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Master's thesis

Potential Benefits of Metal Recovery from Underground Water Using Biomineralization of Schwertmannite in Pyhäsalmi Mine

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Thesis Abstract

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Abstract

In Finland, mining activity has accelerated significantly during the 20th century. Mine waste, including mine drainage waters, generates a potential source of environmental contamination, as heavy metals and acid are released in large amounts. Therefore, waters need to be treated and the generated sludge needs to be disposed of to landfill sites.

The most common acid mine treatment method is alkalization by use of chemicals. However, this treatment method is expensive and it generates large amounts of waste sludge. New passive treatment methods involving microbial activity have been developed recently. The aim of the biological treatment method used in this work is the selective recovery of valuable metals. Due to selective recovery, metals can be utilized as a product instead of disposing them as a waste.

The high metal concentration in mine drainage waters is the main reason of high underground maintenance costs. Metals precipitate on the internal surface of the pipe, and as a result, the pipe becomes clogged. Metal precipitation also increases the required power of pumping. Sludge entering a pump can damage the pump and it reduces its life expectancy. The high metal content of mine dewatering has a cumulative impact on the maintenance needs as well, for example the costs of the heat exchanger.

The aim of this work is to find the benefits of the remediation of underground mine drainage water by utilizing the chemical composition of underground waters from different parts of the mine. The benefits, in regard to this work, are economy of process and of course, sustainable development.

The studied treatment method in this work is selective bio-oxidation of iron and precipitation of schwertmannite. Experimental tests using synthetic Pyhäsalmi mine water were made in Bangor University by Prof. Barrie Johnson and Dr. Catherine Kay. Operational parameters from the laboratory scale experiments were extrapolated to a full scale system and operating costs were estimated.

According to the chemical needs and prices, utilizing a bioreactor system with iron recovery would increase the water treatment costs. Furthermore, the annual operating costs of the treatment system would be less than maintenance expenses caused by iron, and savings could be achieved.

In addition to monetary savings, the annual amount of precipitated schwertmannite would be significant. Several applications of schwertmannite have been studied, and if the mineral could be sold as a product, economic benefits could result.

Place of Storage

Additional Information

OULUN YLIOPISTO **Tiivistelmä opinnäytetyöstä**
Teknillinen tiedekunta

Osasto Prosessi- ja ympäristötekniikanosasto	Laboratorio Vesi- ja ympäristötekniikan laboratorio
Tekijä Haanela, Anu Elena	Työn valvoja Kløve, B., Professori

Työn nimi
Kaivosveden metallien talteenottamisen mahdolliset hyödyt schwertmanniitin biomineralisaatiolla Pyhäsalmen kaivoksella

Opintosuunta	Työn laji	Aika	Sivumäärä
Vesi- ja geoympäristötekniikka	Diplomityö	Helmikuu 2013	76 s., 5 s. 4 liitelehteä

Tiivistelmä

Kaivosteollisuus on kasvanut merkittävästi Suomessa 2000-luvulla. Kaivannaisjätteet, jotka sisältävät kaivoksen kuivatusvedet, muodostavat mahdollisen ympäristön pilaantumisen lähteen, sillä jätteistä vapautuu ympäristöön suuria määriä raskasmetalleja sekä happoa. Tämän vuoksi vedet tulee käsitellä ja käsittelystä syntyvä liete hävittää asianmukaisille loppusijoituspaikoille.

Tavanomaisin happamien kaivosvesien käsittelymenetelmä on kemikaalien avulla tapahtuva alkalointi. Tämä käsittelymenetelmä on kuitenkin kustannuksiltaan kallista ja käsittelystä muodostuu suuria määriä jätelietettä. Viime aikoina on kehitetty uusi passiivinen mikrobiologista toimintaa hyväksi käyttävä käsittelymenetelmä. Tässä työssä käytetyn biologisen käsittelymenetelmän tarkoituksena on metallien selektiivinen talteenotto. Selektiivisen erotuksen tuloksena arvokkaita metalleja voidaan käyttää tuotteena sen sijaan, että metallit hävitettäisiin jätteenä.

Kaivoksen kuivanapitovesien korkea metallipitoisuus on pääsyynä kaivoksen korkeille kunnossapitokustannuksille. Metallit saostuvat putkien sisäpinnoille, jonka seurauksena putket tukkeutuvat. Metallien saostuminen lisää myös veden pumppaamiseen tarvittavaa tehoa. Pumppuihin pääsevä liete voi vahingoittaa pumppuja sekä vähentää niiden odotettua elinikää. Kaivosveden korkeilla metallipitoisuuksilla on lisäksi kumulatiivisia vaikutuksia kunnossapitotoimintoihin, esimerkiksi lämmönvaihtimen kustannuksiin.

Tämän työn tarkoituksena on tutkia kaivoksen kuivanapitovesien puhdistuksesta saavutettavia etuja hyödyntämällä veden kemiallista koostumusta kaivoksen eri osissa. Työssä huomioidut veden puhdistamisen hyödyt ovat prosessin taloudellisuus sekä kestävä kehitys.

Tässä työssä veden puhdistukseen käytetty käsittelymenetelmä on raudan biologinen hapettuminen sekä hapettuneen raudan saostaminen schwertmanniittiyhdisteenä. Kokeelliset testit toteutettiin käyttämällä synteettisesti valmistettua Pyhäsalmen kaivoksen vettä. Testit suoritettiin Bangorin yliopistossa Prof. Barrie Johnsonin ja Dr. Catherine Kayn toteuttamana. Laboratoriomittakaavan toimintaparametrit ekstrapoloitiin vastaamaan täyden mittakaavan systeemiä, jonka avulla arvioitiin reaktorisysteemin käyttökustannukset.

Tarvittavien kemikaalimäärien sekä tämän hetken hintojen perusteella raudan erottaminen kyseisellä menetelmällä lisäisi vesien käsittelykustannuksia. Kuitenkin käsittelysysteemin vuosikustannukset olisivat vähemmän kuin raudan saostumisen aiheuttamat kunnossapitokustannukset vuodessa, jolloin säästöjä olisi mahdollista saavuttaa.

Rahallisten säästöjen lisäksi, saostuvan schwertmanniitin määrä olisi huomattava. Useita käyttökohteita schwertmanniitille on tutkittu. Jos mineraali voitaisiin myydä eteenpäin tuotteena, taloudellista hyötyä olisi mahdollista saavuttaa.

Säilytyspaikka

Muita tietoja

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28.2.2013

Anu Haanela

Table of contents

Abstract

APPENDICES

Symbols and abbreviations

Al	Aluminum
AMD	Acid mine drainage
As	Arsenic
$Ca(OH)_2$	Calcium hydroxide, slaked lime
Cond	Electrical conductivity
Cu	Copper
FDA	Food and Drug Administration
Fe	Iron
Fe^{2+}	Ferrous iron
Fe^{3+}	Ferric iron
FeS_2	Pyrite
$Fe(OH)_3$	Ferrihydrate, oxyhydroxide
$Fe_8O_8(OH)_6(SO_4)$	Schwertmannite
GRAS	Generally Recognized as Safe
GTK	Geological Survey of Finland
H	Hydrogen
H^+	Protons
HCl	Hydrochloric acid
H_2S	Hydrogen sulfide
HNO_3	Nitric acid
IC	Ion chromatography
IPCS	International Programme on Chemical Safety
M^{n+}	Cationic metal
MIWs	Mine impacted waters
Mn	Manganese
NaOH	Sodium hydroxide
NSF	The National Science Foundation
O	Oxygen
PRBs	Permeable reactive barriers
SCH	Schwertmannite
Si	Silicon
SO_4	Sulfate

SRB	Sulfate reducing bacteria
S	Sulfur
Zn	Zinc

1 Introduction

Mine drainage waters are considered to be a widespread environmental problem. Conventional treatment of the mine drainage water produces large quantities of waste sludge. Disposal of the sludge is often very costly and it has a negative environmental impact. In addition to sludge disposal, the high iron content of the mine drainage water causes high maintenance costs for underground mine dewatering. Iron precipitates may clog the pumps and underground pipe lines without regular cleaning and maintenance. Additionally, sludge formed in the clarification tanks and ponds in the mine must be removed and stored. The high iron content of the water also has a cumulative impact on other maintenance needs.

A new passive bioreactor system has been developed to treat mine drainage waters. The object of the bioreactor system is selective iron precipitation from the water as iron oxides through microbiological activity. As follows, iron oxides can be separated from the waste and used as valuable products. Iron oxides are already used for sorption of heavy metals from wastewater and as a pigment for paints. Other heavy metals, such as copper and zinc, can also be selectively precipitated from the waters by microbiological activity.

This Master's thesis compares the benefits of underground water treatment at different parts of the mine. The options for the locations of the bioreactor system were chosen by utilizing the chemical composition of the underground waters. A crucial factor, in choosing the best options, is the aim to lower the high maintenance costs of underground mine dewatering. The technical implementation of the bioreactor system is not within the scope of this thesis.

Another point of interest was the implementation of iron precipitation when discharging tailing ponds after mine closure. The expenses of water treatment after mine closure through alkalization were compared to the benefits of water treatment by bioreactors.

The aim of this particular work is to examine the underground water; to find the locations of larger water flows and to identify and locate waters that contain large concentrations of metals. Another part of this thesis evaluates the cost effectiveness of the iron oxidation and precipitation bioreactor system. This work compares the advantages and disadvantages of water remediation by iron precipitation and evaluates the potential benefits of this system with regard to future operations of Pyhäsalmi Mine. The purpose of this particular work is to examine the advantages of the system when considering the process as a whole.

2 Pyhäsalmi Mine

Pyhäsalmi Mine Oy, owned by Canada-based Inmet Mining Corporation, produces copper, zinc, and pyrite-sulfur at a mine in central Finland. Pyhäsalmi Mine began its operations as an open pit mine in 1962 and operations commenced underground in 1967. The underground mine reached a depth of 1 410 meters in 2001.

Mine production has steadily increased since the operations began. In the 1990s, production reached 1.1 million metric tons per year. At present, the annual production is approximately 1.4 million metric tons. All underground operations are conducted between the levels of 1 050 and 1 410 meters. Figure 1 shows the Pyhäsalmi mine area, ponds A-D and recipient Pyhäjärvi lake area.

Figure 1 – The Pyhäsalmi mine, ponds A-D and recipient Pyhäjärvi lake area (Photo: Pyhäsalmi Mine Oy).

2.1 Underground mine

The mining is carried out underground. The underground mine was gradually deepened after its opening. A new blind shaft, called the Olli shaft, was commissioned in 1985 and it extended to 730 meters. The ore body extended further down and the depth of one thousand meters was reached by the spring of 1996. The most recent phase of furthering the depth of the mine was carried out between 1998 and 2001. At present mining is carried out via the 1 440-meter-deep Timo shaft.

The Pyhäsalmi ore has a north-south trending S-formed surface expression of about 600 meters in length and a total vertical depth extension of 1 420 meters (Figure 2). The width of the ore varies from 10 meters to 80 meters. The contact between the ore and waste rock is sharp. The ore is massive and coarse grained. It contains 75 % sulfides on average; 3 % chalcopyrite, 6 % sphalerite, 2 % pyrrhotite, 66 % pyrite, and minor amounts of galena and sulfosalts. Barite ($BaSO_4$) and carbonates are the main gangue minerals.

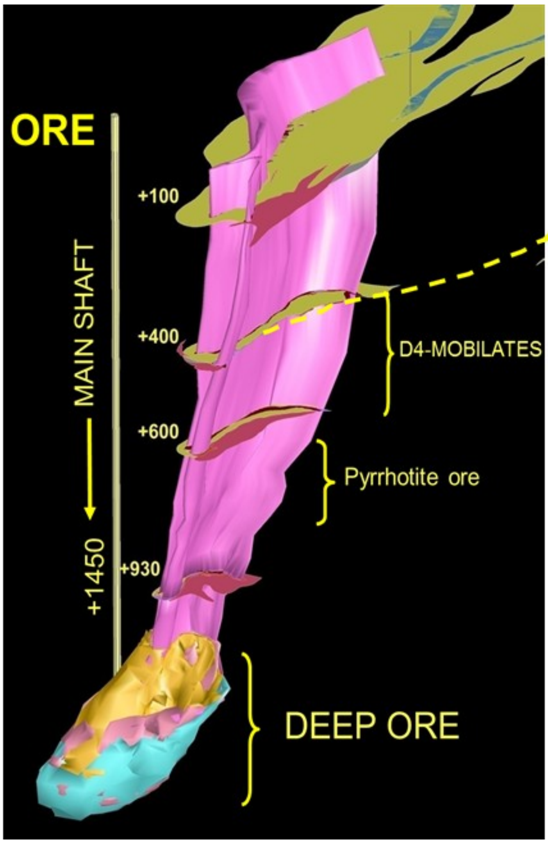

Figure 2 – The Pyhäsalmi ore (Pyhäsalmi Mine Oy).

At present, yearly production is about 1.4 metric tons. The production contains 14 000 tons of copper, 30 000 tons of zinc, and 600 000 tons of chalcopyrite. In addition, annual production includes 12 000 kilograms of silver and 260 kilograms of gold.

The mining methods currently in use are sublevel stoping and benching. The stopes are 25 meters high, 30 to 80 meters wide, with an ore total of 50 000 to 150 000 metric tons. All openings are systematically supported by rock bolting and shotcreting according to occupational safety standards. In addition, all stopes are supported by cable bolting. Empty stopes are backfilled with waste rock which is obtained from a separate open pit. In primary stopes, backfill is consolidated with cemented hydraulic fill produced from classified mill tailings, ground granulated blast furnace slag and lime.

Mine water is pumped out of the mine at a rate of approximately two cubic meters per minute. Prior to pumping, the water is settled in clarification tanks. 50 cubic meters of fresh air per second is blown into the mine. In the winter, mine air is heated through heat energy recovered from mine water.

2.2 Waste rock quarry

The underground mining does not produce a lot of waste rock. Coarse mill tailings and waste rock from development are not enough to backfill all the stopes in the underground. Therefore, the rock material required for mine backfilling is quarried from the open pit mine (Figure 3). The area of the quarry is about 12 hectares and it expands to southeast portion of the mine. The elevation of the quarry is located at + 152 meters and bottom of the mine is at level + 110 meters. (Pyhäsalmi Mine Oy, 2012)

Rock is quarried from the mine by drilling and blasting. The quarried rock material is taken to the mine area by dumpers and dropped to the filling tunnel. From the tunnel, rock material is dropped to the main levels of the underground mine and taken to the stopes which need to be filled. Total amount of the quarried gangue material is about 600 000 – 800 000 metric tons per year. (Pyhäsalmi Mine Oy, 2012)

Rain and underground water coming into the open pit mine are pumped into the tailings pond area during heavy rains and snow melting periods. Even with the pumping, some of the water enters the underground mine which causes an increased amount of water, particularly due to snowmelt.

Figure 3 – The open pit mine can be seen on the left side of the photo (Photo: Pyhäsalmi Mine Oy).

2.3 Tailings pond area

All the waste waters from the mine area are treated in tailings ponds. The tailings pond area is divided into four different pond parts: A, B, C, and D (Figure 4). Pond A was taken out of use and reclaimed in 2001 and 2002. (Pyhäsalmi Mine Oy, 2007)

Chemical water treatment is carried out by the addition of lime milk to the tailings. Lime milk neutralizes acidity and as a result of increased pH, metals precipitate to the bottom. The lime milk is contains 12 % calcium hydroxide ($Ca(OH)_2$). Lime milk is added to the water in the pumping station at the concentrator. After adding lime, water is pumped to the tailing pond area. The amount of lime used is controlled by daily measurements. The pH of Pond D is maintained over 10 to assure that all of the heavy metals are precipitated. (Pyhäsalmi Mine Oy, 2007)

All water from the mine area (including mine drainage water, process water and tailings from the concentrator, surface water from the industrial area, and seepage flow from the tailings ponds) are pumped into Pond D. Pond C is used as a storage pond where chemically-treated and settled water is directed. From Pond C, water is then pumped to a weir where the amount is measured continuously. From the weir, water is directed to northern part of the Pyhäjärvi Lake (Figure 5). Additional lime milk is added to Pond C with a separate pump line if the pH of discharging water is less than 5.5. According to environmental permit pH has to be maintained between 5.5 and 9.5. An automatic meter measures the pH of discharging continuously. (Pyhäsalmi Mine Oy, 2007) The annual discharging amount is 6 Mm^3 (average value of the last five years).

Surface water from the mine area is collected within open ditches and directed to a pumping station P2, and pumped to Pond D. Surface water from the asphalted industrial area is collected in separate rain water wells and directed to the pumping station at the mill. (Pyhäsalmi Mine Oy, 2007)

Surface waters from the southern part of the tailing pond area and the seepage flow from the ponds A and D are directed to a pumping station P5 via open ditches. Pumping station P5 is located near the shores of Pyhäjärvi Lake. From P5, water is pumped to pumping station P2 and to tailing pond D for neutralization. Seepage flow from the northern part of the tailing pond area (Ponds B and C) is directed to pumping station P3, located at the corner of ponds B and C. From P3, water is pumped into Pond B. (Pyhäsalmi Mine Oy, 2007) Locations of the pumping stations are shown in Figure 4.

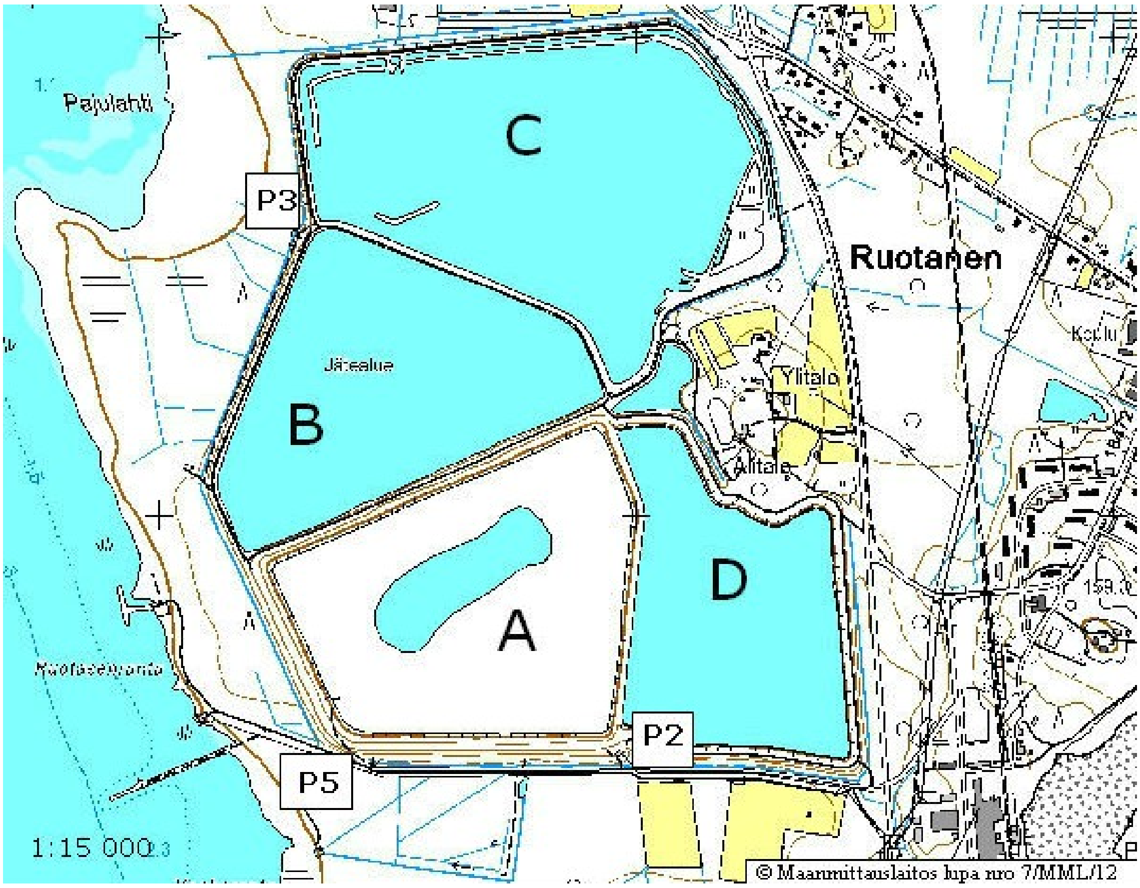

Figure 4 – Tailing ponds A-D and pumping stations.

3 Water balance of Pyhäsalmi Mine

3.1 Water balance during mine operation in 2011

Fresh water used in mining activities, in the concentrator and in other mining operations, is taken from Lake Pyhäjärvi, around 2.5 kilometers south of Tikkalansalmi (Figure 5). The annual fresh water amount is about 5.2 Mm^3 (the average value of the last five years). Environmental permit allows 720 m^3/a water intake. More than 90 % of the fresh water goes into the concentrator. The amount of water pumped into the mine is about 100 000 – 150 000 m^3 per year. The remainder of the water is used for other activities at the mine site. The water balance of 2011 is shown in Figure 6.

4 610 000 m^3 of fresh water was pumped from the lake in 2011, and 90 % of this was used in the concentrator. Only 2 % of the water was used in mining operations. The rest of the water was utilized in other activities such as dust reduction, for fire hydrants, and to supply the residential area located next to the mine site.

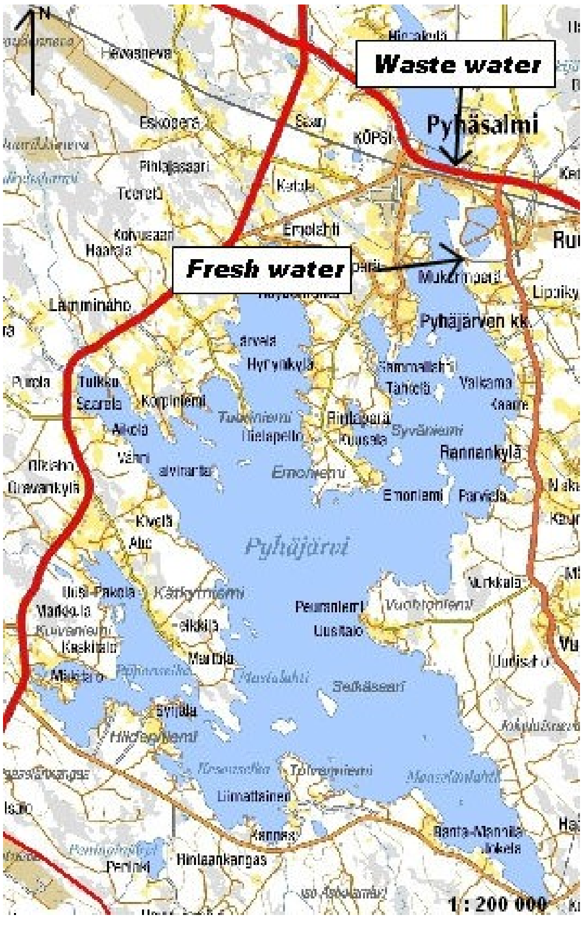

Figure 5 – Lake Pyhäjärvi (Maanmittauslaitos).

The concentrator uses water for the enrichment process and also for backfilling material used for the underground mine. 22 % of the water (923 200 m^3) used in the concentrator was recycled and therefore the total water needed was 5 083 000 m^3. 29 000 m^3 of fresh water and 101 000 m^3 of recycled water were used for backfilling material. The total waste water amount from the concentrator entering the tailing ponds was 4 272 000 m^3.

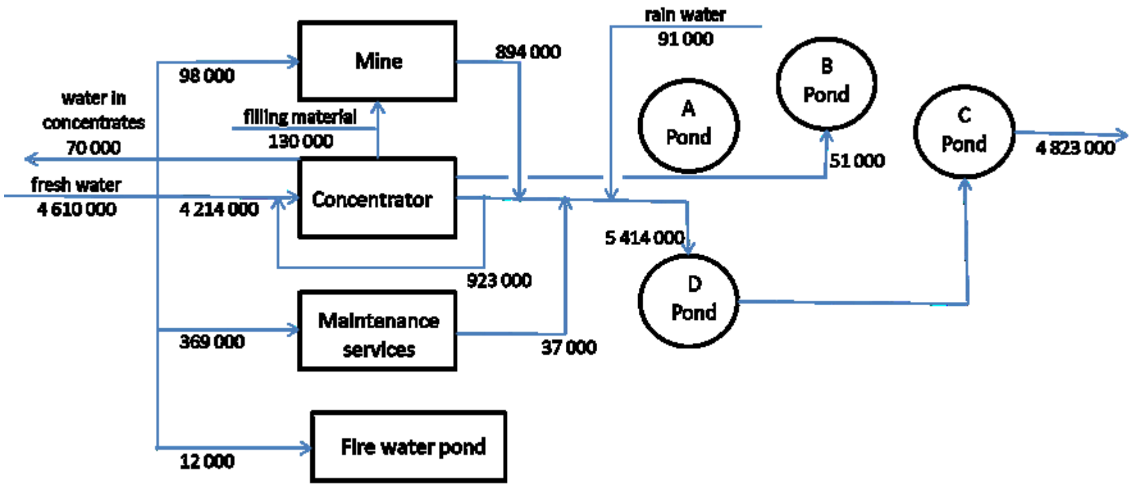

Figure 6 – Water balance for 2011 (Pyhäsalmi Mine Oy).

The underground mine waters consist of: (i) strongly acidic drainage water that has high concentration of metals, (ii) fresh water pumped into the mine for drilling, and machinery and vehicles washings, (iii) waters from backfilling material, and (iv) fresh ground water coming from old drill holes. All mine water is pumped to ground level and further on to the tailing ponds, along with the water from the mill. Mine drainage water goes through the underground clarification tanks before it is pumped to ground level. Amount of the water pumped from the mine was 894 000 m^3 (2011) which is about 20 % of the total discharged amount. According to Figure 6, natural drainage water in the mine is 791 000 m^3, which is about 90 % of the total mine dewatering amount.

3.2 Estimated water balance after mine closure

The amount of rain and snowmelt water from the top of Pond B and the northern part of the dam slopes is estimated to be about 27 250 m^3 yearly. Water drains to the wetland. The annual amount of rain and snowmelt water coming from the western and northern parts of the slopes is about 24 000 m^3. These waters drain to the pumping station at the corner of Ponds C and B. (Pyhäsalmi Mine Oy, 2007)

The area of the Pond D is about 31 hectares. The neutralization ratio (NP/AP) of the tailings is less than 1, which means that acidic runoff is a possibility. The annual amount of the rain and snowmelt water coming from the top the pond is about 19 200 m^3. Waters drain to the wetland. From the slopes of Pond D, rain and snowmelt waters (about 34 500 m^3/a) drain via a side ditch and to the pumping station at the corner of Ponds D and A. (Pyhäsalmi Mine Oy, 2007). Estimated annual water amounts from different parts of the tailing area and the total water amount which needs to be treated are shown in Table 1.

Table 1 – Estimated annual water amounts coming to the tailing pond area, and the water requiring treatment after mine closure.

Pond	**Water from the surface [m^3/a]**	**Water from the side slopes [m^3/a]**	**Contaminated water [m^3/a]**
A-pond	30 000	20 000	50 000
B-pond	27 250	24 000	24 000
D-pond	19 200	34 500	34 500
Total treated water			108 500 m^3

4 Mine closure

The ore reserves of the Pyhäslmi mine are expected to last until 2018. After that, if no further reserves are found, the mine will be closed. In the closure plan, the two most probable scenarios are that mine is closed and the underground mine is allowed to flood, or mine is closed and other operations are moved to the underground mine (Pyhäsalmi Mine Oy, 2011).

If the closed underground mine is allowed to flood, only the water in the tailing pond area needs to be treated. Normally the seepage from the mine after its filling includes heavy metals containing acid at first and the chemistry of this water changes with time but that possibility is not included in this work. After the closure of the mine and halting the mill activities, discharging water includes rain and snowmelt in the tailing pond area and the seepage flow from the ponds. (Pyhäsalmi Mine Oy, 2007) The chemistry of the discharging in the tailing pond area is estimated in section 7.2: Survey of the surrounding waters.

If the other operations are located within the mine, mine drainage water needs to be pumped to the ground level and treated to remove dissolved metals and sulfates. In that case, the pumped water amount is only slightly lower than it is during mine activities. Only the process water will not be used. In addition to the mine drainage water, rain water and seepage flow from the tailing pond area need to be treated. The clean surface run-off is not directed to the seepage collection systems. That will be done by contouring the soil covers and re-vegetation planning. In both situations, sludge generated by metal precipitation needs to be collected and disposed of in appropriate landfill sites. (Pyhäsalmi Mine Oy, 2007)

The area of Pond A is about 41 hectares, and this pond was closed during 2001 and 2002. The annual amount of rain and melted snow water coming from the top of the Pond A is estimated to be about 30 000 m^3. After mine closure, water can be drained to the middle of the Ponds A and B. The water goes via a ditch (at the top of the moraine dam) to the ditch beside Pond B and further on into the pumping station at the corner of the B and C ponds. The annual amount of the water coming from the slopes of the Pond A is estimated to be about 20 000 m^3. The water from the slopes goes to the ditch at the edge of the pond and into the pumping station at the corner of the B and C ponds. (Pyhäsalmi Mine Oy, 2007)

The area of Pond B is about 31 hectares. Pond B is used as storage for the pyrite. It is possible that pyrite ore prices will be low at the time of mine closure and thus the enrichment process would not be economical. In this case, pyrite tailings could be acid forming. (Pyhäsalmi Mine Oy, 2007)

The area of the Pond C is about 47 hectares. Tailings and gypsum are likely settled at the bottom of Pond C. Sludge need to be removed and relocated to Pond B or D, or to the small area separated from Pond C. The moraine dams will be lowered to about 1 – 1.5 meters high, when the wetland is formed from the pond area. (Pyhäsalmi Mine Oy, 2007)

5 Acid mine drainage

Acid mine drainage (AMD) is water that has a high acidity, high concentration of metals and high concentration of dissolved sulfates (Garcia et al, 2001). Often, the pH of AMD is lower than 3 and the sulfate concentration is higher than 3 000 mg/L (Lyew et. al, 1994). Acid mine drainage is considered to be the most significant and widespread mining industry related pollution problem around the world (Tsukamoto and Miller, 1999). AMD-waters must be collected and treated to remove dissolved metals and sulfates. The acidity must be neutralized before being discharged into the environment (Neculita et al, 2007).

Chemical reactions of acid mine drainage formation and iron precipitation in acidic waters are explained in this section. Precipitated iron oxides can be utilized as products and characteristics of schwertmannite are explained. Different treatment methods are introduced shortly and differences between passive and active methods are explained. The advantages and disadvantages of the both methods are also described.

5.1 Formation of acid mine drainage

Underground mining creates channels for water and air that did not previously exist within the rocks. Ground water seeping into the mine can come into contact with fresh rock surfaces which may contain reactive and soluble minerals. (Blodgett et. al., 2002) In addition to the mineralogy of the mine ore, the chemistry of the mine water is related to hydrology. For example rain water, surface run-off and ground water increase the water amount inside the mine. Different factors affecting the mine water amount are presented in Figure 7 (Vestola and Mroueh, 2008).

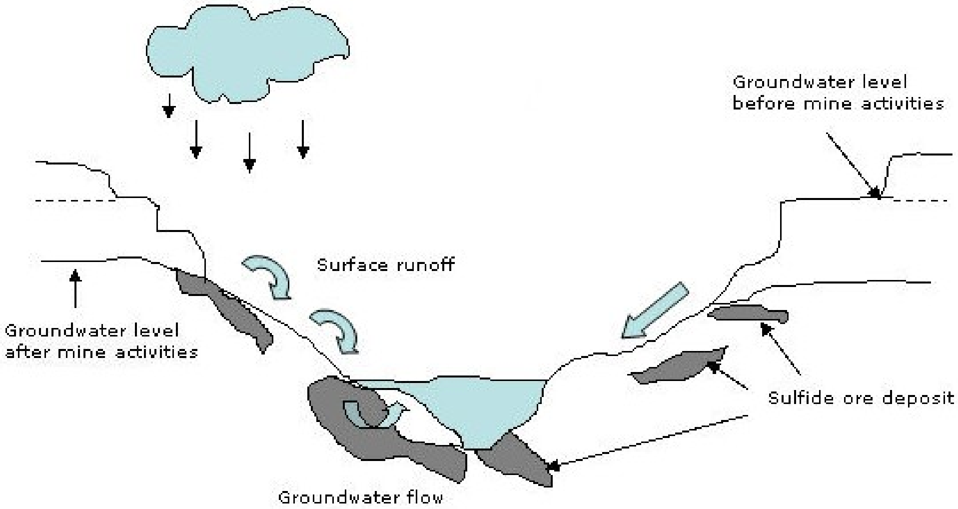

Figure 7 – Factors affecting to mine water amount (Vestola and Mroueh, 2008).

AMD is formed when sulfide minerals are exposed to water and oxygen through a combination of chemical and biological processes (Neculita et al, 2007). AMD generation depends on different factors such as bacterial activity, pH, sulfide mineral surface area, type of sulfide minerals, temperature, and oxygen concentration controls the rates of AMD formation (Berghorn and Hunzeker, 2001). The effects of these factors are explained later on in this chapter.

The first step of AMD formation is pyrite (FeS_2) oxidation in the water. Oxidized pyrite releases ferrous iron (Fe^{2+}) into the solution according to the following reaction (1). The pH of the water is neutral at this point (Neculita et al, 2007).

$$FeS_{2(s)} + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1}$$

Sulfite (SO_4^{2}) is formed by pyrite oxidation in reaction (1). Proton acidity (H^+) and mineral acidity caused by ferrous iron in reaction (1) decrease the pH of the solution. Therefore the next step occurs at lower pH values (<4) (Neculita et al, 2007).

Oxidation of ferrous iron to ferric iron (Fe^{3+}) by oxygen will take place if the oxidation potential is maintained at high values. Figure 10 presents the stability of iron oxides and hydroxides in Eh-pH diagram. Reaction (2) consumes part of the proton acidity produced and therefore pH increases again (Peppas et. al, 2000).

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad (2)$$

pH is a very important determining factor. Chemical oxidation of ferrous iron is very low at pH < 3.5. Therefore iron-oxidation bacteria such as *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* have a significant role in the reaction (Johnson, 2013). Ferric iron is not soluble in water if the pH is higher than 2.3 to 3.5, depending on total iron concentration and in the higher pH levels (>6.5) ferric iron precipitates as ferric oxyhydroxide ($Fe(OH)_3$). The reaction releases proton acidity (H^+) and lowers the pH of solution (Blowes et. al, 2013):

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (3)$$

As the pH decreases, the cycle starts again because ferric iron remains in solution and is reduced by pyrite. Therefore, more ferrous iron and acidity is formed, until either ferric iron or pyrite is depleted. (Neculita et al, 2007) Ferric iron, generated in reaction (2), oxidizes pyrite by the indirect reaction (4) (Peppas et al, 2000):

$$FeS_{2(S)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

Pyrite oxidation rate by Fe^{3+} is much higher than oxidation by O_2. In addition, 1 mol of pyrite oxidation by ferric iron releases 16 mol of H^+ (reaction 4) compared to 2 mol of H^+ released in reaction (1). In acid-generating process, the oxidation of Fe^{2+} to Fe^{3+} (reaction 2) is often referred to as the "rate determining step" (Neculita et al, 2007).

The overall reaction (5) is given by adding reactions (1) through (3) (Neculita et al, 2007):

$$FeS_{2(S)} + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+ \qquad (5)$$

Formed ferric iron (reaction 2) can also precipitate as schwertmannite ($Fe_8O_8(OH)_6(SO_4)$) if the pH of the solution is between 2.8 and 3.5 according to reaction (6), though at low pH (<3), ferric iron precipitation tends to be slow. (Bigham et al, 1994)

$$8Fe^{3+} + SO_4^{2-} + 14H_2O \rightarrow Fe_8O_8(OH)_6(SO_4) + 22H^+ \qquad (6)$$

5.2 Schwertmannite precipitates in AMD

Schwertmannite is an oxyhydroxysulphate of iron (Figure 8), and was found at the Pyhäsalmi mine area in 1994. Schwertmannite occurs in nature as ochreous precipitate from acid and sulfate rich waters (Bigham et al, 1994) with a pH range of 2.8 to 3.5 (reaction 6). Iron precipitates as ferrihydrite (nominally $5Fe_2O_3 \cdot 9H_2O$) if the pH of the water is higher than 6.5. (Bigham et al, 1996)

Figure 8 – Schwertmannite (Mineralogy Database).

Solids formed by mine drainage treatments have chemical and physical characteristics that can be developed into useful products. SCH differs from other iron oxides. Comparing SCH with other iron oxides less Si precipitates, and calcite formation cannot occur due to precipitation in low pH waters. That makes them the purest iron solids collected to date. Iron oxides have chemical characteristics that are valued in remediation applications. Two general uses for mine drainage solids have been identified. (Hedin, 2012)

Schwertmannite has strong pigmentary characteristics and it can be used as crude pigments. After processing (includes drying, calcinations, particle size reduction, and blending) the end product is a dry powder pigment that is used in paints, stains, concrete, and plastics. (Hedin, 2012)

Schwertmannite has chemical characteristics that are valued in remediation applications. Iron oxides are well known for their high sorption capacity. They are particularly good sorbents for oxyanions such as arsenate, selenite, and phosphate. Iron oxide is also a good sorbent of lead, cadmium, copper, and zinc. When they are added to the contaminated soils, sorption onto the solid can decrease extractable metals to safe concentrations and mitigate the need for expensive soil removal and disposal. (Hedin, 2012)

For the last decade, Iron Oxide Recovery, Inc. (IOR), US, has been producing an iron product from the solids precipitated for coal mine drainage. Since 2000, IOR has sold 3 300 tons of dry products to pigment, coal mining, water treatment, and soil remediation companies. (Hedin, 2012)

5.3 Treatment systems for AMD

Acid mine drainage can be treated by active or passive methods. Active treatment methods require continuous addition of alkalization chemicals. Passive treatment methods are based on bio-chemical reactions. Advantages and disadvantages of the methods are compared in this chapter and some classifications of the passive treatment methods are introduced.

5.3.1 Active treatment systems

The most common AMD treatment method is the use of chemical. Chemical treatment is made by the addition of alkaline chemicals to water. Alkali neutralizes the acidity and due to increased water pH, metals precipitates as hydroxides and carbonates. (Gazea et al, 2002) The main disadvantage of this method is that alkalization has to be continuously repeated to be effective (Ledin and Pedersen, 1996).

Chemical treatment has high operational and maintenance costs. In addition, chemical treatment forms large amounts of sludge which requires disposal to designated landfill sites. (Nanucucheo and Johnson, 2012) Other technologies to treat AMD, such as ion exchange, reverse osmosis, electrodialysis, and electrolytic recovery are also available but they are more expensive and not as commonly used (Prasad et al, 1999).

5.3.2 Passive treatment systems

Acid mine drainage from many sites could possibly contaminate the environment for many decades after mine closure. Therefore, alternative low-cost and low-maintenance passive treatment systems have been developed. (Gazea et al, 2002)

Passive treatment systems can be classified by separating chemical passive treatment from biological passive treatment (Figure 9). The biological treatment system involves sulfate reducing or iron-oxidizing bacteria. Permeable reactive barriers can be classified either as biological or as chemical passive treatment systems. (Neculita et al, 2007)

Passive biological methods for AMD treatment have plenty of advantages when compared to passive AMD chemical treatments. Biological methods can produce a high degree of metal removal at a low pH. Furthermore, the sludge formed by biological treatment is denser, less voluminous, and more stable. (Neculita et al, 2007) Operational costs and energy consumption are also lower in comparison to the chemical treatment (Gazea et al, 2002).

"Passive bioreactor" refers to a reactor using a simple flow-through design. The reactor needs to have a solid reactive mixture, acting as a source of carbon for bacteria and as a physical support for microbial attachment and metal sulfide precipitation. (Neculita et al, 2007) The reactors used in this work are semi-passive and passive bioreactors.

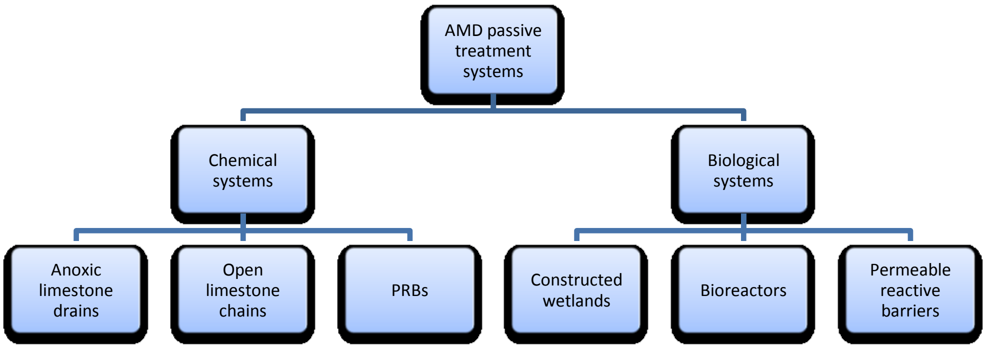

Figure 9 – Classification of AMD treatment systems (Johnson and Hallberg, 2005).

5.3.3 Iron oxidizing bacteria

A great variety of microorganisms have been found from mine waste. Microbiological processes are usually responsible for the environmental hazards created by mine waste. However, microorganisms can also be used for removing the negative impacts on the environment. (Ledin and Pedersen, 1996) This chapter introduces one of the iron-oxidizing bacteria which are used in the iron-oxidizing module in the Bangor University laboratory experiments.

Sulfate reducing and iron oxidizing bacteria are commonly used in passive waste water treatment methods. Bacterial activity can have an effect of mobility of metals in the mine waste in several ways. The influence depends on which of the processes are dominant in a certain environment. Bacteria act as catalysts in geochemical processes through their metabolism. (Ledin and Pedersen, 1996)

Microorganisms that have adapted to highly acidic, metalliferous, environments include bacteria that catalyze the oxidation of iron and sulfur. Iron needs a high oxidation potential for the oxidation from ferrous to ferric forms in acidic solutions. Therefore iron-oxidizing bacteria have a significant role in catalyzing ferrous iron oxidation in biological treatment methods. (Johnson, 1995) The Eh – pH stability diagram (Figure 10) presents abiotic iron oxidations in the order of different pH and Eh values.

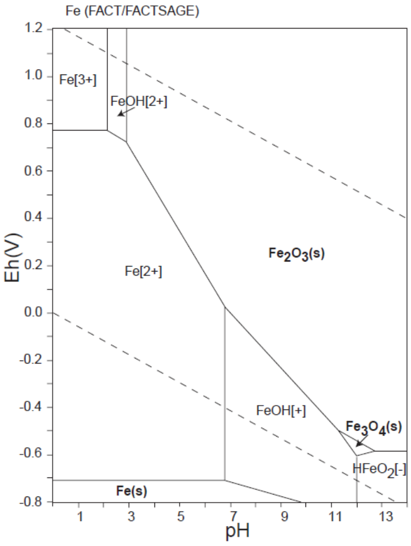

Figure 10 – Eh-pH stability diagram for iron oxides and hydroxides (Atlas of Eh-pH diagrams, 2005).

The iron-oxidizing bacteria species *Ferrovum myxofaciens* (*Fv. myxofaciens)* has recently been isolated from mine impacted waters of an abandoned copper mine (Blowes et al, 2013). This bacterium produces large amounts of extracellular polymeric substances giving a rise to characteristic “acid streamer” growths in mine waters of pH range between 2 and 4. The bacteria can continue to grow on the iron and the reactor becomes more efficient with age. Previous studies have found that *Fv. myxofaciens* is the most efficient species tested in the continuous flow mode reactor. (Johnson and Hedrich, 2012)

6 Bioreactor system for AMD treatment

A modular continuous flow reactor system for the selective bio-oxidation of iron and precipitation has been designed in Bangor University by D. B. Johnson and his colleagues. The basic idea of the reactor system used in the experiments of the synthetic mine water tests is explained in this chapter.

The system includes three modules (Figure 11). The object of the first module is to oxidize ferrous iron to ferric iron by iron-oxidizing bacteria. Ferric iron precipitates in the second reactor as the mineral schwertmannite as a result of increased pH of the solution. A flocculating agent is added to promote rapid aggregation and settling of the schwertmannite particles. The third reactor lowers the remaining soluble iron concentration in the processed water. This module is optional and it is used as a polishing reactor. (Hedrich and Johnson, 2012)

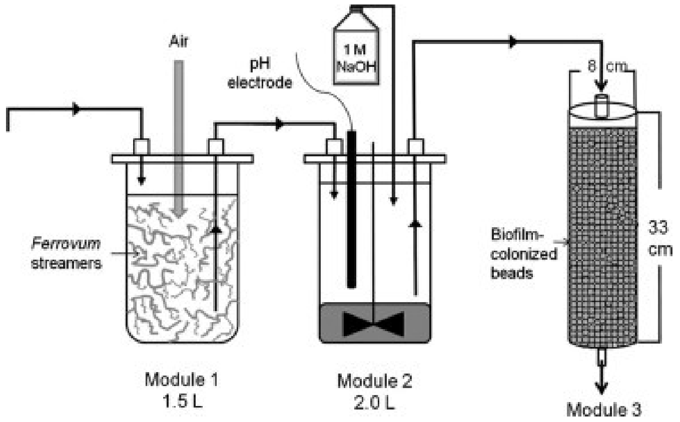

Figure 11 – Schematic of the composite modular bioremediation system. (Hedrich and Johnson, 2012).

6.1 Module 1. Ferrous iron oxidation

The primary bioreactor (module 1) oxidizes ferrous iron to a ferric form. Because of the acidic water (pH < 3.5) abiotic iron oxidation is very slow. Therefore, the reactor contains acidophilic iron-oxidizing bacteria which have a key role in accelerating iron oxidization.

Bacteria used in this reactor are *Fv. myxofaciens*. Bacteria readily attach to the walls of the vessel and other internal structures, and form long streamer like growths that extend into the reactor body. Bacteria can continually grow on the iron and therefore higher dilution rates can be used when the iron concentration of the water is higher.

An additional support matrix is not necessary because of the growth of the bacteria. This maximizes the space available in the reactor vessel for microbial biomass to accumulate. Ferrous iron oxidation is an oxygen-requiring and proton consuming reaction (reaction 2).

6.2 Module 2. Iron-precipitation reactor

Module 2 is the iron-precipitation reactor. The ferric iron generated in module 1 precipitates as schwertmannite according to reaction (6) by the controlled addition of alkaline. According to previous studies, hydrolysis of the ferric iron is very slow (< 1 % within 16 h) because of the low pH (~2.3) of the water. To make this process faster, it is necessary to increase the pH of the solution. (Hedrich and Johnson, 2012)

Results of the previous experiments have shown that the optimal pH for schwertmannite precipitation is 3.5. If higher pH values are used, other metal hydroxides will co-precipitate in this reactor. The increasing of the pH is from an automated addition of NaOH to the reactor vessel. (Hedrich and Johnson, 2012)

Module 2 is operated as a continuous flow reactor. Small flocs of ferric iron precipitate forms as a result of iron hydrolysis. A flocculating agent (FLOCCIN 1105) is used to accelerate the sedimentation of the flocs (from >15 min to <5 min). Because of module 2 is a continuous flow system and it needs to be stirred periodically, two iron precipitation modules are used operating in tandem. (Hedrich and Johnson, 2012)

Precipitated schwertmannite is produced as wet flocculated slurry. Schwertmannite is removed from the reactor by gravity flow via a pipe connected to the base of the module 2.

6.3 Module 3: Iron oxidation/precipitation bioreactor

The purpose of the module 3 is to oxidize and precipitate the small amount of soluble iron remaining from the first two modules. Iron precipitates while flowing through a trickle packed bed reactor by bacterial activity. Because of the pH of the part-processed influent liquor, the ferric iron generated hydrolyzes and precipitates in-situ. (Hedrich and Johnson, 2012)

In the experiments, the iron concentration of the discharging from the module 2 has kept at 5 mg/L in every case. Therefore module 3 is not included to the results.

7 Materials and methods

7.1 Flow rate and quality measurements

All the mine drainage water from the underground mine were studied. The study includes analyses of the water chemistry and water amount and temperature measurements.

All the larger water holes, through which the mine water travels to the next level, were located. Flow rates and temperatures were measured from April 11 to 13, 2012. Water samples were collected April 14, April 19 and May 7, 2012. Samples from the tailing pond area and the open pit mine were taken on May 11, 2012. The last two of the water samples for the ferric/ferrous iron analyses were collected on July 2, 2012.

Volumetric flow rates were measured by using 10, 60, and 200 liter containers. Temperatures were measured using a Delta OHM HD 9218 thermometer. Water samples were collected in 0.5 and 1.0 liter bottles.

The metal concentrations: Cu, Zn, Fe, Mn and SO_4 were analyzed and redox, pH and electrical conductivity were measured by the laboratory of Pyhäsalmi Mine. Metal and pH analyses were made by using Finnish SFS standards, and sulfate was analyzed by in-house method gravimetry. The results and used standards of the analyses are shown in appendix 4.

Redox was measured with a silver/silver chloride reference electrode, and the reported values are E values. According to the instruction manual of meter used (METTLER TOLEDO inlab®) conversion to redox potential related to standard hydrogen electrode (SHE) is: $E_H = E_{meas} + 207$ mV.

In addition, in some of the water samples Al, As, and ferrous iron were analyzed by Lapinvesitutkimus Oy in Rovaniemi (LVT). Methods that were used to analyze metal concentrations were: ICP-OES and SFS-EN ISO 11885. Electrical conductivity was measured according to the standard SFS-EN 27888 and sulfate concentration with ion chromatography method (IC). Ferrous iron analyses were made by a subcontractor of LVT in Germany and the method used was German standard: DIN- 38406-E1. 1:1 diluted sulfuric acid (H_2SO_4) was added for stabilizing the ferrous/ferric iron sample in proportion to LVT. The results of the analyses are shown in appendix 3.

The samples taken July 2, 2012 were analyzed by accredited laboratory Labtium Oy in Espoo, Finland. Samples were pre-treated by adding 2.5 ml of strong nitric acid (HNO_3) to stabilize the metals and 20 ml of strong hydrogen chloride (HCl) was added to the ferrous/ferric iron samples according to the practice of Labtium. Metal concentrations were analyzed by using ICP-OES method and ferrous/ferric iron by in-house method spectrophotometer. To minimize possible error when evaluating the amount of oxidized ferrous iron, samples were sent for analysis on the day of collection and the analysis was carried out the following day.

Possible errors may have occurred in the results of ferrous iron concentrations in the samples analyzed by LVT. Errors could have arisen from possible changes in water quality during the storage period (in this case, it was from one to two weeks). In addition, the used stabilization method was not according to the standard DIN-38406-E1, which was the one used in analyzing the amount of oxidized ferrous iron.

Bangor University in Wales, UK, analyzed the microbes of the mine water from two different locations (levels + 630 m and + 970 m). Microbiological analyses were made by using molecular and cultivation methods.

7.2 Estimation of underground water and mass balance

Metal and sulfite concentrations of the mine water in different depths are explained and temperature changes are described. The amount of oxidized ferrous iron is not taken account in this survey because of the possible errors in the water analyses.

Axonometric view of the mine, where all the levels can be seen, is shown in appendix 2. A flow chart of the mine drainage water (appendix 1) was made based on these results. The results of the study were used to evaluate the benefits of remediation of the water in different parts of the mine. The aim of the study was also to examine if high metal content waters with high flow rates could be found and if selective recovery of the metals would be beneficial to the process.

Based on the water analyses and the existing water collection system, two possible alternatives of locations for the water treatment were pinpointed. The locations of the reactor systems were chosen to lessen the maintenance costs of the pumps and pipe lines. This could be possible if all the iron from the water will be precipitated before water is pumped to the ground level. Two alternative locations of the reactor system were analyzed.

Two mine water samples were chosen for the bioreactor experiments carried out at Bangor University. Combined chemistry of the water analyses were used preparing two synthetic mine water with different iron content used in the bioreactor tests. The bioreactors operate in the continuous flow mode, and a large number of tests were carried out at different flow rates. Based on these results, hypothetic flow rates were calculated in large-scale (10 m^3) bioreactors.

Due to annual changes of the drainage water amount, as well as metal concentration changes, water amount-time and metal concentration-time curves were made based on previous analyses made in Pyhäsalmi laboratory. These Figures were used to evaluate the correlation of the results of the underground water survey to annual average values.

A surrounding water survey was made and evaluations of the water discharge from the tailing pond area after the mine closure were based on these results. Benefits of utilizing the bioreactor system in the tailing pond area after mine closure were assessed. Survey of the underground water shows the water amount in different depths of the mine.

7.3 Survey of surface waters

Water samples from the tailing pond area and open pit mine were used for the estimation of the discharge after the closing of the mining activities. The results of analyses are used for evaluating the benefits of iron recovery after mine closure within the tailing pond areas.

Water samples were collected May 11, 2012 from the tailing pond area and the open pit mine. Locations are shown in Figure 12 (with the exception of the sample from the open pit).

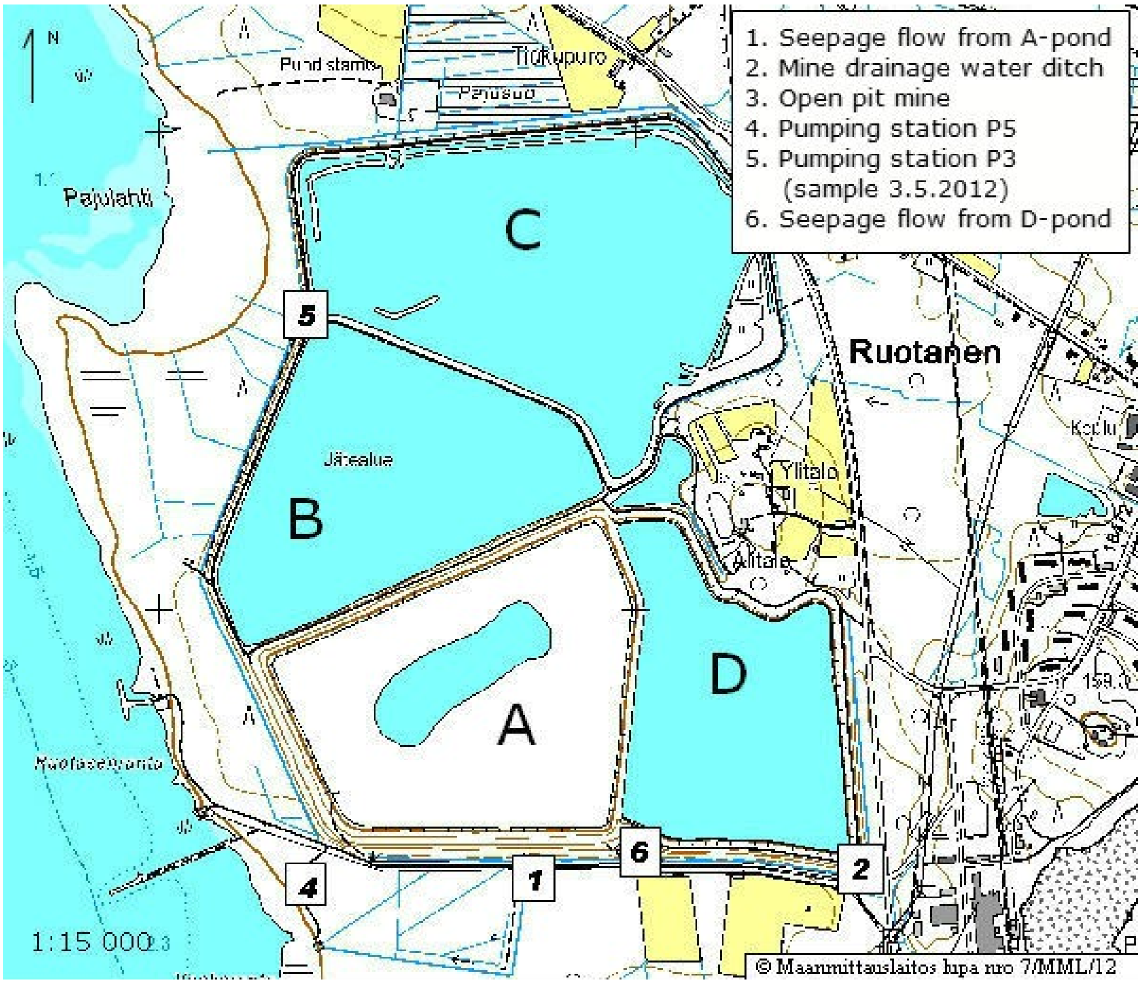

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Figure 12 – Sample points in the tailing point area.

Table 2 – Concentrations of waters in the tailings pond area (May 11, 2012). Locations of the sample points are shown in Figure 12.

	Cu [mg/L]	**Zn [mg/L]**	**Fe [mg/L]**	**Mn [mg/L]**	**SO_4 [mg/L]**	**Redox [E]**	**pH**	**Cond. [mS/m]**
Sample 1	1.99	7.87	60.0	4.15	1150	483	3.2	186
Sample 2	1.12	3.62	7.30	1.91	275	456	3.6	62.1
Sample 3	0.04	1.68	0.10	3.02	280	413	6.3	65.3
Sample 4	1.89	21.9	179	10.9	3240	540	2.9	425
Sample 5	1.20	15.0	50.0	4.60	811	-	3.0	157
Sample 6	71.8	556	568	38.5	9930	525	2.8	937

Results for the water sample from pumping station P3 (average values over the last five years) are used for the estimating the water chemistry of discharge after mine closure.

8 Results

8.1 Underground water flow rate and quality

Most of the drainage water comes to the levels between + 240 m and + 630 m. At level + 630 m the flow rate is about 15 L/s. Smaller amounts of water comes to the mine between the levels + 780 m and + 970 m. The flow rate is about 6 L/s at the level + 930 m. The water located under level + 1300 m, is only ‘fresh’ process water.

Figure 22 presents the flow rates of the underground water at different depths. The flow rate shown at level + 645 m (28.3 L/s) includes a flow rate from the water pumped from the pumping station at level + 970 m. The flow rate at level + 970 m (13.8 L/s), includes the flow rate of the water pumped from level + 1 300 m.

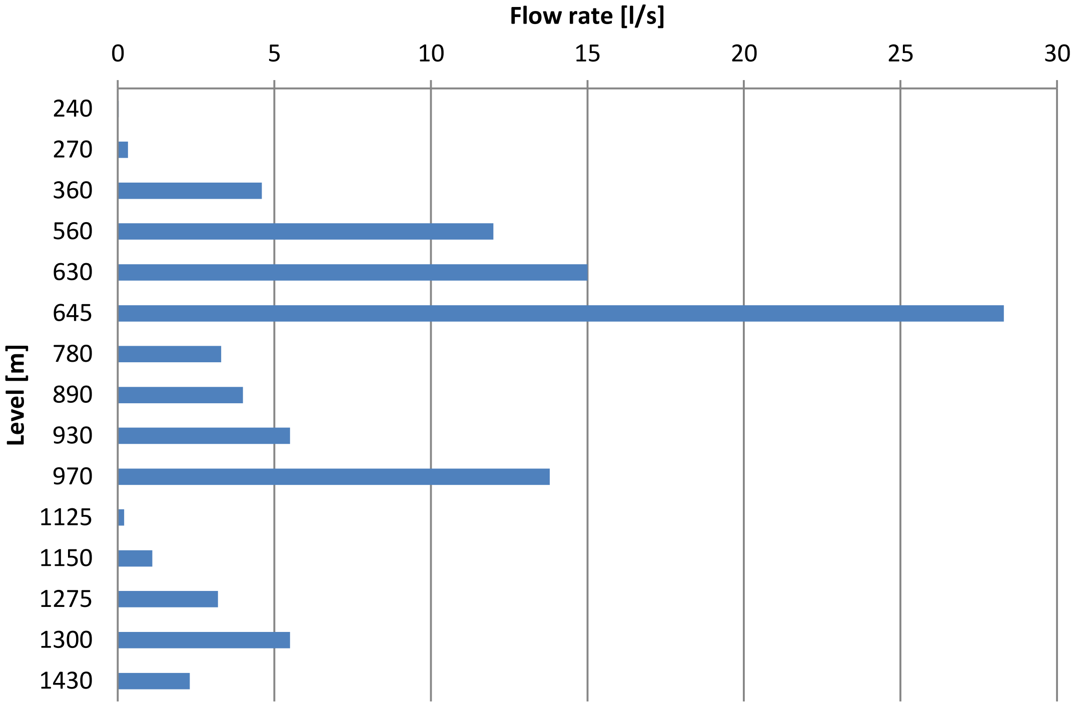


Figure 13 – Flow rates of the mine water at different depths.

As seen from Figures 14 – 17, mine water holds the highest metal and sulfate concentrations between levels + 240 m and + 630 m. At these levels, copper concentration is between 54.0 mg/L and 623 mg/L, zinc is between 820 mg/L and 5 900 mg/L, and iron is between 317 mg/L and 3 400 mg/L. Ground water flows through the old stopes where metals are dissolved into the water from rock surfaces. Figure 15 and 16 show clear changes in copper and zinc concentrations between the upper and lower levels. One reason why concentrations are significantly higher below level + 630 m may be due to the fact that copper and zinc ore could not be quarried during the 1960s and 1970s, and the residual ore at this depth is oxidizing and the metals released are dissolving in the acidic water.

Between levels + 640 m and + 940 m water also contains soluble metals, but concentrations are not very significant. Below level + 940 m to level + 1300 m metal concentrations are lower. Natural waters do not exist under level + 1300 m. All the water located within these levels is fresh water pumped from the ground level. Therefore metal concentrations are nearly zero and the pH is nearly neutral.

Selective recovery of zinc and copper is not included in this work due to their low concentrations. Concentrations are higher in a few locations, but the water amount is so small that economic benefits are not considered. However, if the water from the level + 630 m could be pumped separately to the surface, selective copper and zinc recovery could be advantageous.

Arsenic concentrations are very low (for AMD) in the mine water of all levels. The highest concentration of As (0.2 mg/L) is measured from the water steps at level + 500 m, where other metal concentrations are also high.

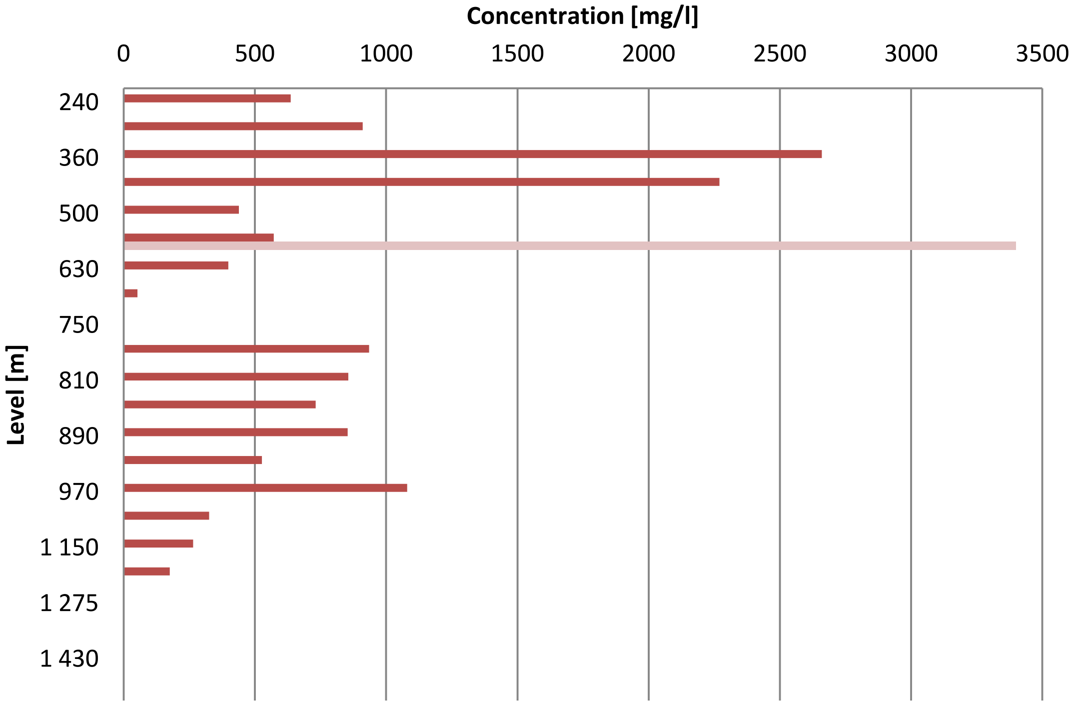


Figure 14 – Concentrations of iron in mine water at different depths.

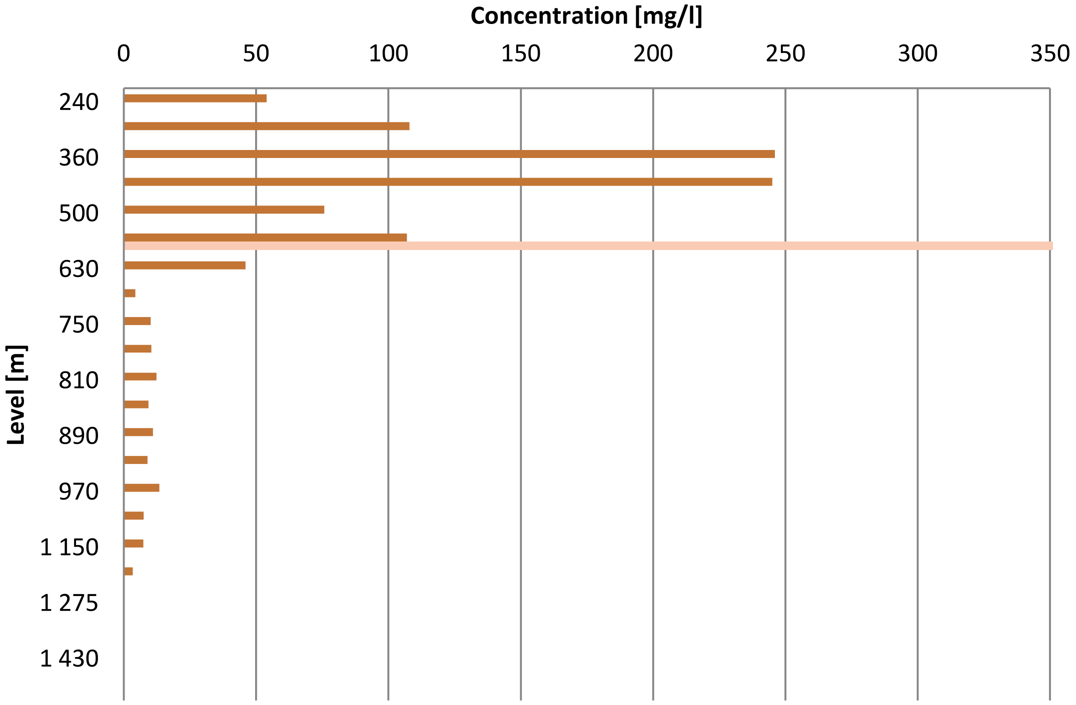


Figure 15 – Concentrations of copper in mine water at different depths.

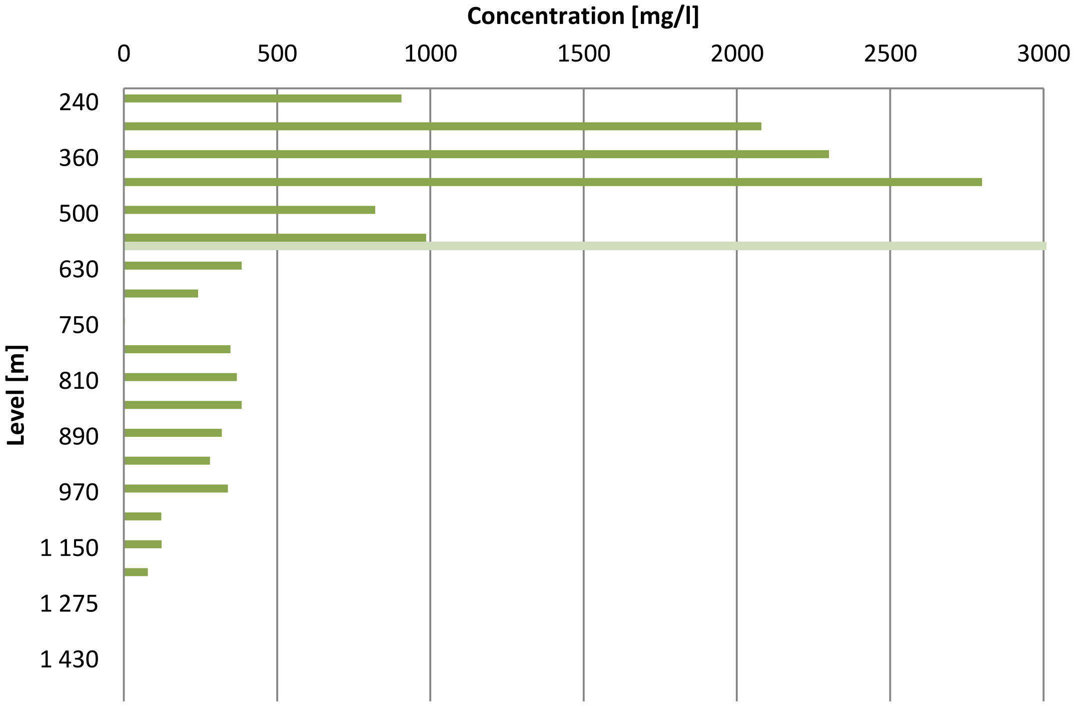


Figure 16 – Concentrations of zinc in mine water at different depths.

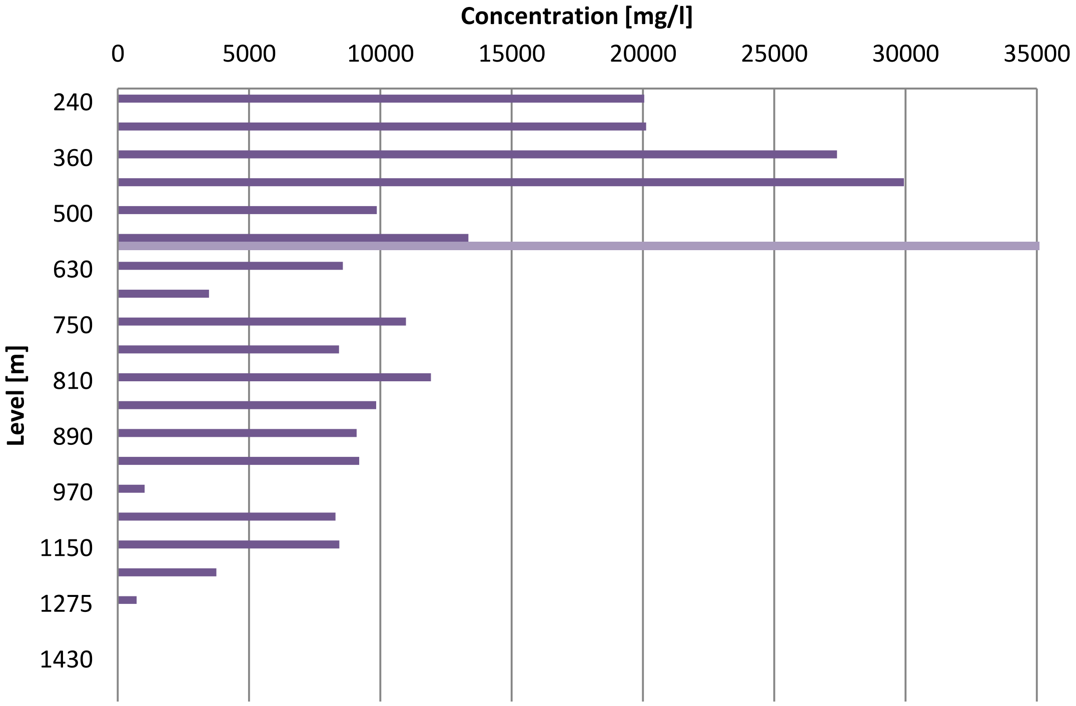


Figure 17 – Concentrations of sulfate in mine water at different depths.

Figure 18 shows the pH of the mine water at different levels. Mine water is extremely acidic at level + 970 m and above, where pH averages about 2.6. At levels below + 970 m the pH is higher, averaging about 4.2.

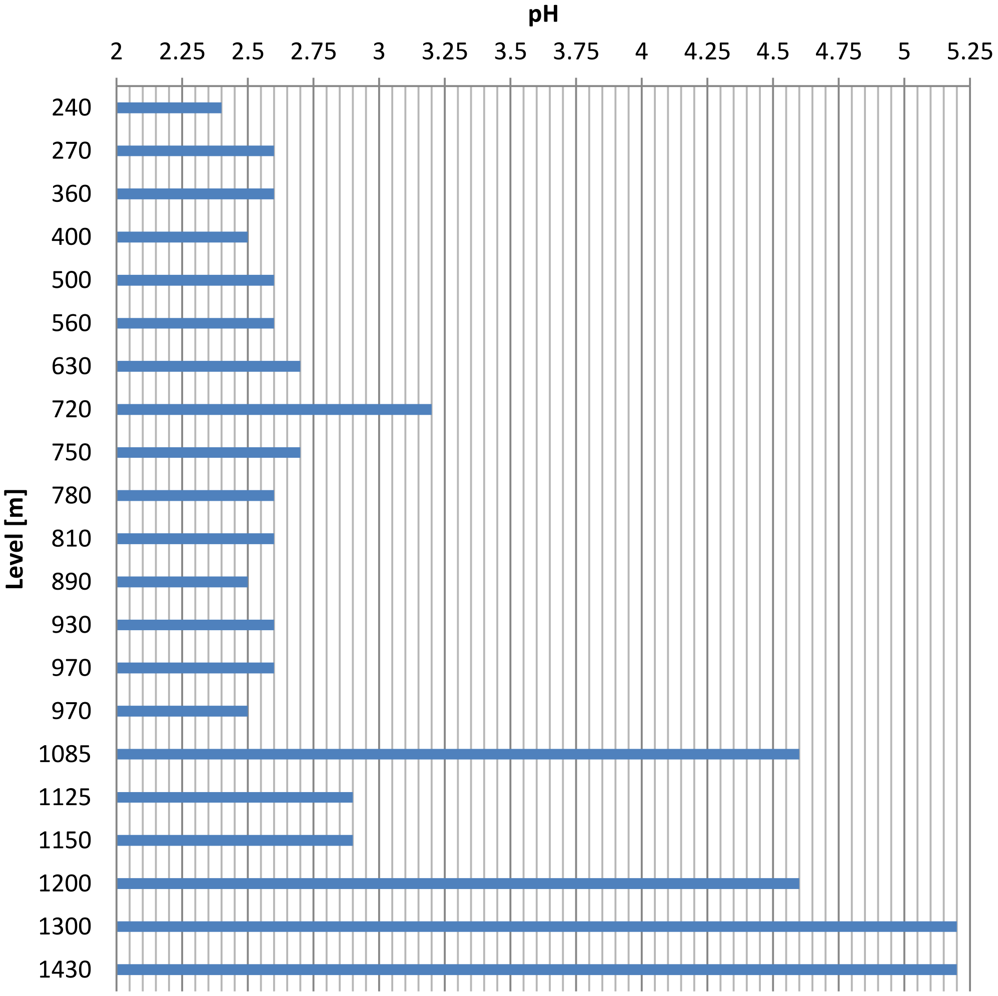


Figure 18 – The pH of mine water at different depths.

The redox potential of the water decreases in the deeper sections of the mine (Figure 19). The E_h values show an inverse relation to pH values, as was expected. According to Figures 10, 18, and 19, in theory, all the iron should be in ferrous form. Nevertheless, 90 % of the total iron amount is present in the oxidized ferric form in the samples taken from the levels + 630 m and + 970 m. As a result of this observation, samples were sent to the Bangor University laboratory, where acidophilic bacteria than can catalyze the oxidation of ferrous to ferric iron were identified.

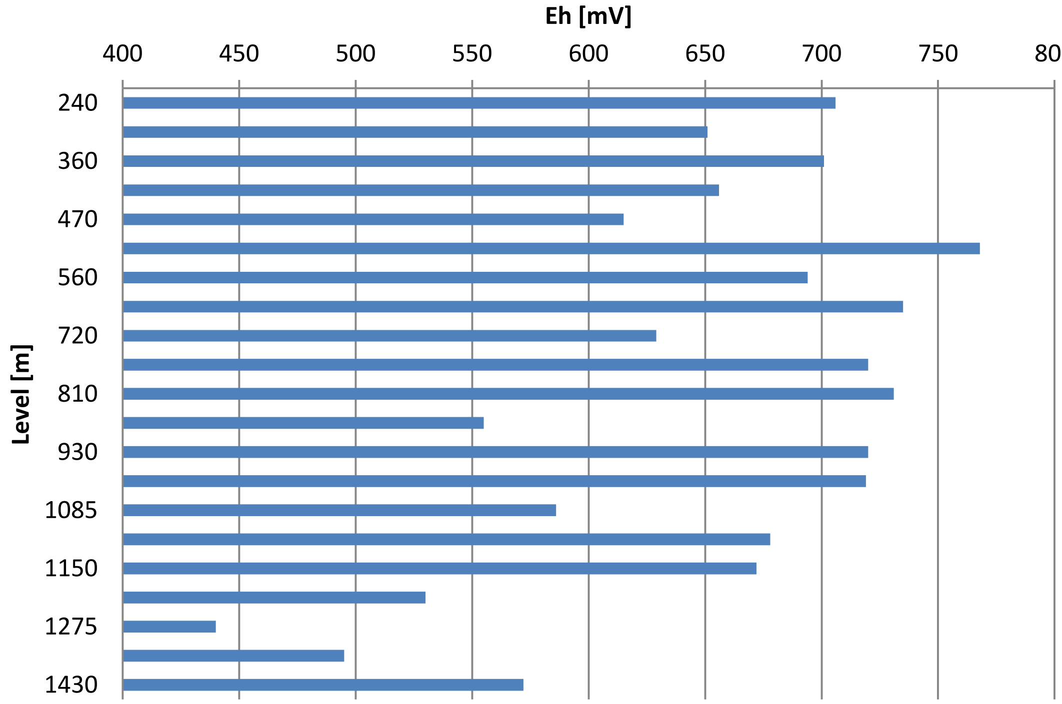


Figure 19 – Redox potentials of the mine water at different depths.

8.1.1 Waters between levels + 240 m and + 630 m

The first underground water hole is located on level + 240 m (240 meters below ground level). The flow rate of the water coming from the hole is low, only 0.03 L/s. The water is extremely acidic with a pH of 2.3. Metal concentrations are also quite high, particularly zinc (906 mg/L) and iron (636 mg/L). Copper concentration is slightly lower (54.0 mg/L). As expected, the amount of sulfate is high (20 100 mg/L) in the water. The temperature of the water is 14.1 ˚C.

On the next level (+ 270 m), the flow rate of the water is 0.30 L/s. Zinc (2 080 mg/L) and copper (108 mg/L) concentrations are 100 % than in the above-level water, though the iron concentration (911 mg/L) does not show the same degree of difference. Temperature is one degree C cooler, and the pH (2.6) slightly higher. The sulfate concentration has remained unchanged.

The amount of water at the + 300 m level was less than at the + 270 m level, and the water flows as a stream on this level. A flow rate measurement of the water was not possible and a water sample was not collected. Water on the level goes to the next level, which is located at a depth of + 360 m.

At the +360 m level, water comes from two holes located beside one another (Figure 20). A clarification pond is located underneath of the holes. The flow rate of the water from the smaller hole is 1.3 L/s. The copper concentration here (157 ml/L) is greater than that in the level above. In contrast, concentrations of iron and zinc are only slightly different from the +270 m level, with iron measured at 974 mg/L and zinc at 1 320 mg/L. The concentration of sulfate at this level (23 300 mg/L) is also greater than in the above level.

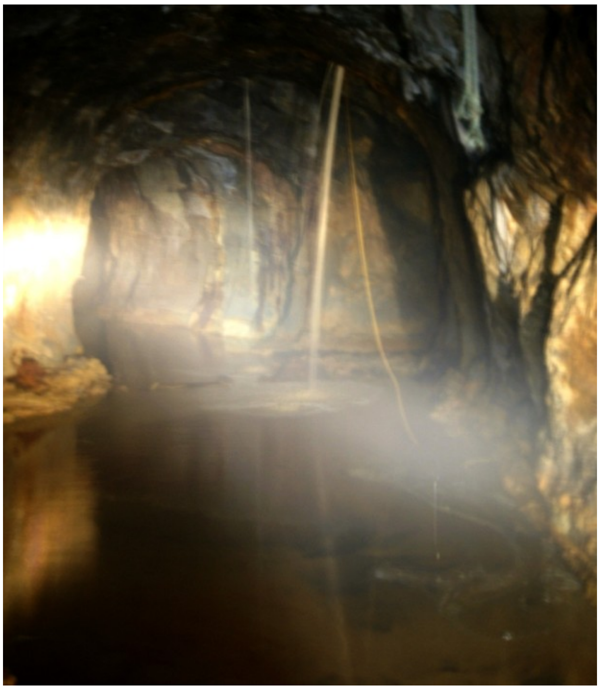


Figure 20 – A clarification pond and the water holes at the +360 m level (Photo: Haanela 11.4.2012).

The flow rate of the larger hole is 3.3 L/s, and the sulfate concentration is higher than in the smaller hole (27 400 mg/L). Metal concentrations are also much higher at this point: Copper is to 246 mg/L, zinc 2 300 mg/L, and iron 2 660 mg/L. Water from this pond goes to the +400 m level.

At the +365 m level, water comes from both a ventilation raise and from a water hole which is situated above the tunnel. Water flows on the level as a small stream and therefore, the flow rate could not be measured, though from previous measurements it was estimated to be ~2.3 L/s. Water from the +365 m level travels to the +470 m level where the measured flow rate of the water is 3.0 L/s. The water here is not acidic (pH 6.3) and metal concentrations are much lower than at higher levels (copper 0.2 mg/L, zinc is 10.6 mg/L, and iron is 14.7 mg/L). The temperature is low at only 5.8 ˚C, but is greater than at the +365 m level, where it is 2.6 ˚C. Because of the low metal concentrations and temperature, water at the +365 m and +470 m levels may come from the water deposit nearby without contacting the surface of the sulfide minerals and for that reason the metals are not dissolved.

Zinc concentration rise even higher (comparing to the + 360 m level) at the + 400 m level (to 2 800 mg/L). Copper concentration is 245 mg/L and iron is 2 300 mg/L. The flow rate of the water coming from the hole is 2.3 L/s, and it decreased (1.1 L/s) from the water at the + 360 m level. Water from level + 400 m goes to the aeration tank located at level + 500 m.

The water at the +500 m level comes from several locations: the aeration tank, the drill hole and the water steps. The flow rate of the water coming from the drill hole is 0.1 L/s and only the zinc (1 410 mg/L) and sulfate (18 800 mg7L) concentrations of the water are high.

The flow rate of the water from the steps is 0.4 L/s (Figure 21). This water originates from level + 455 m. Concentrations of metals are significantly high (copper 623 mg/L, zinc 5 900 mg/L, and iron 3 400 mg/L) in this water. The sulfate concentration is also very high at 61 600 mg/L. The water steps have been made to collect sludge from the water. Sludge was not collected on the steps at all due to the pH of the water being very low (2.3).

Figure 21 – Water steps at level + 500 m (Photo: Haanela. April 11, 2012).

Metal concentrations of the water in the tank are lower than concentrations of the water above (copper 76.0 mg/L, zinc 820 mg/L, and iron 439 mg/L) because the water in the tank is mixed with the low metal concentration water coming from the + 470 m level. The flow rate of the incoming water is about 15 L/s.

All the water coming from level + 500 m travels to the water hole at level + 560 m (Figure 22) via level + 530 m. At the level + 530 m, the flow rate of the water could not be measured. At level + 560 m, water comes from two locations. The flow rate of the water is 12 L/s. Metal concentrations are relatively high (copper is 107 mg/L, zinc is 986 mg/L, and 572 mg/L). From level + 560 m, the subsequent level is + 600 m, where the flow rates could not be measured. The next level is + 630 m.

Figure 22 – Water hole at level + 560 m (Photo: Haanela. April 11, 2012).

Two pumps, a pump tank and three aeration tanks are located on level + 630 m. One of the three tanks is used as a reserve tank, which is in operation while others are emptied and cleaned. All the water from levels above + 630 m is collected and directed to a separate tank. The flow rate of the water coming to the tank is 16 L/s. Water from levels below level + 630 m is pumped into the another aeration tank and the average flow rate of the water is about 12.3 L/s. From the aeration tanks, water goes to the pump tank at level + 645 m and from the pump tank, it is then pumped to the ground level.

8.1.2 Waters between levels + 630 m and + 970 m

At level + 720 m, metal concentrations are lower than in the levels above (copper 4.41 mg/L, zinc 242 mg/L, and iron 52.6 mg/L). The pH of the water is still low (3.2), though not as acidic as water at higher levels.

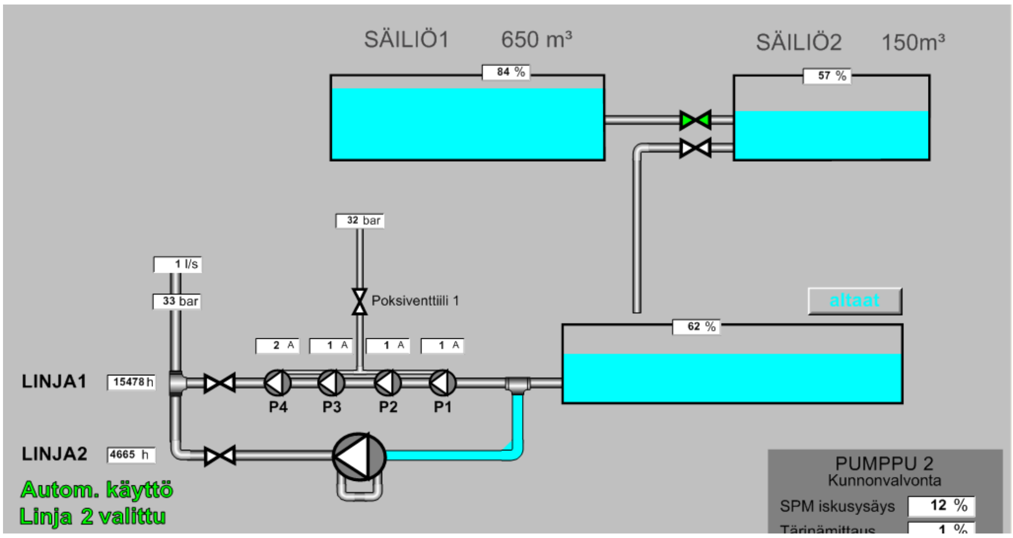
At level +750 m, the flow rate is 3.3 L/s. There is an increase in copper concentration (10.2 mg/L), but zinc and iron are near zero.

The copper concentration at level + 780 is nearly same as level + 750 m. Yet, zinc and iron concentrations were significantly higher (zinc 369 mg/L and iron 856 mg/L). In the levels between + 810 m and + 930 m, metal concentrations remain nearly the same as in level + 780 m. The water temperature rises at these levels to about 21 ˚C.

Other water steps have been built at level + 890 m (Figure 23). As opposed to the steps at level + 500 m, sludge is collected on these steps. The pH of the water is 2.5 which is 0.2 of a pH unit greater than the water steps at level + 500 m. The flow rate of the water going to the steps is 5.5 L/s. From the steps, water goes to level + 930 m and continues on to the aeration tank at level + 970 m.

Figure 23 – Water steps at level + 890 m (Photo: Haanela. April 11, 2012).

Two clarification tanks and a pump tank are located at level + 970 m (Figure 24). Water from levels below level + 630 m and water from below level + 970 m are pumped into the clarification tank, and then directed to the pump tank. Clarifications which occurs in the tank and the water pumped from the levels below the level + 970 m lowers metal concentrations in the tank (copper 5.26 mg/L, zinc 159 mg/L and iron 343 mg/L). Water is pumped to the tank at level + 630 m.



SPM iskusysäys 12 %

Tärinämittaus 1 %

Figure 24 – Aeration and pump tanks at level + 970 m.

8.1.3 Water between levels + 970 m and + 1450 m

An old drilling hole is located at level + 1075 m. The flow rate of the water is high but it could not be measured. Metal concentrations are low, near zero, but electrical conductivity is significantly high (1 020 mS/m) due to high salinity of this water.

The flow rate of the water at level + 1125 m is 0.2 L/s. The metal concentration at this level are lower than in levels above, but the water is still strongly acidic (pH is 2.9). The next level is + 1150 m where the flow rate increases to 1.1 L/s. The metal concentration of the water lowers again (copper 7.44 mg/L, zinc 123 mg/L and iron 265 mg/L). However, the amount of sulfate is higher (8 433 mg/L).

At level + 1300 m and below all the waters consists of fresh water which is pumped to the mine. The pumping station is located at level + 1300 m. Water is pumped from the levels between levels + 630 m and + 970 m to the aeration tank at level +970 m. Metal concentrations are not high in these waters (< 1 mg/L of copper, zinc and iron) and the pH is higher (5.2).

A submersible pump is located at level + 1425 m, which pumps waters from levels + 1325 m and + 1375 m to the pump tank at level + 1430 m. At level + 1430 m, water is pumped from the bottom of the mine (+ 1450 m) and from + 1425 m, to the pump tank at level + 1300 m. An oil separation tank is located at level + 1430 m. The tank is designed in a way that oil floats to the surface and water leaves the tank beneath the surface.

8.2 Annual changes in mine drainage water

The following Figures are compiled from previous water analyses made in Pyhäsalmi Laboratory. Figure 25 presents the changes and the mean of water amount pumped from the mine. As can be seen from the Figure, surface water changes affect the amount of mine drainage water with a time delay. Snow begins to melt in Pyhäsalmi between March and April. Water from the snowmelt period can be seen in the increasing mine water amount by May.

According to the Figure 25 the monthly amount of the pumped underground water in April, 2012 (75 000 m^3) is close to the mean value between January, 2011 and July 2012 (78 000 m^3). Therefore, the flow rates of the underground waters recorded in the present study are considered to equate to mean annual values.

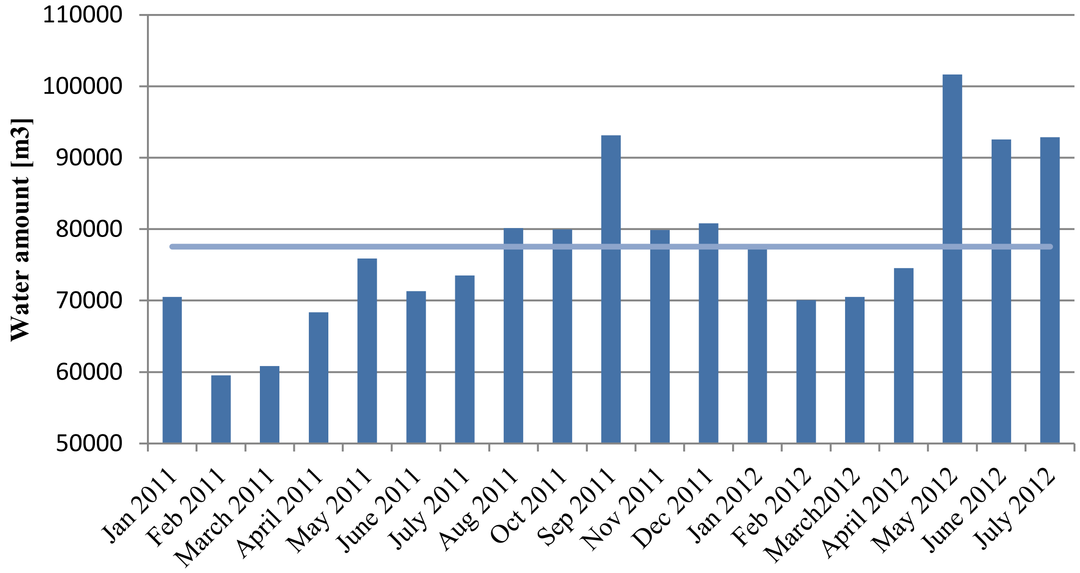


Figure 25 – Amount of water pumped monthly [m^3/month] and a mean value between January 2011 and May 2012.

Variations in water volumes pumped from the mine appear to be inversely correlated to concentrations of dissolved metals. Figures 26 – 29 shows the copper, zinc, iron, and sulfate concentrations measured from the pumping station at the level + 630 between January 2011 and July 2012. From Figures 26 – 29, it can be seen that the volumes of water pumped out of the mine and metal concentrations reach the minimum and maximum values at the same times during the year.

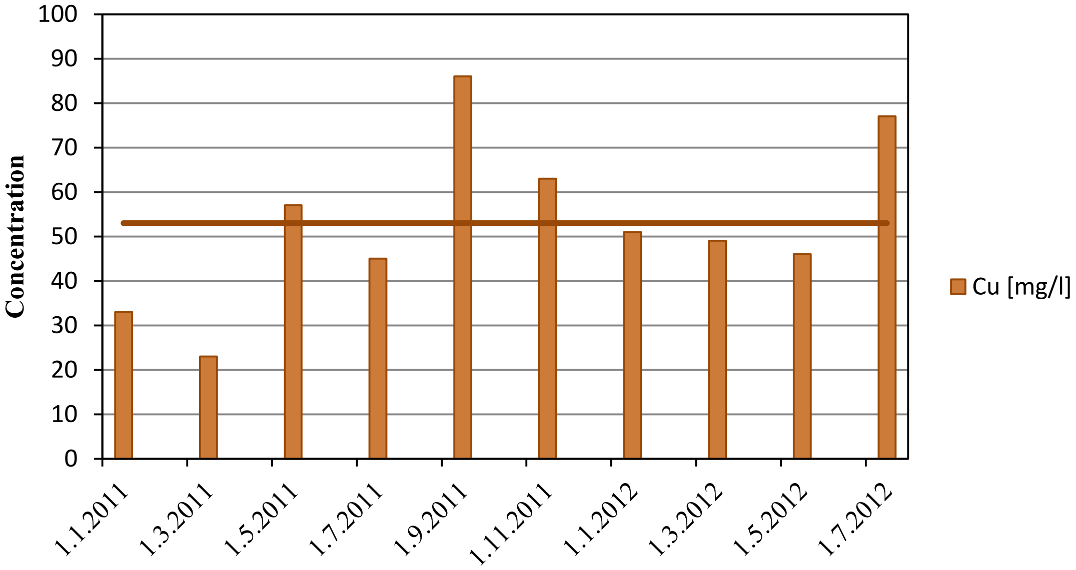


Figure 26 – Copper concentration [mg/L] and a mean value at level + 640 m between January 2011 and July 2012.

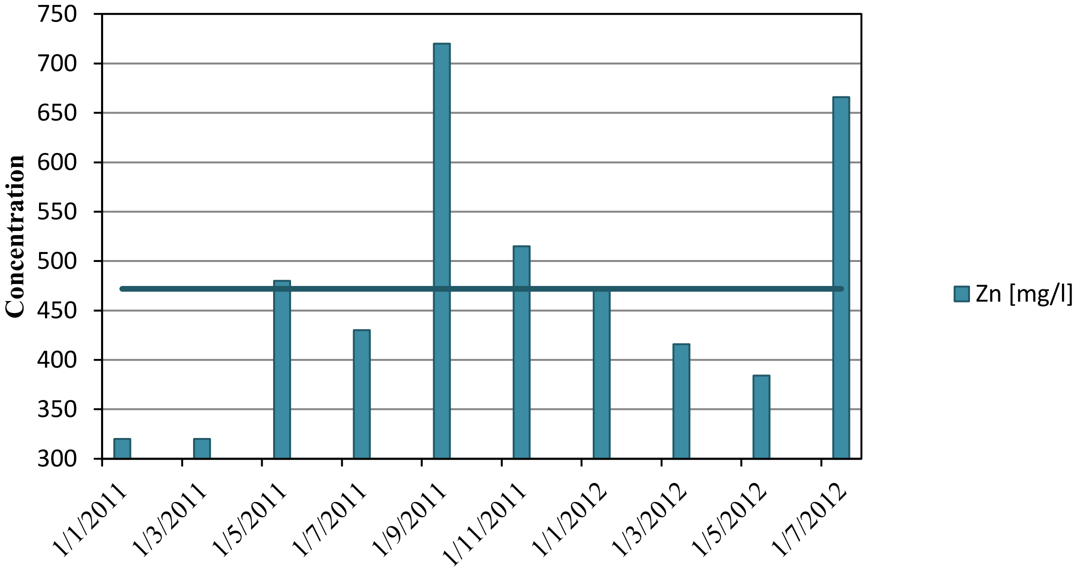


Figure 27 – Zinc concentration [mg/L] and a mean value at level + 640 m between January 2011 and July 2012.

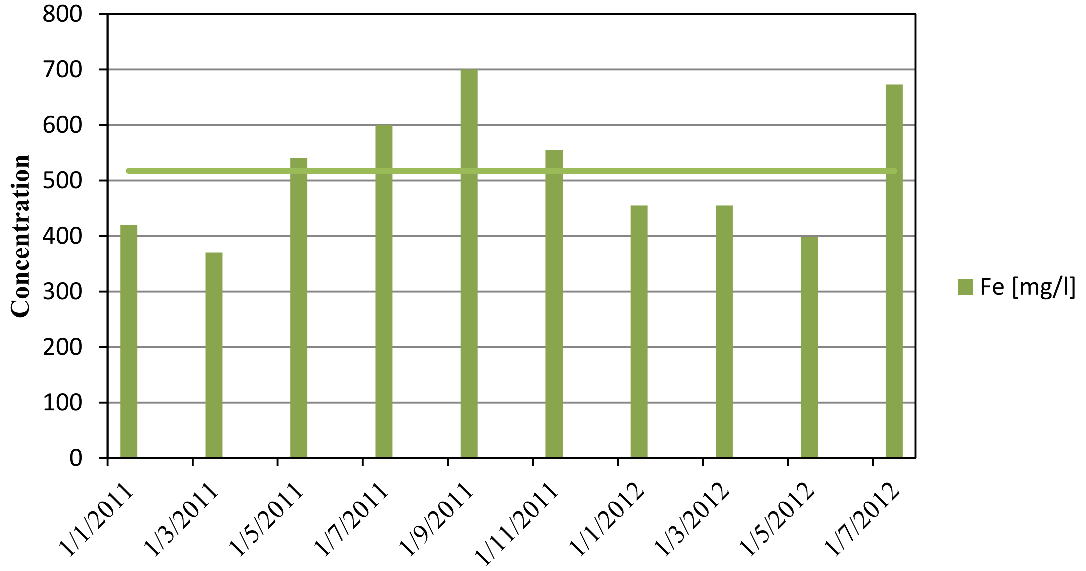


Figure 28 – Iron concentration [mg/L] and a mean value at level + 640 m between January 2011 and July 2012.

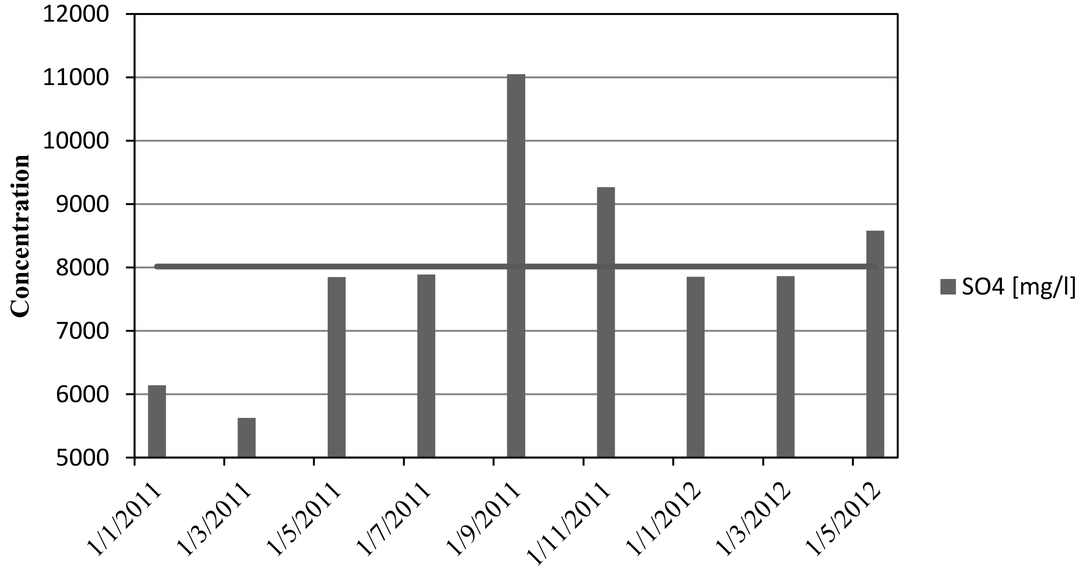


Figure 29 – Sulfate concentration [mg/L] and a mean value at level + 640 m between January 2011 and May 2012.

Sulfate concentration changes are related to the metal concentration changes. According to Figures 26 – 29, it can be assumed that metal and sulfate concentrations are related to the amount of mine drainage water.

8.3 Alternative locations of the bioreactor system

The proposed bioreactor system contains two parts, ferrous iron is oxidised by Ferrovum myxofaciens in the first module, and the ferric iron generated is precipitated as the mineral schwertmannite in the second module. The bioreactor set up is described in detail in the section 6.

Option A

The reactor system could be located at level + 630 m and the iron is removed from all the water before pumping to the ground level. An advantage of option A is that only one reactor system is needed and all the water would be cleaned at the same time. The disadvantage of option A is that the iron still causes lots of problems in the pipe lines and pumps at level + 970 m.

Option B

Two reactor systems would be located at the mine. One system would be positioned at level + 630 m, where iron could be removed from the water coming from above. Another system, at level + 970 m, would see the iron removed from the water coming from the levels between + 630 m and + 970 m. Option B would enable to major cost savings in the maintenance expenses.

The flow rates of the water going through the reactors would be less in option B and the smaller reactor size would be sufficient. Additionally, the amount of precipitated schwertmannite would be significantly more in this option due to all the iron being recovered.

8.4 Operational parameters for biomineralisation of schwertmannite

Total iron concentration used in tests carried out with synthetic mine water was 372 mg/L, and ferrous iron concentration was 33 mg/L in Alternative 1. In Alternative 2, total iron concentration is 748 mg/L, and concentration of ferrous iron is 72.6 mg/L in the water at level +630 m. In the water at level + 970 m total iron concentration is 1 149 mg/L, and concentration of ferrous iron is 119 mg/L. Chemical composition of mine waters is shown in Tables 3 and 4.

Table 3 – Content of the mine water at level + 630 m (Alternative 1).

Analyte	**Concentration [mg/L]**
SO_4	8 580
Fe	339
Fe^{2+}	33
Al	192
As	<0.04
Cu	5.26
Mn	20.3
Zn	159
pH	2.7
Cond. [mS/m]	774
Flow rate [L/s]	28.3

Table 4 – Content of the mine water at levels + 630 m and + 970 m (Alternative 2).

Level	**+ 630 m**	**+ 970 m**
Analyte	Concentration [mg/L]	Concentration [mg/L]
SO_4	10 300	11 400
Fe	675	1 030
Fe^{2+}	72.6	119
Al	503	467
As	<0.05	<0.05
Cu	76.4	12.5
Mn	39.5	41.6
Zn	659	290
pH	2.5	2.5
Cond. [mS/m]	951	1 060
Redox [E_h]	734	718
Flow rate	16 L/s	6.8 L/s

The calculated hypothetic flow rate in iron oxidation/precipitation system in Alternative 1 is 57 L/min. In Alternative 2, the calculated flow rate is 68 L/min. (Table 5)

Table 5 – Operational parameters from the developed iron oxidation/precipitation system. (Data provided by Prof. Johnson and Dr. Kay).

	Alternative 1 Level + 630		**Alternative 2 Level + 970**	
	100 % Fe^{2+}	Combined Fe^{2+}/Fe^{3+}	100 % Fe^{2+}	Combined Fe^{2+}/Fe^{3+}
Fe^{2+} [mg/L]	339	33	1,000	100
Fe^{3+} [mg/L]	0	306	0	900
Fe^{2+} oxidation[%][1]	98.5	85	99.5	95
Dilution rate [h^{-1}]	0.17	0.34	0.19	0.41
Projected flow rate [L/min][2]	28	57	32	68

[1] required to generate the target discharge water (5 mg Fe^{2+}/L in all cases)

[2] 10 m^3 bioreactor

The amounts of NaOH required to raise the pH of the oxidized water to 3.5 is independent of the relative concentrations of ferrous and ferric iron in the pre-oxidized mine water. Based on the amounts consumed in processing the two test mine waters (combined Fe^{2+}/Fe^{3+}), the extrapolation can be made. Required NaOH amounts are showed in Table 6.

The required amounts of the flocculant used by Hedrich and Johnson (2012) (FLOCCIN 1105) are extrapolated from the amounts used in the laboratory. These amounts are shown in Table 6.

Table 6 – The required amounts of NaOH and FLOCCIN 1105 in module 2. (Data provided by Prof. Johnson and Dr. Kay).

	NaOH	**FLOCCIN 1105**
	[kg/m^3]	[kg/m^3]
Option A		
+ 630 m level	0.9	0.15
Option B		
+ 630 m level	1.7	0.6
+ 970 m level	2.2	0.9

8.4.1 Precipitation of schwertmannite

Table 7 – Molecular weights of Fe, O, H, and S.

Element	**M [g/mol]**
Fe	55.845
O	16.000
H	1.0079
S	32.065

The total iron amount of the discharging from module 2 is 5 mg/L.

$$\mathrm{m}_{Fe_8} = 0.339\ \mathrm{g/L} - 0.005\ \mathrm{g/L} = 0.334\ \mathrm{g/L}$$

Molecular weight of idealized schwertmannite (Table 7):

$$\mathrm{M}_{Fe_8O_8(OH)_6(SO_4)} = (55.845 \cdot 8 + 16.000 \cdot 8 + (16.000 + 1.0079) \cdot 6 + 32.065 + 16.000 \cdot 4 \mathrm{g/mol} = 772.9\ \mathrm{g/mol}$$

Molecular weight of Fe_8:

$$\mathrm{M}_{Fe_8} = 55.845\ \mathrm{g/mol} \cdot 8 = 446.8\ \mathrm{g/mol}$$

Amount of Fe_8:

$$n_{Fe_8} = \frac{m_{Fe_8}}{M_{Fe_8}}\frac{0.334\ \text{g}}{446.8\ \text{g/mol}} = 0.000749\ \text{mol}$$

Mass of precipitated schwertmannite:

$$m_{Fe_8O_8(OH)_6(SO_4)} = 0.000749\ \text{mol} \cdot 772.9\frac{\text{g}}{\text{mol}} = 0.578\ \text{g/L}$$

The flow rate of water (coming from levels above) on level + 630 is 16.0 L/s and on level + 970 (water coming from the levels between + 630 and + 970) is 6.8 L/s (April 2012). The annual amount of water in option A is approximately 908 000 m^3. In option B, the annual amount of water at level + 630 is about 505 000 m^3 and at level 970 is about 214 000 m^3. The calculations of the amounts of precipitated schwertmannite are presented in Table 8.

Table 8 – Calculated amount of precipitated schwertmannite in the alternative schemes.

Location	**m_{Fe}**	**M_{SCH}**	**M_{Fe8}**	**n_{Fe8}**	**m_{SCH}**	**m_{SCH}**
	[g/L]	[g/mol]	[g/mol]	[mol/l]	[g/L]	[kg/a]
Option A						
630	0.334	773	447	0.000740	0.578	525 000
Option B						
630	0.670	773	447	0.00150	1.16	586 000
970	1.03	773	447	0.00223	1.77	379 000
Total (Option B)					2.93	965 000

8.4.2 Sulfate removal

Schwertmannite also contains structural sulfate. The amount of sulfate removed from the mine water is calculated in Table 9. Because the total amount of the sulfate that is removed in the precipitated schwertmannite is very small, the change of the discharging is not considered in the results.

Table 9 – Calculated amount of sulfate removed in schwertmannite.

Location	**m_{SO4}**	**M_{SO4}**	**m_{SCH}**	**M_{SCH}**	**n_{SCH}**	**m_{SO4} (in SCH)**	**Removed sulfate**
	[g]	[g/mol]	[g/L]	[g/mol]	[mol/min]	[g/min]	[%]
Option A							
630	8.58	96.1	0.578	773	0.000740	0.0748	0.837
Option B							
630	10.3	96.1	1.16	773	0.00150	0.144	1.40
970	11.4	96.1	1.77	773	0.00223	0.220	1.90

9 Cost estimation

Costs are estimated for the maintenance of the underground pipes and pumps and also for further cumulative effects caused by the iron in the mine water. Operational costs of the reactor system are estimated and the planned running costs after mine closure are explained. In the conclusions, the current costs are compared to the operational costs of the bioreactor system.

9.1 Maintenance costs

The annual maintenance expenses of mine dewatering are significant. Almost all of the maintenance needs are a result of the high concentration of iron in the water needing to be pumped from the mine. In addition to underground maintenance, iron precipitates cause problems to the ventilation system and heat exchanger at ground level. The annual maintenance cost estimation showed in Table 10 is based on the actual annual maintenance cost of between July 2011 and July 2012. The maintenance needs explained in this chapter are based on the long experience of maintenance superintendent Risto Mäkeläinen and maintenance foreman Matti Moisala.

Iron precipitates on the internal surface of the pipes. When the amount of the precipitated iron on the surface increases, the required power of pumping increases and as a result the pipe becomes clogged. To prevent clogging, the pipe lines need to be cleaned regularly. Cleaning usually carried out biannually by use of high pressure hydrocleaning. Discharging pipes need an expensive element cleaning approximately once or twice every two years. Element cleaning of the long pipe lines of more than 100 meters is carried out by inserting the elements into the pipe and water pressure forcing the elements to move through the pipe.

Sludge entering a pump can damage the pump and reduce its life expectancy. Pump repair is a relatively expensive endeavor. The pumps utilized in the mine are Sulzer HPP-high pressure pumps.

Mine drainage water is used in a heat exchanger to heat the fresh air blown into the underground mine areas during the winter. The air blown underground must be at least 4 ˚C. If the air is less than 4 ˚C, ice or snow will form inside of the mine. The heat energy recovered from mine water can raise the air temperature by up to 17 degrees. In the case that the outside air temperature is below - 13 ˚C, district heat is used. If ventilation station heat exchangers become clogged by sludge, only expensive district heat can be used for heating the fresh air. Heat exchangers need to be cleaned as well, when the outside temperature has increased enough.

Sludge is collected in the clarification tanks and ponds in the underground mine. Sludge needs to be removed from the ponds, and tanks need to be cleaned approximately once a month. The removed sludge is relocated to old stopes by shovel loaders.

The heat exchanger and the ventilation station need to be cleaned regularly due to the precipitated iron. The water tanks of the ventilation stations need to be emptied and washed approximately twice a year.

Table 10 – Yearly maintenance cost caused by high iron concentration in the mine drainage waters.

Maintenance unit	**Description**	**Cost [€]**
Pipe lines and pumps	Cleaning, repairing	517 000
Sludge treatment	Sludge removing, cleaning	41 000
Heat exchanger	Cleaning	10 000
	District heating	50 000
Total		618 000

9.2 Reactor system costs

Operating costs of the reactor system related to the consumption of the chemicals required are considered in this section; other running costs of the passive and semi-passive bioreactor systems are considered to be secondary. Annual operating costs are estimated by the information provided by Prof. Johnson and Dr. Kay and the utilized water amounts are based on underground water measurements.

The operating costs of the reactor system include the costs of the required NaOH and FLOCCIN 1021. Based on the current market price of NaOH (around 300 US dollars (USD) per metric ton) the cost of this consumable would be between 0.30 USD and 0.84 USD per cubic meter of mine water. The online price quoted for FLOCCIN 1105, supplied by US-based Integrated Engineers Inc., is 1.65 USD/lb. which is the equivalent of 3.63 USD/kg.

Other consumable costs include the addition of inorganic nutrients to support the growth of the bioreactor. Costs are estimated to be at approximately 0.05 USD per cubic meter of mine water oxidized.

Some cost savings may be achieved by using an alternative flocculating agent. According to Prof. Johnson and Dr. Kay, pre-precipitated schwertmannite itself could be used as a flocculating agent and this use is currently being investigated.

Investment cost of the bioreactor system includes reactor vessels and pumps. The system has two modules. One reactor vessel is needed in the first module and two vessels in the second module. One to two pumps are needed per module, depending on whether gravity is used. According to online prices from various manufacturers, the price of the reactor vessel would run approximately 5 000 – 10 000 euros and a pump would be approximately 5 000 euros. Because of the required reactor size would be large; one possible alternative could be that the existing ponds are used instead of reactor vessels. A challenge for this method is that the pond would quickly become filled with schwertmannite deposits. Schwertmannite removal could be operated for example by sweeping the sludge from the pond.

Based on previous study of underground mine water treatment by sodium hydroxide, the tank needed for the storage of NaOH would be about 20 000 euros and underground dispensing containers cost about 10 000 euros.

The yearly water amount in option A is about 908 000 m^3. In option B, the yearly water amount at level + 630 is about 505 000 m^3 and at level + 970 is about 214 000 m^3. Estimated annual operating costs of the bioreactor system are calculated in Table 11.

Table 11 – Annual operational costs for the bioreactor system in option A and B.

	NaOH US$ / a	**FLOCCIN 1105 US$ /a**	**Nutrients US$ / a**	**TOTAL US$ / a**	**TOTAL €[1] / a**
Option A					
630	245 000	458 000	9 000	712 000	543 000
Option B					
630	258 000	1 018 000	5 000	1 281 000	976 000
970	141 000	647 000	2 000	791 000	603 000
Total (Option B)				2 071 000	1 579 000

[1] Exchange rate used 0.762274 (September 14, 2012).

9.3 Costs incurred following mine closure

The cost estimation of the water treatment after mine closure is based on the “Mine Closure Plan” of Pyhäsalmi Mine (Pyhäsalmi Mine Oy, 2011). This chapter describes the planned operating costs of the water treatment. Biomineralization of iron from the discharge would not affect the planned investment costs and therefore they are not explained. The described expenses are compared to the cost savings estimation through the utilization of bioreactors.

Water treatment is planned to be performed by chemicals. Chemical treatment includes precipitation and clarification. Precipitation is carried out by adding slaked lime ($Ca(OH)_2$) to increase the pH of the water to 10. Due to the increased pH, transition metals and aluminum precipitate as hydroxides and carbonate phases. Following this, the precipitates are separated by settling, and clarified water is directed to the receiving watercourse. The amount of necessary lime is estimated to be about 40 g/m^3 water. (Pyhäsalmi Mine Oy, 2007)

The sludge formed within the settling ponds needs to be removed. The sludge could be stored for example in the area which is separated from the Pond C by an earth dam. (Pyhäsalmi Mine Oy, 2007)

Estimated costs in option 1

The annual treated water amount is estimated to be about 100 000 m^3 (11 m^3/h) if the mine is closed and mine dewatering has been halted. The design flow for the water treatment is 35 m^3/h. The estimated annual operating costs are showed in Table 12. (Pyhäsalmi Mine, 2011).

Table 12 – Annual operating costs of water treatment after mine closure in option 1 (Pyhäsalmi Mine, 2011)

Description	**Cost [€]**
Slaked lime, 200€/a x 4 t/a	800
Electrical energy	1 500
Salary expenses (running and management)	20 000
Observation and monitoring of discharging	10 000
Maintenance expenses	5 000
Sludge removing	5 000
Total	42 000

Estimated costs in option 2

The annual treated waste water amount is estimated to be about 1 000 000 m^3 (114 m^3/h) if the mine is closed but other activities are relocated within the mine. The design flow for the water treatment is 120 m^3/h. The estimated annual operating costs of the option 2 are shown in Table 13.

Table 13 – Annual operating costs of water treatment after mine closure in option 2.

Description	**Cost [€]**
Slaked lime, 200€/a x 4 t/a	8 000
Electrical energy	6 000
Salary expenses (running and management)	25 000
Observation and monitoring of discharging	17 000
Maintenance expenses	10 000
Sludge removing	30 000
Total	96 000

9.3.1 Bioreactor system expenses and schwertmannite production

Based on the iron concentration (Table 14) the amount of precipitated schwertmannite would be 0.13 kg/m^3. In both of the closure options, the estimated water amount which is treated at the ground level is about 100 000 m^3 per year, because the iron from the mine water would be removed underground in closure option 2. The precipitated schwertmannite amount would be 13 000 kg annually.

Table 14 – Estimated content of water in the tailing area after mine closure (average values for the last 5 years from P3).

Analyte	**Concentration [mg/L]**
Cu	2.2
Zn	29
Fe	75
Mn	15
SO_4	2 000
pH	3.2
Cond. [mS/m]	280

Calculated operational costs of the reactor system used in the tailing pond area after mine closure are shown in Table 15.

Table 15 – Estimated operational costs of the reactor system in the tailings area after mine closure.

NaOH US$ / a	**FLOCCIN 1105 US$ / a**	**Nutrients US$ / a**	**TOTAL US$ / a**	**TOTAL €[1] / a**
9 000	10 000	1 000	20 000	15 000

[1] Exchange rate used 0.762274 (September 14, 2012).

10 Safety aspects

Chemicals needed in the bioreactor system can be toxic and work safety needs to be considered when planning new systems. The bioreactor system would be located underground and therefore, special safety precautions need to be taken, especially if the chemicals used are toxic, flammable, or explosive. Safety risks caused by the use of chemicals are explained in this chapter and possible solutions for lowering the safety risks are described.

According to the IPCS, sodium hydroxide (NaOH) is classified as UN hazard class 8. NaOH is a toxic alkaline chemical and it needs to be handled and stored carefully. Solution is a strong base and it has to be stored in an alkali-resistant floor. NaOH is corrosive to soft metals and therefore unsuitable for containers that are comprised of aluminum, zinc, tin, lead, and glass. Solutions reacting with aluminum or other soft metals generate hydrogen, which is a flammable and explosive gas. (ISCS 0360)

The substance is also corrosive to the eyes. Respiratory irritation and chemical burns can result if NaOH particles are inhaled. The solution can cause severe irritation and chemical burns when it comes into contact with the skin. A face shield or eye protection in combination with breathing protection, and protective gloves and clothing should be used if handling of solution. (ISCS 0360)

Sodium hydroxide consumption in iron precipitation reactor would be between 2 500 kg and 3 200 kg per day. Because of the high chemical consumption, NaOH should be stored at the ground level and directed to the underground via pipe line. An old backfilling pipe line could be used at least to level + 470 m. If the existing line is not possible to use below level + 470 m, a new line has to be made by drilling. The old pipe line passes the ramp at levels + 150 m, + 365 m, and + 850 m, where the pipeline must be protected so that passing vehicles do not damage the lines. Locations of containers to store NaOH need to be chosen to prevent any possible overflow of NaOH from causing any damage.

The other chemical required in the current configuration of the bioreactor system is the flocculating agent FLOCCIN 1105 supplied by Integrated Engineers Inc. According to Integrated Engineers Inc., Floccin products are formulated with chemicals that are either approved by National Science Foundation (NSF 10) for drinking water application, approved by Food and Drug Administration (FDA) for direct human contact, or meeting Generally Recognized as Safe (GRAS) status as defined by the FDA. Therefore, the flocculating agent could be safely used underground and no personal protective equipment is necessary for handling the material. (Integrated Engineers Inc., 2012)

11 Conclusions and future operations

The survey of the underground water shows that the mine drainage water has the highest metal concentrations between levels + 240 m and + 970 m. The concentration of iron is especially significantly high within these levels. Based on the laboratory analyses, 90 % of the iron was oxidized underground due to the microbial activity found in the water samples. Water amounts and chemistry changes are significant throughout the year, but based on the previous analyses of the last year, the results correlate with annual average values.

The iron content of the water is the main reason of the existing high maintenance needs of the pipe lines and pumps due its precipitation. In addition, iron precipitation causes large amounts of waste sludge which is stored in the old underground stopes. Furthermore, the sludge may end up back in the pipes and pumps from the repository due to its water content.

Bioreactor experiments with synthetic Pyhäsalmi Mine water showed positive results. Iron-oxidation was quick and the remaining ferrous iron concentrations stayed within the target discharge limits in all of the tests performed. In addition, the used Fe^{2+}/Fe^{3+} ratio existing in the mine water enabled fast flow rates of the bio-oxidation reactor. Alkali addition generated the schwertmannite mineral precipitation, and its fast sedimentation was ensured by flocculating agent.

The needed chemicals in the reactor system are sodium hydroxide and flocculating agent. Sodium hydroxide is a toxic substance and the required amount is high, but with a preventative safety plan, the risks can be controlled. The flocculating agent FLOCCIN 1105 can be safely used without any significant safety risks.

The expenses of the used chemicals in the bioreactor system in the both of the options were high. In the option A, where all the water is treated at level + 630 m, the estimated costs of the bioreactor system were nearly the same as the maintenance costs resulting from the iron in the water. Since the water is treated at level + 630 m, the iron-rich water needed to be pumped from the levels between + 630 m and + 970 m, and this still caused problems with the pipes and pumps on these levels. Therefore, approximately half of the maintenance costs would remain.

In option B, the two reactor systems are located within the mine. One system processes the water at level + 630 m and another at level + 970 m. This option enables all the iron to be removed from the water, and as a result, the pumps and pipes remained clean and sludge was not formed. However, the chemical needs in of the both reactor systems would be four times as much as the existing maintenance costs. If the bioreactor system expenses are compared only to the maintenance expenses, the reactor system would not be realistic. Since the pH of the discharging water is low and it contains heavy metals, it needs to be treated by alkalization. Therefore, cost savings with alkalization are minimal. However, the waste sludge precipitated from the mine water in the tailings ponds would be less if the iron is selectively removed from the water.

The added flocculating agent is the most expensive aspect of the process. According to Prof. Johnson and Dr. Kay some savings could be achieved by using an alternative flocculating agent, such as pre-precipitated schwertmannite which is currently being investigated. If FLOCCIN 1105 is not used, the system could offset the maintenance cost. Furthermore, if schwertmannite could be sold to the customers in the future, the process will be actually cost-effective. The schwertmannite mineral is currently being investigated as a pigment or sorption material in the treatment of water contaminated by materials such as phosphate, selenate, molybdate, antimony and polyphenols.

The bioreactor system does not result in any major cost savings in the treatment of water after mine closure in the tailings area, with only sludge disposal costs benefiting. The operational costs of the bioreactor system would increase the total costs by a factor of two, but as in the other case, significant savings are possible by using an alternative flocculating agent. Also the value of the precipitated schwertmannite would decrease the expenses. In the long term, some benefits could be achieved in the tailing pond area through the decrease in the waste sludge amount.

Table 16 compares the annual operating costs of the bioreactor system to the maintenance cost savings. In addition to the covered operational costs, the reactor system also needs electricity for the pumps, monitoring, and maintenance operations. However these costs would be relatively minor and thus they are not included in these calculations. Operational costs and net costs of the reactor system without FLOCCIN 1105 are also calculated in Table 16.

Table 16 – Estimated net annual costs of the bioreactor system.

	Option A	**Option B**	**After closure**
Operational costs	543 000 €	1 579 000 €	15 000 €
Maintenance cost saving	309 000 €	618 000 €	
Operational costs[1]	194 000 €	309 000 €	8 000 €
Net costs	234 000 €	961 000 €	15 000 €
Net costs[1]	-115 000 €	-309 000 €	8 000 €
SCH production	525 000 kg	965 000 kg	13 kg

[1] Operational costs of the reactor system without the FLOCCIN 1105 agent

The ore deposit of the Pyhäsalmi Mine is estimated to last until 2018. If mine dewatering continues after mine closure, implementation the bioreactor system could be a viable option. In this the case, the operational cost of the reactor system should be less with an alternative flocculating agent and schwertmannite at the existing market value. If the mine is filled with water after the closure, the only option for the bioreactor system would be the discharging of waters from the tailings area. Based on the estimated chemical composition of the seepage flow from the tailing ponds, the iron content is insignificant. Therefore, benefits from iron precipitation would be minimal.

In future operations, iron oxidation and a precipitation bioreactor system could potentially extract valuable minerals from the waste and the need of new raw materials could be potentially less. This would help achieve sustainable development by utilizing waste material as a useful product.

12 Summary

Pyhäsalmi Mine is a copper, zinc, and pyrite mine in central Finland. The ore contains 75 % sulfides on average; 3 % chalcopyrite, 6 % sphalerite, 2 % pyrrhotite, and 66 % pyrite. Ground water seeping into the mine makes contact with fresh rock surfaces and reactive and soluble minerals are dissolved into the water. Acidity is results from the several chemical reactions making the undergrounds water are highly acidic and containing large amounts of metals and sulfates. Mine drainage water is treated at the tailing ponds by alkalization.

The survey of the underground water showed that the most acidic and iron-rich water is located on the levels between + 240 m and + 970 m. On these levels, the iron content of the water is so high that it causes significant maintenance problems to the pumps and pipe lines. Iron precipitates on the internal surface of the pipes and they become clogged without regular cleaning. The sludge formed may damage the pumps and reduce the life expectancy of these costly pumps. In addition, the sludge needs to be removed from the clarifications ponds and stored at the old stopes. Stored sludge may end up back in the pumps and pipes because it is not stabilized.

The chemical composition of the underground water showed that 90 % of the iron has been oxidized underground to a ferric form, despite the highly acidic water. Bacterial analyses proved that it could be due to the microbial activity. The chemistry of the water samples from the two locations were used to prepare synthetic mine water, which was used in iron bio-oxidation and precipitation experiments. Laboratory scale experiments were performed in Bangor Laboratories by Prof. Barrie Johnson and Dr. Catherine Kay. Bioreactor tests showed excellent results, ferrous iron was oxidized in the first module and ferric iron was precipitated as pure schwertmannite mineral, as expected. The results from the laboratory scale experiments were used for extrapolating operational parameters for a full-scale bioreactor system.

The main drawback of the bioreactor system was the operational expenses due to chemical needs. According to Prof. Johnson and Dr. Kay, the total cost of the reagents used in the schwertmannite precipitation is between 0.85 USD and 5.38 USD per cubic meter of water, depending on its iron content. The annual mine drainage water amount is about 900 000 m^3 and the estimated annual costs of the reagents would be between

775 000 USD and 2 914 000 USD depending on the iron content and amount of treated water.

The annual cost saving from the maintenance expenses of the underground mine dewatering is about 618 000 euros. According to Prof. Johnson and Dr. Kay, other cost savings could be achieved in using pre-precipitated schwertmannite instead of FLOCCIN 1105 as a flocculating agent. This is currently being investigated and in this case, it is possible that about 200 000 euros net cost savings would be achieved in the implementation of this agent. Furthermore, schwertmannite itself has market value and it can be sold as a pigment or a treatment for contaminated water due to its efficient adsorption ability. The amount of schwertmannite generated is estimated to range from 0.58 kg/m^3 to 1.77 kg/m^3. Annual production of schwertmannite would be between 525 000 and 965 000 metric tons.

After the projected mine closure in 2018, bioreactors could be used for treating underground mine drainage water, as it is planned in this work, if the other activities are located within the mine. If the mine is to be filled with water, it is not probable that the bioreactor system will be implemented. A reactor system could be also used for treating the seepage and rain water from the tailing pond area after mine closure. Generated amounts of schwertmannite were estimated by using the water chemistry from the last 5 years of the seepage flow. The projected amount is about 0.13 kg/m^3 which results in 13 000 kg per year. The annual operating costs would be about 24 000 USD in the schwertmannite precipitation process. Due to the small amount of the schwertmannite and the operational costs of the process, this scenario is not likely to be implemented.

The flocculating agent FLOCCIN 1105 is the major cost factor in the bioreactor system. If FLOCCIN 1105 could be replaced, the operational cost would be much less. In this case, the bioreactor system could offset all the maintenance costs. Furthermore, if the schwertmannite mineral has a significant market value in the future, the new system would potentially generate a profit.

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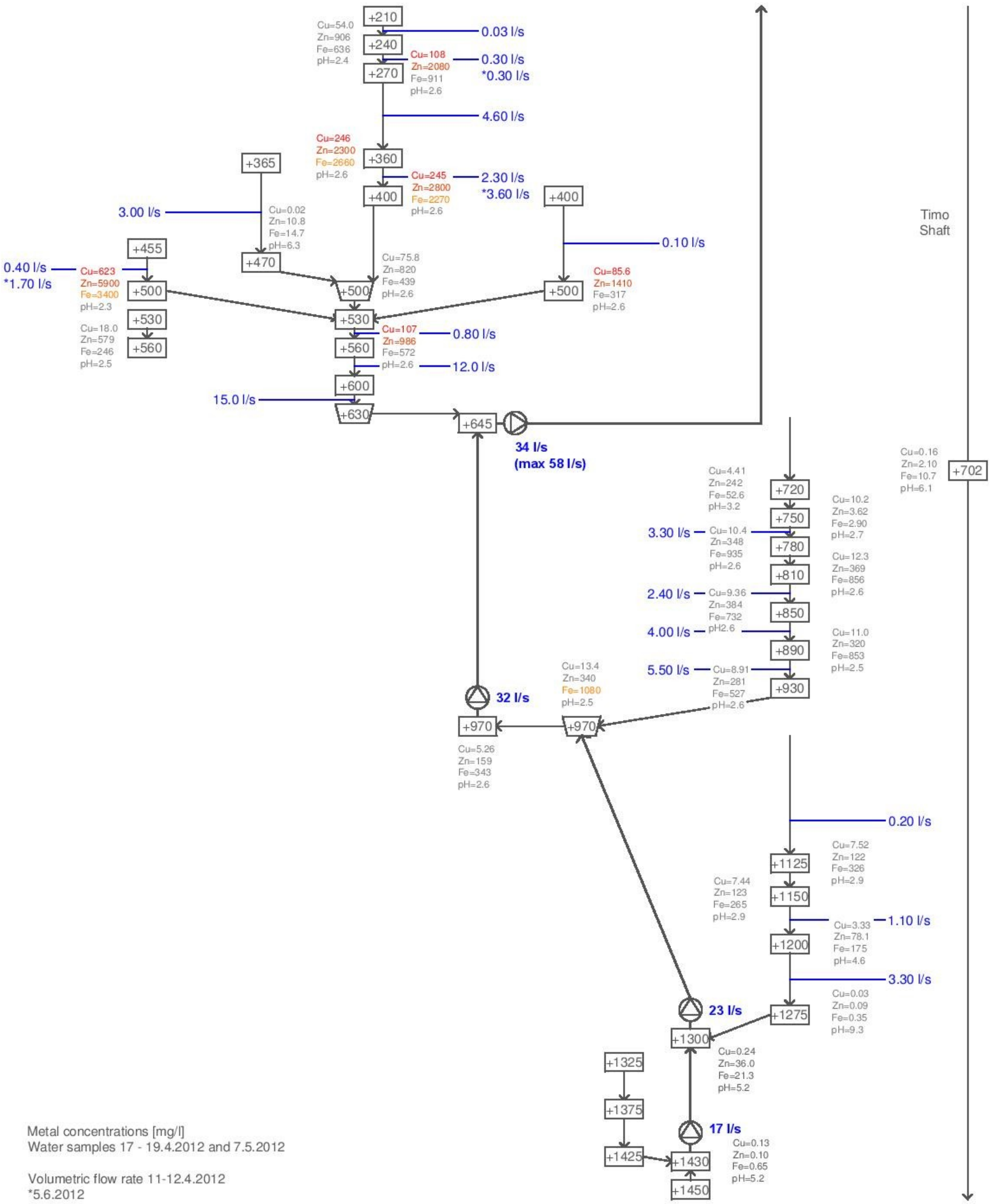
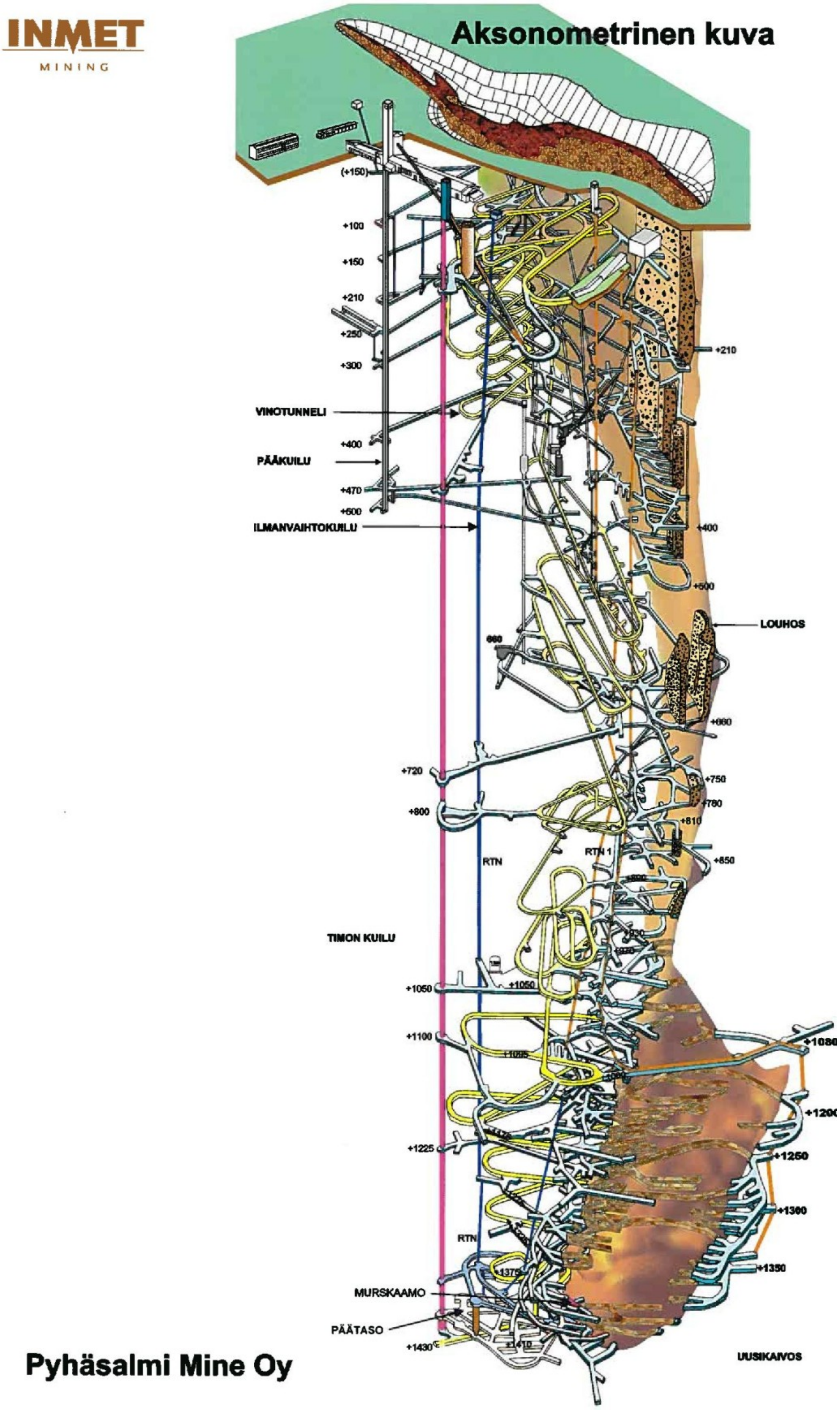
Appendix 1. Flow chart of underground mine waters.



Appendix 2. Axonometric view of underground mine (Pyhäsalmi mine Oy).



Appendix 3(1). Chemical composition of mine water at different depths.

Level	*Location*	*Date*	*T*	*v*	*Cu*	*Cu**	*Zn*	*Zn**	*Fe*	*Fe**	*Fe II*	*Mn*	*Mn**	*As*	*As**	*Al*	*Al**	*Sulfate*	*Redox*	*pH*	*Cond.*
			[˚C]	[l/s]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[E]		[ms/m]
240		17.4.2012	14.1	0.03	54.0	-	906	-	636	-	-	89.70	-	-	-	-	-	20057	499	2.4	1440
270		17.4.2012	13	0.33	108	-	2080	-	911	-	-	80.3	-	-	-	-	-	20120	444	2.6	1540
360	1	7.5.2012	16.8	3.3	246	244	2300	2300	2660	2600	1060	96.3	92.7	0.072	0.062	1660	1660	27400	-	2.6	1740
360	2	19.5.2012	16.8	1.3	157	-	1320	-	974	-	-	91.2	-	-	-	-	-	23300	494	2.7	1670
400		17.4.2012	16.2	2.3	232	-	2280	-	1900	-		113	-	-	-	-	-	29900	449	2.5	2010
400		17.4.2012			245	233	2800	2740	2270	2070	62	112	108	0.077	0.051	1800	1800	31800	-	2.6	2000
470		17.4.2012	5.8	2.3	0.02	-	10.70	-	14.7	-	-	4.16	-	-	-	-	-	683	408	6.3	131
500	POND	17.4.2012	12.7	-	75.8	71.4	820	820	439	434	3.2	39.6	37.7	<0.04	0.016	558	540	9860	-	2.6	876
500	STEPS	17.4.2012	17.5	0.4	623	587	5900	5890	3400	3310	16.2	204	193	0.18	0.17	3780	3730	61600	-	2.3	3010
500	DRILL HOLE	17.4.2012	16.3	0.1	86.0	-	1410	-	317	-	-	78.9	-	-	-	-	-	18800	561	2.6	1510
560		17.4.2012	13.2	12	107	-	986	-	572	-	-	52.1	-	-	-	-	-	13400	487	2.6	1100
560		17.4.2012	19.3	0.75	18	579	246	-	246	-	-	46.3	-	-	-	-	-	9240	504	2.5	928
630	POND (waters above)	12.6.2012	17.4	15	85.0	83.4	764	762	776	593	<0.1	42.8	42.2	0.04	0.023	592	576	10700	-	2.5	973
630	PUMPING STATION	29.5.2012	-	34	46	-	384	-	398	-	-	33.0	-	-	-	-	-	8580	-	2.7	913
		12.6.2012	-	-	71.6	70.7	670	669	643	618	<0.1	41.2	39.5	<0.04	0.021	526	525	10200	-	2.5	949
702	TIMO SHAFT	19.4.2012	-	-	0.16	-	2.10	-	10.7	-	-	0.33	-	-	-	-	-	1560	435	6.1	273
720		19.4.2012	-	-	4.41	-	242	-	52.6	-	-	16.8	-	-	-	-	-	3470	422	3.2	481
750		19.4.2012	-	-	10.2	-	3.62	-	2.9	-	-	42.6	-	-	-	-	-	11000	513	2.7	1000
780		7.5.2012	-	-	10.4	-	348	-	935	436	80	34.6	31.9	0.072	0.016	505	432	8400	-	2.6	820
810		19.4.2012	21.4	2.4	12.3	-	369	-	856	-	-	45.8	-	-	-	-	-	11900	524	2.6	1090
850	DRILL HOLE	19.4.2012	16.2	0.5	0.02	-	0.12	-	0.36	-	-	0.04	-	-	-	-	-	88.0	348	6.4	549
		7.5.2012	20	2.4	9.36	9.17	384	373	732	705	6.14	37.4	35.8	0.041	0.039	471	455	9840	-	2.6	897

Appendix 3(2). Chemical composition of mine water at different depths.

Level	*Location*	*Date*	*T*	*v*	*Cu*	*Cu**	*Zn*	*Zn**	*Fe*	*Fe**	*Fe II*	*Mn*	*Mn**	*As*	*As**	*Al*	*Al**	*Sulfate*	*Redox*	*pH*	*Cond.*
			[˚C]	[l/s]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[E]		[ms/m]
890	STEPS	7.5.2012	20	4	11	10	320	316	853	680	80.8	35.6	33.9	0.045	0.027	456	438	9100	-	2.5	900
930		19.4.2012	21.2	5.5	8.91	-	281	-	527	-	-	37.3	-	-	-	-	-	9190	513	2.6	1000
970	PUMPING STATION	7.5.2012	-	32	5.26	4.77	159	159	343	298	4.30	20.3	18.9	<0.04	0.017	192	185	5260	-	2.6	774
970	AERATION POND	19.4.2012	21.3	-	13.4	11.6	340	325	1080	986	74.0	46.9	43.4	0.05	0.03	510	491	11000	-	2.5	1020
1085	DRILL HOLE	19.4.2012	-	-	0.15	-	0.93	-	1.52	-	-	0.29	-	-	-	-	-	112	379	4.6	4460
1125		19.4.2012	20	0.2	7.52	-	122	-	326	-	-	38.20	-	-	-	-	-	8290	471	2.9	994
1150		19.4.2012	20.9	1.1	7.44	-	123	-	265	-	-	39.9	-	-	-	-	-	8430	465	2.9	996
1200		19.4.2012	-	-	3.33	-	78.1	-	175	-	-	19.7	-	-	-	-	-	3750	323	4.6	513
1275		19.4.2012	19.2	3.3	0.03	-	0.09	-	0.35	-	-	0.03	-	-	-	-	-	719	233	9.3	178
1300	PUMPING STATION	19.4.2012	-	23	0.24	-	36	-	21.3	-	-	4.79	-	-	-	-	-	2170	288	5.2	527
1430	PUMPING STATION	19.4.2012	-	17	0.13	-	0.10	-	0.65	-	-	0.15	-	-	-	-	-	122	365	5.2	5460

Appendix 4. Methodology of the performed analyses.

Analyze	Method
Cu, Zn, Fe, Mn (Pyhäsalmi lab.)	SFS 3044
Al, As, Cu, Zn, Fe, Mn	ICP-OES
Fe^{2+} (LVT)	DIN-38406-E1
Fe^{2+} (Labtium Oy)	Spectrophotometer
Cond. (Pyhäsalmi lab.)	SFS 3022
Cond. (LVT)	SFS-EN 27888
pH	SFS 3021
Sulfate	IC, gravimetry