

## Study of pH Influence on Selective Precipitation of Heavy Metals from Acid Mine Drainage

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Acid mine drainage (AMD) is considered as one of the worst environmental problems associated with mining activity. AMD from abandoned mines is a long-term threat to the environment and directly impacts it by polluting streams, rivers, drinking water, and groundwater, disrupting wildlife habitat, and destroying the natural landscape.

Mining activity in the Slovak Republic has a long tradition, especially in connection with the gold, silver, copper, iron and polymetallic ores mining. One of these mines is mine Smolnik where AMD is produced and discharged from abandoned mine and contaminates the Smolnik creek catchment.

The paper deals with the utilization of precipitation for decrease of the contents of iron, copper, zinc, aluminium and manganese in acid mine drainage from the abandoned mine of Smolnik. In this paper the possibility of selective removal of heavy metals from AMD by precipitation NaOH solution is evaluated.

### 1. Introduction

The abandoned mining area Smolnik in Slovakia belongs to the old environmental loads because of acid mine drainage (AMD) production. Massive pyrite oxidation and free sulphuric acid production are the major reasons of water acidification and dissolving of heavy metals from metallic ores. This AMD contains high metal concentrations that are dependent on rainfall intensity (e.g., Fe 500 - 400 mg/L; Cu 3 - 1 mg/L; Zn 13 - 8 mg/L and Al 110 - 70 mg/L). This AMD acidifies and contaminates the Smolnik creek water, which transports the pollution into the Hnilec river catchment (Bálintová and Komárová, 2007; Bálintová et al., 2009).

One of the possibilities of acid mine water treatment is chemical precipitation, which is associated with increase of AMD pH (Plasari and Muhr, 2007). Increasing the pH of water to the desired value is connected with the metal precipitation in the form of hydroxides. Therefore, the way of AMD treatment depends on the type and concentrations of the metal cations in water. According to literal data by Xinchao et al. (2005), hydroxides of ferrous ions precipitate at pH > 8.5. In the presence of oxygen, iron ions are oxidized to ferric ions and iron (III) hydroxides form orange-yellow precipitate (called yellow boy) at pH > 3.5. Aluminum hydroxide usually precipitates at pH > 5.0 but again dissolves at pH 9.0. Precipitation of manganese depends on the oxidation number of cation, but usually takes place at pH from 9.0 to 9.5. Sometimes

the pH 10.5 is necessary for complete removal of manganese (Sheremata and Kuyucak, 1996).

The literature review showed that to the issue of selective extraction of metals from acid mine water is given considerable attention. Jenke and Diebold (1983) re-acquire the metals from AMD by adding sulfide and subsequent oxidation and selective titration. Cu and Zn have precipitated in the form of sulphides and Fe, Al, Mn and Mg were recovered in the form of hydroxides. Up to 85 % of metal were recovered in different pH regimes. Rao et al. (1996) develop a three-step process of precipitation:

1. Iron was obtained in the form of hydroxide in the presence of dodecylamine at pH 3.5 by adding calcium hydroxide and subsequent oxidation with  $H_2O_2$ .
2. Zinc was precipitated in the form of sulphide by adding  $Na_2S$ ,  $H_2S$  and  $NaHS$ .
3. Finally, at the pH 9.5 have been removed other metals.

Sheremata and Kuyucak (1996) recovered copper at pH 3.5 by cementation with iron powder then iron was precipitated as  $FePO_4 \cdot H_2O$  at pH 1.6 by adding  $H_3PO_4$ . Matlock et al. (2002) tested the precipitation of metals from AMD with low pH using the addition of 1,3-benzenediamidoethanethiol dianion (BDET).

The interaction among the metals can influence the reaction rate and oxidation state of the metals in the precipitate. For example, manganese will be simultaneously precipitated with iron (II) from water at pH 8, only if the concentration of iron in the water is much greater than the manganese content (about 4 times more). If the concentration of iron in AMD is less than four times of the manganese content, then the manganese can be removed from the solution at  $pH > 9$  (Sheremata and Kuyucak, 1996). Because of variability of pH and metal contents in acid mine drainage from individual sources, it is necessary to treat them separately.

## 2. Material and Methods

Test of Fe, Cu, Mn, Al, Zn precipitation in AMD was carried out by raw AMD from the sampling site Smolnik with pH 3.06. The concentration of metals in AMD is shown in Table 1. NaOH (0.5 mol/L) was used as the precipitating reagent.

*Table 1: Contents of selected metals in AMD*

Fe	Cu	Mn	Zn	Al
mg/L	mg/L	mg/L	mg/L	mg/L
256.8	0.46	23.9	7.1	43.4

For the experiment 500 ml of AMD was used, which was neutralized by NaOH under continuous stirring and monitoring of pH (inoLab, WTW, Germany). The resulting precipitate was filtered through a filter funnel with frit (S3) and the filtrate was used for further neutralization. This procedure was repeated at gradually increasing pH values: 3.5; 4; 4.5; 5; 5.5; 6; 6.5; 7; 7.7; and 8.2. The precipitate was afterwards dissolved in the filter funnel with 10 mL of 10 % hydrochloric acid, frit was washed with distilled water and the solution was added to 200 mL. The solution was used for determination of concentrations of Fe, Cu, Mn, Zn, Al.

The second experiment was carried out as follows: First, the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  with 30 % hydrogen peroxide was performed and subsequently the precipitation of metal hydroxides from AMD in the pH range from 3.5 to 12 was realized as described above.

The concentration of  $\text{Fe}^{2+}$  was determined by colorimetric method using 1,1-phenanthroline with DR 890 colorimeter (Hach Lange, Germany). Concentrations of total iron, copper, manganese, aluminium and zinc were determined by flame AAS method (SpectrAA-30, Varian Australia).

### 3. Results and Discussion

In Figure 1 is shown the efficiency of precipitation of metals at different pH values.

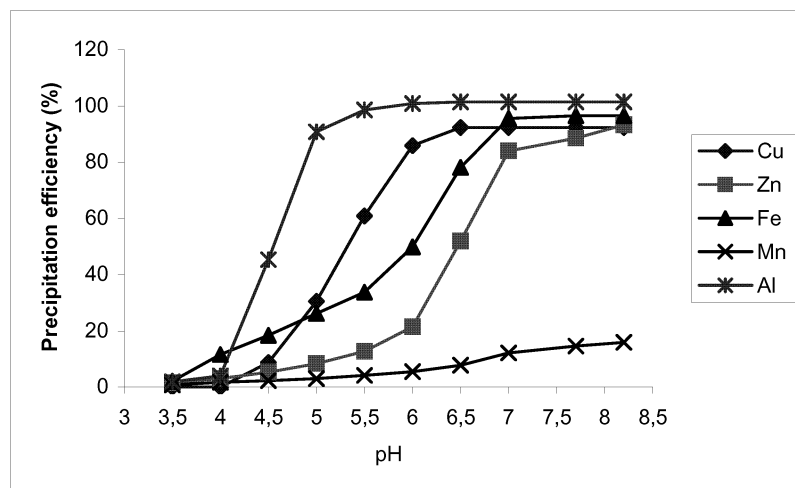


Figure 1: Efficiency of metals precipitation in pH range 3.5 – 8.2

As can be seen in Figure 1, as the first from the monitored elements is precipitated aluminium (98.5 %) in the pH range from 4 to 5.5. Precipitation of copper was carried out in accordance with the literary data, where copper begins to precipitate at  $\text{pH} > 4$  and total precipitation occurs at  $\text{pH} 6$ . The efficiency of the precipitation of copper was 92.3 %. Iron should be in AMD mainly as  $\text{Fe}^{2+}$ , which should be precipitated at  $\text{pH} 8$  in accordance to literature (Xinchao, 2005). The reason for the iron precipitation across the studied range may be progressive oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by oxygen in the air and its precipitation in the form of  $\text{Fe}(\text{OH})_3$ , which starts at  $\text{pH} 3.5$ . According to literature data (Sheremata and Kuyucak, 1996), zinc is precipitated in the range  $\text{pH} 5.5$  to 7. In that interval was precipitated 84 % of Zn.

The fact that in the presence of a large excess of Fe the Mn is precipitated at  $\text{pH} 8$  was not confirmed. At  $\text{pH} 8.2$  was precipitated only 15.9 % of total Mn in AMD. Therefore, in accordance with the literature and the other experiments, metal precipitation was studied up to the  $\text{pH} 12$ .

Based on the results presented in Figure 1 the experiments were oriented to study of the change of the oxidation state of iron in raw AMD and in AMD 72 h after its sampling. As resulted from Table 2, 92 % iron in fresh water was in the form of  $\text{Fe}^{2+}$  and in AMD after 72 h was only 4.2 % iron as  $\text{Fe}^{2+}$ . Based on these results, and literary knowledge (Xinchao et al., 2005; Sheremata and Kuyucak, 1996) ( $\text{Fe}^{3+}$  is precipitated at pH 3.5 and  $\text{Fe}^{2+}$  at pH 8), it confirmed the behaviour of iron in the precipitation (Figure 1). This knowledge was used for further experiments where, after the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by hydrogen peroxide, the effectiveness of the precipitation of iron was 98.82 % at pH 3.65 (Table 3).

Table 2: Oxidation state of iron in fresh AMD and after 72 hours

	pH	$\text{Fe}_{\text{total}}$ mg/L	$\text{Fe}^{2+}$ mg/L
AMD	3.78	280	258
AMD after 72 hours	3.92	250	11

Table 3: Efficiency of Fe removal from AMD

	The efficiency of $\text{Fe}_{\text{total}}$ removal %
pH 3	24.14
pH 3.65	98.82

This knowledge has been applied in another experiment where the precipitation by NaOH was carried out after the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by hydrogen peroxide. Efficiency of metal precipitation is presented in Figure 2. As can be seen from Figure 2, as the first from the monitored elements is precipitated iron. The precipitation occurred immediately after the addition of hydrogen peroxide, and simultaneously the pH decreased from 3.78 to 3.02. At pH 4.05 was precipitated 97.16 % iron. In the pH range from 4 to 5.5 was precipitated 92.9 % aluminium. Precipitation of copper covered the pH range from 4.49 to 6.11. The efficiency of precipitation of copper was 95.23 %. In the pH range from 5.5 to 7.23 was precipitated 88.72 % zinc. Manganese is precipitated at a pH in the range from 5.5 to 9.98 with 89.49 % efficiency. Losses in the precipitation can be attributed to adsorption of metals by the precipitate of  $\text{Fe}(\text{OH})_3$ , which was confirmed by chemical analysis (3.83 % Cu and 2.42 % Zn).

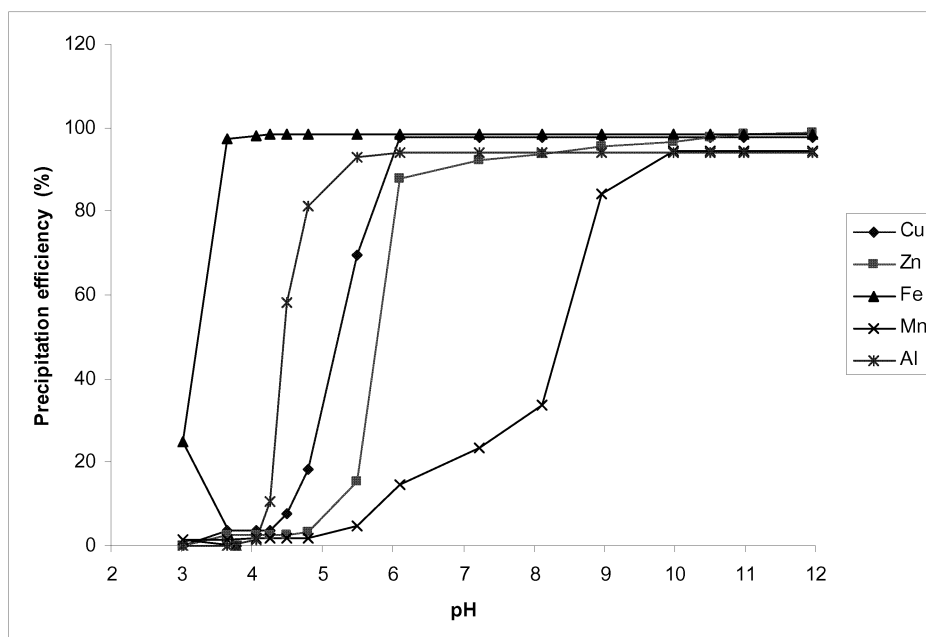


Figure 2: Efficiency of metals precipitation after Fe oxidation

#### 4. Conclusion

The main objective of these experiments was to determine the possibility of selective recovery of metals. Based on the presented results it can be stated that by AMD neutralization with sodium hydroxide to the pH of 8.2 was removed: 92.3 % of copper, 93.3% of zinc, 96.6 % of iron, 99.9 % of aluminum, and 15.9 % of manganese. The reason for the gradual precipitation of iron across the studied range was the gradual oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by oxygen in the air and its precipitation in the form of  $\text{Fe}(\text{OH})_3$ . After the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by hydrogen peroxide, the first of the precipitated element was iron at pH 4.05 (97.16 %). In the range of pH 4 - 5.5 was precipitated 92.9 % of aluminum. Precipitation of copper covered the pH range 4.49 - 6.11. The efficiency of the copper precipitation was 95.23 %. In the pH range from 5.5 to 7.23 was precipitated 88.72 % of zinc. Manganese is precipitated in the pH range from 5.5 to 9.98 with 89.49 % efficiency. These results will be used for design of technology for selective recovery of metals from acid mine drainage.

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