Passive Mine Water Treatment with a full scale, containerized Vertical Flow Reactor at the abandoned Metsämonttu Mine Site, Finland

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Abstract This paper describes the first full scale, containerized VFR operating in Finland. Other than previous installations published, the VFR is sized such that all the mine water discharging from the abandoned Metsämonttu mine site can be treated. The design criteria allow treatment of 1 to 35 L/min of circum-neutral mine water. During a 6 weeks small scale experimental VFR operation, the iron removal rate, flow and the on-site parameters were measured regularly. Based on these data, the full scale reactor was constructed and all before mentioned parameters were measured. In addition, a tracer test with NaCl to evaluate the mean residence time in the reactor and an on-site oxidation text with the mine water was conducted.

The experimental reactor removed more than 80 % of the iron in the mine water. The full scale VFR meanwhile removes 95 % of the iron and about 80 % of the arsenic in the mine water. Electrical conductivities ranged between 250 and 1300 µS/cm, pH between 7.0 and 7.9 and the redox-potential between 140 and 360 mV. Inflow total iron concentrations ranged between 6.3 and 10.7 mg/L and the outflow concentrations 0.2 and 10.0 mg/L. The tracer test revealed a mean residence time of 10 ± 1 h, which is substantially below the design criteria of 48 hours. Oxidation of the mine water reached 90 % after 1 h, staring form an initial oxygen saturation of 30 %. No removal of sulphate or a statistically significant decrease of the mine water's mineralisation was observed.

Key words vertical flow reactor, Finland, passive treatment, Metsämonttu, abandoned mine

Introduction

Mine water treatment at abandoned mine sites is often challenging (Wolkersdorfer 2008; Younger et al. 2002). It is therefore important to provide mine water treatment techniques that can operate independently, which is often the case for passive mine water treatment options (Brown et al. 2002; Gusek 2013; Younger 2000). One of these is the vertical flow reactor (VFR) that was first introduced about a decade ago (Sapsford et al. 2006) and has been described and used at various locations (Florence et al. 2016; Yang et al. 2011; Yim et al. 2014) since then.

Simplified, a vertical flow reactor consists of a tank and a coarse substrate at the tank's bottom that allows microorganisms to grow ("schmutzdecke") and iron sludge to settle. It works similar to a slow sand filtration system, in which polluted water is filtered through coarse gravel and a layer of sand above it. Water flows gravity driven vertically downward, at velocities depending on the size of the gravel bed. To remove Fe from circumneutral mine water, VFRs work more effectively under aerobic conditions (Sapsford et al. 2007).

The precipitation of Fe^{3+}-ochre on the surface is due to adsorption of Fe^{2+} on the existing ochre particles, which is then followed by the auto-catalytic oxidation forming even more ochre (Barnes 2008). Once the ochre bed is building up, the filtration effect and removal properties for Fe of the VFR increase.

So far, VFRs used in the UK, China and Korea are specifically designed tanks for treating mine water on a chosen mine site. Though the Taff Merthyr pilot scale plant was constructed using pre-manufactured parts for a "commercially available bespoke steel panelled water tank" (Sapsford et al. 2005) and other sites used intermediate bulk containers (Dey et al. 2003), they were not in itself containerized VFRs. The new approach described here is using a modified container which allows easy access and removal of the sludge as well as the gravel bed.

The aim of the project was to show that a containerized VFR can be used at the Metsämonttu mine site and that the mine water can be treated to an environmentally better quality than without the VFR.

Description of mine site

Metsämonttu ("forrest pit") is an abandoned underground copper-zinc-lead-silver-gold mine in Aijala, situated in the Salo municipality (formerly Kisko) of the Salo sub-region of Southwest Finland (Varsinais-Suomi). Mining in this area dates back to the 17th century, but the Metsämonttu deposit was only discovered in 1945. A first drill hole was started in 1946 and the mine was operated from 1952–1958 and 1964–1974. As rich ore reserves were discovered, Outokumpo Oy started mining in 1951, initially with an open pit exploration but subsequently, a 3 × 4 m shaft I was sunk to a depth of 135 m (Turunen 1953; Varma 1954) and later deepened to 235 m. Based on the production data, shaft II, which is located 280 m south of shaft I, was very likely sunk between 1961 and 1962 and reached a depth of 545 m. Both shafts are connected with each other through the +190 m level. In the vicinity of the Metsämonttu mine, three other abandoned mines are located: the Aijala, Aurums-Aijala and the Hopeamonttu mines, which operated during various times between the 17th and 20th century (Mäkelä 1989; Papunen 1986; Puustinen 2003). Though the ore processed was still high, the mine was finally closed in 1974. Production numbers vary from source to source, but are around 1.1 t Au, 20 t Ag, 45 kt Zn, 7.1 kt Pb, 1.6 kt Cu and 113 kt S (Geological Survey of Finland (GTK) 2016; Nurmi and Rasilainen 2015).

Tectonically and genetically, the mine belongs to the Orijärvi-Aijala area (Aijala subarea *sensu* Eilu) of the Uusimaa Belt and is classified as a Zn-Cu±Au volcanic massive sulphide (VMS) deposit (Eilu et al. 2012; Hanski 2015; Latvalahti 1979). It is characterised by felsic to mafic volcanics and chemical sedimentary sections. Usually, the volcanics are intensely altered with an increase of K, Fe and Mg and a decrease of Na and Ca with gneisses of varying composition and skarn, all of them highly metamorphosed (Eilu et al. 2012). According to Latvalahti (1979), this alteration results in "dolomitization, silicification, sericitization and magnesium-iron metasomatism" of the ore deposit. This nearly vertical deposit has a maximum thickness of 20 m, but mostly it is less than 10 m thick and the ore itself is located within dolomitic limestones and skarns as well as quartz and cordierite-anthophyllite wall rocks in disseminated or breccia deposits. Typical main ore minerals are pyrrhotite, pyrite, chalcopyrite, sphalerite and galena with a large number of secondary minerals.

Figure 1 *Iron staining at the uncontrolled mine water discharge of the Metsämonttu site (2015-07-02).*

No details about the flooding period of the Metsämonttu mine are known and eventually the mine water started to discharge from the abandoned and decommissioned shaft. Using the iron staining and sludge build up as an indicator (fig. 1), it can be assumed the mine water flooded the cellar of the mine building and discharged form their into a northern direction into waste rock and a natural wetland area. Downstream of the mine, no more iron staining can be observed.

Methods and Material

Initially, a commercially available, 100 L tank was used to identify if the iron concentration of the Metsämonttu mine water can be reduced by means of a VFR. The flow was controlled with a valve to range around 1 L/min and the iron concentration as well as the on-site parameters measured regularly for 38 days. Thereafter, a 20 ft container was modified of-site into a VFR and transported to the Metsämonttu site where it was filled with a gravel bed and the inflow and outflow adjusted to take all the water discharging from shaft 1 (fig. 2). Flow was measured with a van Essen CD Diver through a calibrated ½ V-Weir.

Water analyses were conducted daily to monthly and on-site parameters pH, temperature, redox-potential, oxygen concentration and electrical conductivity (EC) measured with HACH probes. Iron concentrations were measured on-site with a Hach photometer and alkalinity and acidity with a Hach digital titrator. Filtered (0.45 µm membrane filters) and unfiltered samples were analysed with ICP-MS and discrete analysers at Ramboll Oy in Lahti. All containers were rinsed three times and the filtered samples acidified with ultra-pure

HNO_3. Samples were kept cool at below 6 °C after sampling in cooler boxes or fridges and transported to the lab as soon as logistics allowed.

The experimental tank was filled with commercially available, white inert granodiorite of 0.5 to 1 cm diameter (purchased from a garden centre), whilst the full scale containerized tank was filled with 32—64 mm mica gneiss.

A NaCl tracer test was conducted with commercially available food salt (Meira Jodioitu Ruokasuoala) of 2089.79 g mass. EC was measured every minute with a van Essen CTD diver and the EC–NaCl relationship established with a calibration of the mine water and the food quality salt.

Sludge of the experimental VFR was dried and sent for XRF as well as SEM-EDS analysis at LUT in Lappeenranta.

Figure 2 *Picture of the Metsämonttu VFR at the end of the initial filling period (2016-08-08), before the installation of the aeration device.*

Results and Discussion

Though the on-site parameters of the Metsämonttu shaft 1 discharge are fluctuating throughout the year, the chemical parameters are relatively constant (tab. 1). From an environmental point of view, the mine water can't be described as polluting, though the iron precipitates leaves an unesthetical staining around the former, uncontrolled point of discharge (fig. 1). Downstream the mine site, natural attenuation reduces the potential contaminants As and Fe to 1.3 µg/L and 92 µg/L, respectively. These values can be explained by the circum-neutral characteristic of the mine water, with a pH between 6.9 and 7.9, caused by the buffering capacity of the carbonate wall rock of the ore deposit. The mine water sometimes has a slight aromatic smell, which is caused by the PAHs Fluorene (5 pg/L) and Pyrene (7 pg/L), which are usually originating from gasoline, diesel fuel, and heating oils (Ibanez et al. 2007; Weiner 2010) used in the underground mine workings. As the mine water is discharging directly form the shaft, the redox-potential and the oxygen saturation are usually low, with average around 150 mV and 5%, respectively.

Table 1 *Mine Water Quality of the Metsämonttu mine water discharge between 2015 and 2016.*

Parameter (n = 8)	**Value**
Temperature, °C	7.0 – 11.9
Electrical conductivity, µS/cm	579 – 1288
pH, –	6.9 – 7.9
Redoxpotential, mV (SHE)	100 – 290
Fe_{tot}, mg/L	6.7 – 15.6
As, µg/L	52 – 55
U, µg/L	2.7 – 3.5
SO_4^{2-}, mg/L	230 – 290
HCO_3^-, mg/L	180 – 292
O_2, mg/L	0.1 – 18.3
Q, L/min	0.6 – 34.6

Mine Water from the shaft discharge was partly diverted into the experimental VFR for 38 days. Inflow and outflow pH ranged between 7.2 and 7.5, inflow E_h between 70 and 90 mV, while outflow E_h ranged from 150 to 300 mV. Inflow Fe_{tot} was between 6 and 11 mg/L, while the outflow Fe_{tot} ranged between 0.4 and 10 mg/L, resulting in a removal rate starting at 11 % and reaching a value as high as 96 % towards the end of these 38 days (fig. 3). This result was promising enough to design a full scale VFR based on a 20 ft open container, which was commissioned on August 5th, 2016. Removal rates for Fe_{tot} increased from about 20 % to above 85 %, but substantially decreased during the winter months of 2016/2017, which might be contributed to reduced microbial activity during that time of the year. Another reason could be that the redoxpotential of the mine water stayed too high or that the partly frozen aeration system was not capable of oxygenating the mine water high enough. In an on-site aeration experiment it could be shown that the oxygen content of the mine water could rose from about 31 % to 90 % within 1 h, but the redoxpotential stayed low between 90 and 100 mV, which is not high enough to oxidize all of the ferrous iron.

In order to identify the mean residence time of the mine water within the VFR, a tracer test with food quality NaCl was conducted. A recovery rate of only 37% was achieved, as the tracer test might have been stopped to early. Based on the tracer test results, the mean residence time in the VFR is 10 h 17 min, which can be considered too low for all the iron oxyhydrate to

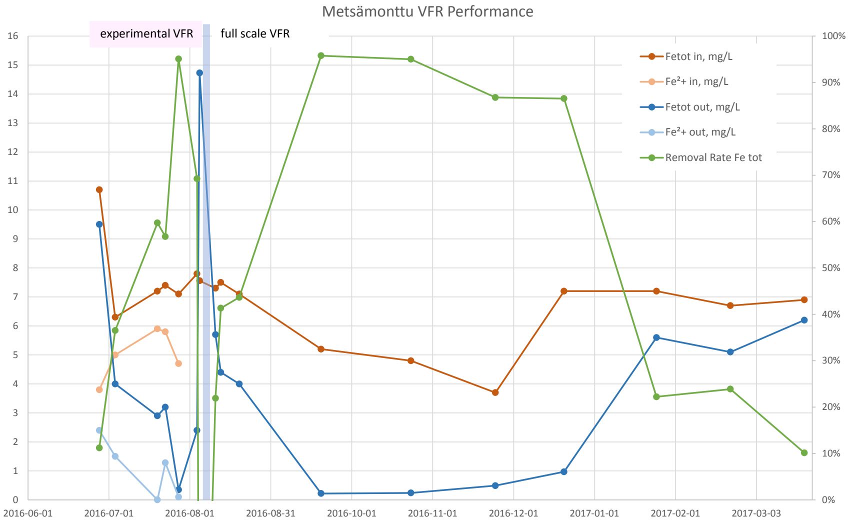


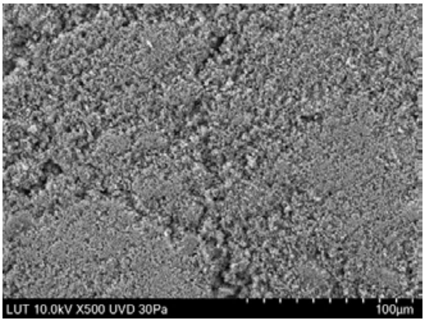
Figure 3 *Performance of the experimental and the full scale VFR between June 2016 and March 2017.*

settle or react. This might be another cause for the reduction in the removal rate over time. Further investigations will be done during the summer months of 2017.

Besides the Fe, also As was removed in the VFR, which is very likely a result of co-precipitation with the Fe oxihydrate. Other semi-metals and metals did not show a statistically significant change in concentration. In the SEM EDS analysis, As could not be found, but the results clearly show that the sludge is primarily iron oxyhydrate with some single particles in the sample showing carbonates (tab. 2). XRF analyses only showed amorphous substances.

Table 2 *Results of SEM EDS analysis of the sludge in the experimental VFR and related image. Averages from area and single particle analysis.*

Element	Average, %	Standard deviation, %	*n*
C	12.3	14.1	8
O	38.9	6.1	8
Mg	0.4	0.2	5
Al	0.7	0.8	5
Si	5.4	6.8	8
S	4.4	7.7	5
Ca	2.1	0.9	8
Fe	34.3	17.4	8
Na	6.4	–	1
Zn	21.3	–	1



Conclusions

The two experimental and full scale vertical flow reactors proved that it is possible to treat circum neutral mine water with this technique and when using correct design criteria, removal rates of up to 95 % can be achieved. The project also proved that it is possible to containerize a VFR so that it can easily be constructed of-site and transported to the treatment site. It could also be shown that the relatively low mean residence time of the mine water in the reactor seems not to affect the removal rate, which might be due to the fact that the water can be oxidised relatively quickly. No precise explanation can be given for the low removal rates during the winter months, but very likely the design needs to be changed so that the aeration system will not freeze in winter.

Another reason for the decreased performance might be that the gravel used in the containerized VFR is too coarse and that the high initial removal rates are an indication for the first sludge that build up. No removal of sulphate or a statistically significant decrease of the mine water's mineralisation was observed and is neither expected nor needed for the relatively low mineralized water.

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