O_2(aq) = 11Fe^{2+} + 12SO_4^{2-}$
Sphalerite	ZnS	$ZnS(s) + 2O_2(aq) = Zn^{2+} + SO4^{2-}$

Figure 1 provides an illustration of the AMD formation process.
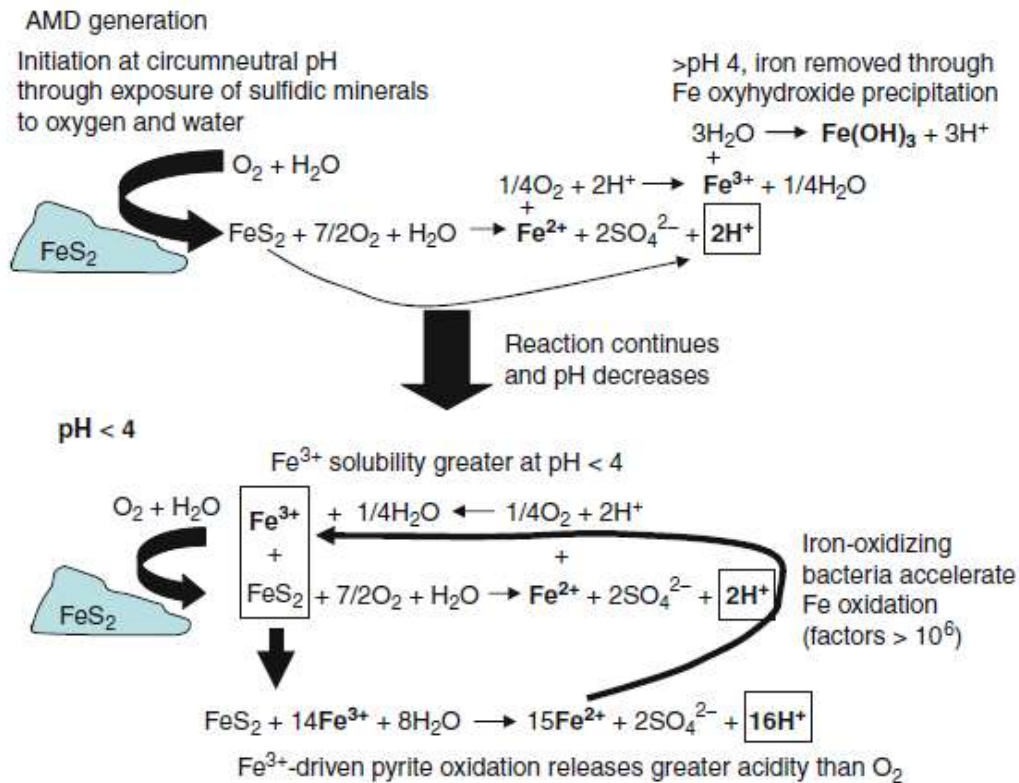
Figure 1. Scheme of AMD formation from pyrite. (Warren, 2011)

Initially, at near-neutral pH AMD occurs through the penetration of ferrous (Fe^{2+}) and acid (H^+) ions into water:

$$FeS_{2(s)}+7/2O_2+H_2O \rightarrow Fe^{2+}+2SO_4^{2-}+2H^+ \tag{3}$$

When the pH level is decreased below 4, the solubility of Fe^{3+} ion sufficiently grows, which causes relatively fast oxidation of pyrite by Fe^{3+}:

$$FeS_{2(s)}+14Fe^{3+}+8H_2O \rightarrow 15Fe^{2+}+2SO_4^{2-}+16H^+ \tag{4}$$
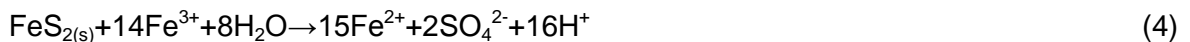
In addition, when pH is lower than 4, iron- and sulphur-oxidizing bacteria, such as *Acidithiobacilli* may increase rates of Fe^{2+} oxidation by factors greater than $1 \cdot 10^6$ (equation 5):

$$Fe^{2+}+1/4O_2+2H^+ \rightarrow Fe^{3+}+3H_2O \tag{5}$$

Therefore, when the pH value of the mine water is lower than 4, the process of Fe oxidation and sulphuric acid formation will continue until the full dissolution of available pyrite. A well known mine site in the Iberian Pyrite Belt in Spain, for example, has been generating AMD for more than 2000 years (Cáceres et al., 2013).

1.3 AMD environmental impact

An impact of AMD in the environment is easily detectable by the death of fish or other aquatic organisms, poor productivity of re-vegetated areas (Figure 2), red-coloured water, orange-brown iron oxide precipitates in drainage lines (Figure 3) and in junctions, where AMD is mixed with background water due to pH higher than 4 at the places (equation 6), and corrosion of concrete or steel structures. (Australian Government Handbook, 2007; Warren, 2011)

Figure 2. Dieback of vegetation on the shore of AMD water body (Australian Government Handbook, 2007).

Figure 3. Acid mine drainage at a sulphide-rich nickel and copper ore deposit (Burtynsky, 1996)

Equation on precipitation of Fe from AMD in the near-neutral solutions:

$$Fe^{3+}+3H_2O \rightarrow Fe(OH)_{3(s)}+3H^+ \tag{6}$$

As a rule, a complex influence of AMD to the environment is difficult to separate for individual components. The release of elements, including toxic ones, and their migration into the groundwater can lead to a wide dispersion of the components, followed by their

concentration in a range of environmental objects. The spreading of the individual components in waters ranges from hundreds of meters to several kilometres (Krainov and Phoigt, 1991).

The toxicity of AMD depends on several factors, such as the total acidity of the contaminated water, the concentration of dissolved metals, the dilution factor when entering the surface water, pH and buffer capacity of the receiving water body (Weed and Rutschky, 1971). pH is the most important factor, since the lower the pH, the greater the potential impact of acidic water on the aquatic flora and fauna (Krainov and Phoigt, 1991).

As in the case with many other pollutants, exposure of AMD to surface water bodies and streams can lead to a decrease in diversity and the total number of aquatic flora and fauna species (Weed and Rutschky, 1971). It was assumed that the increased acidity of the water reduces the food supplies for invertebrates, thereby indirectly affecting their size and number, as well as of other species. However, more recent studies have shown that direct exposure to low pH levels on aquatic biota is more important than indirect effects on food sources (Reclamation Research Group, 2008).

Cooper and Wagner (1973) studied the fish fauna of rivers in Pennsylvania State affected by the AMD. They observed the greatest impact on fish population in water with pH from 4.5 to 5.5: at these rates the complete loss of fish in 90% of the studied streams was observed. Later it was proved that the lack of fish in acidified water may be associated with increased concentrations of dissolved metals. Cooper and Wagner (1973) also indicated that sulphates - the major anion of AMD - are not toxic to fish until the concentration does not exceed several thousand mg/l. Low levels of pH, which are not fatal to aquatic life, can adversely affect fish growth and reproduction.

Heavy metals increase the AMD toxicity and, in addition, act as metabolic poisons. Iron, aluminum and manganese most commonly present in the mine brines can greatly exacerbate the adverse effects of acidic water on the environment.

Of the three major metals presented in AMD, aluminium exhibits the most serious adverse effects on aquatic organisms (Cooper and Wagner, 1973). It was found that the combination of pH less than 5.5 and the concentration of dissolved aluminium greater than 0.5 mg/l, usually leads to death of all aquatic organisms.

Also, some other metals, such as zinc, cadmium and copper also present in mine waters, are toxic at very low concentrations and can act synergistically, inhibiting the growth of

algae, fish and benthic organisms (Weed and Rutschky, 1971). Based on limited studies, Ni causes Mg^{2+} antagonism, respiratory disorder and kidney disease in fish and other aquatic animals (Ptashynski et al., 2002; Jasimchowdhury, 2008). Exceeded nickel level is more harmful for mammal animals. Nickel has the potential to cause the following health effects: decreased body weight, heart and liver damage, dermatitis. (US EPA, Technical factsheet on nickel)

In addition, AMD may cause the secondary pollution effects, such as increased carbon dioxide concentration in water, increased water turbidity caused by soil erosion, and changing the shape of the drainage channels due to the deposition of various metal compounds (Kleinmann and Watzlaf, 1988; Krainov and Phoigt, 1991; Reclamation Research Group, 2008).

The AMD impact on drinking and industrial water supply was described by Reclamation Research Group, 2008: acidic mine waters cause excessive corrosion of the locks and dams, ships and barges, bridges and culverts, pipes and plumbing installations. Iron sulphate, as well as its oxides, often destroys aquatic ecosystems, prevent self-purification of rivers and reservoirs, makes the water unfit for drinking and household use, causes the appearance of unsightly reddish-brown stains on fabrics in laundry and textile factories, increasing scale in the wash-basins, sinks and bathrooms. The water becomes unsuitable for use in boilers, as well as in municipal waterworks.

Another common problem associated with AMD is the growth of bacteria that use iron as an energy source and store it in the cytoplasm. These bacteria produce the bulk material that can clog water systems. As a rule, their activation occurs when the iron concentration exceeds 0.2 mg/l (Shevyakov,1939; Dokukin and Dokukina, 1950; Gray, 1997). In addition, AMD significantly reduces the shelf life of concrete structures. For example, the sulphate contained in the AMD reacts with certain components of the concrete to form calcium sulphoaluminate. This reaction is accompanied by expansion and, consequently, the destruction of concrete structures (Shevyakov, 1939; Dokukin and Dokukina, 1950).

2 STRATEGIES OF AMD MANAGEMENT

In this chapter the conventional methods of AMD prevention, mitigating and treatment are reviewed for their proven sustainability for both environmental and business aspects.

Generally, minimization of AMD formation is preferred to control the contaminant loads and is favoured over the treatment. The treatment, however, in some hard cases is

inevitable for the AMD already produced in huge amounts due to poor planning of mining works in former times that minimization or formation control is impossible. Also, in locations with a limited water supply AMD may to be purified and used for municipal purposes (Zick, 2010). Finally, the metal ions concentrations in AMD may be so high, that commercially profitable recovery becomes available (Strosnider et al., 2011).

2.1 Minimization and control of AMD formation

A preferred option for reducing AMD is to prevent sulphide oxidation at the source (Filion et al., 1990; Evangelou, 1995). If achieved, prevention can provide a permanent solution at low cost (Nyavor and Egiebor, 1995). Minimization and control strategies according to AMD formation implies the reducing of ore oxidation and transport of oxidation products. As both oxygen and water are required to perpetuate the formation of AMD, excluding one or both of these make it possible preventing or minimizing AMD formation (Shevyakov, 1939).

There have been several strategies developed to prevent pyrite oxidation and subsequent formation of AMD (Evangelou, 1995; Brown et al., 2002; Zhang and Evangelou, 1996; Johnson and Hallberg, 2005). Conventional methods are classified into two major types: establishing a physical barrier or blending and co-disposal with alkaline materials.

2.1.1 Physical barriers

The most common and traditional approach for controlling AMD formation is to establish a physical barrier that comprises a wet or dry cover (Kleinmann, 1990; Evangelou and Zhang, 1995). Such covers work because they create barrier for oxygen preventing pyrite oxidation (Belzile et al., 1997; Peppas et al., 2000; Vigneault et al., 2001).

Dry cover

To restore the environment at the place of a closed mine multi-layered covers, with fertile top layer are often used for the emergence of vegetation. Soil covers must also be resistant to breakthrough by erosion, plant roots, or burrowing animals.The limited oxygen ingress is achieved at the case via the capillary barrier effect in unsaturated soils. With the capillary barrier effect one of the cover layers is maintained at a high degree of saturation with water at all times. The high degree of saturation makes the moisture-retaining layer an efficient barrier against oxygen flow by impeding the gas transfer.

Capillary barrier effect is present when a fine grained material is placed over a coarser one. The two materials have different hydrogeological properties because of their different

textures. In the initial desaturation stage, the fine grained material layer keeps water stronger than the coarse layer for its smaller pores. When the coarse material drains, the presence of gas in its pore space reduces the interconnectivity of the voids which reduces its hydraulic conductivity. This reduction of the hydraulic conductivity in the coarse layer reduces the vertical water flow from the fine material (Nicholson et al., 1989; Akindunni et al., 1991; Aubertin et al., 1995; Aachib, 1997; Bussiere, 1999; Bussiere et al., 2003).

Covers with capillary barrier effects usually contain three to five layers of different materials. Figure 4 gives a schematic illustration of a multi-layer cover. The bottom layer is made of a fairly coarse material which functions as both a mechanical support and a capillary break. The fine grained material, utilized as the moisture retaining layer (high air-entry value to maintain saturation), is placed upon the first layer to create the capillary barrier effect; the layer should also have a low hydraulic conductivity ($< 10^{-8}$ m/s) to hold up rain ingress. Another coarse material is placed on the fine grained material layer to prevent water evaporation. The other two layers (protection and surface layers) are protective layers against wind-, water-, and bio- erosion of a cover. Topsoil usually has a sufficient depth (>> 0.5 m) for plant roots. (Bussiere, 2009; Williams et al., 1997)
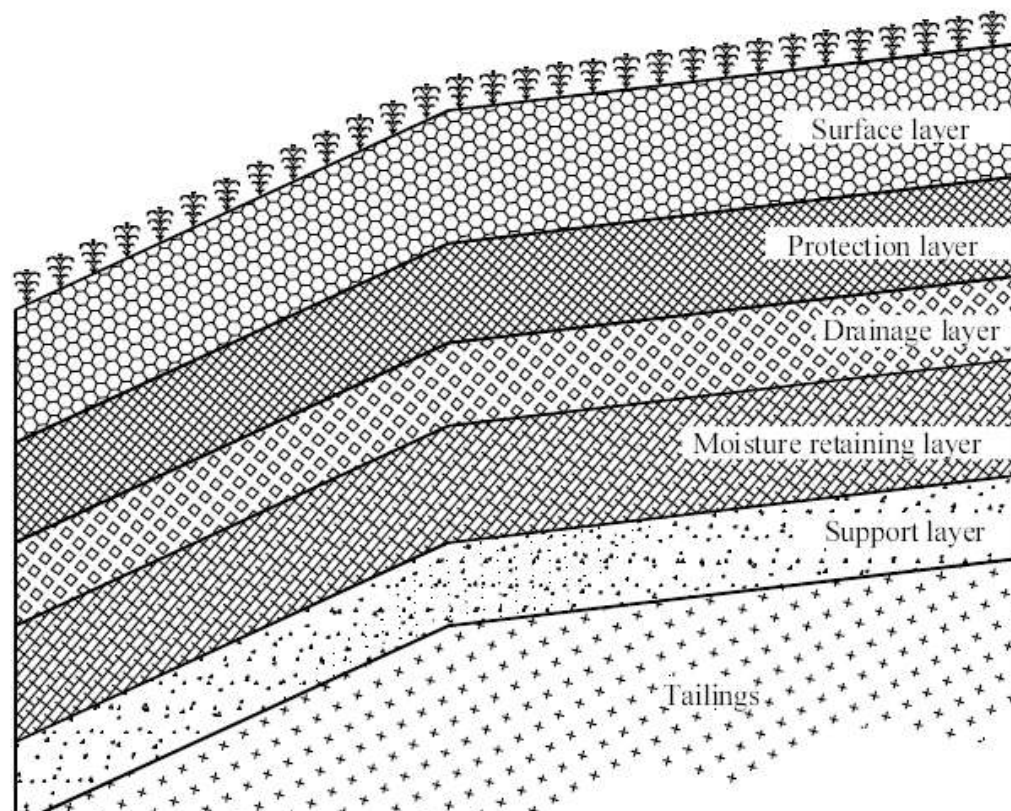

Figure 4. A multi-layer cover of potentially acid-forming materials

In dry climates, where it is difficult to maintain the soil cover in a saturated state, the main function of a soil cover is to limit the percolation of rainfall into the acidic wastes. Rainfall-shedding or barrier covers are likely to perform poorly in seasonal climates and to fail in semi-arid and arid climates, where the vegetation cover would be poor and the sealing layer would be prone to cracking and root penetration, and erosion (Svanson et. al., 1997).

An option to limit water infiltration in arid and semi-arid conditions is the use of "Store-and-Release" (SR) covers. Such engineered systems may represent an alternative to more traditional covers that rely on materials having a low saturated hydraulic conductivity (Morris and Stormont, 1997; Ward and Gee, 1997; Dwyer, 1998; Zhan et al., 2001; Scanlon et al., 2005).

A typical SR cover includes a fine-grained soil layer placed on top of a coarser material. The capillary barrier effect at the interface between the fine and coarse materials allows the finer soil layer to store surface water, which can later be released by evaporation. Additional layers can also be added to help the cover play its role(s) efficiently. Figure 5 shows a typical water transfer into a SR cover.
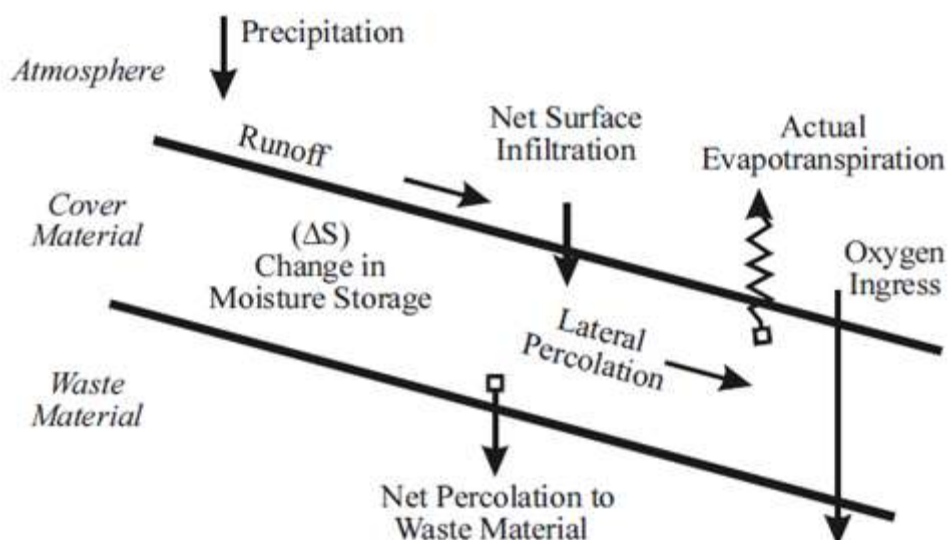

Figure 5. Schematic outline of the SR cover water balance (MEND 2001)

The objective of the cover is to have sufficient evapotranspiration, storage, and runoff to avoid water infiltration into the mine waste. The main advantages of a SR cover lie in its relative simplicity, long-term stability, and potentially lower construction costs compared to

more traditional covers, which utilize natural soils and geosynthetics with a low saturated hydraulic conductivity. (Morris and Stormont, 1997; Williams et al., 2003; Benson et al., 2001)

In wet climates, where it is difficult to stop rainfall ingress, the main function of a cover is to limit oxygen ingress and so limit the oxidation of the stored reactive wastes and the production of AMD. A cover typically comprises a compacted clayey soil seal about 0.5 m thick, overlain by a growth medium as thin as 0.3 m, which may support grasses but is quite inadequate for most bushes and trees. A well-vegetated cover can handle the huge rainfall flux while limiting erosion. (Australian Government handbook, 2007)

When potentially-forming material is stored, the place of storage should be sealed not only from the top, but from all sides. For waste rock piles, reactive waste rock should typically be placed on a base layer of non-acid forming waste rock, tied into the lined natural drainage channels, and encapsulated with a benign rock (Figure 6).
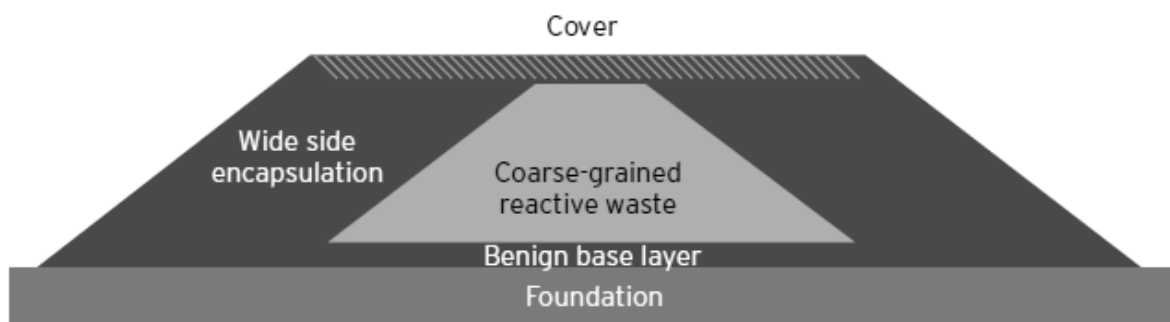
Figure 6. Encapsulation of reactive waste

The initial pyrite ore may be used as non-acid forming material (mainly fine fraction) after the desulphurization (Martin and Fyfe, 2011). Different techniques such as flotation and gravimetric separation can be used to separate the sulphides from the tailings (McLaughlin and Stuparyk, 1994; Humber, 1995). Hesketh et al. (2010(demonstrated the feasibility of froth flotation for desulphurization of copper sulphide tailings, and achieved the content of sulphur in the tailings as low as 0.2% S. Such low-S tailings are classified as being non-acid-producing material.

Wet covers

The most effective way to restrict the oxygen flux to the potentially acid-forming wastes is to deposit them permanently under water. The oxygen diffusion coefficient is 10 000 times lower in water than in air (Li et al., 1997), therefore in water it is the limited amount of

dissolved oxygen. In addition, microbial catalysis, metals hydroxides precipitation, and development of sediment barriers between stored pyrite waste and overlying waters also inhibit oxidation (Kleinmann and Crerar, 1979). Both laboratory and field studies have shown that underwater disposal is one of the most effective ways to stabilize sulphide tailings (Sahoo et al., 2013).

The water cover technique consists of completely covering the reactive mine wastes with water by submerging the mine waste in a lake or by building a dyke to hold both the mine waste and the water that submerges them. Flooded underground workings may also provide the potential for the permanent storage of reactive wastes under water. (Adu-Wusu et al. 2001; Catalan and Yanful 2002; Yanful and Catalan 2002; Mian and Yanful 2004)

To be effective, water covers require the topography and rainfall to provide a minimum water depth of 1.5 to 2 m, preferably more, depending on the potential for the re-suspension of fine-grained reactive wastes by surface wave action and currents. The greater the flushing of the water cover the better (Australian Government Handbook, 2007).

However, a water cover is a complex, dynamic system influenced by factors such as sulphide material erosion and resuspension, oxygen migration, oxidation of sulphide wastes by dissolved oxygen (DO), release of dissolved metals, water exchange with the surrounding environment, etc. (Bussiere, 2009) Johnson and Hallberg, 2005 reported that water cover is problematic at sites where the influx of oxygen-containing water occurs, or where mines are only partially flooded. This is due to rise and fall of the water table and seasonal changes, which allow pyrite to oxidize when exposed to the atmosphere. Finally, flooding of mine wastes requires a rigorous engineering design and proper maintenance to minimize the risk of dike failure, which is often not cost effective (Sahoo et al., 2013).

To reduce the geotechnical risks associated to a water cover, a new approach was proposed and used relatively recently for tailings: the Elevated Water Table (EWT) technique (MEND, 1996; Orava et al. 1997; Dagenais et al., 2005; Dagenais et al. , 2006; Demers et al. 2008). The principle on which the EWT method is based consists of maintaining a degree of saturation sufficiently high in the tailings above the water table in order to reduce the oxygen diffusion rate and prevent sulphide oxidation. A high degree of saturation is maintained by controlling seepage and capillary rise. Similar to water cover, the elevated water table technique is based on the fact that the effective diffusion

coefficient of oxygen is very low in saturated (or nearly saturated) media (Mbonimpa et al. 2003, Aachib et al. 2004).

2.1.2 Blending and co-disposal with alkaline materials

Alkaline compounds inhibit sulphide oxidation in two ways: inhibition the activity of oxidizing bacteria (Nicholson et al., 1988), and neutralizing acids, leading to Fe^{3+} precipitation as Fe-hydroxide colloids, which precipitate on the surface of the pyrite (Evangelou, 1995; Huminicki and Rimstidt, 2009).

There are several ways that alkaline materials are applied to sulphide residues at mine sites. The pumped co-disposal of coal washery wastes is reasonably common in the coal industry (Australian Government Handbook, 2007). For underground mines, alkaline material such as lime was applied into mine spoils through boreholes as lime–water slurry. However, this method was mostly unsuccessful because of slurry settling problems and limited solubility of lime. This problem was solved by using more soluble compounds like sodium carbonate and sodium hydroxide, but these replacement chemicals failed to suppress acid generation significantly. (Kleinmann et al., 1981) For surface mines, alkaline materials are applied as blends with mine spoil, or alkaline material is placed above or below the mine spoil (Mylona et al., 2000; Miller et al., 2003; Taylor et al., 2006).

Blending can be a difficult task, because it is dependent on the degree of mixing, and the nature of the contact between acidic rock and the alkaline materials. Common alkaline materials blended with mine spoils include limestone ($CaCO_3$) and lime (CaO or $Ca(OH)_2$). Geidel and Caruccio (1984) examined the effects of applying limestone mixed with sulphur compounds to the acidic materials at a reclaimed coal mine. They found that the treatment produced alkaline drainage, but it shortly became acidic. The major reason is that abiotic pyrite oxidation continues after applying of alkaline materials (Evangelou 2001).

Potentially acid forming material is sometimes mixed with cement or a mixture of cement and tailings and placed in underground voids as backfill. The cement has inherent neutralising capacity. (Australian Government Handbook, 2007)

2.2 AMD Treatment

AMD treatment can be a costly part of mining operations and potentially an even more costly post closure liability if the probability for sulphide materials to produce AMD is not recognised and managed appropriately from the start of mining operations.

The content of metal ions and pH are the most common targets for treatment of AMD, but the removal of non-metal ions, such as sulphate may also be required.

AMD treatment systems can be categorised as either active or passive. The common attributes of a passive treatment system are absence or minimal requirements for active (electric or diesel) pumping, and absence of need for addition of chemical reagents.

Whether an active or passive method is fitted to a given AMD application, this is determined by estimation of the acidity load of the influent AMD.

Acidity load refers to the product of the total acidity (acid + latent acidity) and flow rate (or volume) and is expressed as 'the mass of $CaCO_3$ equivalent per unit time', or the mass of $CaCO_3$ equivalent for a given volume of water. If the flow rate or volume data are available, the measured or estimated acidity values can be converted into acidity load as shown in Equations 7 and 8.

(7)

Acidity load (tonnes $CaCO_3$/day) = 10^{-9} x 86,400 (conversion factor)x Flow rate (L/s) x Acidity (mg/L $CaCO_3$)

or

(8)

Acidity load (tonnes $CaCO_3$) = 10^{-9} (conversion factor)x Volume (L) x Acidity (mg/L $CaCO_3$).

Passive treatment approaches can be economically attractive in the right circumstances, but have some significant limitations. They are best suited to the treatment of waters with low acidity (<800 mg $CaCO_3$/L) and low acidity loads (100–150 kg $CaCO_3$ per day), with steady flow rates. In the case of near-neutral mine drainage, such as pH 5-8, very large flows can be directly treated by wetland systems at lower cost and with potentially better output water quality than can be achieved by active water treatment.

Figure 7 can be used to determine the applicability of different AMD treatment systems based on the acidity load of influent AMD.
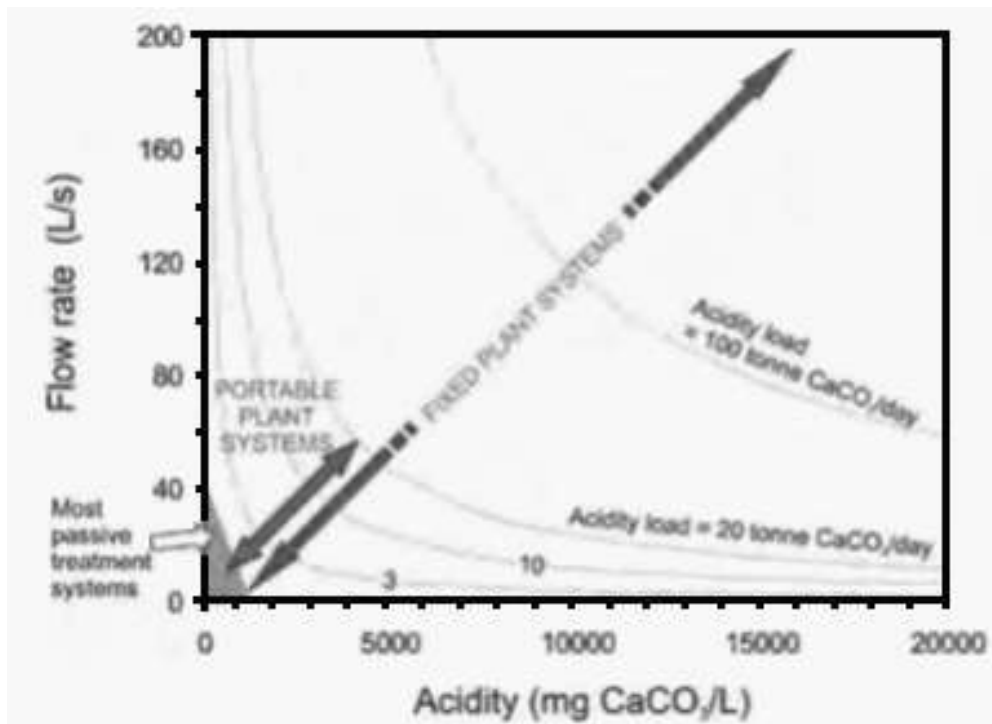
Figure 7. The selection of appropriate treatment approaches.
(Australian Government Handbook, 2007)

2.2.1 Active AMD treatment

The advantage of active treatment systems is that they can be designed to treat a wide range of acidity loads (see Figure 7). However, the selection of a suitable active treatment technology or the combination of treatment technologies that will provide robust and economically viable service is very site-specific. There are four basic types of active treatment technologies: precipitation of metal complexes by addition of neutralising agents to raise pH; ion exchange; membrane separation (reverse osmosis, electrodialysis); bioreactor systems.

Addition of neutralizing agents

The most common and lowest cost form of active treatment is chemical neutralisation. Most metals of concern can potentially be removed by raising the pH to the required level. However, mercury (Hg), molybdenum (Mo), chromium-VI (chromate) and arsenic-III (arsenite) cannot be managed by pH control alone. Design of a plant treating AMD requires calculation of the neutralizing agent demand, and the test work to determine the cost-effective range of potentially available neutralizing agents. (Taylor et al., 2005)

The most commonly used neutralising agents for large-scale treatment of AMD are lime (quicklime, hydrated lime), magnesite, magnesium oxide and limestone. This is due to the

ready commercial availability of these reagents, non-proprietary nature, well-proven technologies for their use, cost-effectiveness and manageable occupational health and safety properties for large-scale application (Australian Government Handbook, 2007).

Various neutralising reagents have been used, including lime (calcium oxide), slaked lime, calcium carbonate, sodium carbonate, sodium hydroxide, and magnesium oxide and hydroxide. These vary in cost and effectiveness; for example, sodium hydroxide is some 1.5 times as effective, but is about nine times the cost of lime (Johnson and Kevin, 2005). Although active chemical treatment can provide effective remediation of AMD, it has the disadvantages of high operating costs and problems with disposal of the produced bulky sludge (Sharma, 2010).

There are a number of process variations reducing the problems of wastes. For example, multiple-stepped addition of reagents accompanied by pH control can result in the selective removal of some AMD components such as arsenic and molybdenum (Aube and Payant, 1997). Various flocculating reagents may be used to promote aggregation of precipitates, thereby aiding their removal in settling ponds. Modifications to the technique, involving partial recycling of sludge into lime-holding tanks can produce high-density sludge with smaller cost of disposal and storage (Kalin et al., 1991).

Ion exchange

It is well-established technology for extracting dissolved salts from AMD water by passing it through beds of ion-exchange resins. (Clifford, 1990). So, the performance of field ion exchangers can be limited by AMD load and plugging with insoluble metal precipitates (Gaikwad, 2010). Therefore, the first stage of AMD treatment should be removal of heavy metals by precipitation.

The dissolved salts in many of the polluted mine waters are mainly calcium and magnesium sulphate. Various authors have investigated the elution of calcium and magnesium ions from cation-exchange resins with sulphuric acid, and the elution of sulphate ions from the anion-exchange resins with lime. The calcium eluted from the cation-exchange resin can be combined with the sulphate in the sulphuric acid to form solid calcium sulphate. Similarly, the sulphate eluted from the anion-exchange resin can be combined with the calcium in the lime to form solid calcium sulphate. Where magnesium is present in sufficient amounts, it can be precipitated from the solution (as a mixture of solid magnesium hydroxide and solid calcium sulphate). The elution of the cation-exchange resin can be performed by neutralising all or a part of the solution with

excess lime. Mixture of acidic gypsum from the cation elution section and alkaline gypsum from the anion elution section could generate high quality gypsum as byproduct. (Feng et al., 2000)

Membrane separation (reverse osmosis, electrodialysis)

This method allows removing both major ion salts and metals to low levels. It is a secondary treatment step that would follow first stage neutralisation of acidity by pH adjustment. Rigorous pre-treatment (precipitation, filtration) is required to remove solutes (especially, iron, manganese, and calcium sulphate and carbonate) that can rapidly and irreversibly foul the costly membranes.

During reverse osmosis treatment, water move through both brackish membranes and sea-water membranes to achieve a high recovery of the treated softened water (Zick, 2010). During electrodialysis water is passed between cation- and anion-selective membranes, in the presence of an electric field. The impurities (ions) are transported across these membranes and concentrated into brine streams, leaving a product stream of purified water. In both cases the calcium in the feed water gives rise to scaling of the membranes, so, for instance, the recovery of purified water in electrodialysis is decreased to levels similar to those achievable with reverse osmosis (Feng et al., 2000).

Bioreactor systems

Much of the biotechnology developments rely on sulphate-reducing bacteria (SRB) to treat AMD. Basically, bioreactors use SRB to drive sulphide precipitation, removing metals from the AMD solution (Equations 9 and 10):

$$2CH_2O+SO_4^{2-} = 2HCO_3^-+H_2S, \tag{9}$$
$$H_2S+M^{z+} = MS_{(s)} + 2H^+, \tag{10}$$

where M^{z+} is a cationic metal that forms insoluble sulphide (copper, cadmium, nickel and lead, as well as arsenic, selenium and molybdenum). In addition, SRB will drive alkalinity generation (Equation 9) (Warren, 2011).

Engineered sulphate-reducing bacterial systems have been developed by BioteQ (www.bioteq.ca, BioSulphide®) and Paques (www.paques.nl,THIOPAQ®). The Biosulphide system consists of two components, biological and chemical ones, which operate independently (Johnson and Kevin, 2005). Raw AMD enters the chemical circuit where it comes into contact with hydrogen sulphide generated in the biological circuit. By

careful manipulation of conditions (pH and sulphide concentration), selective separation of a particular metal sulphide takes place. This may then be removed from the partially processed water ahead of further treatment. Then the treated AMD enters the biological circuit to provide the sulphate source in the bioreactor, containing a mixed culture of sulphate reducing bacteria. The Thiopaq system differs from the Biosulphide process utilising two distinct microbiological populations and processes: one works for conversion of sulphate to sulphide and precipitation of metal sulphides, and the other - for conversion of excess hydrogen sulphide to elemental sulphur. Application of this technology to AMD has also been demonstrated on a pilot-scale at the Kennecott Bingham Canyon copper mine in Utah, where 99% of copper present in a pH 2.6 waste stream was selectively recovered.

This processes can produce water containing <300 mg/L sulphate and also removes metals. The technology has been in operation at full-scale since the mid-1990s and several plants have been installed. This technology is best suited to situations where high levels of control can be provided, and where commercial metal recovery is possible (Boonstra et al., 1999).

2.2.2 Passive AMD treatment

There are two conventional classes of passive treatment systems: oxic/anoxic limestone drains, and wetlands.

Single-stage active or passive treatment systems that use only chemical neutralizing agents, may have difficulty meeting stringent targets in aquatic ecosystems protection, depending on the range of metals and other solutes in the source water. This is where a second-stage passive biological (for example, a wetland) polishing system can provide a distinct advantage, by achieving the required water quality without the large capital and operating costs associated with secondary and tertiary active treatment technologies (Australian Government Handbook, 2007).

Oxic and anoxic limestone drains

Passive-treatment systems quite often incorporate crushed limestone that is flooded continuously with AMD to neutralize the acidity, thereby generating alkalinity. In theory, limestone drains require minimum maintenance once constructed, so their use is considered to be a passive approach to mine water treatment. In drains water flows through a bed of limestone gravel that is impervious to both air and water due to plastic

bottom liner and a clay cover. The dimensions of the drain vary from narrow, 0.6 to1.0 m, to wide, 10 to 20 m diameter, and typically about 30 m in length (Evangelou, 1998).

For example, an ''anoxic limestone drain'' (ALD) consists of crushed limestone of uniform size that is placed in a buried bed to treat AMD before its exposure to atmospheric O_2 (Hedin and Watzlaf, 1994). Excluding O_2 from contact with the water in an ALD minimizes the potential for oxidation of Fe^{2+} to Fe^{3+} and the consequent precipitation of $Fe(OH)_3$ and related solids. As the pH increases to near-neutral values in an ALD, concentrations of dissolved Fe^{3+}, Al and other metals in AMD tend to decrease mainly due to their precipitation; however, concentrations of SO_4, Fe^{2+} and Mn^{2+} generally will not be reduced (Cravotta and Trahan, 1999; Cravotta and Watzlaf, 2002). After passing the AMD through the ALD, the partially treated effluent typically is diverted through ponds and/or wetlands where exposure to the atmosphere promotes Fe^{2+} oxidation and the precipitation and settling of solid $Fe(OH)_3$ (Hedin et al., 1994; Skousen et al., 1998; Watzlaf et al., 2004).

Continuous flow and retention of CO_2 can enhance limestone dissolution and alkalinity production because the rate and extent of limestone dissolution tend to increase with increased partial pressure of CO_2 (P_{CO2}) and/or decreased pH (Unger-Lindig et al., 2010). Alkalinity may reach up to 275 mg $CaCO_3$ /L compared to an open system which, in equilibrium, would produce only 50–60 mg $CaCO_3$ /L (Kleinmann et al., 1998). Furthermore, the dissolution rate tends to increase as the exposed surface area of limestone increases (particle size decreases) (Morse, 1983), and/or the $CaCO_3$ content of the limestone increases (Watzlaf and Hedin, 1993). Consequently, Hedin et al. (1994) and Watzlaf et al. (2004) have recommended crushed limestone fragments with a maximum diameter of 5 cm and with a minimum $CaCO_3$ content of 90% for use in passive-treatment systems for AMD.

The precipitation of Fe^{3+} and Al oxyhydroxides or oxyhydroxysulphates, gypsum, and various other compounds within a bed of limestone can ''armour'' the limestone surfaces, causing the failure of the drain within a few months. Furthermore, the accumulation of precipitated compounds can decrease the porosity and permeability of the limestone bed. (Hammarstrom et al., 2003) Hence, design criteria for ALDs as proposed by Hedin et al. (1994) and Hedin and Watzlaf (1994) generally are conservative with respect to the permissible concentrations of dissolved O_2, Fe^{3+} and Al in influent (<1 mg/L O_2, Fe^{3+} or Al) to minimize potential for clogging or armoring by Fe^{3+} or Al solids.

Stringent requirements for low concentrations of O_2, Fe^{3+} and Al in the influent make ALDs inappropriate for treatment of oxic or highly mineralized AMD. For example, of 140 AMD samples from abandoned bituminous and anthracite coal mines in Pennsylvania, only 17% were net acidic and had <1 mg/L of dissolved O_2, Fe^{3+} and Al (Cravotta, 2008a). Alternative treatments, including a buried "oxic limestone drain" (OLD) that includes flushing pipes to remove precipitated solids could be useful for the neutralization and removal of metals from acidic effluent that does not meet criteria for an ALD (Skousen et al., 1998).

As the pH increases within OLD systems, metalrich solids tend to precipitate. Because dissolved CO_2 is retained in an enclosed ALD or OLD, limestone dissolution and alkalinity production are enhanced. Despite the accumulation of Fe^{3+} mineral coatings, limestone dissolution can be rapid in OLDs compared to ALDs. (Cravotta et al., 2004) According to Cravotta and Trahan (1999), the hydrolysis of Fe and Al within the OLD releases H^+ that reacts with HCO_3^- and limestone before exiting the system. In contrast with Al-hydroxysulphate and Ca-sulphate minerals that could form coatings on the limestone surfaces in contact with AMD, freshly precipitated Fe^{3+} minerals tend to be loosely bound to the limestone (Loeppert and Hossner, 1984).

Nevertheless, OLDs could fail due to clogging of the limestone bed by the precipitated metal hydroxides. By incorporating perforated piping within the limestone bed, solids potentially can be flushed from the OLD, thereby reducing potential for clogging (Cravotta, 2008b). Although some studies have reported on systems designed for the efficient flushing of metal-rich solids from limestone beds (Schueck et al., 2004; Weaver et al., 2004), consensus has not been reached on the implementation and management of flushable passive-treatment systems to achieve treatment goals.

Limestone drains are often used in combination with active treatment systems, which may result in dramatic improvement of the treated waters quality (Kleinmann et al., 1998). For instance, during lime treatment, the most commonly used method, AMD is discharged directly into a rapid mix chamber where hydrated lime is added in dry form or as slurry. Low ferrous iron concentrations (<50 mg/L) are treated to a pH of 6.5-8 and then diverted directly to a settling chamber. Higher concentrations have pH 8-10 and are passed through an aeration tank, where the ferrous hydroxide precipitate is converted to ferric hydroxide. The water then flows to a settling chamber, where heavy metals are precipitated from the solution (Silva et al., 2012b).

Wetlands

The bioremediation of AMD is derived from the ability of some microorganisms to generate alkalinity and immobilise metals, thus reversing the reactions originating AMD (Boonstra et al., 1999). There are three conventional types of wetlands: aerobic wetlands, anaerobic compost bioreactors, and composite aerobic and anaerobic wetlands.

Aerobic wetlands are generally constructed to treat alkaline mine waters. These are relatively shallow ponds operating with a surface flow. Macrophytes are planted for aesthetic reasons and to regulate water flow, e.g. preventing channelling, and to filter and stabilise the accumulating ferric precipitates (ochre). They also provide additional surface area for precipitation of other ferric compounds and minerals. In addition, some aquatic plants may accelerate the rate of ferrous iron oxidation by delivering oxygen from aerial parts to their root systems.

Most aerobic wetlands operate at near-neutral pH using neutrophilic iron-oxidising bacteria living at the interface of aerobic and anaerobic zones, e.g., *Gallionella ferruginea*. The big advantage of aerobic wetlands consists of their possibility to remove arsenic from AMD (Boonstra et al., 1999).

The term "compost bioreactor" describes the systems entirely enclosed below ground level not supporting any macrophytes. The composts itself are prepared by mixing relatively biodegradable materials, e.g. manure or mushroom compost, with more recalcitrant materials, such as sawdust, peat, or straw. The slow biodegradation of the latter is presumed to act as a long-term provision of appropriate substrates and ammonium for the indigenous iron- and sulphate-reducing bacteria, which are considered to be responsible for AMD remediation. The choice of bulky organic materials varies according to their local availability and, when possible, their effectiveness.

The microbially catalysed reactions in compost bioreactors generate net alkalinity and biogenic sulphide. Therefore, these systems may be used to treat acidic mine waters with high content of metallic ions, such as AMD from abandoned metal mines (Boonstra et al., 1999). However, there are little quantitative data on the relative significance of iron and sulphate reduction in compost reactors and nothing is known about how the microbiology of these systems changes with the ecosystem age, especially with regard to substrate provision.

Passive bioremediation systems that utilise a combination of aerobic and anaerobic wetlands, such as Acid Reduction Using Microbiology (ARUM) system (Kalin et al., 1991), have been used for full-scale treatment of AMD. The system is comprised of two oxidation cells, within which iron is oxidised and precipitated. Beyond these, AMD passes first through a detention reservoir prior to the passage through the ARUM cells generating alkali and sulphide. The organic materials that promote sulphate reduction in the ARUM cells originate from floating macrophytes, e.g., cattails. The ARUM systems have been shown to be effective in treating AMD in both northern and subtropical locations (Johnson and Kevin, 2005).

Wetlands cannot rapidly adjust to a sudden changing in water quality or to a huge short-term increase in flow rate. They work in the appropriate way at pH values above 4.5, under steady-state conditions, with a residence time of 10–15 days. They require a relatively constant inflow rate from a pond in which the mine water is initially collected (and pre-neutralised if required).

The design lifetime of a passive treatment system is a key issue. In some cases, significant volumes of mine water requiring treatment may only be produced during the operations phase, before to rehabilitation of source material (such as waste rock piles). In the cases, there would be less emphasis on long-term, post-closure environmental safety. The need for self-sustaining systems becomes much more critical following site decommissioning, because passive treatment systems accumulate toxic metals during own operational life-cycle (Australian Government Handbook, 2007).

3 TREATMENT OF NICKEL CONTAINING AMD WITH NEUTRALIZING MATERIALS

A large body of data concerning application of neutralizing materials to AMD treatment has been reported. pH control with cost-effective neutralisation reagents will remain for some time the most widely used and the lowest cost first-stage approach to both passive and active AMD treatment. The most abundant minerals that can neutralize acidic waters are carbonates: calcite $CaCO_3$, magnesite $MgCO_3$, dolomite $Ca_{0.5}Mg_{0.5}CO_3$, etc. Active treatment using calcium-based reagents is likely to remain the primary choice for neutralising medium to high-strength (low pH) AMD, and for treating those systems where the acidic water flow rate varies over a large range. Passive treatment systems are restricted to low acidity load situations where the flow rate of the water to be treated is relatively steady through time. (Australian Government Handbook, 2007)

It is generally accepted that limestone (calcite) is the most effective neutralising agent. (Lottermoser, 2007; Solomin and Krainov, 1994). Limestone is the most common neutralizing agent for acid waters (Douglas and Degens, 2005) due to its availability (Hammarstrom et al., 2003) in many countries and it is likely to be either the first option for metal removal from many wastewaters, or to be combined with other treatment technologies (Martins et al., 2010). Although limestone application produces a lower volume of sludge, it is not widely used, largely because carbon dioxide buffers the reaction, therefore making it difficult to raise the pH above 6. Calcite has slow rate of dissolution and tendency for an impermeable metal-hydroxide coating, termed armouring, to form on grain surfaces. Limestone is not recommended for sites with acidity levels greater than 50 mg/l as $CaCO_3$ or Fe concentrations above 5 mg/l because of armouring (Skousen et al., 1995). In addition, there may be biological growth, which inhibits solid-liquid interface interaction with mine water (Silva et al., 2012a).

Data have been presented in the literature showing that limestone can be an option for sulphate sorption, particularly from neutral mine drainages because calcium ions on the solid surface can bind sulphate ions. Also, limestone can effectively reduce concentration of iron and aluminium in drainage waters, even with low pH values, when the surface of calcite is partially dissolved and passivated by the sulphuric acid. (Hammarstrom et al., 2003; Silva et al., 2012b)

Although these experiments were carried out in the conditions, which are close to natural ones in AMD (low pH values, high concentrations of metal and sulphuric ions), they were performed on a limited number of metal ions. On the other hand, the waters are contaminated not only with iron and sulphate ion. In some cases, releasing of heavy metals ions occur during chemical processes of pyrite oxidation even without mining. One example of natural contamination is in groundwater supplies from chalk aquifers in Denmark and South-Western Sweden, where trace concentrations of nickel are present as a solid solution in pyrite nodules. As pyrite is oxidised by draw-down of the water table, Ni is released (Larsen and Postma, 1997). Depending on groundwater conditions, nickel concentrations can vary from barely detectable to a few hundred ppm (~5 μM), well above the Danish legal limit and the World Health Organisation (WHO) recommended value of 20 ppb (0.34 μM) (Lakshtanov and Stipp, 2007).

There is a group of articles related to precipitation of nickel, cadmium, copper and zinc on the calcite in neutral and alkaline conditions (Lakshtanov and Stipp, 2007; Zhigang et al., 2009).

Also, there are several articles on heavy metals (Ni, Cd, Zn, Cu) precipitation with calcite, they all are conducted with quite low concentrations of heavy metals (less than 1 ppm) and with the absence of sulphuric ions in the solution, i.e. without passivation of the calcite surface. At the same time, the study conducted by Honghai et al. (1999) showed that the sorption behaviour of cations such as Cd^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} on calcite surface differs significantly with the change of metal ions concentration: at low concentrations it can be modelled by surface exchange reaction, at the high concentrations - by both surface complexation and exchange reaction, or by precipitation. Therefore, the results of the research on heavy metal interaction with calcite, which was carried out with small concentrations of metal ions cannot be compared with the ones usually occurred in AMD in high concentrations. (Honghai et al., 1999; Hoffmann and Stipp, 2001; Lakshtanov and Stipp, 2007)

Finally, the co-precipitation phenomenon of heavy metals with iron and aluminium on calcite was reported (Liang-qi et al., 2010; Miller et al., 2011).

Although all AMD waters contain iron and very often aluminium, the question on heavy metals precipitation characteristics in high acidic conditions under variable conditions remains. Thus the data on solitary precipitation of selected heavy metals in natural AMD conditions are necessary at the first place.

4 OBJECTIVES OF RESEARCH AND WORKING HYPOTHESIS

This paper evaluates the effect of active neutralizing with Nordkalk Oy calcite-containing side-products on nickel removal from nickel acidic solutions: the effect of neutralizing material dosage on pH was studied together with the removal of nickel ions from solutions.

It was assumed that the first contact of the materials with acidic water will induce the appearance of rising pH gradient in the layer of solution close to the surface of the sorbent due to the neutralization of acid by carbonates contained in the material. An example of a chemical interaction that may occur in the system is described by the following reaction:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \hspace{4cm} (11)$$

As a result, a medium with conditions close to the neutral pH may occur in the boundary layer between the solid and liquid phase, and nickel will start to form surface hydroxide and carbonate complexes there being trapped at the surface of neutralising agents. Thus

the concentration of metal in the bulk solution may decrease. Also, adsorption of nickel from acidic solution may be observed.

Further, the chemical interaction of carbonate and hydrogen ions will continue, and the thickness of the layer will increase with higher pH. The general increase of solution pH may also be observed.

The formation of gypsum on the surface of the calcium containing materials contacting the acidic solutions is also foreseen, which could also significantly affect the degree of nickel removal.

Figure 8. Pore plugging on calcite during gypsum formation

Besides calcium carbonate reaction with sulphuric acid, the formation of amorphous silica gel with good adsorption properties on the surface of wollastonite contained in the tested materials is also expected as a result of calcium silicate hydrolysis according to the equation:

$$CaSiO_3 + 2H^+ = Ca^{2+} + H_2O + SiO_2 \tag{12}$$

5 MATERIALS AND METHODS

5.1 Materials

The materials, proposed for the use as neutralising agents, were provided by Nordkalk Oy.

The materials are the by-products of mining and processing of limestone. One of them, named by the manufacturer FS, is a filter pulp for water purification. The second one named MTK-F (further called MTK) is used as an acidity stabilizer of the soil. The third material was the limestone from the Gotland island mine (further called Gotland), and the

fourth limestone specimen arrived from Raahe mine (further called Raahe). These materials were produced by grinding the wastes of the primary limestone boulders crushing. The composition of the Nordkalk Oy materials is given in Table 3.

Table 3. The composition of the limestone processing by-products, Nordkalk Oy

Constituent	FS (filter pulp)	MTK-F (soil stabilizer)
Calcite ($CaCO_3$)	15.48 %	74.79 %
Dolomite ($CaMg(CO_3)_2$)	2.2 %	3.55 %
Wollastonite ($CaSiO_3$)	29.55 %	12.63 %
Other silicates	52.78 %	9.01 %
Particle size		
<200 µm	91.3 %	100 %
<75 µm	19.4 %	99.1 %
<32 µm	3.5 %	88.5 %

It is well seen that both materials comprise significant amounts of calcium carbonate (17,7% for FS and 78,3% for MTK-F in total) that are able to lower AMD acidity. At the same time wollastonite may be regarded as potential adsorbent for insoluble compounds formed by AMD metals under conditions of low acidity. So both test materials are likely to be used for AMD treatment in a complex way.

If to speak about particle sizes of materials, it is well know that the smaller the particle size, the greater the surface, and the adsorption capacity. So even though both materials particles are rather small, additional grinding is required.

Composition of Gotland is CaO 49.9%, SiO_2 3.86%, Al_2O_3 1,96%, Fe_2O_3 0.7%, MgO 1.78%, K_2O 0.48%, clay 40,98%; the mineral totally contains 92,5% $CaCO_3$. Fractions are <25 mm 99.9%, <20 mm 98.4%, <10 mm 74.3%, <6.3 mm 53.7%.

Raahe contains at least 90% of $CaCO_3$; samples were not grinded.

Gotland and Raahe samples contained significant part of calcite, therefore, they appear to be an effective neutralasing agents. Grinding of samples was applied to provide better reaction kinetics during the experiments and for averaging the samples.

All samples of calcite materials were dried in drying cabinet during 2 days with the temperature 105 ºC. Further the samples were left for cooling in desiccators for 4 hours. Afterwards it was grinding on a ball mill. Obtained after grinding mean particle sizes were measured with laser diffraction analysis (Appendix 1). Measured mean diameters are the following (Appendix 2): MTK 6.29 μm; FS 30.5 μm; Gotland 7.56 μm; Raahe 8.34 μm. It is not necessarily that kinetics of experiments with FS would be noticeably worse in comparison with other materials due to coarser grinding. For example, in the article of Zhigang et al. (2009) calcite material with grain size of 0.55−0.25 mm showed practically the same removal characteristics toward nickel as material with grain size of 0.25−0.18 mm.

5.2 Experiment methodology

The four series of batch experiments were performed:

- the experiments establishing the equilibrium pH of studied calcite materials in water; these experiments were required to find the maximum pH available;
- the experiments establishing the dependence of the treated solutions pH on the neutralising material dose;
- the experiments establishing the equilibrium pH in synthetic acidic nickel solutions; these experiments were required to find the time necessary for reliable batch experiments results close to equilibrium;
- the experiments establishing the dependence of nickel concentration on the neutralising material dose.

5.3 Equipment

The equipment and reagents used in the experiments are listed in Table 4.

Table 4. Equipment and reagents

Equipment	Reagents
pH-meter Metrohm 744	Millipore water
Magnetic stirrers for each sample	Nickel sulphate hexahydrate $NiSO_4*6H_2O$
Volumetric flasks Duran A-class 1L, 100 ml, 50 ml	Buffer solutions with pH=4, 7 and 10
	Solution of 96% H_2SO_4
Graduated cylinder VitLab 100 ml	Solution of 32% HNO_3
Automatic pipettes Biohit Proline Plus 1, 10 ml	
Analytical scale Precisa 400M	
Sleeved jars Schott Duran for each sample, 100 ml	

5.4 Analyses

The atomic absorption spectrometry (AAS, Appendix 1) was used for measurement of nickel content in synthetic AMD samples. The solution samples were filtered and acidified with 32% solution of HNO_3 in order to obtain pH=2 or lower, according to instructions for AAS spectroscopy. Also, it was prepared 2 standard 100 ml solutions for AAS graduation: 0 ppm and 1 ppm of nickel.

pH was measured by the Metrohm 744 pH-meter.

6 RESULTS

6.1 Alkalinity of neutralising materials

For the first series of experiments the pH measuring was performed for calcite-containing materials mixed with Millipore water. The doses of materials were placed into stirred jars for 24 h.

The equilibrium state between aqueous solution, calcite and atmospheric CO_2 is characterized by pH value 8.3, but it takes an extended period of time to obtain such state during neutralizing of AMD by calcite in the open system. On the other hand, the experimental treatment using milled neutralizing material samples may have an advantage in an increased reaction rate. Also, the jars are sleeved, therefore, partial pressure of CO_2 (P_{CO2}) and, consequently, dissolution rate of calcite under these condition increased (Kleinmann et al., 1998; Lottermoser, 2007; Unger-Lindig et al., 2010).

The results are given in Table 5.

Table 5. Dependence between pH of Millipore water – neutralising agent

Neutralising agent	pH in 24 h
No neutralising agent	9.12
FS	10.34
Raahe	9.13
MTK	9.16
Gotland	9.34

It is preferably to estimate material's pH according to British Standard ISO 10390 (2005), the international standard that specifies an instrumental method for the routine determination of pH using a glass electrode in a 1:5 (volume fraction) suspension of soil in water (pH in H_2O), in 1 mol/l potassium chloride solution (pH in KCl) or in 0,01 mol/l calcium chloride solution (pH in $CaCl_2$).

However, one can see (Table 5) that Raahe, MTK and Gotland materials are able to negligibly adjust the pH of Millipore water indicating small presence of active alkaline ingredients. Only FS shows active pH adjustment ability. These observations indicate that most probably the materials with negligible alkalinity will not be able to raise pH in acidic solutions higher than 7 in a sensible time. The FS material may be able to show an advantageous performance in AMD neutralization.

6.2 Neutralising materials in pH adjustment in acidic solutions

The initial acid solution for the subsequent series of experiments for determination of the dependence of pH on neutralising agent dosage dependence had pH around 1.3, and nickel concentration 0.15 ppm (Hoffmann et.al., 2001). One ml of 96% H_2SO_4 was added to each litre of the modelled AMD water. The activity of water with these concentrations of acid and nickel is higher than 0.989, thus leading to faster chemical reactions (Kobylin et al., 2013).

Acidity under these conditions calculated according to the equation (1) is 2512.8 mg/L $CaCO_3$.

During batch experiments, the dosages of the neutralasing agents were mixed with magnetic stirrers with the initial solution for 3 min and then left under ambient conditions for 17 h. The results of the experiments are shown in Figures from 9 to 12.
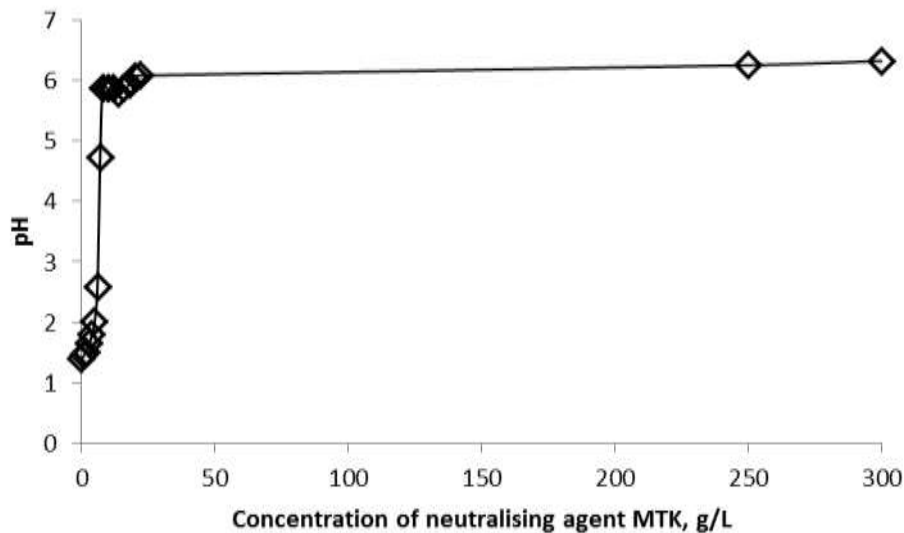

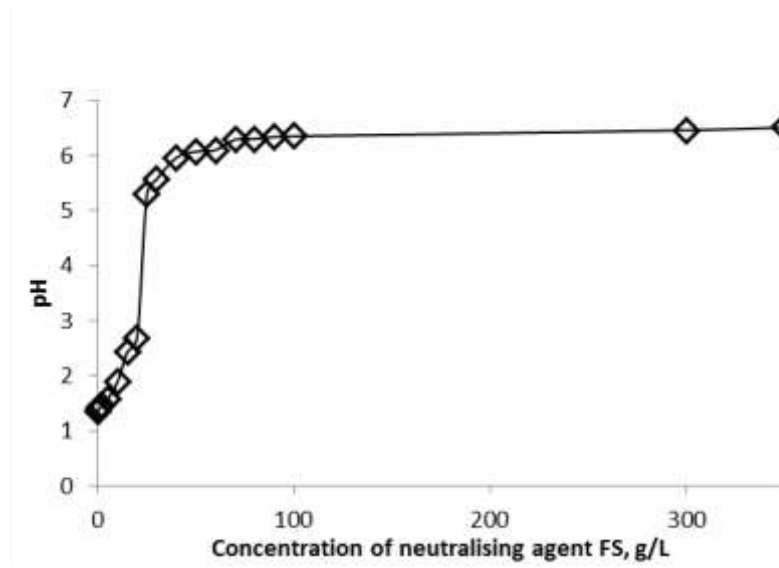Figure 9. The acidity neutralization with MTK material

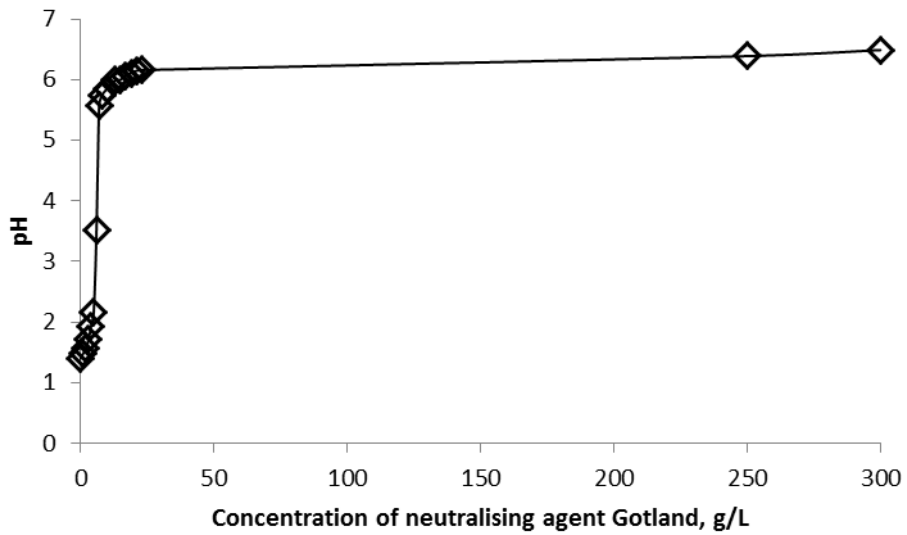Figure 10. The acidity neutralization with FS material

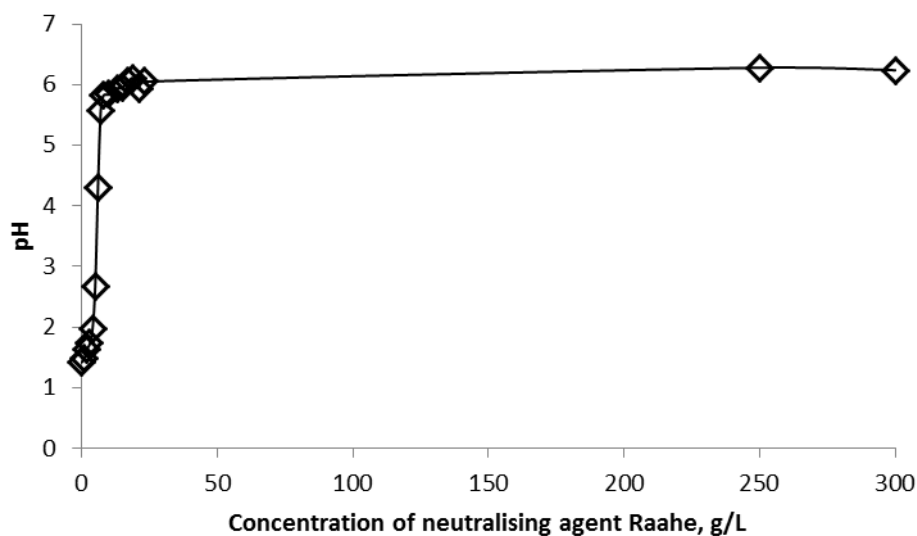Figure 11. The acidity neutralization with Gotland material

Figure 12. The acidity neutralization with Raahe material

It was found that pH level of water became practically constant after adding of approximately 20 g of MTK, Raahe and Gotland, and 90 g of FS per litre. The difference between the doses of FS and others is possibly due to difference in content of calcium carbonate, although FS indicated more alkaline properties than others. Apparently, FS contains minor amount of active alkaline constituents, the action of which is compensated by the bulk amount of inert silicates. Therefore, in the further experiments on nickel abatement the neutralising agent dosages varied between 0 to 20 and from 0 to 90 g per litre.

6.3 Treatment time

The series of experiments for assessment of the time sufficient for the chemical reaction's practical completeness was carried out. Samples with various dosages of neutralising agents in acidic solutions from the previous series were left standing under ambient conditions for several days. The pH measurements were performed for each 24 h. The initial acidity (according to eq. 1) for high-calcite samples was 1250 mg/L $CaCO_3$ (pH=1.6), for low-calcite 3150 mg/L $CaCO_3$ (pH=1.2).

The results of the experiments are shown in the Table 6, where the removed fraction of acidity is given in dependence of treatment time and the neutralising material dose.

Table 6. The fraction of acidity removed (%) in time of treatment

Material and its dose, g/L	Time of treatment, h		
	17	41	65
MTK, 250	99.99	99.99	99.99
FS, 300	99.99	99.99	99.99
Raahe, 250	99.99	99.99	99.99
Gotland, 250	99.99	99.99	99.99
MTK, 3	53.22	61.09	65.32
FS, 5	47.52	60.19	63.69
Raahe, 3	56.35	65.33	69.80
Gotland, 3	54.29	64.52	66.12

One can see from the Table 6, the concentration of H+ ions was changing less than for 5 % between 41 and 65 h of treatment. Therefore, 41 h was considered further to be sufficient for chemical interaction between calcite and acidic water under defined conditions and was used in experiments.

6.4 Nickel removal

Samples of synthetic nickel-containing AMD were analysed for nickel content after the treatment for 41 h.The results of measurements are shown in Figure 13.
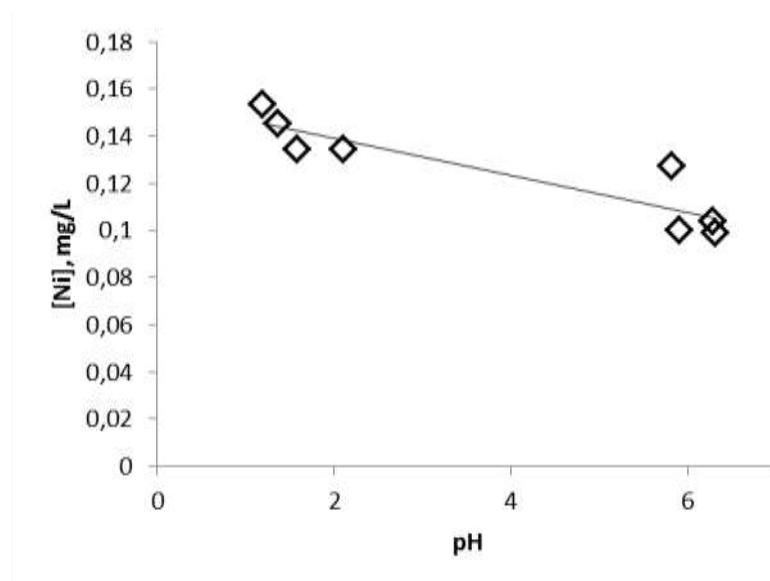

Figure 13. The dependence of nickel ions concentration in samples treated with MTK on pH

One can see that the concentration of nickel in the solution treated with MTK neutralising agent decreased negligibly, from the initial 0.154 ppm to 0.1 mg/L as the the lowest concentration registered after the treatment (see Appendix 2). Such removal presents only 35.5% of performance. These data is in contradiction with the ones available in literature: Hoffmann et al. (2001) observed almost full adsorption of nickel and even its burial under calcite surface in acidic conditions. The present experimental research showed poor removal ability of MTK under the conditions given.

As we did not observe the sufficient removal of nickel via adsorption mechanism at very low nickel concentration, we moved to the higher concentration, where surface complexation and exchange reaction are possible (Honghai et al., 1999).

The further series of experiments were performed with the same sulphuric acid content and the higher nickel concentration, 4 ppm. The activity of water under these conditions is also higher than 0.989, thus leading to better kinetics of chemical reactions (Kobylin et al., 2013). Duration of experiments was 41 h as established for acidity neutralisation.

After the treatment, samples were filtered and diluted for 5 times in order to fit the previously obtained calibration curve from 0 to 1 mg/L.

The results obtained for higher nickel concentrations are shown in the Figures from 14 to 17. Full data are available in the Appendix 2.
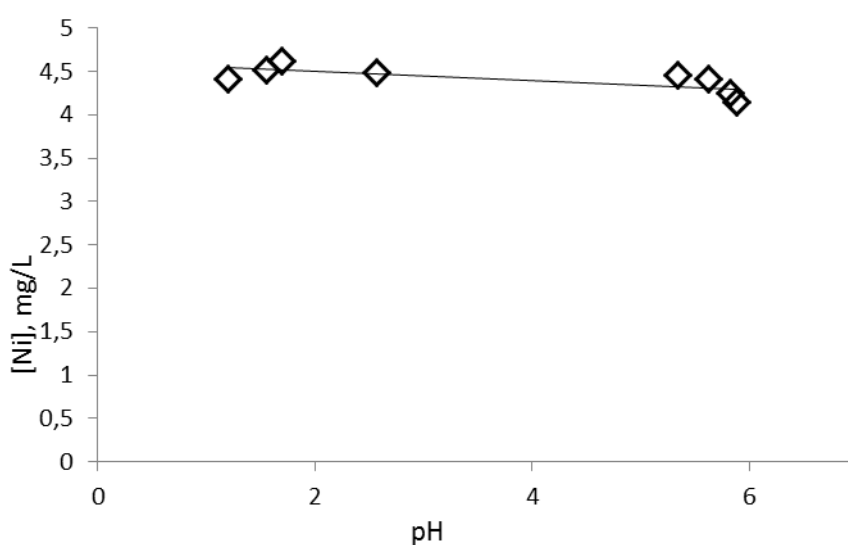

Figure 14. The dependence of nickel ions concentration in samples treated with MTK on pH
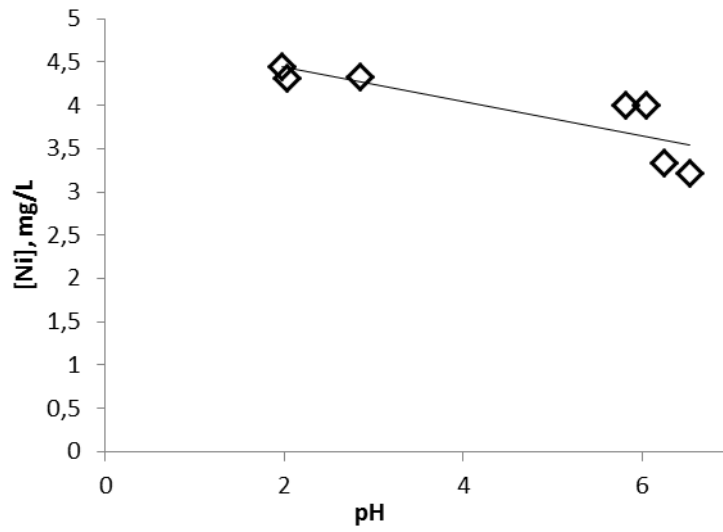
Figure 15. The dependence of nickel ions concentration in samples treated with FS on pH
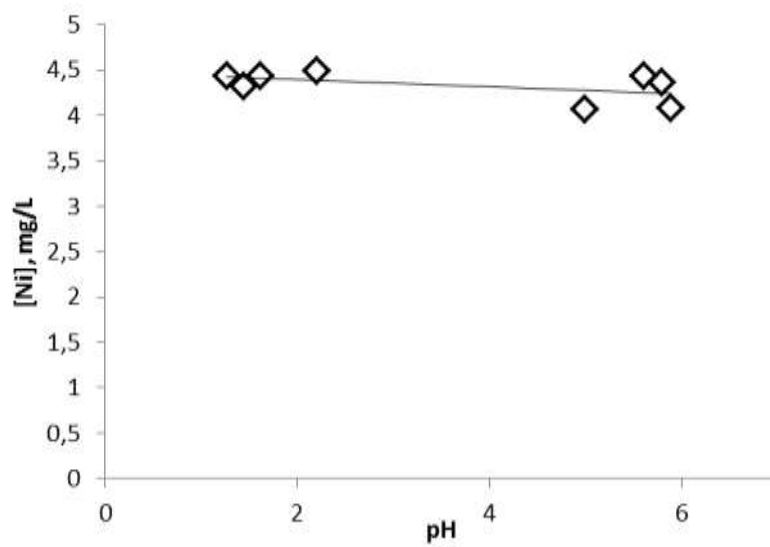

Figure 16. The dependence of nickel ions concentration in samples treated with Gotland on pH
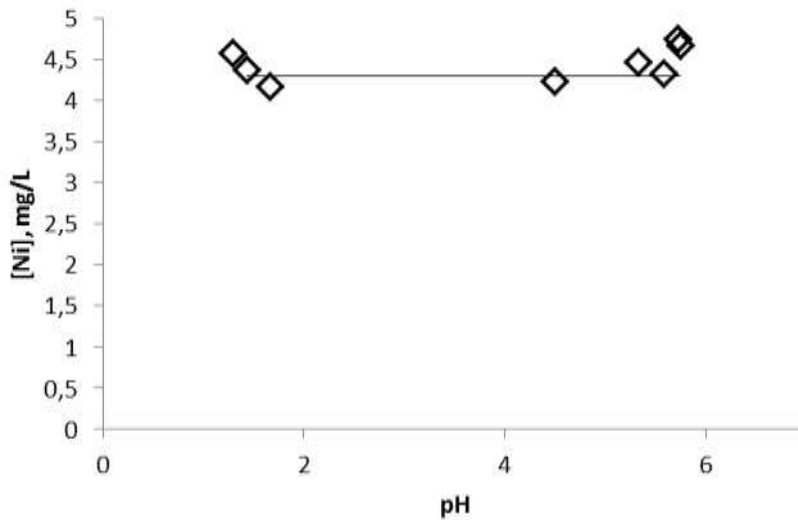
Figure 17. The dependence of nickel ions concentration in samples treated with Raahe on pH

One can see the minor or negligible removal of nickel with the pH increased from 1.6 to 6.0 provided by addition of the neutralizing agents under the scope.

Only the FS material showed more noticeable slope with the nickel removal efficiency not exceeding 26 % (see Appendix 2). The better performance of FS material may be explained by its higher alkalinity, and possibly by higher content of wollastonite. For instance, Zhigang et al. (2009) found that sand material showed better nickel removal performance in alkaline solution than calcite with the same gravimetric characteristics.

7 DISCUSSION

It was found that adsorption of nickel from diluted solutions (less than 1 ppm Ni^{2+}) on calcite surface is low, which may be explained with the presence of sulphate ions in the AMD: the reason for that maybe the gypsum crust formation obstructing adsorption.

Also, the best removal efficiency demonstrated by the low-calcite neutralizing agent FS supported by the published data brings to the conclusion of minimum adsorption performance of calcium carbonate suface towards nickel adsorption: the interactions between Ni and the calcite surface were found to be minimal with the low pH of AMD and presence of sulphuric ions. Further research in nickel removal from acidic water with silicone-containing sand-like low-cost materials may be more successful. The higher pH may also bring better results.

Based on previous studies, there are three possible ways to improve removal efficiency of nickel with calcite under acidic conditions. Firstly, it is the removal of gypsum crust. Secondly, it is co-precipitation with iron and aluminium, because these metals are common for AMD and their precipitation in form of hydroxides is possible with lower pH values despite of nickel (Callender, 2003). Lastly, it is the sufficient growth of pH up to 9 with addition of alkaline substances.

Removal of gypsum crust is possible with the help of CO_2: it promotes the dissolution of carbonates. Therefore, unused calcite in the sludge can raise the alkalinity more effectively by the application of carbon dioxide. Furthermore, it was shown that remobilization of nickel will not affect the water quality (Unger-Lindig et al., 2010). Remobilization of nickel will not affect the water quality due to its better binding with calcite during co-precipitation with calcite, than just during adsorption on the calcite surface. Nickel become "immobilised" within the calcite structure in the form of solid solution during co-precipitation (Hoffmann and Stipp, 2001; Lakshtanov and Stipp, 2007). When it is quite high pH of the water, nickel can precipitate in the form of hydroxide, as it is shown on Figure 18.
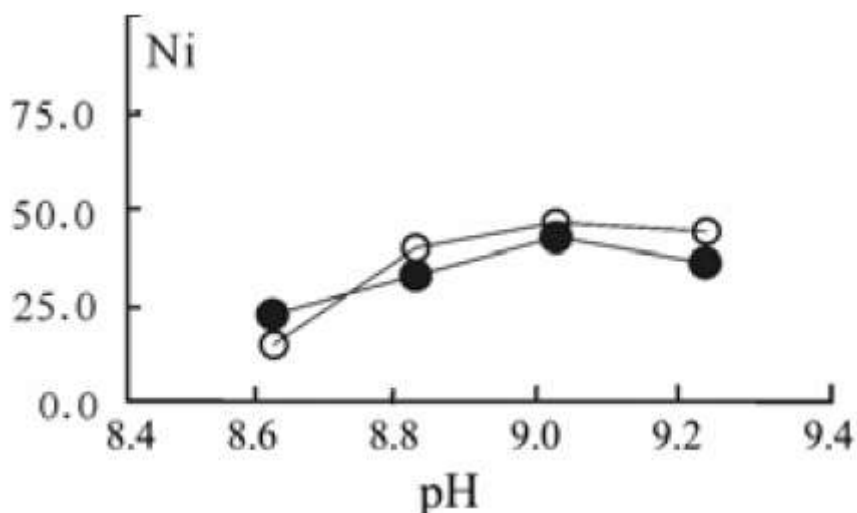
Figure 18. Effects of pH on the efficiency of nickel removal (Zhigang et al., 2009)

Co-precipitation with iron and aluminium remains the most applicable solution. Miller et al. (2011) found that nickel interaction at its concentration of 27 ppm with both Fe and Al hydroxide surfaces was occurred via cation sorption: increasing pH or the total number of surface sites $Fe(OH)_3$ and $Al(OH)_3$ increased the amount of Ni removal. The best results during their experiments were achieved under the following conditions: acidity 113-125 mg/L $CaCO_3$, pH 6.18-6.68, Fe:Ni ratio 28:1. There was 55% of nickel precipitated, 12%

adsorbed making the total removal 67%. The cited paper brings the Ni distribution data as a function of pH, acidity, and Fe and Al concentrations: increased the total Fe content improved the Ni removal, although for Al did not improve the situation. No removal was observed when the pH values were below 4,0. Appreciable Ni removal (>10%) did not occur unless the pH was $\geqslant$6.0.

SUMMARY

In the present paper the formation mechanism and the sources of AMD, and its impact on the environment was described. Also, conventional methods of AMD prevention, mitigation and treatment with their limitations were mentioned.

Limestone treatment of AMD concerned to be the most cost-effective method. Iron, aluminium, acid and sulphate ions are easily removed with limestone. However, the research data available on behaviour of nickel in aqueous solutions at the presence of calcite under acidic conditions are insufficient. Therefore, the research on nickel removal with calcite treatment in modeled AMD solution was undertaken.

The results show poor nickel adsorption on calcite surface with the presence of sulphate ions in the solution. Also, precipitation of nickel in acid neutralized with calcite appears to be insufficient: we observed the lack of nickel removal ability with calcite in the modelled AMD solutions.

Further research is desirable for achieving better efficiency of water treatment process. The possibility to improve the nickel removal lays possibly in usage of alkalinity-producing materials in order to obtain high-pH conditions, or in co-precipitation of nickel with iron or aluminium.

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APPENDIX 1. Analytical methods

1. Atomic absorption spectroscopy (AAS)

The method of atomic absorption spectroscopy (AAS) is based on the phenomenon of selective light absorption by free atoms in the gaseous state. The absorption can be observed by passing light from an external source of continuous spectrum through a layer of free atoms of an element. The natural analogue of such system is the Fraunhofer lines in the solar spectrum (Auriga Research Ltd).

Absorbing light selectively, most of all - at the frequency of the resonance transition, the atoms pass from the ground to the excited state. The intensity of the transmitted beam of light at the resonance frequency (or wavelength) decreases exponentially with increased atomic concentration according to the Bouguer - Lambert - Beer law:

$$I = I_0 \exp(-k_v l), \tag{1}$$

where I_0 and I are the intensity of the incident and transmitted radiation, respectively; k_v - coefficient of light absorption by free atoms, l - thickness of the absorbing layer (optical path length in an absorbing medium). The magnitude of k_v depends on the concentration of free atoms in the absorbing layer (N) and the characteristics of the spectral line (the oscillator strength corresponding to this transition, the parameters of the broadening and hyperfine structure of lines, etc.). In practical measurements the value of the optical density of an atomic vapour (absorption capacity, absorption) is usually used:

$$A = \lg\left(\frac{I_0}{I}\right) = k_v l \cdot \lg(e) = \alpha \cdot N \tag{2}$$

where α is the coefficient of proportionality.

Under constant conditions of atomization the density of atoms in the atomizer is directly proportional to the concentration of the element in the sample(s):

$$A = a \cdot c \tag{3}$$

The proportionality factor a is a purely empirical quantity, which depends on the conditions of the analysis, and it is usually found empirically by calibration.

To measure the atomic absorption A it is necessary to observe the two conditions set forth by Walsh:

1) The wavelength corresponding to maximum absorption of the atomic vapour must be equal to the wavelength of maximum intensity of the radiation source;

$$\lambda_{max.emitted} = \lambda_{max.absorbed}$$

2) Half-width of the atomic vapour absorption lines must be greater than the half-width of the source emission line, i.e. these quantities must meet the ratio $\alpha = \dfrac{\Delta \nu_{1/2 emit.}}{\Delta \nu_{1/2 abs.}} \leq 1$

If the first condition is not met, atomic absorption does not occur. If the second Walsh condition is not satisfied, then only a small part of the radiation source is absorbed by the atoms due to the fact that the shape of the emission lines is broader than the absorption line (Rust et al., 2005).

Known methods of light monochromatization (prism, grating, interference filters) do not provide needed narrow bands. Therefore, the atomic absorption analyzers use sources that emit narrow bands of the spectrum. These sources are gas discharge tubes: hollow cathode lamps or high-frequency lamps without electrodes.

Standard outline of the atomic absorption spectrophotometer is shown in Figure 1. The sample solution 9 in the form of aerosol goes from the sprayer 10 into the flame 2 (acetylene-air flame with the temperature from 2000 to 3000K). Solvent evaporation, melting and evaporation of solids, thermal dissociation of molecules to free atoms take place.

The luminous flux from the lamp passes through the burner flame 2 and monochromator 3. The monochromator selects a narrow spectral line (typically 0.2 - 2.0 nm) characteristic for the element under consideration. The atoms of that element absorb the light. The outgoing light beam is converted into an electrical signal by photomultiplier 4 and then, after passing the amplifier 5, is recorded by galvanometer 6.
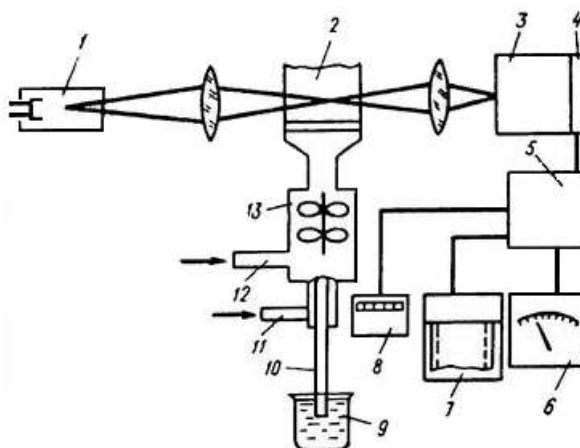

Figure 1. Outline of atomic absorption spectrophotometer: 1 - the source of resonance radiation, 2 - burner, 3 - monochromator, 4 – detector, 5 – amplifier, 6 –galvanometer, 7 - recorder, 8 – output device, 9 - a vessel with a solution, 10 - sprayer, 11 and 12 – input of the oxidizer and fuel, 13 - spray chamber (Auriga Research Ltd)

In the present work, the double-beam atomic absorption spectrometer, Thermo Scientific iCE 3000 Series (Figure 2), with acetylene-air flames and lamps with full cathode was used. The algorithm of analysis is as follows.

After the AA spectrometer turning on, the SOLAAR software was started. There the method of analysis, number of standard solutions and number of samples were identified. The following analysis was done according to the program recommendations, and the whole process is automated. At first, oxygen and acetylene flows were enabled; flame and lamp for nickel concentration analysis were turned on and warmed up. Also the necessary maintenance including gas flow, burner position and flame height calibration was carried out.

Further, the calibration curve was plotted. Two calibration solutions with nickel concentration of 0 and 1.0 ppm were used. The standard solutions were prepared by dilution of Perkin-Elmer AA standard (1000mg/kg) with addition of 1ml of 7N nitric acid per 100ml of calibration solution.

Then all samples, including initial solutions, were analyzed. The spectrometer sprayer tube was plunged into the flask with sample, sample's name was introduced into the program in the format "name of test material-its dosage-number of initial solution", after that the procedure of analysis started. The sprayer was washed with distilled water for a few seconds after each measurement. Millipore water was used as the blank solution. The results were reflected on the computer screen in the form of tables.

Figure 2. Atomic absorption spectrometer Thermo Scientific iCE 3000 Series (Intertech Corp.)

2. Laser diffraction analysis

Laser diffraction is one of the most effective and widely used methods for particle size analysis. The measuring principle is as follows (Figure 3): the laser beam illuminates the cell, through which the cloud of particles is pumped. Radiation, scattered by particles, is recorded at different angles with photodiode matrix, which is a multielement detector. Then measured dependence of the scattered light intensity on the scattering angle is used for particle size distribution. The particles cloud is created by introducing the test object (in the form of powder, suspension or emulsion) in liquid-filled chamber of a centrifugal pump, where the exposure conditions of ultrasound by thorough mixing. Suspension, passed through the cell, re-enters the chamber pump, therefore all particles repeatedly pass through the laser beam several times during one measurement (Eshel et al., 2004).
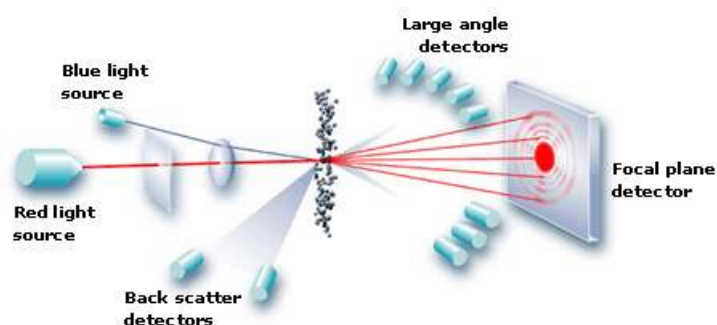

Figure 3. Laser diffraction system (Malvern Instruments Ltd)

Light scattered by particles forms a series of concentric rings of alternating maximum and minimum intensities, often called the Airy disk. The first minimum (closest to the centre of the Airy disk) provides information to determine the mean size of the distribution. Subsequent maxima and minima contain information on the shape and width of the distribution.

Based on principles of integrated mathematics, particle size distribution in a group of the scattered particles can be calculated from the distribution of the scattered light intensity. This calculation can be performed both on the basis of the theory of Fraunhofer, and on the basis of Mie theory (Eshel et al., 2004).

The main idea of Fraunhofer theory is about the light diffraction at the edges of the particle. However it is valid only when the particle diameter is greater than the wavelength of the light and particles are opaque. It is also assumed that all particles scatter light equally (Eshel et al., 2004).

For particles, the size of which is comparable to the wavelength, as well as when it is needed to take into account optical properties of the particles, Mie theory is used. This theory describes the radiation for all spatial directions in a homogeneous, non-absorbent medium. Furthermore the particles may be not only transparent, but completely absorbing. Optical properties are included in the calculations as a comprehensive index of diffraction.

In the described laboratory study, a laser diffractometer LS13320 of Beckman Coulter (USA), shown in Figure 4, was used. Measurement of particle size in this device is based on laser diffraction by both Mie and Fraunhofer methods in conjunction with registration of the differential intensity of polarized light (PIDS).

Polarisation Intensity Differential Scattering (PIDS) is a technique that overcomes the limitations of conventional laser diffraction to give high resolution submicrometre analysis (Eshel et al., 2004). PIDS uses three different wavelengths of light (450, 600 and 900 nm) in two planes of polarisation (vertical and horizontal) to irradiate the sample. The PIDS detectors are placed at angles of up to 150 degrees to collect the high angle scatter data. The resultant scatter patterns of differently sized submicrometre particles are easily differentiated from each other to provide well resolved particle size distributions.

The light source used in device is solid-state laser (wavelength - 750 nm), and detector is presented by photodiode array detector with 126 elements.

Figure 4. Laser diffracto-meter LS13320 Beckman Coulter (USA)

The LS-13320 usage foresses was to preliminary cleaning of the analysis module. Subsequently, the module was filled with water and grinded sample of material was added slowly. The sufficient obscuration in the module was preset at about 8%, after the reaching this value, the sample analyses started.

APPENDIX 2. Full data with results of the measurements and experiments
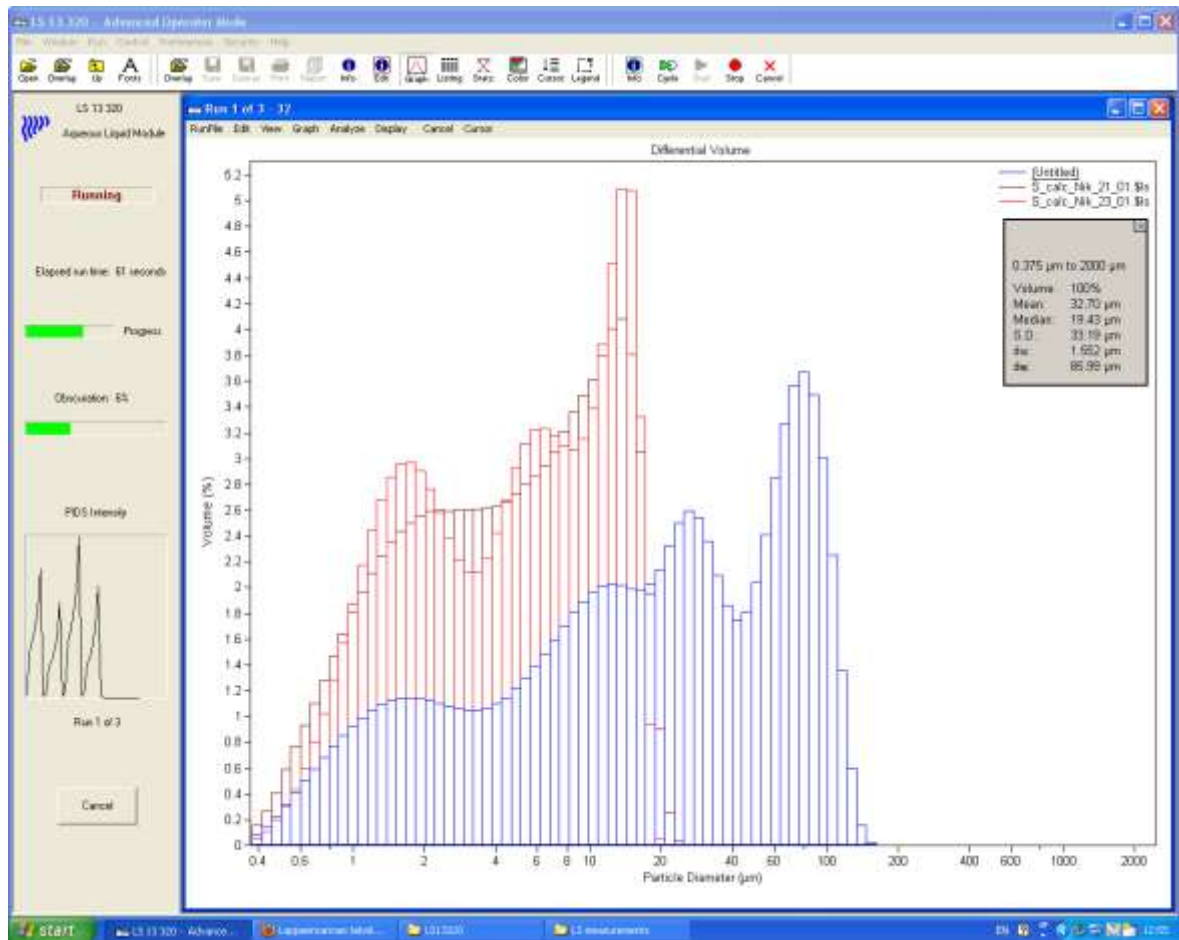
Figure 1. Results of laser diffraction analysis: red line – MTK material; blue line – FS material

MTK first measurement: Mean Diameter: 6.298 µm, Median: 4.646 µm.
2nd measurement: Mean Diameter: 6.282 µm, Median: 4.855 µm
3rd measurement: Mean Diameter: 6.282 µm, Median: 4.855 µm
Mean size: diameter 6.2873 µm.

FS first measurement: Mean: 32.66 µm, Median: 19.49 µm.
2nd measurement: Mean: 30.03 µm, Median: 17.59 µm
3rd measurement: Mean: 28.72 µm, Median: 16.81 µm
Mean size: 30.47 µm.
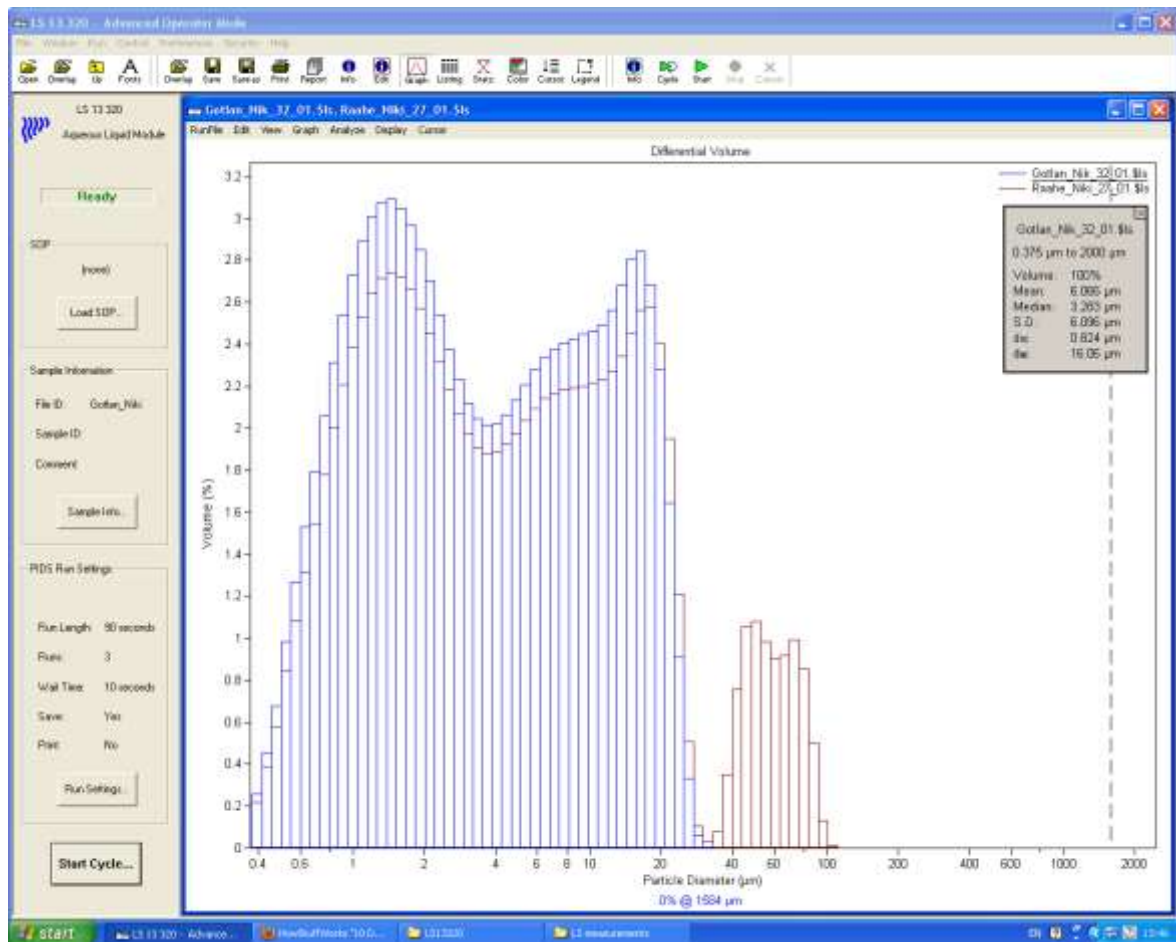
Figure 2. Results of laser diffraction analysis: red line – Raahe material; blue line – Gotland

material

Gotland 1st measurement: Mean: 10.48 μm, Median: 3.988 μm.
2nd measurement: Mean: 6.125 μm, Median: 3.262 μm
3rd measurement: Mean: 6.066 μm, Median: 3.283 μm
Mean size: 7.557 μm.

Raahe 1st measurement: Mean: 11.02 μm, Median: 4.326 μm
2nd measurement: Mean: 7.646 μm, Median: 3.818 μm
3rd measurement: Mean: 6.366 μm, Median: 3.634 μm
Mean size: 8.344 μm.

Series on estimation of pH-dosage of neutralizing agents dependence (Table 1). There are columns "Neutralant, g" about weight of neutralant per 1L of initial acidic solution. Columns "Neutralant, pH" are on obtained after 17 h pH of the solution.

Table 1. pH-dosage of neutralizing agents measurements

	MTK, g	MTK, pH	FS, g	FS, pH	Gotland, g	Gotland, pH	Raahe, g	Raahe, pH
0	0	1,4	0	1,35	0	1,4	0	1,42
1	1	1,46	1	1,41	1	1,48	1	1,48
2	2	1,51	2	1,46	2	1,57	2	1,64
3	3	1,66	5	1,58	3	1,71	3	1,73
4	4	1,8	10	1,89	4	1,94	4	1,98
5	5	2,02	15	2,43	5	2,17	5	2,68
6	6	2,58	20	2,69	6	3,51	6	4,31
7	7	4,73	25	5,3	7	5,57	7	5,57
8	8	5,88	30	5,57	8	5,74	8	5,82
9	10	5,86	40	5,96	10	5,85	10	5,84
10	12	5,87	50	6,07	13	5,99	13	5,94
11	14	5,79	60	6,1	15	6	15	5,95
12	16	5,86	70	6,29	17	6,07	17	6,05
13	18	5,93	80	6,3	19	6,11	19	6,11
14	20	6,07	90	6,34	21	6,15	21	5,94
15	22	6,08	100	6,35	23	6,16	23	6,05
16	250	6,25	300	6,46	250	6,39	250	6,28
17	300	6,32	350	6,51	300	6,49	300	6,24

Data on obtained nickel concentration after the treatment with MTK during 41 h of the acidic solution with initial pH 1.18 and initial nickel content 0.1537 ppm shown in Table 2.

Table 2. Nickel concentration-pH measurements, with the initial nickel concentration 0.15 ppm

MTK, g	pH	Ni concentration, ppm
0	1,18	0,1537
2	1,36	0,1453
4	1,57	0,1348
6	2,1	0,1346
8	5,81	0,1273
12	6,27	0,1042
16	6,3	0,0992
20	5,89	0,1002

Data obtained on nickel concentration after the treatment with all neutralants during 41 h of the acidic solution with initial nickel content around 4 ppm. Here "Unscaled Ni concentration" is the measured nickel concentration of the diluted solution after the calcite treatment.

Table 3. Nickel concentration-pH measurements after MTK treatment, with the initial nickel concentration 4 ppm

MTK, g	pH	Unscaled Ni concentration, ppm	Ni concentration, ppm
0	1.2	0,8829	4.4145
2	1.56	0,904	4.52
4	1,7	0,9245	4,6225
6	2,57	0,8968	4,484
8	5,34	0,8903	4,4515
12	5.62	0,8816	4,408
16	5,82	0,8489	4,2445
20	5,89	0,8279	4,1395

Table 4. Nickel concentration-pH measurements after FS treatment, with the initial nickel concentration 4 ppm

FS, g	pH	Unscaled Ni concentration, ppm	Ni concentration, ppm
0	1.19	0,8696	4,348
2	1,98	0,88967	4,44835
10	2,03	0,8641	4,3205
20	2,85	0,866	4,33
30	5,82	0,8013	4,0065
50	6,05	0,8007	4,0035
70	6,24	0,6658	3,329
90	6,54	0,6431	3,2155

Table 5. Nickel concentration-pH measurements after Gotland treatment, with the initial nickel concentration 4 ppm

Gotland, g	pH	Unscaled Ni concentration, ppm	Ni concentration, ppm
0	1,27	0,8872	4,436
2	1,44	0,8644	4,322
4	1,61	0,8883	4,4415
6	2,2	0,9004	4,502
8	4,99	0,8154	4,077
13	5,6	0,8873	4,4365
17	5,79	0,8725	4,3625
21	5,88	0,8178	4,089

63

(Appendix 2 continued)

Table 6. Nickel concentration-pH measurements after Raahe treatment, with the initial nickel concentration 4 ppm

Raahe, g	pH	Unscaled Ni concentration, ppm	Ni concentration, ppm
0	1,29	0,9167	4,5835
2	1,44	0,8738	4,369
4	1,66	0,8358	4,179
6	4,49	0,8466	4,233
8	5,32	0,8949	4,4745
13	5,58	0,8652	4,326
17	5,72	0,9511	4,7555
21	5,75	0,9335	4,6675