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Minerals Engineering 17 (2004) 195–203

MINERALS ENGINEERING

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Adsorptive retention of copper from acidic mine water at the disused sulphide mine at Løkken, central Norway—initial experiments using olivine

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Received 30 July 2003; accepted 4 September 2003

Abstract

This paper investigates the chemical potential of using forsterite olivine to remove copper from acidic mine water through the actions of neutralisation and adsorption. The study was initiated by The Norwegian Directorate of Mining in order to asses the potential for employing such a concept as a remediation measure at the disused sulphide mine at Løkken in central Norway. A number of batch experiments have been conducted in order to study a suspension system containing olivine flour and an acidic synthetic mine water solution. The synthetic solution had an initial pH close to 3 and contained 15 mg/l copper, 50 mg/l zinc and various amounts of iron. With iron present in the system, both the neutralisation isotherm and the retention isotherm exhibited an initial rapid increase before separate pH and retention maxima were reached. After this stage, a gentle decrease was observed for both parameters as a function of reaction time. This can be explained by the oxidation and precipitation of iron. With 250 mg/l of iron in solution and a solid/solution ratio of 10 g/l, approximately 79% retention was obtained after 10 min of reaction time. During the following desorption phase retention was significantly reduced. Further investigations are required in order to assess the practical feasibility of the concept.

Keywords: Acid rock drainage; Environmental; Ion exchange; Pollution

1. Introduction

In Norway, robust low-tech solutions have always been the preferred measure for minimising and controlling the release of pollutants from disused sulphide mines. These measures include various capping solutions, sub-aqueous deposition, backfilling and the utilisation of natural water bodies. The main criterion for such solutions, in addition to low operating and maintenance costs, has always been to exploit naturally occurring geochemical reactions in order to come as close as possible to a geochemically stable situation. However, the complexity of the system usually makes it difficult to predict the accurate outcome of a given remediation measure and surprises will occur. Sometimes already implemented measures will have to be amended, preferably by new robust low-tech solutions. This paper describes such an attempt.

A good example of a remediation measure based on exploiting naturally occurring geochemical reactions is found at the disused Løkken mine in central Norway (Fig. 1) where a flooded mine has been used as a 'geochemical treatment plant' in order to remove copper from acidic surface drainage. As described in detail in later sections, the remediation measures implemented at Løkken have, up until now, been considered a huge success. However, during the last two years episodes of increased copper emissions have occurred and the future development is uncertain.

Faced with the recent copper emission data from Løkken, The Norwegian Directorate of Mining has started a search for other low-cost solutions which could be employed if the situation continues to deteriorate. One interesting alternative lies in mixing the mine water with naturally occurring minerals in order to remove copper through the actions of partial neutralisation and adsorption. The aim is to remove copper from solution without simultaneously removing substantial amounts of iron, thus avoiding the problems associated with handling and depositing huge volumes of

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0892-6875/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/j.mineng.2003.09.014

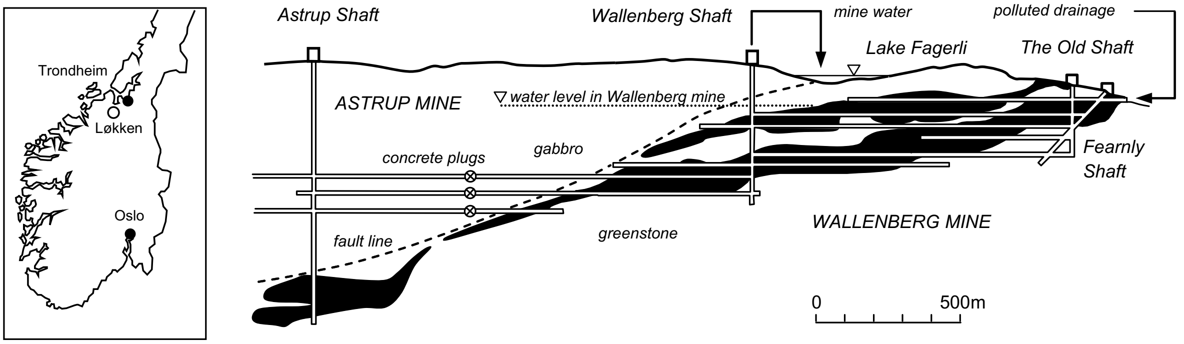

Fig. 1. Schematic presentation of the Løkken mine. The diagram shows Løkken's location in Norway as well as a cross-sectional profile of the mine itself.

copper contaminated iron sludge. The problem is caused by the very low solubility of ferric iron. In a system where the iron is initially present as ferrous iron, as is the case for the mine water at Løkken, the rate of oxidation to its ferric form will increase exponentially with increasing pH once pH exceeds pH 4 (Singer and Stumm, 1970). Hence, the potential of adsorptive removal, when compared with hydroxide precipitation, lies in the fact that retention can be achieved at a significantly lower pH.

Based on previous research (Kleiv, 2001; Kleiv and Sandvik, 2002) forsterite olivine (Mg_2SiO_4) was seen as a promising mineral as it constitutes both a neutralisation agent and an adsorbent with high affinity for copper. As explained in Section 2.1, the absence of calcium in the olivine is also advantageous. In addition, the process of separating the copper contaminated adsorbent from the liquid phase would benefit from the relatively high density of forsterite (i.e. 3.3 g/cm^3). As a consequence, this study was initiated by The Norwegian Directorate of Mining in order to asses the feasibility of a remediation measure based on forsterite olivine. This paper describes the initial experiments and focuses on the chemical potential of the concept.

2. Background

2.1. Olivine—adsorbent and neutralising agent

The crystal structure of olivine ($(Mg,Fe)_2SiO_4$) is built up of isolated negatively charged SiO_4^{4-} tetrahedra held together by octahedrally co-ordinated divalent cations. The absence of strong interconnecting Si–O–Si bonds between the isolated SiO_4 tetrahedra makes olivine the fastest weathering silicate mineral. The dissolution of olivine has been studied by a number of investigators (Sanemasa et al., 1972; Luce et al., 1972; Blum and Lasaga, 1988; Herk et al., 1989; Wogelius and Walther, 1991, 1992) and a review of existing literature is given by Jonckbloedt (1998) who studied olivine dissolution in sulphuric acid at elevated temperatures. In his study Jonckbloedt used magnesium rich olivine from *A/S Olivin* in Norway, and most investigations are performed using natural magnesium-rich olivines or synthetic forsterite. The reaction mechanism presented in the majority of these studies can be expressed using the following equation:

$$Mg_2SiO_{4(s)} + 4H^+ \rightarrow 2Mg^{2+} + Si(OH)_4 \qquad (1)$$

During dissolution in acid the Mg^{2+} ions are replaced by hydrogen ions, yielding $Si(OH)_4$ monomers and Mg^{2+} ions in solution. The reaction results in a large reduction of acidity. Most investigators have reported a reaction order of approximately 0.5 for the hydrogen ion, i.e. the logarithm of the reaction rate is proportional to −0.5 pH (Rosso and Rimstidt, 2000). The strong pH dependence means that forsterite goes from being a virtually inert mineral to a fast weathering mineral within a rather limited pH range.

The utilisation of olivine's capacity to neutralise sulphuric acid is described by several investigators (Schuiling, 1986, 1998; Jonckbloedt, 1998; Kleiv et al., 2001, Morales and Herbert, 2001; Kleiv and Thornhill, 2002). Due to the high solubility of magnesium sulphate, the use of olivine as a neutralising agent will not result in voluminous sulphate precipitates. This, however, can be a problem when using calcite as the calcium ions leached from the mineral combine with sulphate ions to form gypsum.

Kleiv (2001) showed that forsterite olivine is a good copper adsorbent, and that adsorption is most likely of an inner-sphere nature (i.e. chemisorption). As for most systems containing divalent metal ions in the presence of a silicate surface, the tendency of copper to adsorb to the olivine will increase with increasing pH. In a previous study using copper concentrations and solid/solution ratios similar to those described in this paper, Kleiv and Sandvik (2002) found that the adsorption became significant around pH 4 and reached 100% at around pH 6.

2.2. The Løkken mine

The disused Løkken mine is situated in central Norway, approximately 50 km south-west of Trondheim

(Fig. 1). The Løkken deposit, originally comprising some 30 million tonnes of ore with pyrite, chalcopyrite and sphalerite as the main ore minerals, is the largest massive sulphide deposit ever found in Norway. Mining at Løkken started in 1654, when the orebody was exploited for its copper content. Later both pyrite and zinc became valuable products. From 1974 copper and zinc concentrates were produced by selective flotation. At the end of the 1970s the ore reserves in the eastern part of the mine, known as the *Wallenberg mine*, were more or less exhausted. Production continued in the western part of the mine; the *Astrup mine*, until 1987 when the mining operations finally came to an end.

With exception of the period 1983–1992, mine water has always been the main source of pollution from the Løkken mine (Arnesen, 1999). Originally, it was introduced directly to the local water system, thus causing a significant negative impact on the water quality of the river *Orkla*. From 1952 a 30km long wooden pipeline was employed in order to transport the mine water to the fjord at Orkanger. Here it was initially treated in a sulphide precipitation plant, but from 1962 it was introduced to the fjord untreated. By the late 1970s, some 500–600,000 m^3 of very acidic (i.e. close to pH 2) mine water was produced annually, typically containing 500 mg/l of copper (Arnesen, 1999).

More than 90% of the mine water from Løkken originates from the Wallenberg mine. In 1983 the Wallenberg mine was sealed off from the Astrup mine with concrete plugs and left to be flooded. During the remaining four years of operation mine water from Astrup was pumped to Wallenberg. This caused a temporary cease in the emission of mine water from Løkken that was to last for nine years.

In 1992, the storage capacity of the Wallenberg mine was reached and mine water was once again emitted from the mine and introduced to the local recipient. It was then found that the increased residence time had changed the pH of the water from approximately pH 2 to pH 6. This change was accompanied by a dramatic reduction in the copper concentration from approximately 500 to 1 mg/l.

To exploit the geochemical processes taking place in the Wallenberg mine, acid mine drainage from waste rock dumps and other surface sources has since 1992 been collected and introduced to the mine through the old eastern adit (Fig. 1). This drainage, comprising almost 200,000 m^3 per year, typically contains from 100 to 200 mg/l of copper. When the water is finally pumped and emitted from the Wallenberg shaft (Fig. 1) the copper concentration is in the range of 0.1–5 mg/l (Arnesen, 1999). At this point, the bulk of the iron present in the emitted mine water occurs in its ferrous form.

The flooding of the Wallenberg mine and the use of the mine as a geochemical treatment plant for surface drainage led to a 95% reduction in the total copper load from Løkken (Iversen and Arnesen, 2001), and the remediation measure has been considered a huge success. However, in the autumn of 2001 the quality of the emitted mine water started to change and several episodes of lowered pH and elevated copper concentrations have been observed during the last two years (Norwegian Mining Directorate, pers. commun.). Although the increase in copper concentration, peaking at 14.5 mg/l, is far from dramatic compared to the concentrations prior to 1983, it could result in a violation of the water quality limits for the local recipient given by the Norwegian Pollution Control Authority.

3. Materials and methods

3.1. General procedures

Prior to use, all glassware, bottles and containers were thoroughly cleaned with detergent before being left to soak in 10% nitric acid (HNO_3) for 24 h. Finally, the objects were rinsed several times using deionised water. Great care was taken to minimise the risk of contamination throughout the study.

All pH measurements were performed using a Metrohm 744 pH Meter with a combined electrode. The instrument was calibrated prior to each series of measurements using suitable Metrohm buffer solutions.

All the reagents used in this study were of pro analysi quality. Only deionised water was used for dilution and dissolution.

3.2. The synthetic mine water solution

To ensure a maximum amount of control of the system, it was decided to conduct the experiments by using a relatively simple synthetic solution instead of actual mine water samples from Løkken. The composition of the synthetic mine water solution was chosen to reflect the pH and metal concentrations in the mine water produced at Løkken during a peak in the emission of pollutants from the mine. Based on data from The Norwegian Directorate of Mining, the synthetic solution was designed to contain 15 mg/l copper, 50 mg/l zinc and 0.5 mM sulphuric acid, resulting in a pH close to 3. In addition, ferrous iron was included at a varying concentration ranging from 0 to 500 mg/l with 250 mg/l representing the pollution peak.

The initial synthetic mine water solution used in the combined neutralisation/adsorption experiments was prepared by dilution of an acidic metal containing stock solution by a factor of 100. The stock solution had been prepared by dissolving copper and zinc sulphates in sulphuric acid ($CuSO_4$ and $ZnSO_4 \cdot 7H_2O$, respectively). To prevent the oxidation of ferrous iron during storage, the iron was not added to the stock solution. Instead, as described in Section 3.4, ferrous iron was added to the synthetic mine water solution immediately before the beginning of each experiment.

3.3. The olivine flour

The olivine flour used in this study originates from the production of fine-grained olivine products from milling and air classification of high quality olivine sand (AFS50) supplied by A/S Olivin. The sand had been produced at the company's sand production plant at Åheim in western Norway. Milling and air classification were conducted at The University of Science and Technology (NTNU) in Trondheim using a ball mill and a SINTEF Air Classifier (SAC 200) in a closed circuit. The olivine flour represents the finest material obtained from this process. After samples of the olivine flour had been retrieved, the material was given no additional treatment prior to its use in the combined neutralisation/adsorption experiments.

The chemical composition of the olivine flour was obtained from X-ray fluorescence analysis (XRF-analysis) and the results are shown in Table 1. The analysis was performed at A/S Olivin's laboratory at Åheim, according to the current internal procedures. As part of the analytical procedure, the sample material to be analysed was exposed to a temperature of 900 °C for 30 min prior to the XRF-analysis. The loss on ignition (LOI) value was determined from the observed reduction in sample weight.

Pure olivine from Åheim is comprised of approximately 93 mol% forsterite (Mg_2SiO_4) and 7% fayalite (Fe_2SiO_4) (Osland, 1998). The feed to the sand production plant at Åheim contains 90–95% olivine, whereas the remaining fraction comprises accessory minerals like chlorite, chromite, enstatite, serpentine and talc. Hence, these minerals can all be found in the olivine flour. Based on the results from XRF-analysis, the olivine flour probably contains close to 90% olivine. The approximate mineralogical composition is listed in Table 1.

The size distribution of the process dust was obtained from laser diffraction analysis using a Coulter LS 230 Particle Size Analyser, whereas specific surface area was determined using the N_2-adsorption technique (i.e. the BET equation (Brunauer et al., 1938)) and a Flow Sorb II 2300 volumetric gas adsorption analyser. The results are shown in Table 1.

Table 1
Material characteristics of the olivine flour

Approx. mineral phase composition (XRD)	
Forsterite	90%
Chlorite	<5%
Chromite	<5%
Magnetite	<5%
Pyroxene	<5%
Serpentine	<5%
Talc	<5%
Chemical composition (XRF)	
SiO_2	41.5%
MgO	49.9%
Fe_2O_3	7.3%
Al_2O_3	0.4%
NiO	0.3%
Cr_2O_3	0.3%
CaO	0.1%
MnO	0.1%
Loss on ignition	0.6%
Sum	100.6%
Size distribution (laser diffraction)	
d_{90}	10.5 μm
d_{50}	1.57 μm
d_{10}	0.26 μm
Specific surface area (BET)	4.3 m^2/g

3.4. The experiments

Previous initial experiments conducted according to the procedures described in the following paragraphs showed that the concentration of zinc changed very little under the experimental conditions of interest. These experiments also showed that the concentration of iron in solution went down as the pH of the system increased. Note that although both iron and zinc have been included in the initial synthetic mine water solution in order to achieve a more realistic composition, samples obtained from the experiments reported in this paper were analysed for copper only.

The combined neutralisation/adsorption experiments were performed by first adding 1000ml of the synthetic mine water solution to a glass beaker. The beaker was placed on a magnetic stirrer and the required amount of ferrous iron sulphate ($FeSO_4 \cdot 7H_2O$) was added to the solution in order to obtain the desired initial concentration of ferrous iron.

Following the addition and dissolution of the iron sulphate, the pH of the initial solution was determined. A carefully weighed amount of olivine flour was then added to the solution and the resulting suspension was stirred continuously at 500 rpm. The pH of the suspension was measured and recorded repeatedly throughout the duration of the experiment.

In some of the experimental runs the suspension was also sampled at pre-defined intervals by extracting and filtering a volume of 5 ml using a syringe and a 0.45 μm syringe filter. At the same time, the corresponding pH of the suspension was recorded. The filtrates were collected in glass vials and acidified using 20 μl of 65% nitric acid.

No more than five samples were collected from one experimental run, thus keeping the total suspension volume more or less constant throughout the experiment.

Finally, the filtrates were analysed for copper using atomic absorption spectrometry and a GBC Avanta Σ flame atomic absorption spectrometer. Each determination was obtained by taking the average of three replicate measurements. More than 90% of the determinations had a relative standard deviation of less than 2%, and only those with a relative standard deviation less than 2.5% were included in the reported results. The calibration curve was based on four standards ranging from 0.500 to 10.00 mg/l. Prior to analysis, all samples were diluted by a factor of two.

Multiple experimental runs were conducted with solid/solution ratios and initial iron concentrations ranging from 2 to 10 g/l and 0 to 500 mg/l, respectively. All experiments were conducted at 21 ± 1 °C. The recorded reaction times for all measurements refer to the amount of time elapsed since the olivine flour had been added to the synthetic mine water solution.

4. Results and discussion

4.1. Neutralisation capacity

The acid neutralisation capacity of the olivine flour is illustrated in Fig. 2, which shows the pH of the suspension as a function of reaction time for three different solid/solution ratios. Following an initial rapid increase of the pH, all the isotherms reach a peak value before a significant decrease of the pH can be observed. As indicated by an observed change in suspension colour from grey to reddish brown and directly supported by previous initial experiments, this behaviour can be explained by the oxidation and subsequent precipitation of iron. The combined effect of these mechanisms, illustrated by Eqs. (2) and (3), is the release of two moles of protons per mole of ferrous iron oxidised (Eq. (2)) and precipitated (Eq. (3)):

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

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

Consequently, the pH of the system is effectively buffered by the precipitation of ferric iron hydroxide. The observed pH of the suspension represents a 'kinetic compromise' between olivine dissolution (Eq. (1)) and iron oxidation and precipitation.

In order to test the buffering effect of iron, a series of experimental runs were conducted with varying initial iron concentrations. The results, shown in Fig. 3, clearly demonstrate how the pH of the initially iron-free system continues to increase with time, whereas the three other isotherms, representing initial iron concentrations of 100, 250 and 500 mg/l, decline slowly after having reached their respective peak values. Note the break on the horizontal axis. It is also worth noting that the height of the peak is negatively correlated with the initial iron concentration, i.e. the lowest peak is obtained for the system with the highest initial iron concentration.

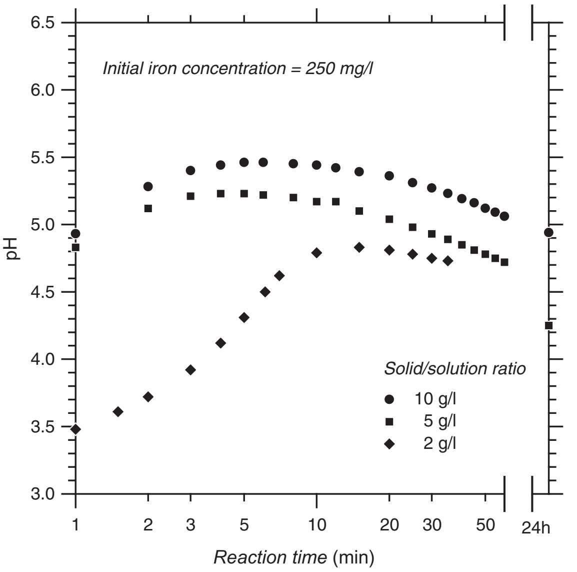

Fig. 2. Neutralisation isotherms showing pH as a function of reaction time for various solid/solution ratios. The initial iron concentration was kept at 250 mg/l.

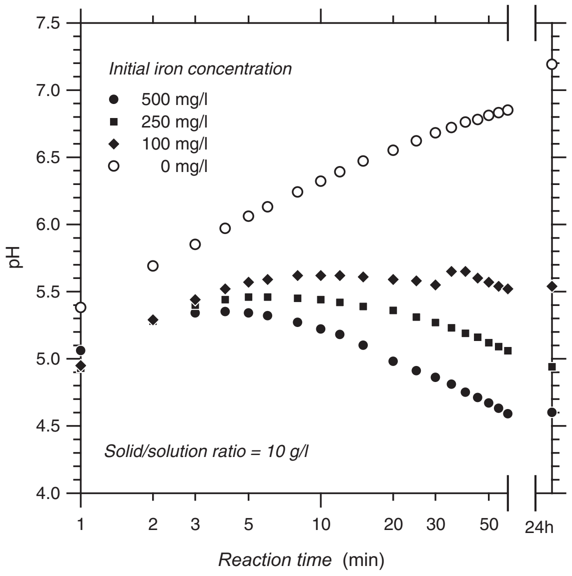

Fig. 3. Neutralisation isotherms showing pH as a function of the reaction time and the initial concentration of iron. All isotherms refer to a solid/solution ratio of 10 g/l.

4.2. Adsorptive retention of copper

The amount of copper retained by the olivine flour is calculated from the difference between the amount of copper initially present in the synthetic mine water solution and the amount remaining in solution after sampling and filtering. Thus, the degree of copper retention, represented by *%Retained*, can be expressed as a unit-less fraction according to the following equation:

$$\%\text{Retained} \equiv 100\% \cdot \frac{[\text{Cu}]_\text{i} - [\text{Cu}]_\text{f}}{[\text{Cu}]_\text{i}}, \tag{4}$$

where $[\text{Cu}]_\text{i}$ is the initial concentration and $[\text{Cu}]_\text{f}$ is concentration of copper in the filtrate.

Fig. 4 shows the retention of copper as a function of reaction time for three different combinations of solid/solution ratio and initial iron concentration. As is apparent from these results, the presence of iron in the initial solution has marked effect on copper retention. The two isotherms representing experimental runs conducted with an initial iron concentration of 250 mg/l exhibit the same behaviour; after a rapid increase the retention reaches a maximum value before a slow but significant decrease is observed. Here, the maximum retention is found to be close to 79% for a solid/solution ratio of 10 g/l, whereas the 5 g/l isotherm peaks at approximately 33%. In contrast, the isotherm representing the initially iron-free system increases monotonically as a function of time until virtually all the copper is retained. The isotherms obtained at a solid/solution ratio of 10 g/l and an initial iron concentration of 250 mg/l are hereby referred to as the '10:250' isotherms, whereas the isotherms obtained at the same solid/solution ratio, but without iron initially present, are referred to as the '10:0' isotherms.

Adsorptive retention of copper on olivine is predominantly governed by the pH of the system (Kleiv, 2001; Kleiv and Sandvik, 2002). As is apparent from the obtained results, the post-maxima decrease (i.e. the desorption phase) displayed in Fig. 4 is in agreement with the corresponding neutralisation isotherms of Fig. 2, even though there is a slight off set between the pH peaks and the retention peaks. The '10:250' neutralisation isotherm peaks at pH 5.45 after approximately 5 min, whereas the corresponding retention peak occurs some 5 min later. The fact that the observed retention continues to increase although the pH of the system is decreasing must be contributed to kinetic factors.

Kinetically speaking, adsorption of metal ions on silicates is usually a fast process, but the off set from equilibrium could be considerable during the first 5–10 min of the reaction. This is illustrated in Fig. 5, showing pH as a function of reaction time both with and without iron initially present in the synthetic mine water solution. Due to the significant 'peak-and-decline' behaviour of the suspension pH, the retention isotherm for the iron containing system is exhibiting hysteresis. This is further illustrated by Fig. 6, where the '10:250' isotherm is shown in a 3D scatter plot, i.e. *%Retained* is plotted against both pH and *Reaction time*.

The hysteresis of the '10.250' isotherm is very distinct. At a reaction time of 1 min pH 5.07 is reached and approximately 41% of the copper is retained by the

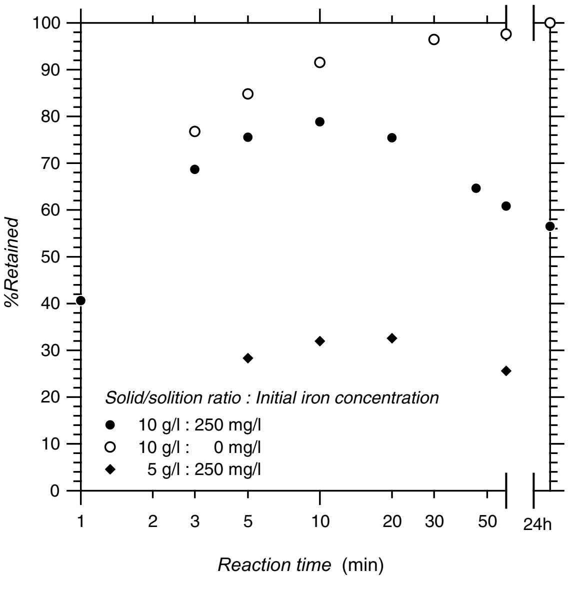

Fig. 4. Copper retention isotherms showing *%Retained* as a function of reaction time for three different combinations of solid/solution ratios and initial iron concentration.

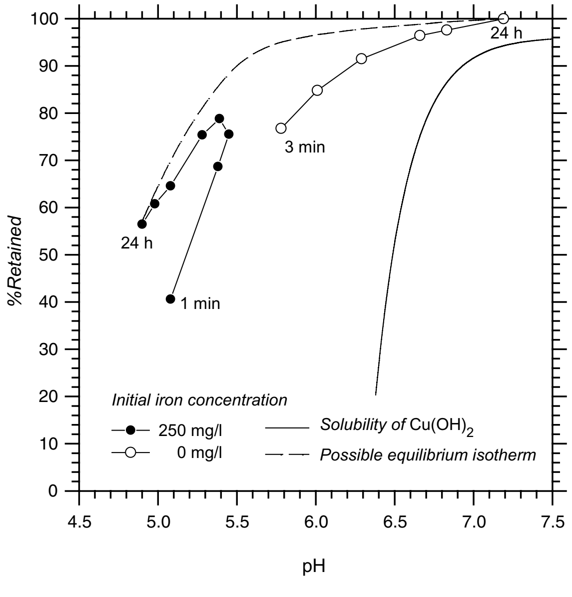

Fig. 5. Non-equilibrium copper retention as a function of suspension pH. The graph displays both the '10-250' and '10-0' isotherms. The lines connecting individual data points indicate the time sequence.

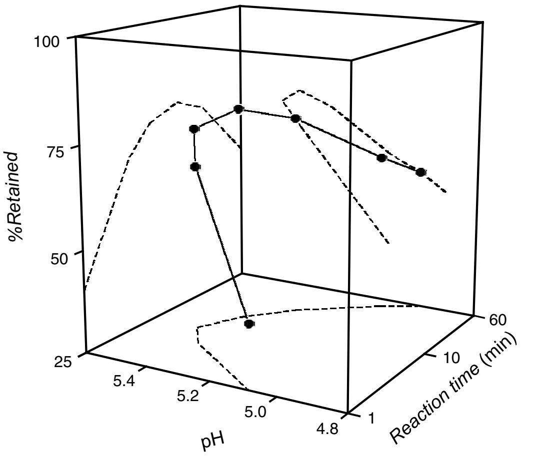

Fig. 6. 3D presentation of the '10-250' isotherm. Dashed lines indicate the respective 2D projections.

olivine flour. At a reaction time of 45 min, after both the pH and retention peaks have been reached, the pH is back at 5.08, but now *%Retained* is found to be close to 65%. One would expect retention values obtained at higher reaction times to be even closer to the equilibrium state. In Fig. 5 a possible equilibrium isotherm is indicated to illustrate the kinetic response of the system. This isotherm is drawn simply by assuming that the difference between the observed retention and the equilibrium value will decrease with increasing reaction time and that the system will be very close to equilibrium after 24 h. It is further assumed that the pH is the governing variable, i.e. that the equilibrium isotherm represents both the iron containing and initially iron-free system.

As shown by Eq. (4), *%Retained* is nothing more than a ratio calculated from the actual observations. However, when the pH of the system is lower than that required for hydroxide precipitation, the amount of retained is usually interpreted as the amount adsorbed to the mineral surfaces. In Fig. 5 the theoretical solubility of copper hydroxide ($Cu(OH)_2$) is shown for comparison. The solubility isotherm, referring to an initial copper concentration of 15 mg/l, is calculated using the MinteqA2 v.3.0 computer model (Allison et al., 1991) and is based on thermodynamic data given by Allison and Brown (1987). As seen in Fig. 5, the experimentally obtained retention isotherms are located approximately 1–1.5 pH units to the left of the solubility isotherm, thereby suggesting adsorption/desorption as the predominant mechanisms controlling retention.

The results obtained from the combined neutralisation/adsorption experiments demonstrate how olivine flour has the potential of removing substantial amounts of copper from the mine water at Løkken. After the required retention has been achieved, the adsorbent can then be separated from the iron containing solution and deposited in a chemically stable environment. However, in practice, a number of problems must be solved prior to implementing such a solution.

As is evident from Figs. 4 and 5, desorption of copper from the olivine surfaces reduces the effective capacity of the material. As a result of this, a relatively high solid/solution ratio is required to achieve the desired amount of retention. It also means that the reaction time of the process must be high to ensure a kinetically stable product. In theory, since desorption is caused by the iron induced pH changes, the problem could be overcome by either removing iron from solution prior to the retention of copper, or by preventing the ferrous iron from oxidising until the copper loaded adsorbent has been separated from the iron containing solution. Iron removal, depending on the method, would result in either huge volumes of iron hydroxides or high operation costs, thus cancelling the potential benefits of the subsequent process of copper removal using olivine flour. The latter alternative, however, is worth a closer look. Here, when the pH of the system exceeds pH 4, the rate of oxidation of ferrous iron to its ferric form increases exponentially with increasing pH (Singer and Stumm, 1970). Hence, the introduction of a reducing agent is probably required since merely stopping the supply of new oxygen to the system could prove to be insufficient.

When studying the '10-250' isotherm of Fig. 4, it is evident that the amount of copper retained does not change much in the time interval from 5 to 20 min. Hence, a third possible strategy for avoiding desorption lies in separating the copper loaded olivine flour from the iron containing solution within this narrow interval. In practice, separating solid from liquid within a time span of 20 or maybe 30 min represents a considerable challenge. However, if achieved, the chemical potential of the process could be fully utilised without introducing other chemical mechanisms. In consequence, such a system could prove to be more robust.

Regardless of how the process is implemented, the end product will consist of significant volumes of copper contaminated olivine flour. This material must be deposited in a chemically stable environment to avoid subsequent desorption. As shown by Kleiv (2001), pH is the main factor controlling the stability of the copper–olivine surface complexes, whereas the ionic strength of the system plays a negligible role due to the inner-sphere nature of the adsorption. Consequently, the copper contaminated olivine flour should be deposited in a system where the pH is higher than that of the adsorbent/solution system prior to phase separation. From a pure chemical point of view, most natural lakes will qualify.

As indicated in the previous paragraphs, the feasibility of the concept depends on more than chemistry. Further investigations are required in order to evaluate the potential for rapid solid/liquid separation as well as the possibilities of implementing reducing operating conditions to prevent iron from oxidising. Problems regarding handling and depositing of the resulting volumes of contaminated olivine flour will also have to be addressed.

5. Conclusions

The following conclusions were drawn from batch experiments in which olivine flour was added to an acidic synthetic mine water solution containing copper, zinc and various amounts of ferrous iron:

1. Both the amount of copper retained and the pH of the suspensions are positively correlated with the solid/solution ratio. With ferrous iron present in the initial solution, both parameters demonstrate an initial rapid increase as a function of reaction time, before separate pH and retention maxima are reached. After this stage, both the neutralisation isotherm and the retention isotherm exhibit a slow decline.
2. When comparing retention isotherms to the solubility of copper hydroxide, adsorption of copper to the olivine surfaces suggests itself as predominant mechanism responsible for the observed retention.
3. The post-maxima decrease of pH with respect to reaction time can be explained by the oxidation and subsequent precipitation of iron. The iron induced pH decrease results, in turn, in a decrease in copper retention as copper is desorbed from the olivine surfaces. When excluding iron from the initial synthetic mine water solution no pH maximum is reached within the time frame of the experiments and much higher pH and retention values are obtained.
4. When using a synthetic mine water solution design to represent a peak in the emission of pollutants from the Løkken mine, the maximum observed copper retention was obtained at a solid/solution ratio of 10 g/l after approximately 10 min of reaction time. At this point close to 79% of the 15 mg/l initially present was retained by the solid phase. After 10 additional minutes retention was still above 75% while it had dropped to approximately 60% after 60 min of total reaction time.
5. If adsorptive retention is to be used as a remediation concept at Løkken, the copper loaded adsorbent must be separated from the iron containing solution. To prevent significant desorption, minimise the adsorbent dose and fully utilise the chemical potential of the system, separation must be achieved within a time span of 20–30 min. Alternatively, desorption can be avoided by preventing the ferrous iron from oxidising until separation has been completed.

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