

DIFFERENT NEUTRALIZING AGENTS USED FOR TREATMENT OF ACID MINE WATER

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ABSTRACT – Different neutralization agents are investigated for neutralization process of acid mine drainage from Robule Lake aim to precipitate the metal ions in a different sludge type. $\text{Ca}(\text{OH})_2$ and CaCO_3 are used as neutralization agents and the neutralization process was done in several stages. After solution reached pH 3 or 4, each sample was filtered. AMD samples neutralized in the first neutralization step were used as start samples for second neutralization step to reached pH 7; 7.5 or 8. Metal ions concentrations at different pH values, as well as the consumption of the neutralizing agents were monitored.

Keywords: Neutralization, Acid Mine Drainage, Calcium Hydroxide, Calcium Carbonate.

INTRODUCTION

Acid mine drainage (AMD) as a consequence of the mining activities in the Eastern Serbia causes water systems pollution around the mine. Aim to protect water system around the mine, AMD require treatment through different treatment methods. Mine wastewater from the area of active or closed copper mines contains heavy metal ions where the concentrations of copper and iron ions are dominant [1]. The concentration of the other heavy metal ions (Mn, Cd, Zn, Pb, Ni, etc.) depends on the mineralization of an ore body but their concentration is much lower than the concentration of copper or iron ions. pH value of those water is, as a rule, mostly between 2.5 and 4 and those wastewaters have the acidic characteristics [2].

The neutralization method is a very effective for removal the dissolved metals from the wastewater due to the pH dependence of the metal solubility. However, removal of some metal ions, such as Ni and Mn, a higher pH value over the effluent standard is required. In this case, additional treatment methods are needed to decrease the pH value according the effluent standard. In Bor area in Serbia, all of the wastewater from the mine area is released out to natural environment and through the tributaries of Bor River and Timok River flowing in Danube River without any treatment, and has the negative environmental impact [3].

The aim of this work was to investigate the possibility of neutralization the AMD from Bor mine area by using various neutralizing agents. Also, the aim was to select the most suitable neutralizing agent for further use on the basis of the obtained chemical results

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after the neutralization of water and the amount of consumed neutralizing agent.

EXPERIMENTAL

Real AMD sample from Robule Lake was used for neutralization. Start pH of this water was 2.67. As a neutralizing agent are used $\text{Ca}(\text{OH})_2$, in a form of lime milk with concentration of 25 g/L, and CaCO_3 p.a. quality.

Neutralization of selected AMD with $\text{Ca}(\text{OH})_2$ and CaCO_3 was done in several stages up to different pH values depending on chemical characterization of neutralized water, and depending on the legislation for surface water. Lime milk and CaCO_3 was used as a neutralizer to reached pH 3 or 4 in a first neutralization step. To AMD sample continually was added a certain amount of neutralization agent in a batch reactor. Stirring was performed with a magnetic stirrer, at a constant speed of 400 rpm/min, in order to avoid precipitation. After solution reached pH 3 or 4, each solution sample was filtered by vacuum filtration to separate solid from liquid phase. Dewatered sludge was dried to constant mass at 40 °C. Liquid sample was collected and given on chemical analyses according to the chemical characterization of the real sample. AMD samples neutralized in the first neutralization step up to pH 3 or 4 were used as start samples for second neutralization step to reached pH 7; 7.5 or 8. As in the first neutralization step, liquid and solid phase were separated by vacuum filtration. Liquid phase was used for the chemical analyses and solid phase was dried at 40 °C and measured after reaching the constant mass value

RESULTS AND DISCUSSION

In the Table 1 are given the results of chemical analyses of AMD from the site.

Table 1 Chemical analysis of real AMD samples

Neutralizing agent	Elements								
	Fe	Mn	Cu	Zn	As	Ni	Pb	Cd	S
	concentration, mg/L								
$\text{Ca}(\text{OH})_2$	322.6	90.8	34.7	12.8	0.0042	0.413	0.007	0.04	2376
CaCO_3	506.2	86.1	51.0	19.5	<0.020	0.56	<0.020	0.11	3973

Neutralization with $\text{Ca}(\text{OH})_2$

Neutralization process is carried out with 2000 ml of real AMD to reach pH 3 or 4. As a neutralizing agent is used $\text{Ca}(\text{OH})_2$, as a lime milk with concentration of 25 g/L. After reached the pH 3 or 4, solution is filtered by vacuum filtration with aim to separate solid from liquid phase. Dewatered sludge was dried to constant mass. Results of the chemical analyses of solution are shown in the following Table 2.

From the Table 2, it can be seen that at pH 4 there is a significant drop in the concentration of iron ions while the concentrations of the other metal ions remained unchanged. It can be concluded that the iron ions precipitated in the sludge while the other metal ions remained in solution.

AMD neutralized up to pH 3 or pH 4 was used as start samples for neutralization up

to 7, 7.5 and 8. As in the first neutralization stage, liquid and solid phase are separated by vacuum filtration. Liquid phase is used for the chemical analyses and solid phase is dried and measured after reaching the constant mass value. Chemical analyses of solution are shown in the following Table 3 and 4.

Table 2 Chemical analysis of solutions after neutralization

Neutralization from start pH value (2.67) to different pH values	Elements								
	Fe	Mn	Cu	Zn	As	Ni	Pb	Cd	S
	concentration, mg/L								
pH 3	274.1	62.1	31.6	12.6	0.004	0.4	0.017	0.04	2245
pH 4	0.98	62.7	31.4	12.4	0.001	0.4	0.003	0.04	2022

Table 3 Chemical analysis of solutions after neutralization from pH 3 to pH7, 7.5 or 8

Neutralization from pH 3 to different pH values	Elements								
	Fe	Mn	Cu	Zn	As	Ni	Pb	Cd	S
	concentration, mg/L								
to pH 7	0.14	38.2	0.06	0.44	0.0004	0.15	0.0007	0.01	1950
to pH 7.5	0.03	28.3	0.04	0.13	0.0004	0.08	0.0007	0.006	1976
to pH 8	0.09	20	0.03	0.03	0.0004	0.03	0.0007	0.002	1994

Table 4 Chemical analysis of solutions after neutralization from pH 4 to pH 7, 7.5 or 8

Neutralization from pH 4 to different pH values	Elements								
	Fe	Mn	Cu	Zn	As	Ni	Pb	Cd	S
	concentration, mg/L								
to pH 7	0.01	42.2	0.04	0.65	0.0009	0.21	0.001	0.02	1962
to pH 7.5	0.01	39.8	0.05	0.22	0.0008	0.14	0.0002	0.015	1949
to pH 8	0.01	36.8	0.03	0.11	0.0008	0.1	0.0004	0.009	1936

Table 5 Consumption of Ca(OH)₂ and sludge mass

Sample	Consumption of 25 g/L Ca(OH) ₂ , ml/L	Sludge mass, g
pH start to pH 3	3.5	0.7
from pH 3 to pH 7	65.4	2.9
from pH 3 to pH 7.5	67.2	3.3
from pH 3 to pH 8	70	3.7
pH start to pH 4	25	3.93
from pH 4 to pH 7	31.8	1.1
from pH 4 to pH 7.5	33.8	1.3
from pH 4 to pH 8	40.3	2.1

From the Tables 3 and 4, it can be seen that all the metals ions from the solution precipitated into a sludge. Only the concentration of manganese ions remained unchanged due to the fact that manganese precipitates at higher pH values, which is

around 10. In the Table 5 is shown the lime consumption during the neutralization as well as the mass of the obtained sludge.

Neutralization with CaCO₃

Neutralization process is carried out with 2000 ml of real AMD to reach pH 3 or pH 4. CaCO₃ is used as a neutralizing agent. After reached the pH 3 or 4, solution is filtered by vacuum filtration with aim to separate solid from liquid phase. Dewatered sludge was dried to constant mass. Chemical analyses of solution are shown in the following Table 6.

Table 6 Chemical analysis of solutions after neutralization to pH 3 or 4

Neutralization from start pH 2.67	Elements								
	Fe	Mn	Cu	Zn	As	Ni	Pb	Cd	S
	concentration, mg/L								
to pH 3	39.9	79.4	47.3	18	<0.02	0.53	<0.02	0.06	3384
to pH 4	196	85.9	47.3	18.6	<0.02	0.58	<0.02	0.08	3163

AMD neutralized to pH 3 or 4 was used as start samples for neutralization to pH 7, 7.5 or 8. As in the first neutralization stage, liquid and solid phase are separated by vacuum filtration. Liquid phase is used for the chemical analyses and solid phase is dried and measured after reaching the constant mass value. Chemical analyses of solution are shown in the following Table 7 and 8.

Table 7 Chemical analysis of solutions after neutralization from pH 3 to pH 7, 7.5 or 8

Neutralization from pH 3 to different pH values	Elements								
	Fe	Mn	Cu	Zn	As	Ni	Pb	Cd	S
	concentration, mg/L								
to pH 7	<0.007	46.1	0.11	1.8	<0.02	0.24	<0.02	0.014	1772
to pH 7.5	<0.007	11.6	0.04	0.18	<0.02	0.16	<0.02	0.007	2622
to pH 8	<0.007	0.23	0.03	0.03	<0.02	<0.007	<0.02	0.012	2240

Table 8 Chemical analysis of solutions after neutralization from pH 4 to pH 7, 7.5 or 8

Neutralization from pH 4 to different pH values	Elements								
	Fe	Mn	Cu	Zn	As	Ni	Pb	Cd	S
	concentration, mg/L								
to pH 7	<0.007	32.1	0.05	1.1	<0.020	0.37	<0.020	<0.008	1962
to pH 7.5	<0.007	8.8	0.03	0.2	<0.020	0.16	<0.020	<0.008	1949
to pH 8	<0.007	8.4	0.03	0.21	<0.020	0.1	<0.020	<0.008	1936

From the Tables 7 and 8, it can be seen that all the metals ions from the solution precipitated into a sludge. Manganese concentration also decreased, which was not the case when Ca(OH)₂ is used as a neutralizing agent. The assumption is that a large amount of CaCO₃ consumption led to decreased manganese.

Table 9 shows the lime consumption during the neutralization process as well as the mass of the obtained sludge.

Table 9 Consumption of CaCO_3 and sludge mass

Sample	Consumption of CaCO_3 , g	Sludge mass, g
start to pH 3	2	2.15
from pH 3 to pH 7	125	128.9
from pH 3 to pH 7.5	200	202.3
from pH 3 to pH 8	275	279.6
start to pH 4	4	4.15
from pH 4 to pH 7	101	103.7
from pH 4 to pH 7.5	175	175.3
from pH 4 to pH 8	250	254.6

From the Tables 5 and 9, it can be seen that the consumption of calcium carbonate is much higher than the consumption of calcium hydroxide. As chemical analyzes have shown almost the same results of changes in metal ions concentration, it can be concluded that it is better to use calcium hydroxide to neutralize acidic mine water.

CONCLUSION

The experiment results suggest that the two-step pH control neutralization method is effective and practical to recover iron and copper ions separately in the sludge generated along the process and are reliable in processing the water quality to the required levels. The use of both neutralizing agents gave good results. however, since the consumption of calcium hydroxide is much lower compared to the consumption of calcium carbonate, the conclusion is that it is more justified to use calcium hydroxide to neutralize acidic mine wastewater.

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