Declining element concentrations in groundwater after remediation in sulphide-rich tailings at Kristineberg, northern Sweden

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Abstract In 1996, pyrite-rich tailings exposed to aerobic oxidation for 50 years at a site in northern Sweden were remediated using two different approaches: water saturation and dry cover. Between 1998 and 2009, notable improvements of the site's groundwater were observed. The improvement was faster below dry cover, but more extensive in the saturated tailings. Elements such as Al, Cd, Co, Cr, Cu and Ni were almost entirely removed. The formation of Al-hydroxides was important in the removal of Co, Cr and Ni, while Fe-oxy-hydroxides, sulphide formation, and sorption on pyrite surfaces were important in the removal of Cd and Cu.

Key Words sulphide tailings, groundwater, remediation

Introduction

It has been estimated that approximately 2,900 million tonnes of mine waste are generated annually in European mines (Eurostat), and 60 million tonnes per year in Swedish mines (Swedish EPA). More than 700 million tonnes of sulphide-containing wastes have accumulated in Sweden. Sulphide-rich mine wastes can cause environmental problems due to the formation of acidic drainage waters, commonly referred to as acid rock drainage (ARD; see for example Nordstrom et al., 1999). The Swedish approach to eliminating this problem centres around preventing the generation of ARD rather than actively treating it once it has been formed. The most common methods for this prevention involve covering the sulphide tailings with water or with dry material in order to decrease the rate at which oxygen can diffuse into them. The Kristineberg mining area in the Skellefte Ore District of northern Sweden contains a large amount of pyrite-rich tailings that have been exposed to aerobic oxidation for up to fifty years. In 1996, these tailings were covered. Where possible, the tailings were saturated with water with a layer of till above. In areas where saturation was not possible, the tailings were sealed using a layer of clayey till, and an unspecified till above that. This article describes the effect that this remediation has had on groundwater quality in areas with pyrite-rich tailings at Kristineberg over over a period of 13 years.

Methodology and study site

The Kristineberg mining area is located in the western part of the Skellefte Ore District in northern Sweden. It contains five impoundments, of which impoundment 1 is the oldest, having an area of approximately 0.11 km^2, an average thickness of 5 m. When first deposited, the unoxidised tailings contained pyrite (26%), sphalerite (1.3%), copper (0.28%), galena (0.08%) and arsenopyrite (0.05%) and minor amounts of carbonates. The major gangue minerals were silicates. In 1996, impoundment 1 was remediated. Fourteen groundwater pipes were installed in the impoundment, along with a reference pipe P outside the impoundment. Sampling of the groundwater began in August 1998, two years after remediation, and continued until the winter of 2009. GeoN groundwater technology was used to collect water samples without exposing them to air. The samples were filtered through 0.22 µm Millipore ® nitrocellulose membrane filters that had been pre-washed with acetic acid; after filtration, the samples were stored under cool and dark conditions until analysis. Their pH and electrical conductivity were determined. The samples' dissolved phases were analysed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS).

Results and discussion

The predominant cations in the groundwater were Fe, Mg and Ca; some samples also contained significant quantities of Al and Zn. The predominant anion in solution was S; only very low levels of bicarbonate were present in the groundwater.

Pipe P is a reference pipe situated in the surrounding till outside Impoundment 1, and was used to measure background groundwater levels of the various contaminants of interest. In the reference pipe the pH was around 6 and EC <1 mS/cm. The pre-remediation concentrations of Fe and S were c. 3000 mg/L, while those of Cu and Zn were approx. 2500 µg/L and 300 mg/L, respectively. In 2009, the concentrations of Mn, Fe and S were still higher in most pipes than in the reference pipe P. The concentrations of Mn and S in the effluent water were relatively high; it is likely that this is attributable to high levels of the reduced forms of Mn and Fe, which was displaced through the impoundment and then undergoes oxidation on contact with the more oxidising conditions and higher pH outside the impoundment. It is likely that the limited scope for redox chemistry within the pipes decreased the rate of formation of Mn and Fe-oxy-hydroxides.

The changes in the measured concentrations of Fe and S over time are illustrated in Figure 1; similar trends were observed for Mg, Mn and Zn. In general, relative to pre-remediation levels, the elemental concentrations decreased and the pH increased in both the water-saturated and the dry covered areas of impoundment 1 over the course of the study period. In the water saturated areas, it is likely that an initial wash-out of the oxidised zone would have increased the con-

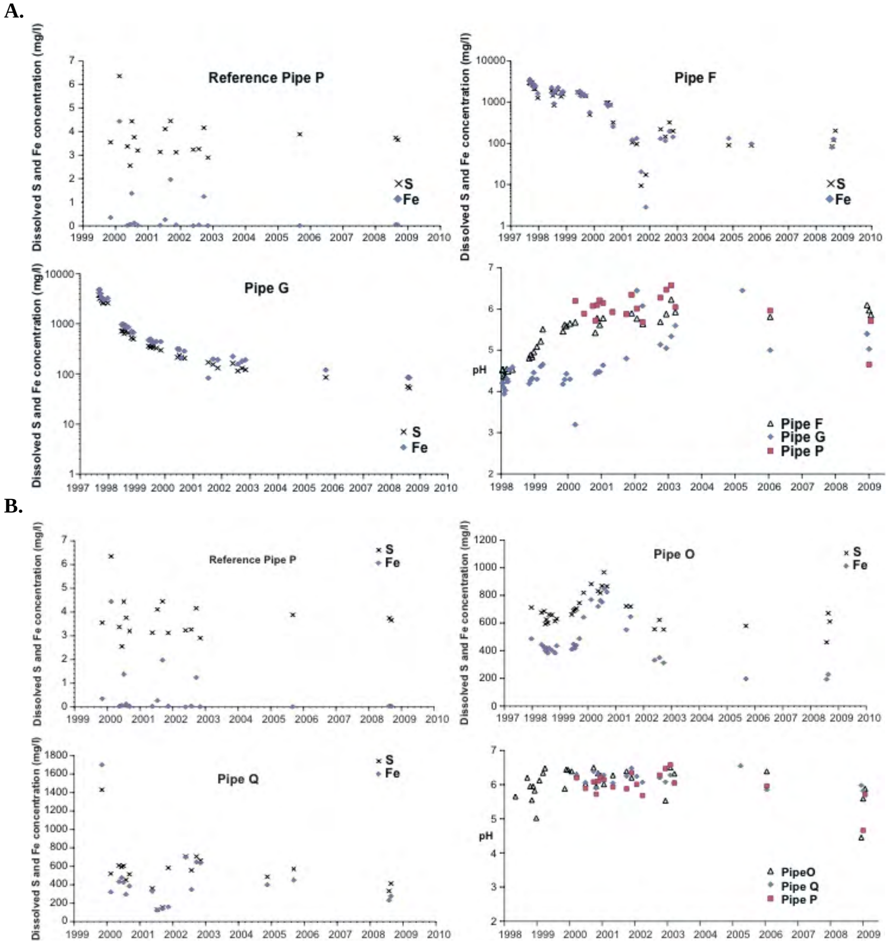

Figure 1 *The variation in the dissolved concentrations of Fe and S, and in the pH in selected pipes in the groundwater in the sulphide rich tailings in Impoundment 1 at Kristineberg and in the reference pipe P, A) In the saturated tailings, exemplified by pipes F and G; B) In the tailings under dry cover, exemplified by pipes O and Q. The trends in the concentrations of Mg, Mn and Zn were similar to those of Fe and S*

centrations of elements such as Fe and S. The groundwater may have become enriched in these species by dissolution of soluble minerals or salt and release from pore water in the oxidised zone. As the remediation progressed, a decrease in the rate of sulphide oxidation and replacement by the local groundwater with less contaminated water caused the concentrations of these elements to decrease (Figure 1A). In the tailings under dry cover, the concentrations of elements such as Fe and S decreased rather rapidly after remediation compared to those saturated with water, and the levels of these elements stabilised over the course of the sampling period (Figure 1B). The decreased rate of sulphide oxidation below the dry cover is due to decreases in the rates of diffusion of oxygen and infiltration of water.

The concentration of heavy metals in the effluent groundwater was low throughout the sampling period, which suggests that these species may be retained within the impoundment after remediation. In 2009, the concentrations of heavy metals such as Cd, Cu, and Zn in the groundwater of the impoundment were lower than before; in some cases, they were even lower than those observed in the reference pipe P (Figure 2). The concentrations of most of the metals studied were found to be strongly sensitive to the pH, with the concentrations decreasing as the pH increased. Lead, Co and Ni were barely detectable at pH 5, while the concentration of Cd was low throughout the pH range (Figure 2).

The concentrations of Al, Cd, Co, Cr, Cu, Ni and Pb exhibited different trends with respect to pH than did those of Fe, Mn, Mg, S and Zn, which behaved in accordance with the dilution effect. This suggests that Cd, Co, Cr, Cu, Ni and Pb were more affected by changes in the environmental conditions than by dilution. Results obtained in a previous study indicated that As, Cu, Cd and Pb were retained just below the oxidation zone in the tailings (Holmström et al. 2001). Some copper was retained as covellite, CuS, and it is likely that some additional copper would have been adsorbed onto mineral surfaces (Holmström et al. 2001). Similar Cu enrichment zones have been observed in other sulphide-rich mine tailings (for examples Boorman and Watson 1976). A study using laser ablation ICP-SMS showed that As, Cu and Cd were also enriched on pyrite surfaces in the tailings (Öhlander et al. 2007). Metals such as Co, Cr and Ni are known to be sorbed onto or coprecipitate with Al and Fe hydroxides (Stumm and Morgan 1996). Aluminium was rapidly removed from the groundwater in the tailings as the pH increased towards 5 and the initial concentration was high, which agrees with other published results (Nordstrom and Ball 1986). This removal of Al as the pH increased was mirrored by a simultaneous decrease in the concentrations of Ni, Co and Cr. In the case of Impoundment 1, it seems that Al-hydroxides were more important in the removal of trace elements than were Fe-oxy-hydroxides, the formation of which might have been hampered by the unfavourable redox conditions within the sealed impound-

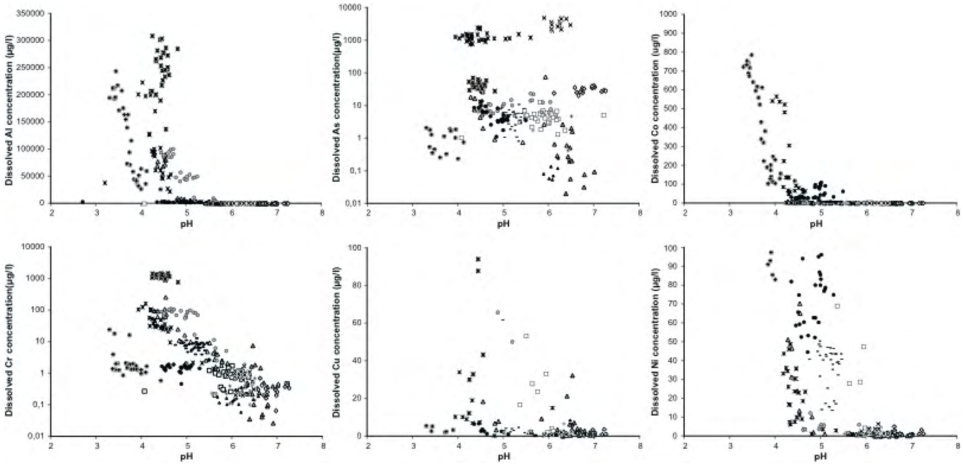

Figure 2 The relationship between pH and the concentrations of selected trace elements in the groundwater in tailings at Kristineberg

ment. Selective extraction indicated the presence of large amounts of amorphous and crystalline Fe-oxy-hydroxides deep within the tailings where the pH was >5 (Carlsson 2002). Nickel, Co and Cr were detected along with these species, suggesting that these trace elements may have been co-precipitated or adsorbed to Fe- hydroxides at these depths. The primary As-containing species in Impoundment 1 was arsenopyrite. After remediation, the concentrations of As in most of the locations sampled were <10 µg /L. However, some of the locations contained high concentrations (>1,000 µg /L) even after lengthy remediation.

Conclusions

It is important that measurements should be taken over a long period of time when evaluating the effects of remediation, especially in water-saturated tailings. The water quality in the remediated sulphide-rich tailings at Kristineberg, Northern Sweden improved significantly, but the effect was not immediate. In general, elemental concentrations decreased and pH increased between 1998 and 2009. Remediation caused the redox potential to decrease and the pH to increase within the remediated areas; this in turn caused the concentrations of trace elements such as Cu, Cd, Co, Ni, and Cr to decrease. Aluminium hydroxides, Fe-oxy-hydroxides and pyrite surfaces were found to play important roles in the removal of trace elements.

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