Precipitation of heavy metals from acid mine drainage and their geochemical modeling

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Abstract

Geochemical modeling plays an increasingly vital role in a number of areas of geoscience, ranging from groundwater and surface water hydrology to environmental preservation and remediation. Geochemical modeling is also used to model the interaction processes at the water - sediment interface in acid mine drainage (AMD). AMD contains high concentrations of sulfate and dissolved metals and it is a serious environmental problem in eastern Slovakia. The paper is focused on comparing the results of laboratory precipitation of metal ions from AMD (the Smolnik creek, Slovakia) with the results obtained by geochemical modeling software Visual Minteq 3.0.

Key words: geochemical modeling, precipitation, acid mine drainage

1 Introduction

Acid mine drainage from coal and mineral mining operations is a difficult and costly problem. The abandoned Smolnik mine is regarded as an environmental loading in the eastern Slovakia, where acid mine drainage (AMD) is generated and discharged from abandoned mine and contaminates the Smolnik Creek catchment (Fig. 1).

AMD forms when sulfide minerals in rock are exposed to oxidizing conditions in coal and metal mining. There are many types of sulfide minerals, but iron sulfides common in coal regions, pyrite and marcasite are the predominant AMD producers. Upon exposure to water and oxygen, pyritic minerals oxidize to form acidic, iron and sulfate–rich drainage. The drainage quality emanating from underground mines or backfills of surface mines is dependent on the acid-producing (sulfide) and alkaline (carbonate) minerals contained in the disturbed rock. In general, sulfide -rich and carbonate-poor materials are expected to produce acidic drainage. In contrast, alkaline-rich materials, even with significant sulfide concentrations, often produce alkaline conditions in water [1].
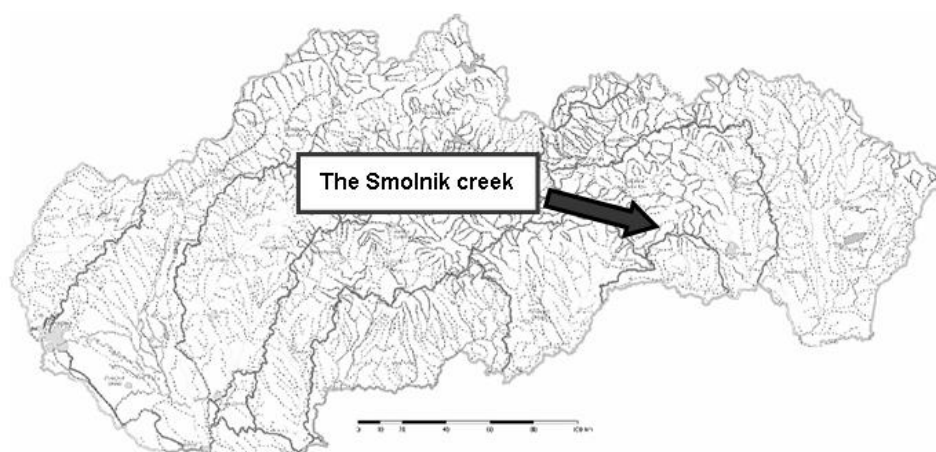
Figure 1: The Smolnik creek catchment

Predicting the evolution of acid mine drainage (AMD) is of increasing interest to the mining industry due to its potential for long-term environmental damage. AMD is characterized by its low-pH water and typically by high concentrations of sulfate, iron and dissolved metals [2,3,4]. The behavior of this acidic water is controlled by the hydro-geochemical environment in which water - sediment interactions play an important role. Methods that have been used for prediction of AMD generation in tailings are both laboratory and model based, with standardized methods of static and kinetic laboratory testing being often applied [5].

However, static tests can at best only predict whether leachate pH will become acidic at some point in time, and typical application of kinetic laboratory testing to prediction of field scale leachate quality is associated with a high degree of uncertainty. Furthermore, these methods assume geochemical control of AMD quality [6], and thereby largely neglect the crucial interaction with oxygen availability. A number of modeling studies of AMD generation from mines exist in the literature [7,8,9], where models have been produced as tools to examine effects of dominant processes and compares different tailings remediation measures. However, the predictive capability of many of these models is limited [5 & 10], due to, for example, over simplification or neglect of some important geochemical processes.

The paper is focused on comparing the results of laboratory precipitation of metal ions from AMD (the Smolnik creek, Slovakia) with the results obtained by geochemical modeling software Visual Minteq 3.0.

2   Material and methods

For the evaluation of pH changing on the concentration of dissolved ions (Fe, Al, Mn, Zn and Cu) in the laboratory testing, 500 mL of AMD (pH 3.78) from Smolnik creek (shaft Pech) were used. The chemical composition of AMD is shown in Table 1.

Table 1: Chemical composition of AMD used for precipitation

	Fe	Cu	Al	Zn	Mn
mg/L	351	1,4	43,2	5,5	21,8

The samples of 500 mL of AMD were sequentially neutralised by NaOH under continuous stirring and pH measuring (inoLab, WTW, Germany). The resulting precipitate was filtered through a filter funnel with the frit (S3) and the filtrate was used for further neutralization. This procedure was repeated at gradually increasing pH values from 4.05 to 11.95 (4.05, 4.26, 4.49, 4.79, 5.5, 6.11, 7.23, 8.11, 8.97, 9.98, 10.5, 10.99, and 11.95). Afterwards, the precipitate was dissolved in the filter funnel with 10 mL of 10 % HCl, the frit was washed with distilled water and the solution was filled up to 200 mL by H_2O. Such prepared filtrates were used to determine the concentrations of total Fe, Cu, Mn, Al and Zn with colorimeter DR 890.

Geochemical modeling was used to verify the results of the laboratory experiment of the pollutants transport in the aquatic environment. For the modeling the free downloading Visual Minteq 3.0 software was used.

The concentrations of metals in AMD used in laboratory experiments were the input data to the software. Modeling has been transferred under the terms of which have fugacity of carbon dioxide value 0.0003 (log f CO_2 (g)) = -3.5 (value is corresponding to the fugacity of atmosphere). The reason for the award of the fugacity of carbon dioxide was that, in laboratory experiments, working with AMD taken at the place of discharge from the shaft Pech, creek Smolnik (AMD brought into contact with the atmosphere).

The presence of hematite (Fe_2O_3), goethite (α-FeO(OH)) and magnetite (Fe_3O_4) were within the modeling neglected, since these minerals, which are rather regarded as products of transformation of metastable Fe^{3+} phases [11]. While goethite and hematite commonly exhibit a much lower growth rate than schwertmannite, ferrihydrite and jarosite and their emergence in "fresh" precipitates is just improbable [12].

3   Results and discussion

The comparing of the results of precipitation of metal ions from AMD by changing the pH, which were predicted by geochemical modeling software Visual Minteq 3.0 and with laboratory results of precipitation are showed in Fig. 2 -6.

Fig. 2 shows the simulation of pH changes in the concentration of Cu. From this figure it is clear that the results of laboratory experiments are consistent with the literature, e.g. Cu is precipitated at the pH range of 4 to 6 [13]. The software Visual Minteq 3.0 analyses that the precipitation of Cu begins up at the pH 6 where the complete precipitation occurred at pH 8.

The effect of the gradual increase of pH on the concentration of Zn is shown in Fig. 3. The comparison of Zn precipitation is similar to that observed for Cu, whereas the software determines a gradual precipitation of Zn up to pH of 7.5, and the complete precipitation of Zn occurs up to pH 8.5, which is not in accordance with literature [14,15,16].
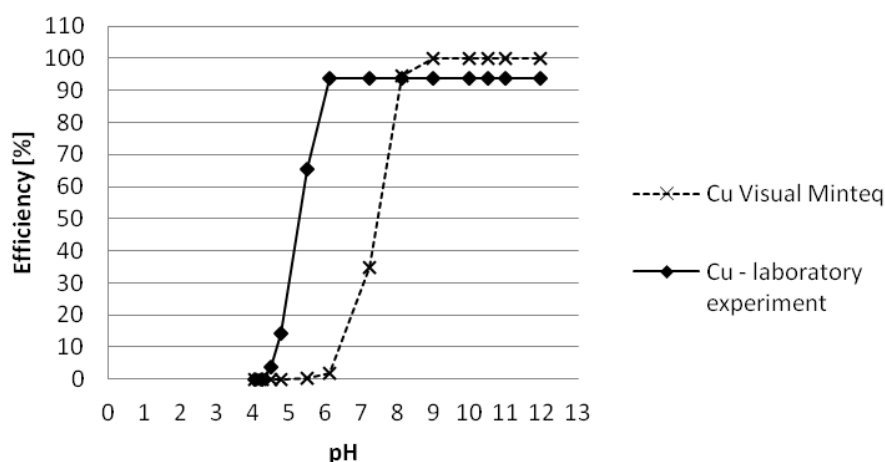
Figure 2: Comparison of changes in Cu concentration with the pH at geochemical modeling and laboratory results

Laboratory results show that the precipitation of Zn has already begun at pH 5 and at pH 7.5 were precipitated approximately 92% of Zn, which is in accordance with the literature [14,15,16].
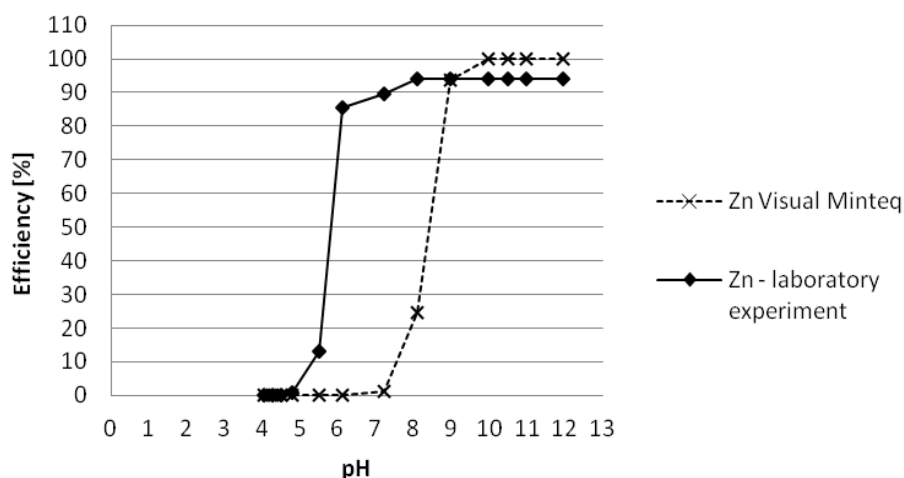

Figure 3: Comparison of changes in Zn concentration with the pH at geochemical modeling and laboratory results

Fig. 4 shows the changes in concentration due to an increase of pH, where the curve of the geochemical modeling results describes the line of the curve of the measured results under laboratory conditions. Accordance with the literature [14 & 17], above 90% of Al was precipitated at pH 6.

The comparison of the results of changes in the concentration of Mn by increasing the pH (Fig. 5) shows that in the laboratory experiments there was a gradual precipitation of Mn already at pH 6, while the results of the software shows that the concentration of Mn should begin to precipitate at pH 7. According to software Visual Minteq 3.0 there is an efficiency of

precipitation 50% at pH 8, which is also in accordance with the literature [18]. Increasing the pH leads to consistency in efficiency of precipitation, whereas at pH 8.5 is already efficiencies of precipitation of Mn the same.
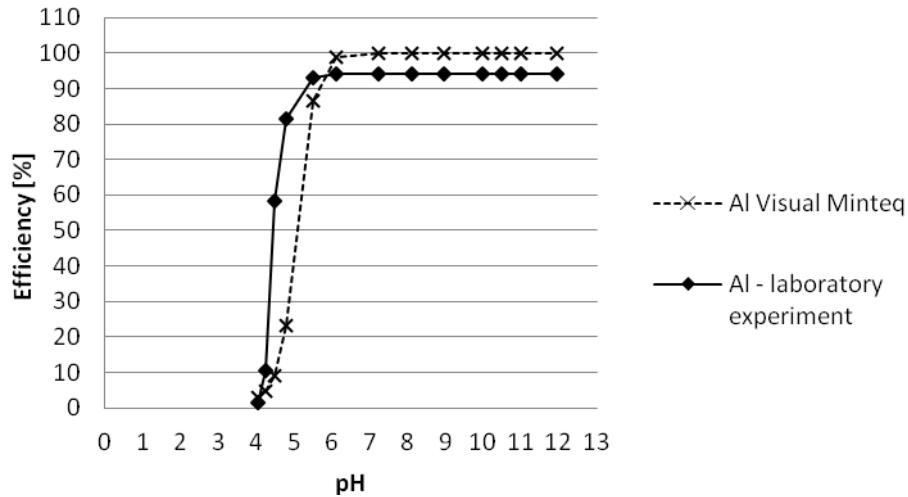

Figure 4: Comparison of changes in Al concentration with the pH at geochemical modeling and laboratory results
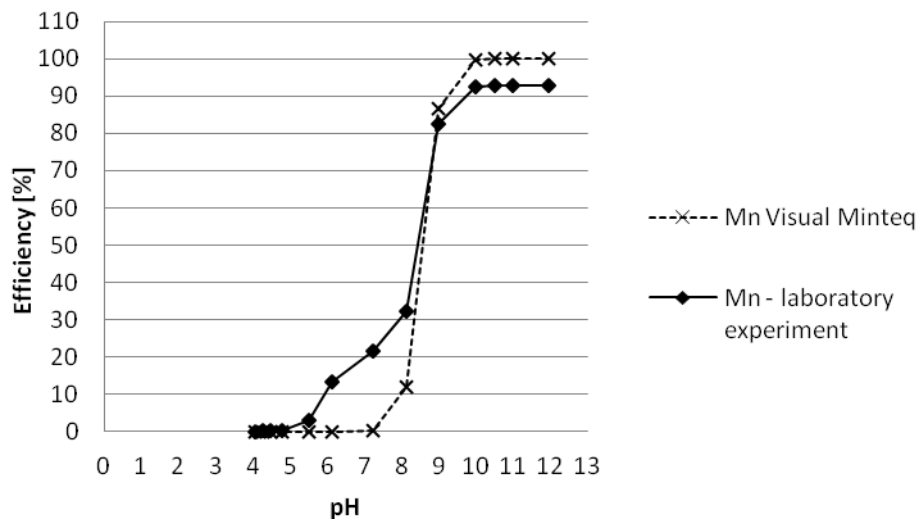

Figure 5: Comparison of changes in Mn concentration with the pH at geochemical modeling and laboratory results

The Fe^{2+} and Fe^{3+} ions create a wide range of organic and inorganic complexes. Fe^{3+} complexes are more stable than Fe^{2+} which is present in the reducing conditions in uncomplexed form [19]. Fe^{2+} is very portable, but exception is the oxidizing environment with extremely low pH, which usually passes through quickly into insoluble compounds. Under oxidative conditions, the Fe is rapidly oxidized and precipitates as oxides, hydroxides

and hydrous oxide. In contrast, in reducing conditions occurs to almost to the quantitative precipitation of sulfides [19].
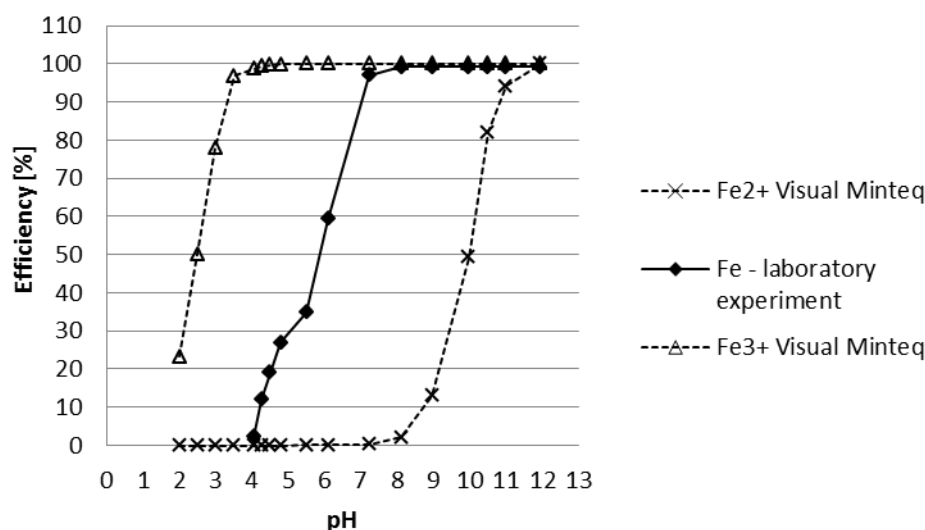

Figure 6: Comparison of changes in Fe concentration with the pH at geochemical modeling and laboratory results

The reason of the precipitation of Fe in the whole range pH (laboratory experiment) may be due to the oxidation of Fe^{2+} to Fe^{3+} in the presence of oxygen and the subsequent precipitation in the form of $Fe(OH)_3$. In contrast, the software modelled only the precipitation of Fe^{2+} or Fe^{3+} (Fig. 6) as it is stated in the literature, e.g. precipitation of Fe^{2+} occurred up to pH > 8.5 [16] and Fe^{3+} to pH < 3,5 [20].

4   Conclusion

By comparing the experimental results (heavy metals (Al, Mn, Zn, Cu and Fe) of precipitation from AMD (shaft Pech, Smolnik, Slovakia) and evaluation of software Visual Minteq 3.0 it was found that the curve of the effect of pH on the precipitation of Al and Mn describe approximately the same line. The comparison of the effectiveness of the precipitation of Zn and Cu ions on the basis of experimental results and evaluation of the Visual Minteq 3.0 has shown that the precipitation were up to two pH values above. This phenomenon could be caused by the fact that the Visual Mitneq 3.0 is freely downloading and it is not specialized in acidic mine waters, ie. because of its versatility could lead to inaccuracies in modeling the precipitation of ions in AMD.

The reason for the precipitation of Fe in the whole range pH may be due to the oxidation of Fe^{2+} to Fe^{3+} in the presence of oxygen and the subsequent precipitation in the form of $Fe(OH)_3$, while the software is modelled only the precipitation of Fe^{2+} and Fe^{3+} separately.The results will be used for further experiments aimed at acid mine drainage treatment based on the sorption and precipitating reactions.

Acknowledgements

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