I

Foreword

The meticulous process of crafting this thesis has been a long and arduous endeavor. At times I have doubted I would ever finish this task at all and countless hours have been spent in frustration and despair. Actually the longevity of this struggle has outlasted no less than five computers which for some reason or another broke down in rapid succession shortly after being introduced to my work of doom. I guess they crumbled under the immense weight of my worries…

It has not been all doom and gloom though. The time spent has certainly not been spent in vain. Many a life lesson has been had and personal growth has been the reward. *Per aspera ad astra!*

I would like to thank my supervisors: Dr. Hans-Christian Teien who has shown great patience and understanding during a hard time, with guidance that has been decisive, and Professor Brit Salbu for tutoring and excellent proofreading!

I would like to express my outmost gratitude to my sister Ingeborg. Without your support and patience I would not have been able to finish this project!

Thank you Harald Askilsrud (my good friend, helper and brother-in-arms) and Silje Vang! Excellent Accomodation, cuisine and god-sent help!

I would also like to thank the following persons: Marit Nandrup Pettersen, Karl Andreas Jensen and Solfrid Lohne for helping me with the ICP-OES, Johnny Kristiansen for TOC and anion measurements, Anne Grete Kolnes for help, waffles and coffee, and Ingrid Bugge for guidance and optimism.

And last, but not least I would like to thank my parents Anne Elisabeth and Øivind.

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Abstract

Metal run-off from derelict mining sites poses serious environmental concerns. Discharge water is usually enriched with a series of heavy metals such as aluminum (Al), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), manganese (Mn), and zinc (Zn), which may exert toxic effects to aquatic organisms. Fish dwelling in the associated draining streams are exposed, and metal accumulation in gills may induce mortality due to ion regulation failure or suffocation

The uptake and toxicity of metals is dependent upon speciation and bioavailability. Water samples from Nordgruvefeltet in Røros were collected in order to identify metal run-off from the site into the Orva river catchment area. *In situ* size and charge fractionation (SCF), *i.e.* filtration and cation exchange chromatography, was utilized in order to characterize the speciation and bioavailability of the metals. Run-off from mine Arvedalsgruva is characterized by low pH water in combination with high concentration of metals, present mainly as low molecular mass (LMM) cationic species.

In rivers in the south of Norway increased levels of Al due to acid rain has been found to cause fish mortality episodes. As a result, researchers at NMBU in collaboration with the Norwegian Institute for Water Research (NIVA) have added sodium silicate (NaSil) to remediate the adverse effects of Al when levels were believed to cause detriment to the fish. This countermeasure has generally been found effective and successful.

To mitigate toxic metal fractions and assess the eligibility of NaSil as a suitable remediation technique for runoff mining waters, dose-response laboratory tests were carried out using sampled water prior to *in situ* testing with acid mine drainage (AMD) water. Fractionation of water demonstrated that the addition of NaSil formed Cu and Al colloids. Using NaOH in parallel tests at similar pH demonstrated, however, formation of Cu and Al particles *i.e.* species larger than colloids. Thus, results indicated that silicate formed colloids, probably due to complexing processes, with metals in the AMD. The formed Cu and Al colloids are most probably less bioavailable than the LMM species and probably more inert than Cu and Al particles formed by pH change only, that potentially can remobilize over time.

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1   Introduction

Norway is a nation built on mining, amongst other industries. Today most of the mining infrastructure has been dismantled and only mere remnants of this epoch remain in the Norwegian landscape. Nevertheless, rivers continue to receive discharge water containing heavy metals from old mining areas. The Norwegian government has tried to manage the problem with limited success and the situation still remains to this day precarious in most of the affected rivers.

Cu is considered one of the most problematic elements found in drainage water from mines, and can *e.g.* disrupt protein function (Harris and Gitlin, 1996) and induce oxidative stress due to its redox properties (Grosell, 2012). Cu is easily taken up by aquatic life such as fish, even at low concentrations, and can disturb numerous mechanisms in fish, such as metabolism, ionoregulation and immunological function, (Grosell, 2012). The Cu toxicity, however, will vary between fish species and life stages (Taylor *et al.*, 2000). Water chemistry and metal speciation will also affect the toxicity of Cu (Taylor *et al.*, 2000).

The River Glåma receives annually through one of its tributaries, the Orva River, 3-6 metric tons of Cu from the "Nordgruvefeltet" mining area in the municipality of Røros (Thyve & Iversen, 2013). Nordgruvefeltet comprises the "Kongens gruve", the "Arvedalsgruva", and the "Christianus Sextus" mines, amongst others. A community was early established at Nordgruvefeltet, in 1657, and the first fire-setting was conducted in the mine "Arvedalsgruva", the oldest amongst the mines at Nordgruvefeltet. After shut down in 1972, Kongens gruve and Arvedalsgruva were flooded with water and closed off. Most of the buildings and infrastructure were dismantled, with the exception of the processing facility at Kongens gruve.

Previous investigations carried out by the Norwegian Institute for Water Research shows Nordgruvefeltet to be a major polluter, contributing to approximately 60 % of the total release of Cu in the upper part of River Glåma (Thyve & Iversen, 2013). The "Storwartz" mining area, the "Slagghaugan" tailings pile and the old "Smelthytta" foundry in Røros town center, the "Folldal hovedgruve" mine through the tributary "Folla", also contributes to the pollution of River Glåma. In addition to Cu, metals such as iron (Fe), aluminum (Al), zinc (Zn), cadmium (Cd), as well as anionic sulfate (SO_4^{2-}) have since 1966 been monitored in run off at

four different sites in the River Orva catchment area (Iversen & Arnesen, 2001; Thyve & Iversen, 2013).

According to Iversen & Arnesen (2001) there are mainly three sources of contaminants in River Orva:

1. Drainage from Lake Orvsjøen infused with run-off from Christianus Sextus, surface water drainage from Kongens gruve, and run-off from Fjellsjøgruva through the creek Naustbekken. Additionally, there is a submerged waste rock pile possibly releasing zinc in the deepest part of Lake Orvsjøen.
2. Acid mine drainage (AMD) from Kongens gruve and Arvedalsgruva.
3. Seepage from the large tailing pond at Arvedalsgruva and diffuse run-off from Kongens gruve and Arvedalsgruva.

Further, the annual transport of contamination in the catchment area increased after the old tailings pond at Arvedalsgruva almost collapsed and had to be bolstered in 1992-1994 (Thyve & Iversen 2013). After this incident, levels increased from 1996 and stabilized after spiking in 2004-2005. According to previous investigations, the manipulation and translocation of contaminated tailings implicate high risk of pollution (Iversen & Arnesen, 2001). There have also been found a strong correlation between water contamination levels and the intensity of precipitation in the area, and in 2011 a worsening of the situation in River Orva was seen as a result of frequent downpour episodes (Thyve & Iversen 2013).

To further outline the necessity to manage the problem, the Norwegian framework regulation on water management (2006) has incorporated to a large extent the Water Frame Directive (2000) into Norwegian law. The framework provides environmental goals for water bodies in Norway, and the general goal is that all water bodies must at least maintain or achieve "good status" in accordance with specific criteria. Good status implies both good ecological and chemical status.

To meet these criteria a range of options are available. However, because of its association with the old mining town of Røros, Nordgruvefeltet is subjected to conservational policies dictated by the world heritage protection act (UNESCO 2010). This implies some limitations to the implementation of potential remedial interventions. Further, conventional

countermeasures against AMD, such as precipitation, osmosis and ion exchange are often expensive, impractical and may also be a threat to the environment (Gavrilescu 2004).

To counteract this problem and assure water meeting environmental criteria, effective countermeasures must be initiated in order to reduce run-off and mitigate toxic metal species. Countermeasures such as addition of plaster, lime, carbonate, sulfide scavenging, constructed wetlands and ion exchange resins are all valid options that do not infringe upon limitations.

Another option is the use of sodium silicate (NaSil) as countermeasure. NaSil is believed to have positive impact upon metal-toxicity due to increase in pH and complexing ability of metals (Teien *et al.*, 2006). NaSil is assumed to react with metals to form stable and relatively inert Me-Si complexes and is thereby inhibiting metal uptake in organisms. This assumption is based on research made in rivers in the south of Norway where increased levels of Al due to acid rain caused fish mortality episodes (Teien et al; 2010). As a result, researchers added NaSil in the river water to remediate the detrimental effects of Al on fish. This initiative was generally deemed successful (Teien *et al.*, 2006; Teien 2010). When NaSil form metal complexes, the resulting composite will remain permanently stable in solution and be resilient to changes in physico-chemical conditions, such as pH.

Finally, NaSil will increase pH levels due to the fact that it is a strong base (pH 11.5, Teien *et al.* 2006; Teien *et al.*, 2012). At high pH, most metals will hydrolyse and form colloidal or particulate species, or form anionic species being less associated with to negatively charged fish gill surfaces than cationic species. Subsequently, elevated pH levels will cause additional change in metal speciation. Following particle sedimentation, less AMD is also transported downstream. Thus, the pH increase should also generally improve the living conditions for aquatic biota residing downstream.

1.1 Objective

The overall objective of the present work is to utilize NaSil as countermeasure to AMD in mining areas to detoxify metals in the water by changing the metals speciation. It is hypothesized that the efficiency of NaSil in AMD should be similar to that obtained when NaSil is added to acid water with high levels of Al. The effect of NaSil on AMD, with emphasis on bioavailable species of Cu, is still unknown as there is no significant research on

the subject to date, thus further investigation is required. Thus, the present thesis will focus on the effects of NaSil on the speciation of Cu.

To reach the overall objective, the work has been separated into the following sub-objectives:

(1)   identify metal concentration and metal speciation in AMD, with main focus on Cu, in waters from the Nordgruvefeltet mining site in Røros, and

(3)   investigate the remediating properties of NaSil and its usefulness as a countermeasure for metals, especially Cu, in AMD waters.

2 Background

2.1 AMD (acid mine drainage)

The term AMD pertains to acidic water draining both active and abandoned mining sites and it is generally laden with solubilized metal species originating from the native rock. All mining industry operations have the potential to generate AMD. Mining sources that can release AMD is spent ore from waste rock piles and overburden material, tailings, heap leach operations, and the walls of surface and underground mining operations (EPA, 1994; Gundersen *et al.*, 2001; Olsvik *et al.*, 2000). Water from for instance rainfall, streams draining the area, interstitial water, ground water and process water from the mining operations facilitates generation of AMD in the structures mentioned above.

One of the main origins of AMD is sulfide rich ore, most commonly pyrite and marcasite (both FeS_2). When such ores are subjected to water and air, the sulfidic constituents are oxidized and thereby releasing ferric iron (Fe^{3+}) and sulfuric acid (H_2SO_4), which subsequently further dissolves the rock and its metal contents. For instance, pyrrhotite ((Cobalt (Co),Cu,Ni)$Fe_{(1-1.17)}$S), chalcopyrite ($CuFeS_2$) and sphalerite ((Zn,Fe)S) generally undergo similar oxidative mechanisms in order to release Co, Cu, Ni, Fe and Zn (Jennings *et al.* 2008).

The process is in varying degrees accompanied and catalyzed by acidophilic microbial activity, *e.g. Thiobacillus ferrooxidans* (Jennings *et al.* 2008, Hindar og Iversen 2006). In sum, high acidity, depletion of water oxygen levels, hampered carbonate buffer ability, and elevated levels of bioavailable heavy metal species from the dissolved rock ensure that the discharge poses serious environmental implications downstream (Akcil & Koldas, 2006).

As this problem extends beyond mining industry, the more general term Acid Rock Drainage (ARD) is preferred to describe all sources, both natural and anthropogenic, which generate and enable acid drainage to escape from rock formations, such as quarries, tunnels, road cuts and road fillings as well as those associated with mining operations. However, the term AMD shall henceforth be used throughout this thesis since it solely concerns mining and mining related pollution.

2.2 The chemistry of pyrite oxidation and AMD generation

Sulfide minerals, with pyrite being the most abundant sulfide ore on the planet, generally undergo complex multistep oxidation processes in order to yield AMD. There are scores of other sulfide minerals as well as chemical and biological mechanisms that result in AMD generation, but for the sake of simplicity oxidation of pyrite is used as an example below as it is the chief constituent of AMD generating processes.

Equation 1: The pyrite oxidation process in general.

$$4FeS_{2\,(s)} + 15O_{2\,(g)} + 14H_2O_{(l)} \rightarrow 4Fe(OH)_{3\,(aq)} + 8SO_4^{2-}{}_{(aq)} + 16H^+{}_{(aq)} \qquad (1)$$

The above equation describes in general the dissolution of pyrite from solid to liquid phase.

Oxidation of pyrite converts sulfide into soluble SO_4^{2-}, which releases ferrous ions into the solution. The draining water will appear colorless and be strongly acidic (pH < 3).

Equation 2: Conversion of pyrite to ferrous iron.

$$2FeS_{2(s)} + 7O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}{}_{(aq)} + 4SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)} \qquad (2)$$
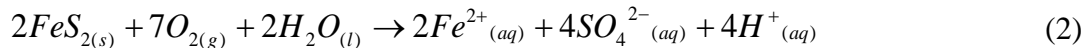
Further the ferrous iron is oxidized and yields ferric iron.

Equation 3: Oxidation from ferrous to ferric iron.

$$4Fe^{2+}{}_{(aq)} + O_{2(g)} + 4H^+{}_{(aq)} \rightarrow 4Fe^{3+}{}_{(aq)} + 2H_2O_{(l)} \qquad (3)$$
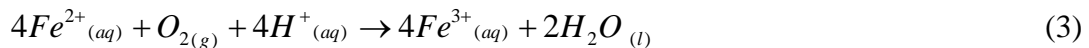
Both of the above reactions (equation 2 and 3) can occur spontaneously or be catalyzed by acidophilic microorganisms (Jennings *et al.* 2008).

Ferric iron then acts as an oxidizer and interacts with pyrite to generate even more ferrous ions and free protons which in turn contribute to keep additional ferric ions in solution, thus boosting the self-perpetuating nature of the pyrite oxidation process.

Equation 4: Ferric oxidation of pyrite to ferrous iron.

$$FeS_{2(s)} + 14Fe^{3+}{}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}{}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 16H^+{}_{(aq)} \qquad (4)$$
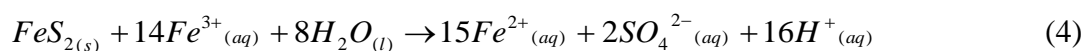
If conditions are right (pH usually above 3.5), ferric iron will react with water to form iron(III)oxide species, an ochre precipitate called "Yellow-boy". This usually happens when the drainage becomes diluted in the stream and the pH is increasing.

Equation 5: Precipitation of iron(III)oxide.

$$2Fe^{3+}{}_{(aq)} + 6H_2O_{(l)} \rightarrow 2Fe(OH)_{3(l)} + 6H^+{}_{(aq)} \tag{5}$$
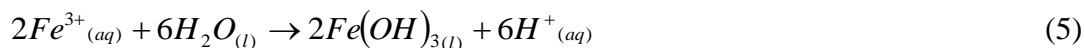
Precipitation of significant quantities of Yellow-boy will coat the stream beds, and eventually destroy the water ecosystem when habitation of organisms become impossible due to substrate being covered up and smothered. (Kirby, 2007; Kirby, 2008)

2.3   Metal concentration in AMD-receiving River Orva.

AMD is laden with metals and could potentially contain a fraction of every metal bearing compound representative of the composition of the rock it originated from. A table with the most significant metals encountered in AMD at Nordgruvefeltet is shown in table 1 below. The list is compiled from reports based on NIVA's previous investigations in Nordgruvefeltet (Thyve & Iversen, 2013).

Table 1: Composition of the metal concentration (average) in River Orva 2009-2010 *(Thyve & Iversen, 2013).*

Metal	Average Concentration [mg/L]
pH	4.74
Cond.	9.52
SO_4^{2-}	31.9
Al	0.65
Cd	0.01
Cu	0.26
Fe	3.69
Zn	0.78

Cu is one of the metals that are presented in relatively high concentration in AMD in Norway, also in Nordgruvefeltet. In addition, Cu is considered to be toxic to aquatic organisms and has therefore been one of the main elements in focus by The Norwegian Environmental Agency

According to guidelines set by the Norwegian Environmental Agency (figure 1), more than 6 µg Cu–/L are strongly polluted water. The further focus in this thesis is therefore mainly limited to Cu.

Effects of pollutants (heavy metals)	Parameters	Water condition class				
		I "Negligibly polluted"	II "Moderately polluted"	III "Distinctly polluted"	IV "Heavily polluted"	V "Strongly polluted"
	Copper, µg Cu/L	<0.6	0.6 - 1.5	1.5 - 3	3 - 6	>6
	Zink, µg Zn/L	<5	5 - 20	20 - 50	50 - 100	>100
	Cadmium, µg Cd/L	<0.04	0.004 - 0.1	0.1 - 0.2	0.2 - 0.4	>0.4
	Nickel, µg Ni/L	<0.5	0.5 - 2.5	2.5 - 5	5 - 10	>10
	Chromium, µg Cr/L	<0.2	0.2 - 2.5	2.5 - 10	10 - 50	>50

Figure 1: Water condition classes of some heavy metals in water (Klif, 1997).

2.4 Speciation of metals in aquatic environments

In chemical parlance, speciation refers to how an element can be present in a range of different forms. Thus, metals present in AMD can be present in different physical and chemical forms, *i.e.* species. Metal species change distribution when AMD enter into receiving water bodies, such as rivers and lakes. Depending on factors such as the element's physico-chemical properties (*e.g.* nominal molecular mass, charge properties, oxidation state, structural configuration and morphology) and environmental factors (*e.g.* temperature, pH, the nature of the medium in which it is solved and the properties of any extraneous element therein) it will conform into a quantitative distribution of species (*e.g.* ions, complexes, polymers, colloids and particles) (Salbu, 2006). In environmental water chemistry, species are usually categorized into size classes as expressed in table 2 below.

Table 2: Distribution of size classes of species (after Salbu, 2009).

Diameter [nm]	1 nm	10 nm	0.1 µm	0.45 µm	1 µm	10 µm
Molecular mass [Da]	$\times 10^2$	$\times 10^4$	$\times 10^6$		$\times 10^8$	
Category	simple compounds	hydrolyzates/colloids	polymers / pseudocolloids		suspended particles	
Cases	inorganic, organic ions, complexes, molecules etc.	nanoparticles polyhydroxo complexes polysilicates fulvic acids fatty acids	metal hydroxides clay minerals humic acids proteins		inorganic mineral particles organic particles microorganisms	

Low molecular mass (LMM) species are defined as compounds below 1 nm in diameter (Salbu 2009). Species in this size class are generally thought to be mobile, potentially reactive and bioavailable, and comprise ions, complexes and simple molecules. High molecular mass (HMM) species are defined as compounds above 1 nm in diameter. These compounds are mainly considered biologically inert and comprise the colloidal range (1 nm to 0.45 μm in diameter) and particulate matter (above 0.45 μm in diameter). Colloidal species generally stay in solution and are therefore mobile. Suspended particulate species settle out of solution at the bottom due to gravity.

Chemical speciation of an element is in no way absolute. The distribution of chemical species is impermanent and continually subject to change as conditions in aquatic environments is rather dynamic and unstable by nature. Chemical species are converted into new species driven by transformation processes such as desorption, dissolution, dispersion, hydrolysis, complexation, polymerization and aggregation, as illustrated in figure 2 below (Salbu, 2006).
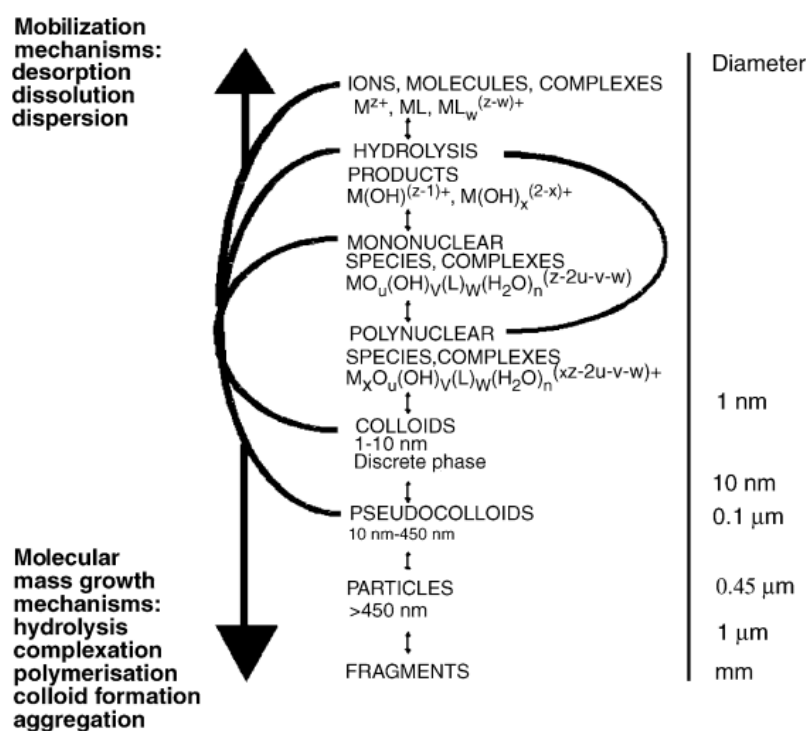
Figure 2: Physiochemical forms of metals, divided into size classes, with the transformation processes changing the distribution of species indicated (Salbu, 2000, after Salbu et al., 2004).

2.5 Speciation of Cu

Cu is an essential element for all aerobic organisms due to its relevance as a reducing agent in the mitochondrial cytochrome c oxidase process and its role as a cofactor in various other enzymes (Grosell, 2011). However, when encountered in sufficient concentrations (>10 µg/L), Cu will exert toxicity towards aquatic organisms. Hence Cu has a significant impact on the living conditions and reproduction of fish dwelling in streams draining mining sites. Studies have shown Cu to affect ion regulation in fish gills at a concentration as low as 12.5 µg/L (Lauren & McDonald, 1985). Cu is considered one of the most problematic elements found in rivers polluted with AMD in Norway, and is found in great abundance at Nordgruvefeltet.

Cu can exist in the following oxidation states:

0   Elemental Cu which is inert and non-toxic in most environmental concentrations.

$+$ Monovalent Cu which is toxic, but of lesser significance than the $2+$ form.

$2+$ Divalent Cu which is the most toxic form of Cu and the main focus of this thesis.

$3+$ Trivalent Cu which is not found in nature and must made artificially *i.e.* only from anthropogenic sources.

There is a general consensus that Cu^{2+} is the main toxic form of Cu, although $CuOH^+$ and $Cu(OH)_2$ have been proven to exert toxicity. In fresh waters with intermediate to low alkalinity Cu^{2+} becomes predominant at neutral to low pH. Cu-carbonate complexes are generally assumed to be non-toxic (but available for accumulation) (Grosell, 2011). Cu toxicity has also been demonstrated for $CuOH^+$ and $Cu_2(OH)_2^{2+}$ (LaGrega *et al.*, 1994). Thus, according to the size classes of metals expressed in table 2, LMM positively charged Cu species are associated with Cu species that may exert toxicity towards aquatic organisms.

2.6 Parameters which affect the speciation and toxicity of Cu

The toxicity of Cu towards aquatic biota has been reported to be affected by various physical-chemical parameters which are shown to change the chemical speciation of Cu. Erickson *et al.* (1995) found that the toxicity of Cu to fathead minnows varied widely depending on the chemical characteristics of the test water. It is worth stating that even though certain Cu species contribute to toxicity, there are also factors in the water that have protective effects for fish (*e.g.*, Ca) without affecting Cu speciation (Erickson *et al.* 1995). Figure 3 illustrate the key factors influencing the speciation and the bioavailability of Cu. These key factors are pH and concentration of organic and inorganic complexing agents. In addition, the concentration of competing ions could also influence the uptake of Cu directly and also the formation of Cu complexes (Erickson *et al.* 1995).
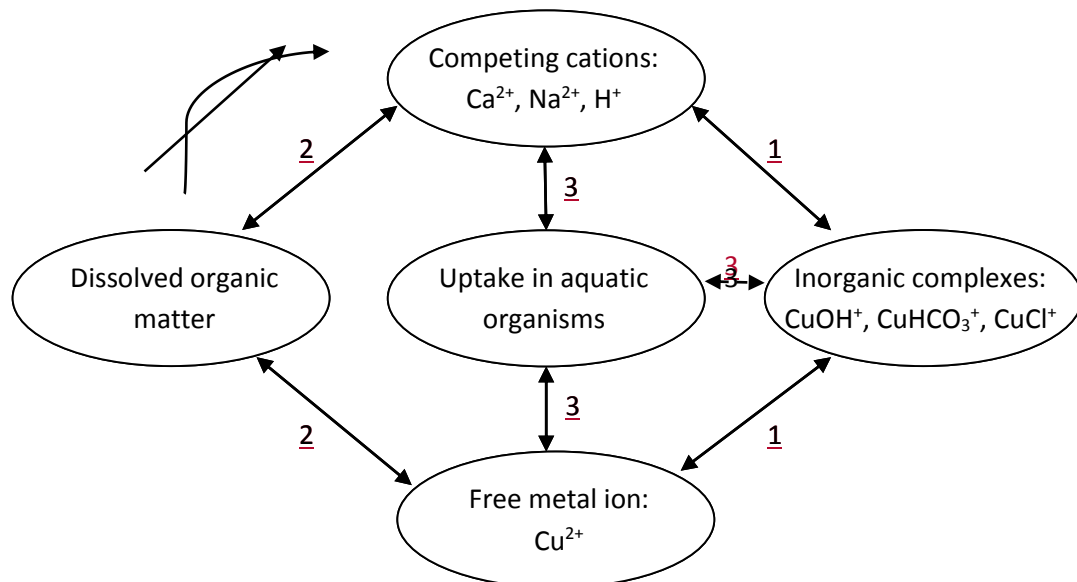
Figure 3: Model illustrating the (1) speciation models, (2) interactions with organic matter and (3) interactions with the aquatic organism.

2.6.1 Competing ions

High concentrations of dissolved cations compete with cations of toxic metals such as Cu and might reduce the sorption or uptake of metals on gills and thereby the toxic effect. Ca and Magnesium (Mg) are ions that typically are reported to influence the toxicity of metals. High levels of Ca and Mg may act as a competitor with other metal ions such as Cu (Perschbacher

& Wurts 1999), and can also protect fish against toxic effects of metals. Water hardness is one measure to report the concentration of both Ca and Mg in water. According to Meade, (1989), the critical concentration of Cu is 6 µg/L if water hardness is less than 100 mg/L, at higher water harness the critical concentration is 30 µg/L. Conductivity is a measure reflecting the concentration of dissolved major ions generally in solution. Electrical conductivity is expressed as the eligibility of a solution to transfer electrical current and it is expressed as the inverse function of resistivity. When ionic activity increases in a solution, so does electrical conductivity as well. Typical conductivity for regular lake water in Norway is 22 µS/cm (Økland & Økland 1996), *i.e.* low conductivity waters.

2.6.2   Water acidity

Water acidity will have a great impact on metal speciation and hence bioavailability. Metal dissolves far easier when the solution is acidic. Cu will mainly exist as cupric ions when pH drops below 5 as shown in figure 4 below. Cupric ions are the most bioavailable Cu species. Increased pH levels result in Cu being converted to complexes, hydroxides or form colloidal species following hydrolysis, thus decreasing the bioavailability. To conclude, toxic fractions of Cu may be greatly reduced by increasing the pH only.
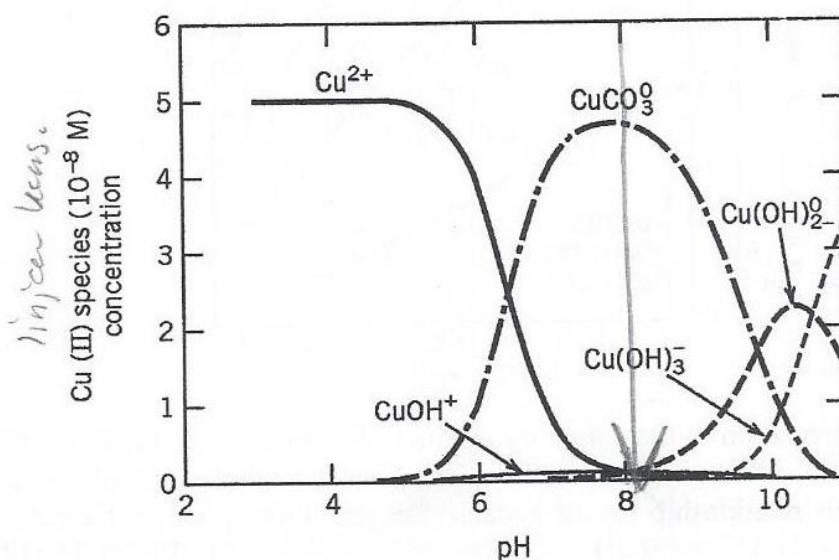
Figure 4: Distribution of Cu species as a function of pH (Stumm and Morgan, 1996).

Studies from Norway have shown that pH historically is the single most important factor explaining fish status of brown trout (*Salmo trutta*), arctic charr (*Salvelinus alpinus*) and perch (*Perca fluviatilis*) (Hesthagen *et al.* 2000). Variations in arctic char viability can be seen at higher water qualities compared to brown trout, while perch can withstand more poor water qualities before variations in fish status is detected (Hesthagen *et al.* 2000; Tammi *et al.* 2003). Although there are major geographical differences between lake systems, a lower limit of brown trout viability is often detected around pH 5.0 (Hesthagen *et al.* 2000, Tammi *et al.* 2003).

2.6.3 Complexing agents

Several investigators have reported that dissolved organic carbon (DOC) species, such as humic and fulvic substances and simple organic ligands, may mitigate the toxicity of Cu towards aquatic organisms. Positively charged Cu will readily adsorb or bind to DOC species and hence reduce the bioavailability and thereby toxicity of Cu. It is worth noting that colloidal humic substances and LMM fulvic substances act as transporting agents for metals such as Cu, and the total concentration and mobility of Cu can be high during deluvial episodes, such as spring freshets and heavy rain falls Inorganic ligands forming complexes with Cu will also influence the toxicity of Cu. Silicon (Si) is one such element assumed to form stable complexes with Cu (Erickson *et al.*, 1996; Grosell, 2011).

2.6.4 Episodic events

Changes in precipitation or temperature can have dramatic effects on the concentration of metals in AMD. During heavy rainfall or spring melt, large amounts of water can flush out metals that have accumulated during periods of low flushing rates Under such events, the largest fraction of metals will be associated with particles and colloids.

High temperatures increase kinetic rates of chemical reactions while lower temperature results in reduced reaction rates. When subjected to subzero temperatures the sulfide oxidation halts due to inhibited transport of reactants and oxidation products. Time of sampling is therefore

essential when evaluating the concentrations of metals such as Cu in AMD and receiving rivers.

2.7 Remediation of AMD with NaSil

NaSil, is also known as sodium silicate, water glass or liquid glass (Iler, 1979). The chemical formula for NaSil is Na_2SiO_3, or more precisely $SiO_2 \cdot Na_2O$. It is available as solids, powders, hydrated forms and solutions. NaSil has a wide range of application, *e.g.* cleaners and detergents, adhesives, binders in concrete, flocculants in water treatment, fireproofing, lumber treatment, sealing agents and corrosion inhibitors, amongst others (Iler, 1979).

In industry NaSil is produced by heating, melting and reacting sodium carbonate and silicon dioxide to above 1300 °C to form sodium silicate and carbon dioxide:

Equation 6: Sodium carbonate reacts with silicon dioxide to form sodium silicate.

$$3SiO_2 + Na_2CO_3 \rightarrow 3SiO_2 \cdot Na_2O + CO_2 \qquad (6)$$

Different grades of sodium silicate are characterized by their $SiO_2:Na_2O$ molar ratios, which mostly vary between 1.6:1 and 3.9:1. Grades with $SiO_2:Na_2O$ molar ratios below 2.85:1 are deemed alkaline. Those with molar ratios above 2.85:1 are classified as neutral (Iler, 1979).

When NaSil is diluted in freshwater at low concentration (< 50 mg/L) silicate will be present as silicic acid (Iler, 1979).

Equation 7: Dissolution of NaSil in water to form silicic acid.

$$Na_2SiO_3 + H_2O + 2H^+ \leftrightarrow Si(OH)_4 + 2Na^+ \qquad (7)$$

Aqueous NaSil shares many properties with water as stated by Iler, (1979): "Some properties of water and silica are so similar that the transition between hydrated silicic acids and the aqueous matrix is a gradual one." Depending on the conditions in the water, such as concentration and pH, silicic acid will start to polymerize (Iler 1979).

There are three modes in which water soluble NaSil can interact with metals such as Cu in water (Iler, 1979; White *et al.*, 1998):

1. Metal solubility is to a high degree dependent on pH. Metal speciation will change by increasing the pH with NaSil.

2. Silicate ions react with salts of metals (other than the alkali group) to form amorphous insoluble metal silicates, *i.e.* Me-Si complexes. The reaction mechanisms are often difficult to characterize.

3. Polymerization of silicate forms flocs and colloids which act as substrate for metal adsorption and encapsulation. The way in which a metal adsorbs onto silicate polymers and colloids are difficult to characterize due to the amorphous nature of the resulting silicate compounds.

According to Teien *et al.* (2009), NaSil has been demonstrated to counteract Al toxicity in acidic water with respect to aquatic organisms, as it rapidly converts Al into less reactive Al-Si complexes (Teien, 2005). The use of NaSil has generally been found to be a successful countermeasure for acidic Al containing water and NaSil is presently being applied in three salmon rivers and in several fish farms to detoxify Al (Teien, 2005)

It is likely that adding NaSil to AMD in mining areas also should be an effective countermeasure, providing similar results for Al as in acidic waters. However, the effect of NaSil on AMD on other metals such as Cu is still unknown.

3   Material and method

The studies have been conducted, throughout the year 2012 (February to December, and were divided into three phases:

- Pilot laboratory experiments at NMBU (Norwegian University of Life Sciences) with AMD water obtained at the tailings pond at the Storwartz mining area (Pilot, figure 5),

- At site test at Nordgruvefeltet mining area (Site 1, Site 2 and Site 3; see figure 5) and

- Data handling after analyses using ICP-OES at NMBU (see appendix).

The study area is mapped in figure 5, showing the Pilot site at the Storwartz mining area and the Site 1, Site 2 and Site 3 at the Nordgruvefeltet mining area.
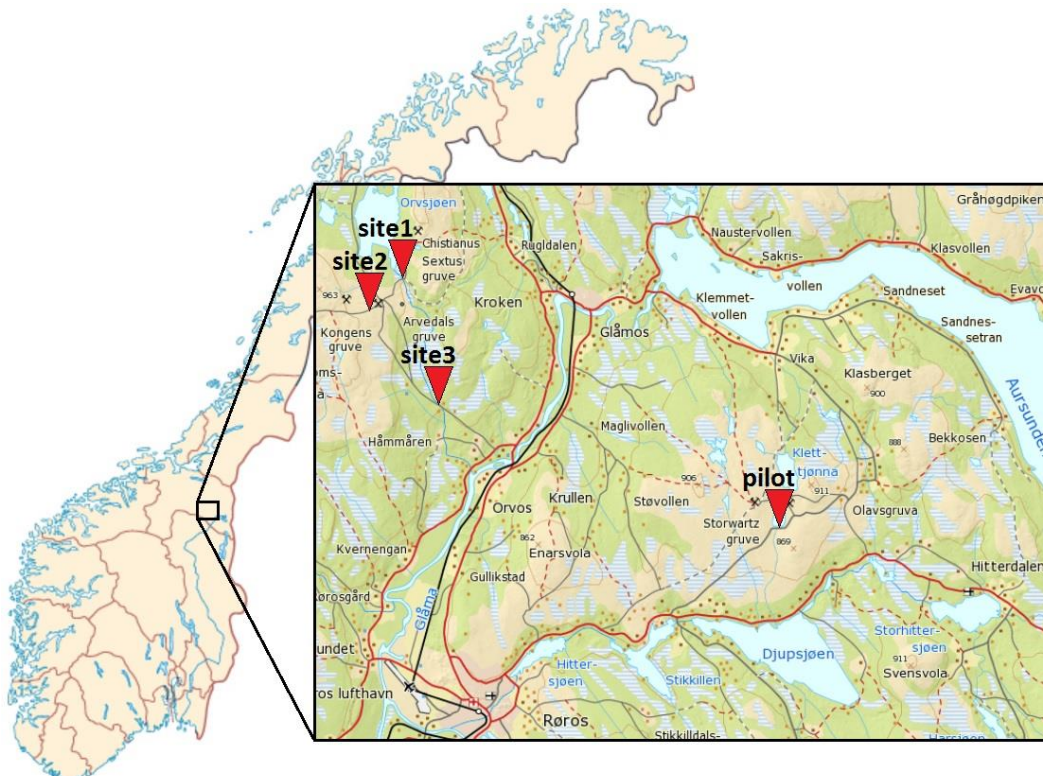
Figure 5: Map of the study area showing Site 1, Site 2 and Site 3 at the Nordgruvefeltet mining area and the Pilot site at the Storwartz mining area (by H. Askilsrud; source: norgeskart.no).

3.1   Pilot studies

In February 2012, 20 L of sample water was collected in a large plastic can at the tailings pond at "Storwartz" mining area 9 km north east of Røros (figure 6). This was brought to the laboratory at the NMBU. The sample was stored at $4^{O}C$ before laboratory experiments was initiated in March, May and September. Sample water from Storwartz was used instead of water from Nordgruvefeltet because all useable water bodies at Nordgruvefeltet were covered by thick ice or were frozen to the bottom at the time of field sampling. A series of preparatory experiments (*i.e.* pilot experiments) were then conducted with water from Storwartz in order to predict what could be expected when running at site tests at Nordgruvefeltet later that year.

Figure 6: The tailings pond at Storwartz (Pilot) located 9 km north east of Røros, where AMD water for the pilot studies were gathered.

3.1.1   Metal speciation in AMD test water from Storwartz

SCF (size charge fractionation) is a method to separate chemical species based on size and charge. 0.45 µm membrane filtration and 10 kDa ultra filtration coupled with cation exchange chromatography was used to sort species by physical size and ionic charge properties. The SCF was set up and prepared according to the procedure described in chapter 3.3.

However, the pilot speciation experiment conducted on AMD from Storwartz was set up to just coarsely separate colloids and LMM metal species from inert particles. Therefore only 0.45 μm membrane filtration coupled with cation exchange chromatography was used.

3.1.2 AMD optimization of SCF

Optimizing ion chromatography for SCF using AMD water in the study, the cation exchange resin, Amberlite IR-120 in Na form was used to obtain information of positively charged fractions of the metal ions. To optimizing the flow velocity of sample through the cation exchange column used in the SCF studies, a series of tests were made at three different pump intervals; 30, 70 and 90 rpm. The reason for doing this was that sorption of cations is dependent upon the contact time with the cation exchange resin. Letting the sample through the column at too high speeds could lead to low contact time and that cations were not being retained, resulting in significant underreporting on the reactive LMM species fraction. The sample velocity for each interval was determined by measuring the volume of sample that went through the column in 60 seconds. A 9.5 mL sample was taken for each of the three pump intervals and was added 0.5 mL of UltraPure HNO_3 to conserve the sample, and 250 μL of internal standard to identify sample loss during storage.

An experiment was also conducted to assess the volumes of processed sample water at which the cation exchange resin became saturated and started to suffer inability to adsorb and retain metals efficiently.

The SCF was set to continuously filter sample water through the cation exchange column at 70 rpm (approximately 20 mL/min), and a 9.5 ml sample was taken for every 200 mL of processed sample water and were added 0.5 mL of 5% UltraPure HNO_3 to conserve the sample, and 250 μL of internal standard to identify sample loss during storage.

3.1.3 Dose response test of NaSil in AMD water

To obtain information about potential changes in Cu speciation due to addition of NaSil, a dose response test was performed at NMBU based on water from the Storwartz AMD. SCF

(without ultrafiltration) was used to obtain information on Cu speciation after addition of 0.87 ml K40 NaSil/L AMD water.

To obtain information about effects of the pH change alone without addition of Si on Cu speciation, dose response test of 4 M NaOH was performed at NMBU based on water from Storwartz AMD at similar condition as for NaSil.

3.2 Field work

The Nordgruvefeltet mining area is located km north of Røros. The tributary River Orva is running from Lake Orvsjøen to the River Glomma through the mining area in a north-south direction. Nordgruvefeltet comprises numerous mines, where the most important are Kongens gruve, Arvedalsgruva, Christianus Sextus, Lergruvbakken gruve, Killingdalen gruver, Fjellsjøen gruver, Muggruva and Rødalsgruva. All these mines drained into the River Orva catchment area except Muggruva and Rødalsgruva.

Furthermore, the area is spangled with remnants of various mining operations, such as derelict buildings and mining equipment, piles of overburden, tailing ponds, tailing heaps, tips, pits, shafts, stalls, and dry and wet deposits, all of which poses as potential emitters of pollution into the surrounding environment (Thyve & Iversen, 2013).

Site 1 (figure 7): Located at the outlet of Lake Orvsjøen into River Orva and represented water quality before running through the Kongens area. Measurements conducted included: temperature, pH, conductivity, TOC, major anions, major cations and concentration and speciation of metals in the water.

Figure 7: Sampling and fractionation in situ (Site 1) in River Orva located near the outlet of River Orvsjøen 1 km upstream of the Kongens area.

Site 2 (figure 8): Located at the outlet of Arvedalsgruva. Samples from this site represented the main source of AMD from the mining area. Measurements conducted in this site included: *in situ* testing of the effect of NaSil and NaOH on metal speciation, as well as temperature, pH, conductivity, TOC, major anions, major cations and concentration and speciation of metals in the water.

Figure 8: Sampling site (Site 2) at the submerged outlet of Arvedalsgruva.

Site 3 (figure 9): Located at a bridge 3 km downstream of Kongens gruve and Arvedalsgruva. Samples from this site represened water quality after running through the Kongens area. Measurements conducted included: temperature, pH, conductivity, TOC, major anions, major cations and concentration and speciation of metals in the water.

Figure 9: Sampling site (Site 3) located in River Orva 3 km downstream of the Kongens area.

Based on the study from the laboratory, two different investigations were performed at the Nordgruvefeltet mining area.

1. *In situ* fractionation of metals in AMD and water from River Orva to obtain information about Cu and metal speciation. Tests were conducted at three separate sites in Nordgruvefeltet.

2. At site remediation test with NaSil of AMD from Arvedalsgruva to study the change in metal speciation as a measure of changed bioavailability.

The associated fieldwork was conducted 10.06.2012 to 10.07.2012 at Arvedalsgruva and along River Orva at the Nordgruvefeltet mining site, 12 km north of Røros. The samples were

taken from points in the Orva catchment where contamination levels where known *a priori* to be high or could give clues about the origins of the discharge.

3.2.1 Metal speciation in AMD from Arvedalsgruva and receiving River Orva

Water directly from River Orva close to the outlet of Lake Orvsjøen (site 1), AMD from Arvedalsgruva at Kongens (site 2) and AMD affected water from River Orva 3 km downstream of Kongens (site 3) was processed *in situ* with SCF in order to obtain information on the size distribution of metal species, as well as the total concentration of metals. The water sampling protocol (chapter 3.3) was used to obtain information on water quality. This was used to follow changes in water quality and metal speciation downstream of the mixing point between of River Orva (site1) and AMD from Kongens (site 2).

3.2.2 At site remediation test with NaSil

NaSil in the form of Krystazil 40 (K40), manufactured by BIM Norway AS, was used in the experiments. K40 had a $SiO_2:Na_2O$ molar ratio of 3.31 and contained 36% dry weight. It had a density of 1360 kg/m^3 and a pH of 11.5 (BIM Norway AS, 2013). 4 M NaOH was also used in the experiments.

AMD from the outlet of Arvedalsgruva was treated *in situ* with K40 NaSil to study if NaSil had any mitigating effects on the toxic LMM fraction of the metal species distribution. In addition 4 M NaOH was used in a parallel test to be distinguish the effect of pH only from that of silicate following NaSil addition.

The study was conducted at the outlet of Arvedalsgruva (Site 3). Water acidity and conductivity was measured at the site first. A 5 L plastic can was then conditioned with AMD. 5 L of AMD was extracted into the 5 L plastic can from the site. Water acidity and conductivity was then measured in the sample. NaSil were added with a Brand Handy Step pipette until neutral pH levels in the sample. The sample with NaSil was ultimately fractioned at site according to the SCF protocol detailed in chapter 3.3.

A similar study was conducted with NaOH instead of NaSil to map the effect on metal speciation by pH alone. Water acidity and conductivity was measured in the site. Subsequently a 5 L plastic can was then conditioned with AMD water from the site. After that 5 L of AMD was obtained in the 5 L plastic can. Water acidity and conductivity was measured in the sample. 4 M NaOH was added with a Brand Handy Step pipette until the sample had neutral pH. The sample with NaOH was then fractioned at site according to the SCF protocol detailed in chapter 3.3.

3.3   SCF and water sampling

SCF (size charge fractionation) was utilized in both laboratory work and *in situ* measurements. The procedures and principles for the SCF are the same in both instances, thus operational procedures are elaborated in this chapter on a general basis.

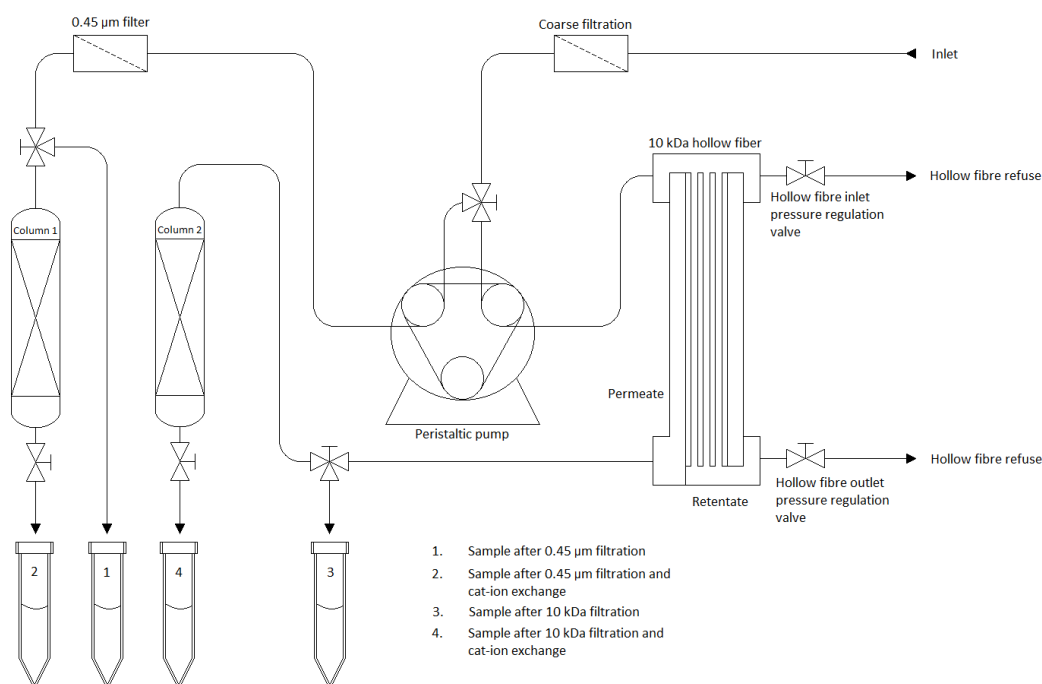The SCF array came fully assembled in the manner shown in the figure 10 below:

Figure 10: Flow scheme of the SCF array used in the water fractionation experiments (by M. Lunde).

3.3.1 Preparation and regeneration of cation exchange columns

Preparation cation exchange chromatography column:

The columns with its valves and fittings were thoroughly washed with 5% UltraPure HNO_3. After drying, the columns were filled with approximately 20 cm^3 IR-120 Amberlite cation exchange resin and assembled.

Regeneration of the cation exchange resin:

The cation exchange resin had to be properly prepared and cations retained by previous sampling removed before further testing could be conducted. Each column with resin was rinsed with 50 mL 3 M HCl, with the last 20 mL of the HCl solution being retained in the column for about 30 minutes. The columns were washed with 100 mL of distilled water (MilliQ) and added 50 mL of 3 M NaCl. After treatment with NaCl solution, the columns were washed with MilliQ until the pH was in the vicinity of the acidity of the sample water.

3.3.2 SCF sampling procedure

All fraction samples from the SCF were taken in three parallels (n=3) to ensure statistical integrity of the results. 9.5 mL of each fraction were transferred to a 15 mL Falcon tube (which was first conditioned 3 times with a little bit of sample), added 0.5 mL of 5% UltraPure HNO_3 to conserve the sample, and then 250 µL of internal standard (rhodium (Rh)) to identify sample loss during storage. All samples were shut tight and stored cold (4°C) and absent from light until being analyzed with ICP-OES at NMBU.

The following five types of fractions were gathered with SCF:

S_{tot} Total sample

$S_{0.45µm}$ Sample after 0.45 µm membrane filtration

$S^+_{0.45µm}$ Sample after 0.45 µm membrane filtration and cation exchange chromatography

S_{10kDa} Sample after 10 kDa ultra-filtration

S^E_{10kDa} Sample after 10 kDa ultra-filtration filtration and cation exchange chromatography

The following distribution classes of metal species could be derived from the fractions stated above:

Me_{tot} *Equation 8: Total metal concentration.*

$$Me_{tot} = S_{tot} \tag{8}$$

This represented the total concentration of all metal species in the sample and was taken unfiltered directly from the sampling site.

Me_p *Equation 9: Concentration of particulate metal species:*

$$Me_p = S_{tot} - S_{0.45\mu m} \tag{9}$$

This represented the concentration of all particle bound and therefore inert metal species above 0.45 μm in diameter in the sample.

$Me_{0.45\mu m}$ *Equation 10: Total concentration of colloidal metal species:*

$$Me_{0.45\mu m} = S_{0.45\mu m} - S_{10kDa} \tag{10}$$

This represented the total concentration of colloidally bound metal species between 0.45 μm in diameter and 10 kDa in the sample.

$Me^E_{0.45\mu m}$ *Equation 11: Concentration of inert colloidal metal species:*

$$Me^E_{0.45\mu m} = S^E_{0.45\mu m} - S^E_{10kDa} \tag{11}$$

This represented colloidally bound metal species considered inert and/or anionic and therefore nontoxic.

$Me^+_{0.45\mu m}$ *Equation 12: Concentration of reactive colloidal metal species:*

$$Me^+_{0.45\mu m} = Me_{0.45\mu m} - Me^E_{0.45\mu m}$$

$$Me^+_{0.45\mu m} = (S_{0.45\mu m} - S_{10kDa}) - (S^E_{0.45\mu m} - S^E_{0.45\mu m}) \tag{12}$$

Reactive charged metal cationic species of the colloidal range. This represented the concentration of positively charged and therefore possibly toxic colloidal metal species between 0.45 µm in diameter and 10 kDa.

Me_{LMM} *Equation 13: Total concentration of LMM metal species:*

$$Me_{LMM} = S_{10kDa} \tag{13}$$

This represented the total concentration of LMM metal species (below 10 kDa) in the sample.

Me^E_{LMM} *Equation 14: Concentration of inert LMM metal species:*

$$Me^E_{LMM} = S^E_{10kDa} \tag{14}$$

This represented the concentration of inert and/or anionic and therefore nontoxic LMM metal species in the sample (below 10 kDa).

Me^+_{LMM} *Equation 15: Concentration of reactive LMM metal species:*

$$Me_{0.45\mu m} = S_{10kDa} - S^E_{10kDa} \tag{15}$$

This represented bioavailable cationic LMM metal species, such as simple ions, ligands and complexes that would exert toxicity.

3.4 Water analyses

3.4.1 Temperature, pH and conductivity measurements

Parameters such as temperature, pH and conductivity were measured by WTW multi 340i pH meter with SenTix® 41-pH electrode and TetraCon® 325-conductivity probe in the water in order to map conditions which could influence the metal speciation.

3.4.2 DOC/TOC and anion measurements

In order to assess the concentration of organic matter and anions in the water, three parallels of 50 mL sample were taken from each site. Each sample were either taken under water or filled to the brim in a 50 mL Falcon tube, in order to exclude as much oxygen as possible, thus preventing oxidation of the samples. The samples were kept refrigerated and absent from light in order to further increase shelf life before final analysis. TOC was analyzed using organic analyzer (Shimadzu TOC cpn, Kyoto, Japan) and anions using Iachat IC5000 ion chromatography.

3.4.3 Metal analyses using ICP-OES

The determination of the metal and cation concentrations in collected and acidified (5% HNO_3) samples and SCF fractions, were performed using ICP-OES. A house control solution, 1643H, was included in the analyses to eliminate errors and ensure the correct measurements. Three types of solutions were made: blank and standard solution for calibration and quality check for control. The quality check was analyzed in-between the samples from SCF on the ICP-OES analysis run.

3.5 Data handling and accuracy

In order to determine the detection limits 10 blanks were measured and the standard deviation multiplied by 3. The values obtained in measurements were given as mean values (n=3) with standard deviation (SD). To obtain the information on the accuracy, standard house reference material 1643h were included in analyses using ICP-OES.

4   Results and Discussion

4.1   Pilot studies

4.1.1   AMD water quality at Storwartz

The water quality variables and the concentration of metals in the AMD water from Storwartz are given in Table 3.

Table 3: General water quality of Storwartz AMD water (n=3).

Variable	Unit	Date		
		03.01.2012	05.12.2012	11.13.2012
Temperature	[°C]	5.2±0.0	19.9±0.1	20.3±0.1
pH		2.8±0.1	2.8±0.0	2.9±0.1
Conductivity	[µS/cm]	1265	983	967
Al	[mg/L]	2.9±0.1	2.9±0.1	3.1±0.0
Ca	[mg/L]	132±1	133	125
Cd	[mg/L]		0.002±0.000	
Cr	[mg/L]		0.003±0.000	
Cu	[mg/L]	0.69±0.03	0.73±0.01	0.84±0.01
Fe	[mg/L]	66	15.9±0.0	15.3±0.0
K	[mg/L]	7.5±0.1	7.1±0.1	34
Mg	[mg/L]	50	47±1	49
Mn	[mg/L]	2.8±0.1	2.8±0.0	2.7±0.0
Na	[mg/L]	1.9±0.0	1.6±0.0	1.7±0.1
Ni	[mg/L]		0.009±0.000	
S	[mg/L]		221±2	
Si	[mg/L]	5.6±0.2	5.6±0.2	5.5±0.2
Zn	[mg/L]	1.3±0.0	2.2±0.0	2.3±0.0

*Where SD < ±0.05 and SD < ±0.005, SD-values are given as ±0.0 and ±0.00 respectively.

Collected water from Storwartz was characterized as acidic with pH 2.8±0.1, and the high conductivity of 1265 µS/cm suggested high levels of dissolved ions. High water hardness was detected with Ca and Mg concentration at 132 mg/L and 50 mg/L respectively. This allowed for mitigation of toxicity by competition amongst cations. However the concentration of heavy metals such as Cu and Al was high, 0.69 mg/L and 2.9 mg/L respectively, as expected for AMD. There were only minor changes in concentration of Al and Cu by storage. The concentration of Fe in the water changed however from 66 mg/L to 15.9±0.0 mg/L due to

storage from January to May. The change in Fe concentration is probably due to oxidation of ferrous iron and formation of ferric iron particles that settled during storage.

4.1.2 AMD optimization of SCF cation exchange chromatography

Optimization of cation exchange chromatography contact time of sample:

In order to optimize the SCF procedure an experiment was run to study optimal contact time between AMD water and the cation exchange resin with respect to retention of cationic metal species (figure 11).
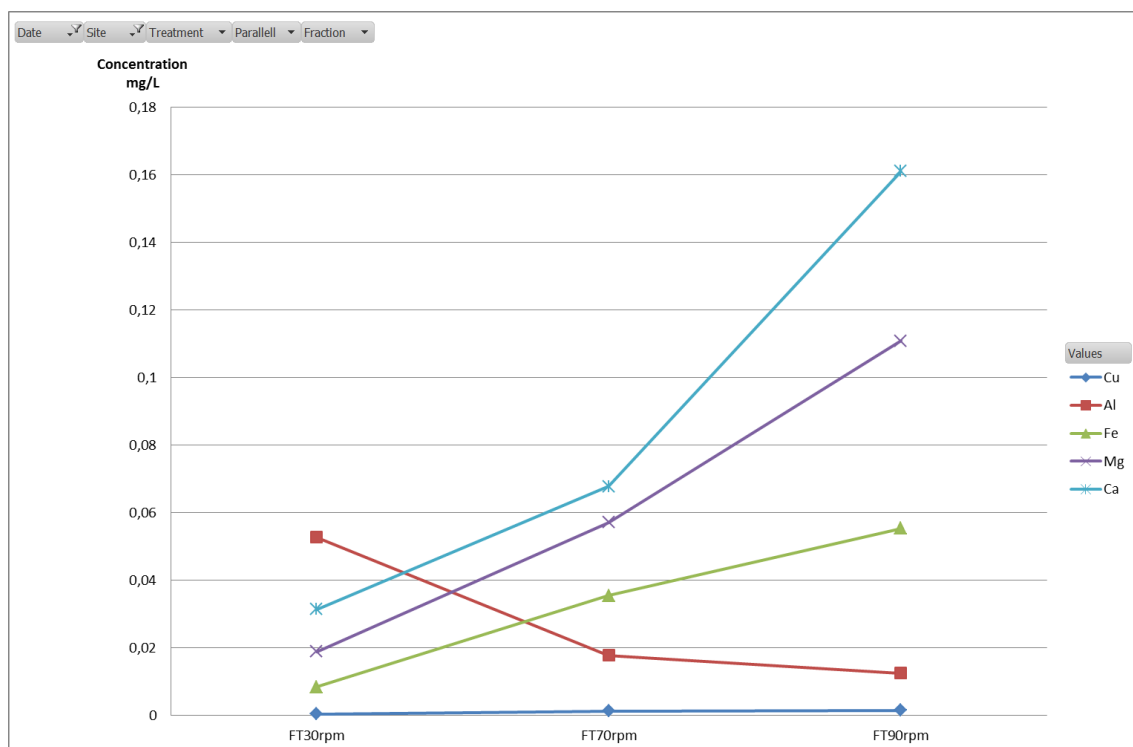
Figure 11: Metal concentration in eluate of cation exchange resin IR-120 Amberlite at different flow rates (FT30rpm = 9 mL/min, FT70rpm = 20 mL/min, and FT90rpm = 26 mL/min).

Using AMD from Storwartz results demonstrated no change in retention of Cu, Al etc. by changing the contact time within the range of 0.4-1.3 mL water /ml resin/ min. 1 mL water/mL resin/min (70 rpm) was therefore used in the SCF procedure.

Optimization of cation exchange chromatography maximum sample volume:

In order to optimize the SCF procedure an experiment was run to study maximum sample volume of cation exchange using pr 20 ml of resin (figure 12).
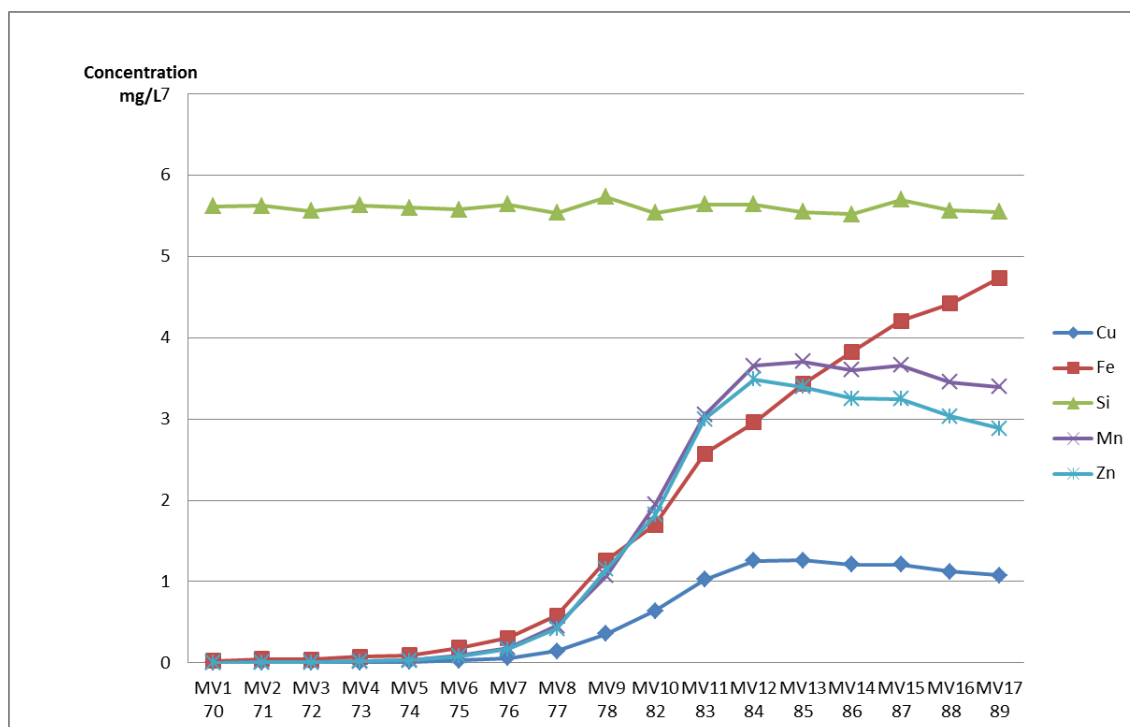
Figure 12: Metal concentration in eluate of cation exchange resin IR-120 Amberlite at increasing number of samples per 200 mL intervals passing 20 mL resin.

Using AMD Storwartz results demonstrated no change in retention of metals such as Cu, Fe, Mn, Al etc within the volume of 1000 mL pr 20 ml resin. A maximum water volume of 200 ml/20 ml resin was used as guidance in the SCF procedure. When maximum volume used, regeneration (see chapter 3.3.1) of the resin performed before reuse.

4.1.3 Dose response tests with NaSil and NaOH in Storwartz AMD test water

Figure 13 shows the distribution of Cu species in AMD water before and after the addition of NaSil and NaOH to a pH of 6.5. As shown in the figure, both additions influenced the Cu speciation. Due to hydrolysis, particles and colloids were formed by NaOH, while colloids were formed by NaSil. The Cu-silicate colloids were more reactive than Cu species formed by NaOH.
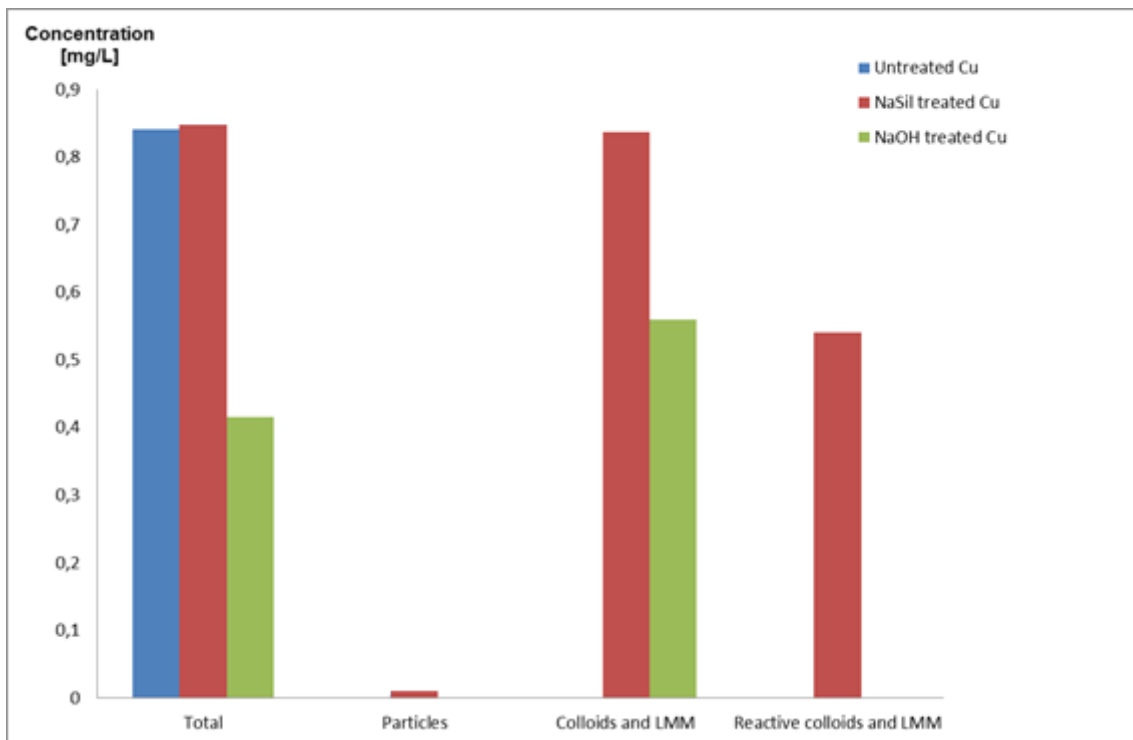
Figure 13: Distribution of Cu species in AMD (Pilot) before and after addition of NaSil and NaOH.

4.2 At site field study at Nordgruvefeltet

Water from three different sites at Nordgruvefeltet were studied; outlet of Lake Orvsjøen, AMD at Arvedalsgruva and River Orva downstream of Arvedalsgruva. Water was sampled and analyzed with regards to general water quality, and SCF was performed *in situ* to obtain information of water metal speciation.

Yellow-boy was observed in the creek draining Arvedalsgruva (including Site 2) and in River Orva downstream of Arvedalsgruva (including Site 3; figure 14), giving visual clues of the polluted state of the water.

Figure 14: Yellow-boy observed at Site 3 in River Orva downstream of Nordgruvefeltet, indicating high levels of precipitated iron species.

The drainage from Nordgruvefeltet was highly acidic, as the mineralogy in the area was rich with sulfide ores. In certain at site measurements conducted in the field studies, the pH was occasionally as low as 2 (in Site 2). Not only was this enough to decimate all aquatic life downstream, but this would also contribute to the pyrite weathering process resulting in elevated rates of dissolution of contaminant metals from the native rock formations.

Water directly from River Orva close to the outlet of Lake Orvsjøen (Site 1), AMD from Arvedalsgruva at Kongens (Site 2) and AMD affected water from River Orva 3 km downstream of Kongens (Site 3) was processed *in situ* with SCF in order to obtain information on the distribution of metal species, as well as the total concentration of metals. The water sampling protocol (chapter 3.3) was used to obtain information on water quality

and change in water quality and metal speciation downstream of the mixing of River Orva (site1) and AMD from Kongens (Site 2).

Table 4: General water quality and metal concentrations in River Orva upstream (Site 1) and downstream (Site 2) of Kongens and at the outlet of Arvedalsgruva (Site 3) (n=3).

	Variable	Unit	Site 1	Site 2	Site 3
Water conditions	Temperature	[°C]	5.5±0.0	2.9±0.0	3.9±0.1
	pH		6.6±0.1	2.8±0.0	4.6±0.0
	Conductivity	[μS/cm]	34	1706	99
	TOC	[mg/L]	1.6±0.1	2.0±0.0	0.95±0.08
	F^-	[mg/L]	0.04±0.00	0.54±0.08	0.05±0.01
	Cl^-	[mg/L]	1.0±0.0	0.97±0.14	1.1±0.0
	NO_3^--N	[mg/L]	<0.01±0.00	0.03±0.01	0.02±0.00
	SO_4^{2-}	[mg/L]	7.8±0.0	916	37±2
Water cations	Ca	[mg/L]	3.2±0.0	39	5.9±0.0
	K	[mg/L]	0.41±0.00	2.0±0.0	0.75±0.02
	Na	[mg/L]	0.86±0.01	2.4±0.0	1.0±0.0
	Mg	[mg/L]	0.70±0.01	29	1.8±0.0
	S	[mg/L]	2.47±0.08	245	11.6±0.0
	Si	[mg/L]	1.3±0.0	20	2.0±0.0
Heavy metals	Al	[mg/L]	0.11±0.00	30	0.76±0.0
	Cu	[mg/L]	0.08±0.00	12.3±0.1	0.26±0.00
	Cd	[mg/L]	0.0007±0.0001	0.05±0.00	0.002±0.0001
	Cr	[mg/L]	0.0001±0.0001	0.043±0.000	0.0006±0.0002
	Fe	[mg/L]	0.043±0.001	80	4.7±0.0
	Mn	[mg/L]	0.033±0.001	1.0±0.0	0.17±0.00
	Ni	[mg/L]	0.001±0.000	0.13±0.00	0.005±0.0003
	Zn	[mg/L]	0.36±0.00	26.7±0.1	1.1±0.0

4.2.1 General water quality in River Orva at the outlet of Lake Orvsjøen upstream of Arvedalsgruva (Site 1)

Sampling of water was performed directly in River Orva, by the outlet of Lake Orvsjøen, approximately 1 km upstream of Arvedalsgruva. The water quality at the time of sampling is presented in table 4, and shows that the water exiting Lake Orvsjøen and entering into River Orva (Site 1) is not acidic, but have moderate concentrations of metals. Measurements

showed the water pH was 6.6±0.1 and the water conductivity to be 34±0 µS/cm, both adequate levels. TOC was measured to be 1.6±0.1 mg/L indicating relatively low concentrations of dissolved organic species which potentially could mitigate the bioavailability of metals. Generally, the combination of low ionic strength and low TOC water made this aquatic ecosystem sensitive to acidification. Low concentrations of water cations were detected indicating reduced ability to compete with the eventual uptake of heavy metal ions in aquatic biota.

However, the heavy metal concentrations were relatively low and, with the exception of Zn (0.36±0.00 mg/L), Cu (0.08±0.00 mg/L) and Al (0.11±0.00). This confirms Iversen & Arnesen's (2001) observation of Zn leaking from the submerged waste rock pile in Lake Orvsjøen. The Cu concentration and Al concentration was in the range classified as strongly polluted (see Chapter 2.3) and the distribution of Cu and Al species would likely play a crucial role in resulting toxicity.

Some of the values measured (Cd, Cr and Ni) were approaching the detection limits of ICP-OES, making them prone to a relatively low tolerance for error margins. Making a conclusion based on these values should not be done before taking the facts mentioned into consideration.

4.2.2   General water quality at the outlet of Arvedalsgruva (site 2)

Water samples collected from AMD at Arvedalsgruva (site 2) were taken directly from a pond NIVA had previously built at the outlet of Arvedalsgruva. The outlet was submerged in the pond. Discharge water ran from the pond into a creek which drained to River Orva 1 km to the east.

The water smelled of sulfur and appeared colorless. However, rapidly increasing levels of yellow-boy were observed when exploring further down the creek. This indicated ferric iron precipitating as "Yellow-boy" when the drainage became sufficiently diluted in the stream and the pH was rising.

The water quality at the time of sampling is presented in table 4. The drainage from Arvedalsgruva was highly acidic (pH 2.8±0.0), as the mineralogy in Arvedalsgruva was rich with sulfide ores. Not only was this enough to decimate all aquatic life downstream, but this

would also contribute to the pyrite weathering process, resulting in elevated rates of dissolved contaminant metals from the native rock formations.

The high conductivity of 1706 μS/cm measured indicated large amounts of ions dissolved in the water. Mitigating factors such as TOC and anions, with the exception of SO_4^{2-}, were quite low, giving the water insufficient ameliorating capabilities. The enormous concentration of SO_4^{2-} came as no surprise as the AMD originated from pyrite weathering inside Arvedalsgruva. The levels of competing cations at Site 2 were high, but would not be sufficient to counteract the severe levels of heavy metals. The concentration of Cu was much higher than the reported critical levels in very Ca rich freshwater (Grosell, 2012).

Massive levels of heavy metals were detected in Site 2. The concentration of each individual metal was sufficient enough to kill all aquatic life in the creek many times over. As an example, Cu was measured to 12.3±0.1 mg/L which was about 1000 times the given water quality criteria for very Ca rich freshwater (Grosell, 2012), and limits set by the Norwegian Environmental Agency (figure 1) The AMD discharge from Arvedalsgruva would undoubtedly cause serious environmental repercussions in the receiving River Orva.

4.2.3 General water quality in River Orva downstream of Arvedalsgruva (site 3)

The water quality in River Orva changed significantly after passing through the area at Arvedalsgruva (site 2), to more acid and higher concentration of metals. This suggests that the the mining area around site 2 was a major source of pollution in the Orva catchment area. The extremely contaminated conditions of the water running out of the Arvedalsgruva (Site 2) affirmed this assumption.

The conditions in the river downstream of Kongens (including Site 2) were critical. The water acidity was very low (pH 4.6±0.0), which was sufficient to cause problems to water dwelling organisms. *E.g.* fish species like brown trout generally don't manage to produce livable offspring under these conditions, while perch will have serious trouble (Lane, 2003). Species like salamanders, snails and mayflies will go to extinction in these conditions (Lane, 2003). The levels of TOC and anions were higher than in Site 1, but nevertheless insufficient to mitigate heavy metal bioavailability. Competing cation levels in the river were elevated, but generally not enough to counter the high concentrations of heavy metals.

The studies showed elevated levels of heavy metals in River Orva at Site 3, compared to Site 1. As an example, the level of Cu was 0.26±0.00 mg/L. This is about 20 times higher than the limits set by the the Norwegian Environmental Agency and reported suggestions for water quality criteria for Ca rich freshwater (Grosell, 2012)

To conclude, the highly concentrated AMD run-off from the Kongens area would certainly have an impact on downstream in the River Orva, establishing Arvedalsgruva as the main source of pollution in the river exiting Nordgruvefeltet.

The levels of measured TOC and anions were generally low in all three sites with the exception of SO_4^{2-}, which was abundant in the Arvedalsgruva discharge water (including Site 2) and downstream in River Orva (including Site 3), due to weathering and dissolution of the sulfur (S) containing pyrite rock in the area. The capability of the water to mitigate the pollution (*e.g.*, buffer capacity) was generally poor in these sites.

Comparing the concentrations of S and major cations such as Ca at site 1, 2 and 3, results indicated that the AMD coming from Arvedalsgruva was diluted 25 times by River Orva at the sampling station downstream. Measured concentrations of metals in water indicated high levels of Al, Cu and Zn at levels associated with strong pollution (Chapter 2.3).

4.2.4   Concluding statements

The water quality in River Orva changed significantly after passing through the area at Arvedalsgruva (site 2), to more acid and higher concentration of metals. This suggests that the the mining area around site 2 was a major source of pollution in the Orva catchment area. The extremely contaminated conditions of the water running out of the Arvedalsgruva (Site 2) affirmed this assumption.

4.3   Speciation of metal run-off at Nordgruvefeltet

In situ speciation with SCF was conducted in River Orva upstream of Arvedalsgruva (Site 1) to assess the composition of metal species in the water draining Lake Orvsjøen.

4.3.1 Metal speciation in River Orva upstream of Arvedalsgruva (Site 1)

Total metal concentrations in Site 1 were generally low except for Al, Cu and Zn. Using SCF results demonstrated that Al was mainly present as Al particles, some Al colloids and at low concentration as LMM AL species (< 5 µg/L). For Cu, about 30% was present as LMM Cu cations, and the rest as particles and colloidal species.
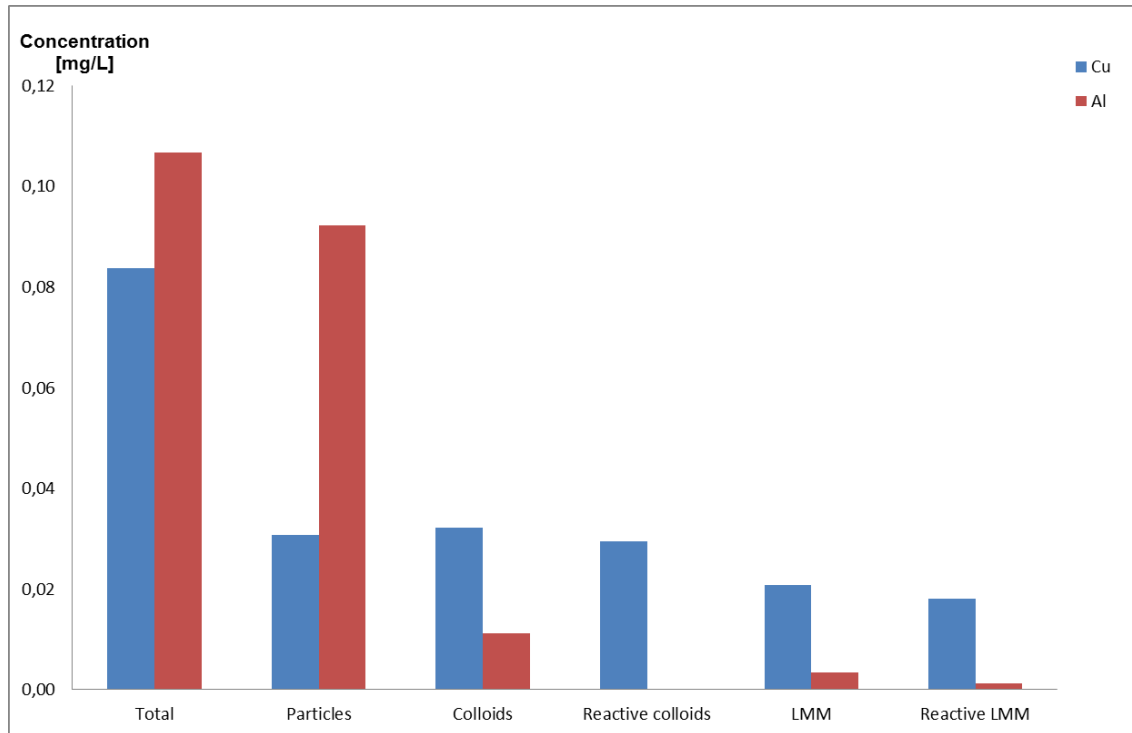

Figure 15: Speciation of Cu and Al in in River Orva upstream of Arvedalsgruva (Site 1).

Cu was almost evenly distributed amongst the size classes, with the concentration of species in the LMM fraction being about 30% smaller than the concentration of species in the particulate and colloidal range according to the *in situ* measurements shown in Figure 15. Nevertheless, most of the LMM species (0.018±0.01 mg/L or about 90%) existed as bioavailable cations, which is still fairly high. Al existed mainly as particle bound species, which were assumed to be inert. A small fraction existed as colloids, and an even smaller (one third or 0.003 mg/L) fraction existed as LMM Al species. Thus, the results from the fractionation indicated that a high fraction of Cu and Al is present as particles and colloids, assumed less toxic than LMM Species. The concentration of LMM Cu species was approximately 20 µg/L and still higher than critical limits. The concentration of LMM Al species was low and below critical limits.

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4.3.2 Metal speciation at the outlet of Arvedalsgruva (site 2)

Utilizing *in situ* fractionation with SCF at the outlet of Arvedalsgruva (Site 1) results indicated that metals such as Al and Cu was mainly present as LMM species (figure 16).
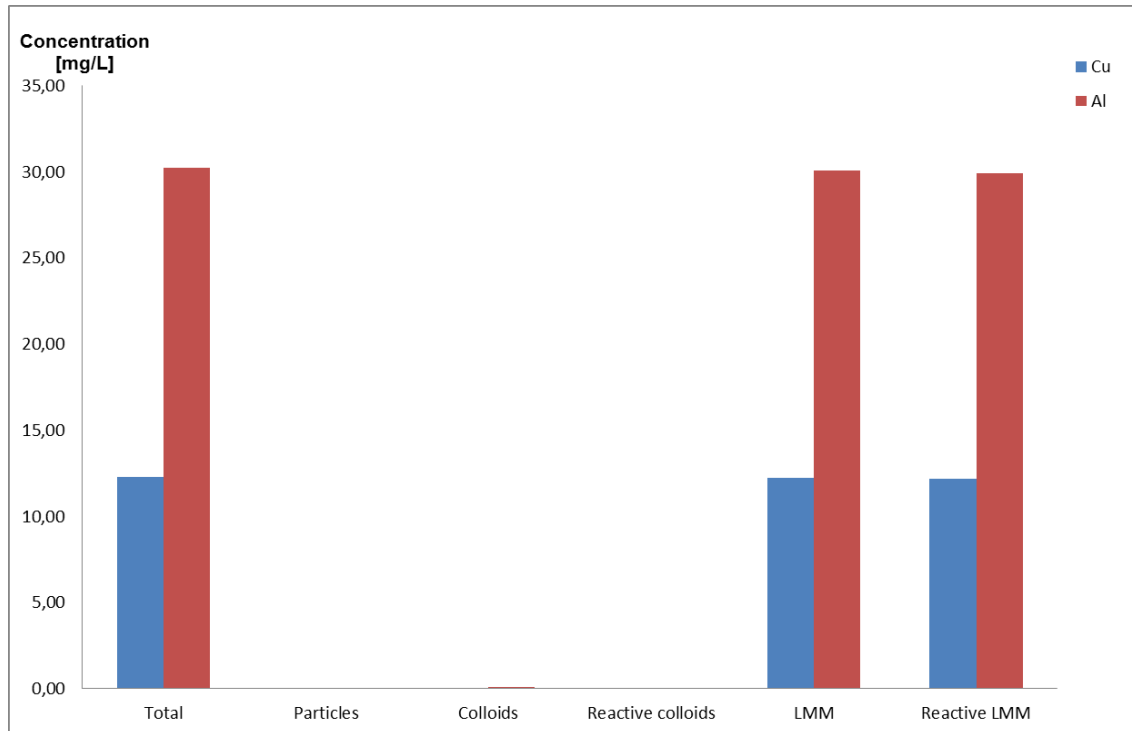

Figure 16: Speciation of Cu and Al at the outlet of Arvedalsgruva (Site 2).

The results showed that the AMD from Arvedalsgruva was very acidic (2.8±0.0), which made metal solubility high. High concentrations of metals were registered. Measurements showed very high levels of Cu and Al exclusively present in reactive LMM forms. Thus, almost all metal species were bioavailable.

4.3.3 Metal speciation in River Orva downstream of Arvedalsgruva (site 3)

In River Orva (including Site 3) downstream of Kongens the water quality was strongly influenced by the AMD from Arvedalsgruva that significantly reduced the pH and increased the metal concentration in the river water compared to upstream water quality. Using SCF results (figure 17) demonstrated that Cu was mainly present as LMM species. Al was present mostly in LMM form, but also some in particulate form and at similar level as upstream the point of mixing with the AMD affected creek draining Arvedalsgruva (including Site 2). This indicated generally high bioavailability for both elements and that speciation of Cu and Al of

AMD were maintained after mixing with River Orva. This was probably due to the relatively low pH at 4 in combination with low TOC.
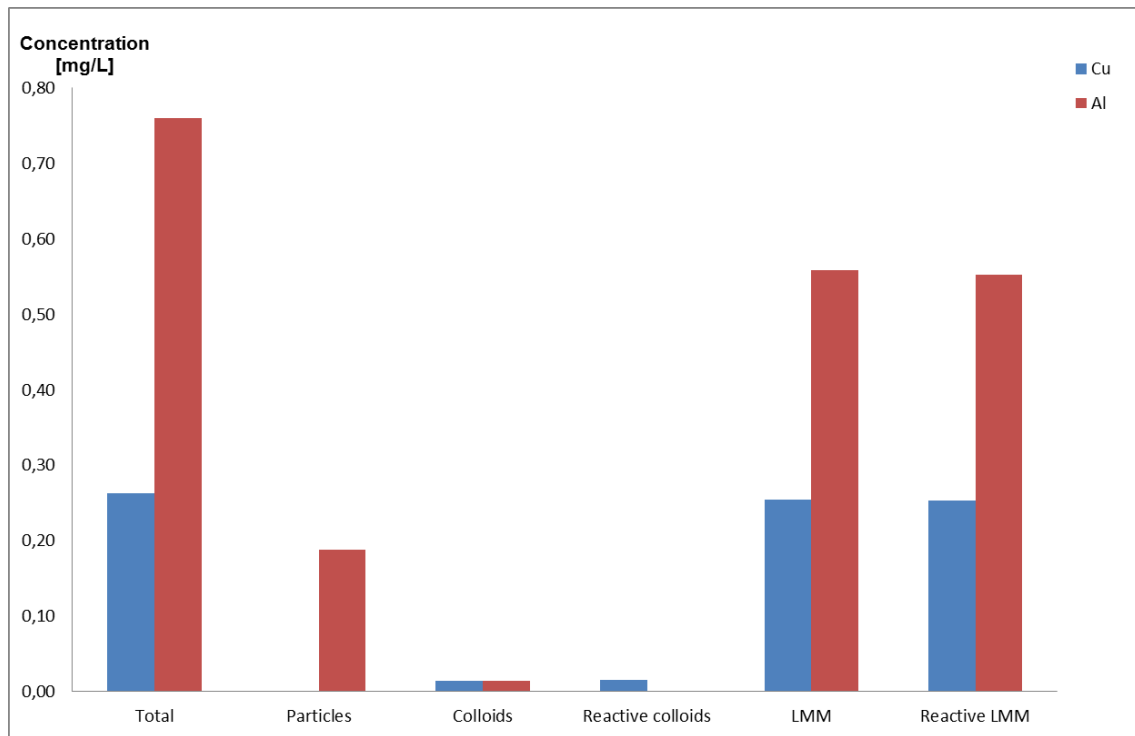

Figure 17: Speciation of Cu and Al in in River Orva downstream of Arvedalsgruva (Site 3).

4.3.4 Concluding statements

In River Orva (including Site 3) downstream of Kongens the water quality was strongly influenced by the AMD from Arvedalsgruva that

4.4 *In situ* test with NaSil in AMD at Nordgruvefeltet.

Remediation testing of AMD from the outlet at Arvedalsgruva (Site 2) with NaSil was conducted 10.06.2012 to 10.07.2012. The water conditions in Site 2 were measured (pH was 2.8 at 2.9°C). 2.57 ml K40 NaSil/L were added in 5 L plastic can with the AMD test sample from Site 2 (5.15 pm) and fractionation with SCF was conducted shortly after (5.30 pm). PH increased from 2.8 to 6.5 but was unstable.

A complementary experiment with addition of NaOH to AMD was also conducted to study the effects of increased pH alone on the AMD from Arvedalsgruva (Site 2). 0.95 ml 4 M NaOH/L was added in the AMD test sample (8.30 pm) which made the pH rise from 2.9 to 6.7. A yellow-brown precipitate (shown in figure 18 below) formed immediately after addition of NaOH, and subsequent fractionation with SCF was delayed (9.10 pm) until conditions in the sample had stabilized.

Figure 18: Precipitation after addition of NaOH in 5 L plastic can with sample water (AMD) from Site 2.

The Cu concentration in the sample decreased from 12.3 ± 0.1 mg/L to 11.9 ± 0.2 mg/L after addition of NaSil (figure 19). Though no precipitation was visible it could still be possible that some precipitate could form, or that a fraction of the newly formed Cu-species would adsorb to the walls of the sample vessel (5 L plastic can).

The following distribution of Cu species was obtained from the SCF results.
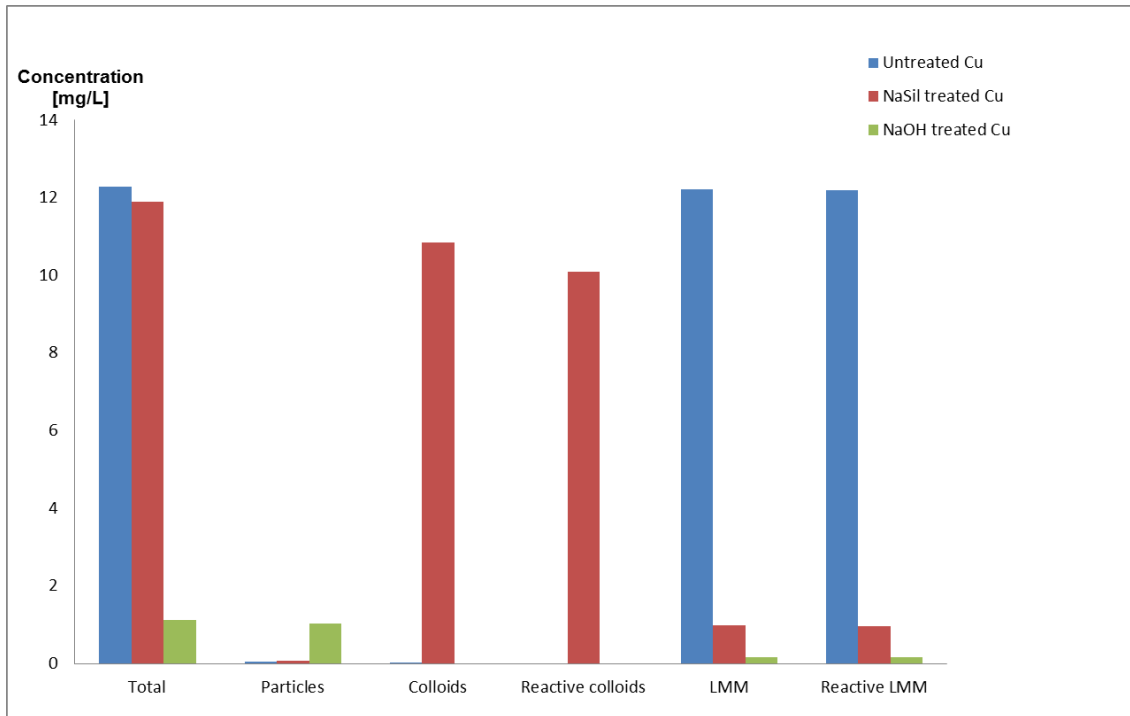
Figure 19: Distribution of Cu species in AMD from Arvedalsgruva (Site 2) before and after treatment with NaSil and NaOH.
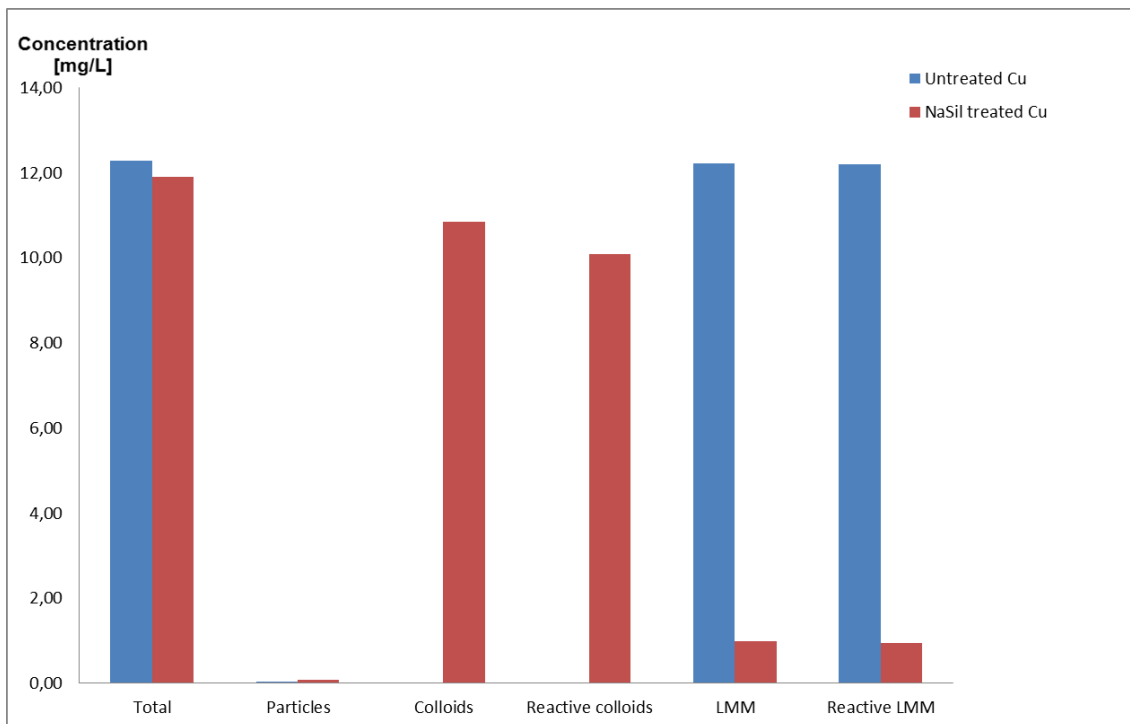

Figure 20: Distribution of Cu species in AMD from Arvedalsgruva (Site 2) after treatment with NaSil.
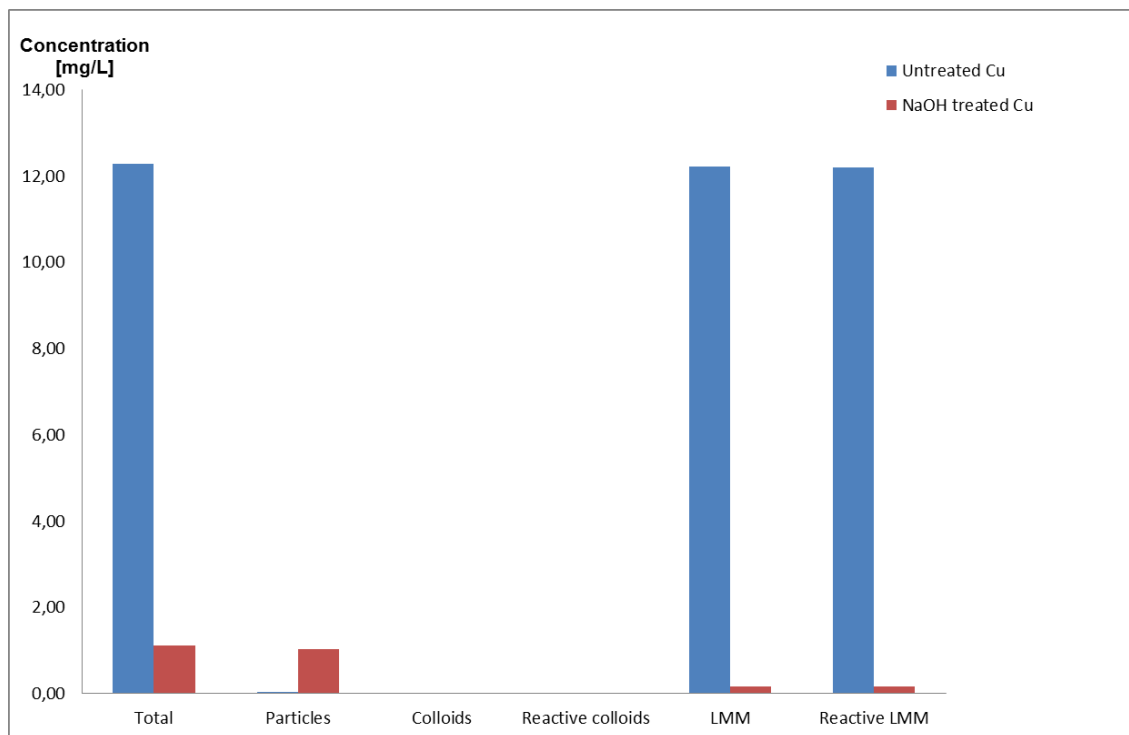
Figure 21: Distribution of Cu species in AMD from Arvedalsgruva (Site 2) after treatment with NaOH.

Judging by figure 20, Cu in junction with silicate would predominantly form compounds in the colloidal range (10.9±0.2 mg/L). The levels of bioavailable LMM species plummeted about ten-fold from 12.2±0.1 mg/L to 0.95±1.27 mg/L. However, most of the Cu-silicate colloids formed were in reactive form and possibly bioavailable.

Addition of NaSil to AMD at Arvedalsgruva (site 2) changed the distribution of Cu species (Figure 20). Results demonstrated that the Cu concentration decreased from about 12.3 to 11.9 mg/L due to addition of NaSil, but from 12.3 to 1.2 mg/L using NaOH at similar pH value.

Treatment with NaOH made almost all Cu precipitate as shown in figure 21. This observation was further reinforced by the fact that a yellow-brown precipitation was detected after addition of NaOH to the sample water, as shown in figure 21. The precipitate was colored by precipitation of Fe species.

When using NaOH, Cu was mainly transferred from LMM species to particulate species that precipitate (figure 21). Addition of NaOH to the AMD removed more reactive LMM Cu compared to addition of NaSil. However, the Cu precipitates could eventually be remobilized.

Similar trends were observed for both Al and Cu. Results demonstrated thus that silicate influencing the speciation of both Al and Cu.
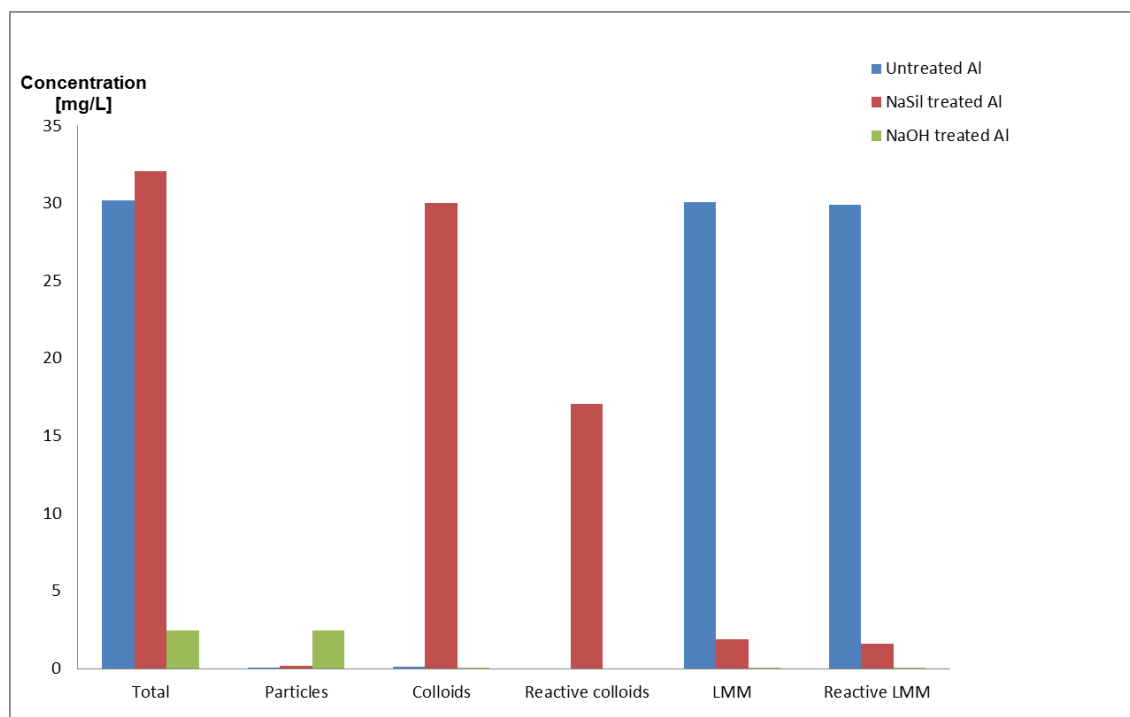
Figure 22: Distribution of Al species in AMD from Arvedalsgruva (Site 2) before and after treatment with NaSil and NaOH.

Reactive Al LMM species, like Cu, converted into colloidal form when treated with NaSil (figure 22). Unlike Cu, about half of the Al formed unreactive colloidal species.

Al was transferred to relatively inert particles, while Cu-silicate was present as reactive colloids. The bioavailable LMM species were significantly reduced.

5   Conclusion

In river Orva upstream of the Kongens area (Site 1) the water was polluted and showed moderate levels of metals. However, the conditions were not as extreme as downstream Kongens area in Site 3.

In river Orva downstream of the Kongens area (Site 3) the water conditions deteriorated after mixing with run-off at the Kongens area and the river was classified as strongly polluted.

The origin of the pollution in River Orva was attributed to the Kongens area with run-off of AMD from Arvedalsgruva (Site 2) as the main source.

The results from the *in situ* SCF studies showed the water in River Orva upstream of Kongens (including Site 1) to change from a relatively even distribution of species size classes to mostly reactive LMM downstream of Kongens (including Site 3) after mixing with the AMD run-off from Kongens (including Site 2). This further proves Arvedalsgruva (including Site 2) at the Kongens area to be the main source of AMD in River Orva.

The general quality of the water in River Orva implied that countermeasures should be implemented. As a test NaSil was added to AMD water obtained at the outlet of Arvedalsgruva (Site 2) in the Kongens area. Results demonstrated thus that silicate influencing the speciation of both Al and Cu, transforming LMM species to less toxic species. Al was transferred to relatively inert particles, while Cu-silicate was present as reactive colloids. The bioavailable LMM species were significantly reduced. Using NaSil, the concentration of Cu was kept at high level in water at pH close to neutral (measured pH was 6.5) and Cu was mainly present as colloids.Using NaOH, Cu is mainly transfered from LMM species to particulate species and that precipitated. Future studies on silicate reaction rates, stability and dose-response lethality on fish should be conducted in order to further assess NaSil as a remediator to the AMD problem in Nordgruvefeltet and to evaluate if the bioavailibility of the colloidal Cu-sil species formed.

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7 Appendix

7.1.1 Materials

List of equipment used with SCF.

Equipment
SCF fractionation array
Hoses, tubes and fittings
Columns
Spatula
WTW combined conductivity- and pH-meter
Zipperbags
15 mL Falcon tubes
50 mL Falcon tubes
Ring stand
Utility Clamps
Peristaltic pump
Millipore 0.45 µm filter
10 kDa hollow fibre w/ vessel
Biohit Automatic pipette

List of equipment used with pH measurement.

Equipment	Quantity
PH-meter	1
PH electrode	1
PH electrode sheath	1
Conductivity electrode	1

7.1.2 Chemicals

List of chemicals used with SCF.

Chemical	Volume
3M HCl solution	1 L
3M NaCl solution	1 L
MilliQ water	10 L
K40 sodium silicate solution	50 mL
4 M NaOH solution	50 ml
IR-120 Amberlite Column Fillings	20 mL

List of chemicals used with pH measurement.

Chemical	Volume	Quantity

Calibration buffer pH 7.00	25ml vial	1
Calibration buffer pH 4.01	25ml vial	1
MilliQ (<18 ohm)	unlimited	

Preparation of Standard Solution for ICP-OES.

The volumetric flask [1L] was filled half-way with MilliQ-water. UltraPure HNO_3 [50 ml] was added to the water (10x5ml) and mixed together by shaking the flask thoroughly. Standards for each element to be analyzed were added to the solution in concentrations shown in the table below.

List of elements used in the standard solution

Element	Concentration in Solution	Standard Concentration	Added
Rh	100 μg/L	20 μg/L	5 mL
Cu	1 mg/L	1 mg/L	1 mL
Mn	10 mg/L	1 mg/L	2x5 mL
Fe	10 mg/L	10 mg/L	1 mL
Al	1 mg/L	1 mg/L	1 mL
Zn	10 mg/L	1 mg/L	2x5 mL
Ca	10 mg/L	10 mg/L	1 mL l
Mg	10 mg/L	10 mg/L	1 mL
K	10 mg/L	10 mg/L	1 mL
Na	10 mg/L	10 mg/L	1 mL
Si	10 mg/L	10 mg/L	1 mL
S	10 mg/L	10 mg/L	1 mL
Cd	500 μg/L	1 mg/L	500 μL
Ni	500 μg/L	1 mg/L	500 μL
Cr	500 μg/L	1 mg/L	500 μL

Again the flask was shaken. Then the flask was filled with MilliQ-water to the 1L-mark and shaken one last time. The ready standard solution was transferred to a 1L plastic bottle and kept in refrigerating conditions.

Preparation of Quality Check for ICP-OES

The volumetric flask [1L] was filled half-way with MilliQ-water. UltraPure HNO_3 [50 ml] was added to the water (10x5ml) and mixed together by shaking the flask thoroughly. Standards were added to the solution in concentrations shown in the table below.

List of elements used in the Quality Check.

| Element	Concentration in Solution	Standard Concentration	Added
Rh	100 μg/L	20 μg/L	5 mL
Cu	1 mg/L	1	1 mL
Mn	10 mg/L	1	2x5 mL

|			
Fe	10 mg/L	10	1 mL
Al	1 mg/L	1	1 mL
Zn	10 mg/L	1	2x5 mL
Ca	10 mg/L	10	1 mL
Mg	10 mg/L	10	1 mL
K	10 mg/L	10	1 mL
Na	10 mg/L	10	1 mL
Si	10 mg/L	10	1 mL
S	10 mg/L	10	1 mL
Cd	500 µg/L	1	500 µL
Ni	500 µg/L	1	500 µL
Cr	500 µg/	1	500 µL

Again the flask was shaken. Then the flask was filled with MilliQ-water to the 1L-mark and agitated one last time. The ready quality check was transferred to a 1L plastic bottle and kept in refrigerating conditions.

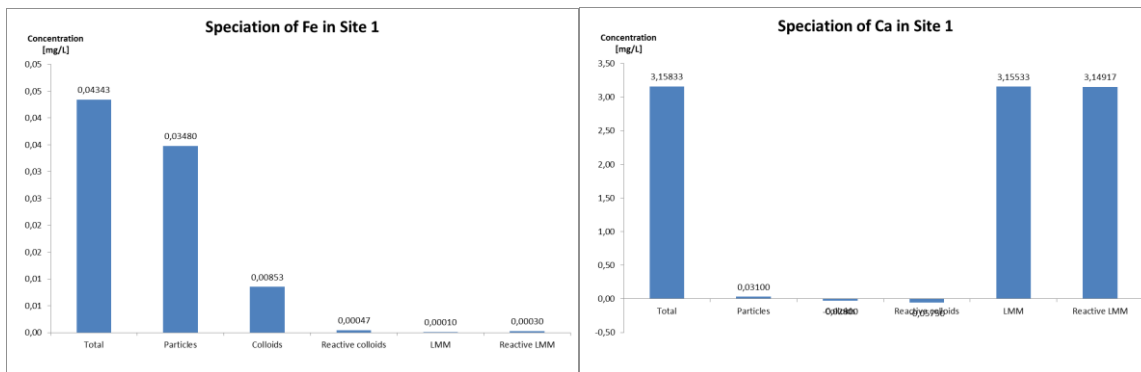*Preparation of 5% HNO$_3$ Blank Solution For ICP-OES.*

An acid washed plastic bottle [1L] was filled half-way with MilliQ-water. UltraPure HNO$_3$ [50 ml] was added to the water (10x5mL) and the contents were mixed together. The bottle was then filled up to the 1L-mark and the contents mixed.

Miscellanesous tables
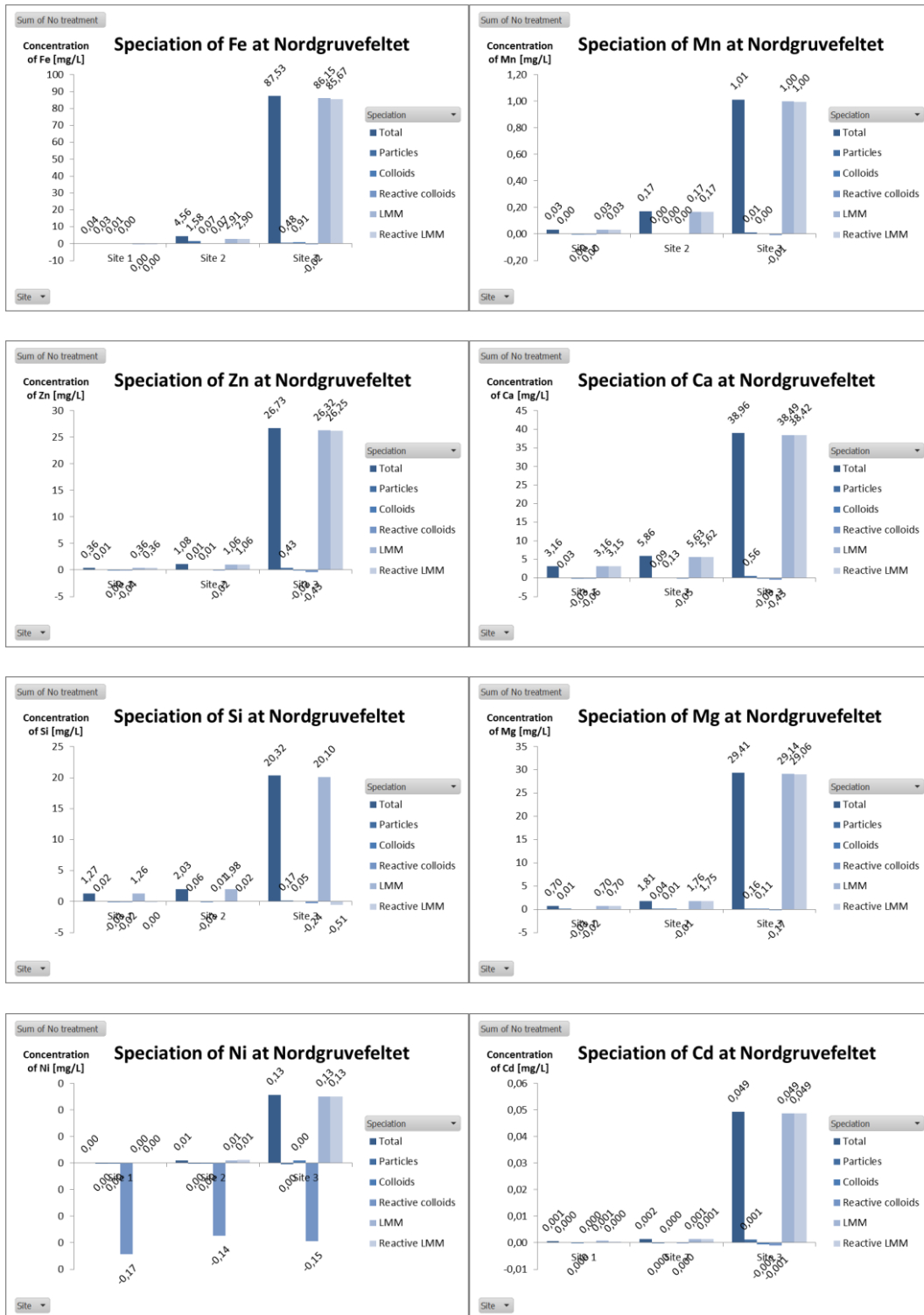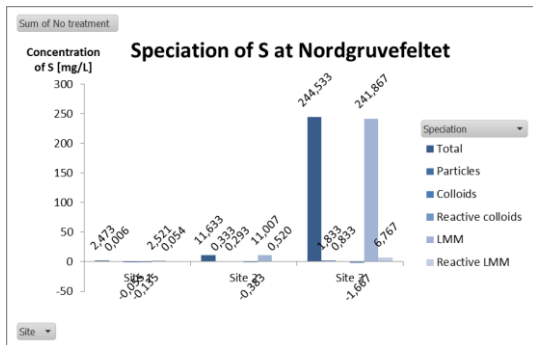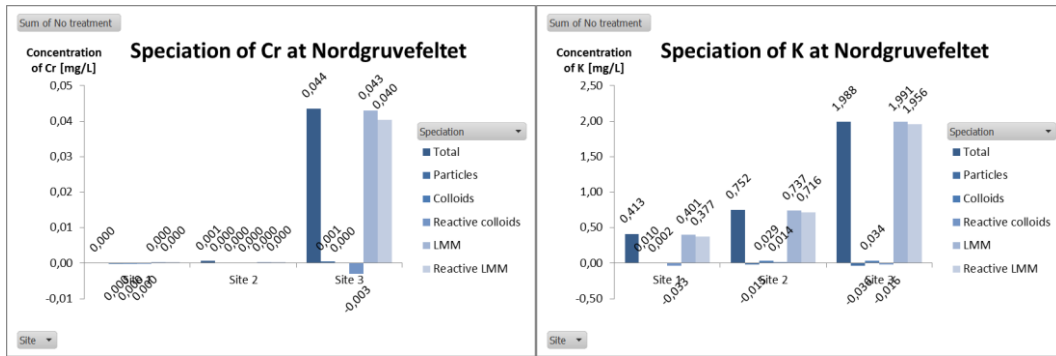
Speciation of Fe and Ca in River Orva upstream of Arvedalsgruva (Site 1).