Experiment Results of Metal Recovery by a Two-Step Neutralization Process from AMD from a Copper Mine in Serbia

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Abstract

A two-step neutralization process is proposed to recover iron and copper separately. A new experiment equipment for continuous operation of this process was developed and manufactured. Three types of Acid Mine Drainages (AMD), which are most environmentally influential in Bor copper mine area in Serbia, were selected for the experiment. They were supplied for the experiment without any pre-treatment. Approximately 1.8 cubic meters of AMD for each type was treated by 5L/min by the new equipment using industrial hydrated lime. As a result, it was confirmed the proposed process is effective for AMD treatment and metal recovery. Iron and copper were recovered in the sludge separately.

Keywords: AMD, neutralization, metal recovery, copper mine, pH control

Introduction

Acid Mine Drainage (AMD) treatment is a serious matter for mining industry especially the case of abandoned or long-time operating mines. The cost for such treatment is perpetually incurred by the industry or the public sector. It is a heavy burden to them for long time. Metal recovery processes for AMD have been proposed in previous researches (e.g. Mongi et al., 2007, Masud et al. 2008, Macingova & Luptakova 2012), however the process should be simple and practical to apply for real situation. This research purpose is to confirm the possibility to recover iron and copper separately by simple and practical process to mitigate the treatment cost by metal recycling benefit.

In Bor area in Serbia, all of the waste water from the mine area is flowing out to natural environment without any treatment now. Bor mining complex is located 230km south-east of Beograd, Serbia. The mine drainage water in the area is released to the downstream without any treatment through tributaries of Danube River. It is suggested that the mine drainage water in Bor mining area gives environmental impact to the river water of Danube River (UNEP 2002).

There are two major mines and copper smelter/refinery in the area. The Bor underground mine has a history of more than 100 years, and Bor open-pit mining opened in 1923. The total amount of ore mined from the open-pit was approximately 100million tons with the waste of approximately 170 million tons. There are other mines which are the Veliki Krivelj open-pit mine and the Cerovo open-pit mine. Waste rocks, low grade ores and flotation tailings are left in surrounding areas, and causing environmental problems. The mining influenced water including waste water from the copper smelter and refinery plant flow into Krivelj and Bor Rivers, then down to Danube. Not only the Serbian government and municipal people but also international organizations have strong concern to such environmental situation (JICA 2008, Stojadinovic et al. 2011).

Previous research conducted between 2011 and 2013, financed by Japan International Cooperation Agency (JICA) and Japan Society for the Promotion of Science (JSPS), showed that the environmental impacts to the river water of River Danube caused by the mine drainage and various mine wastes are not clear. However, serious environmental impacts were recognized in Bor mining area to the downstream basin by 30 km along Bela River (Masuda et al. 2017, Masuda et al. 2016). There exist flotation tailings, waste rocks and AMD with relatively high content of copper in the mine area (Masuda et al. 2012).

Experiment

Experiment equipment

Figure 1 shows the process diagram of the Two-Step Neutralization Experiment Equipment. It was installed in the storage house in Mining and Metallurgical Institute Bor, Serbia in 2016. The equipment is separable to 5 units and transportable by a small track to settle and use at any AMD site.

The pH is controlled by Proportional-Integral-Differential Controller (PID). The pH meters are installed at outlet points of each pH control tank. PID calculates and controls each tank's pH by adjusting each Lime Slurry Pumps automatically to the set up values on the 1st and 2nd steps. Operator can set up the pH values by PID prior to or during the experiment. The pH data is indicated on the display in front of the controller and recorded on SD memory card.

Waste water is fed to the Waste Water Tank at first and pumped up to the pH control tank A in the 1st step, then mixed with the neutralizer from the Lime Slurry Tank. From this point, the waste water flows down to the end of the process, which is the outlet of the Thickener B of the 2nd step, by gravity. It is continuously running down to this point. After the 1st step consists of the pH Control Tank A, the Flocculation Tank A and the Thickener (A) follows by the 2nd step consists of the pH Control Tank B, the Flocculation Tank B and the Thickener (B). Agitators to mix the tanks are attached to each pH Control Tanks and Flocculation Tanks to mix the reagent with the waste water. Sludge is precipitated in the bottom of the Thickener A and B incrementally during the experiment. Precipitated sludge can be discharged by manually using the pump and fed to the Filter Press for dewatering. The flow rate capacity of the equipment is from two to five litter pre minutes (2-5L/min.)

Figure 2 is a picture of the equipment installed in the storage house. A new experiment equipment was developed and manufactured in Japan. It was shipped from Japan to Serbia and installed in a storage house of 9.5m x 4.5m space area in MMI-Bor.

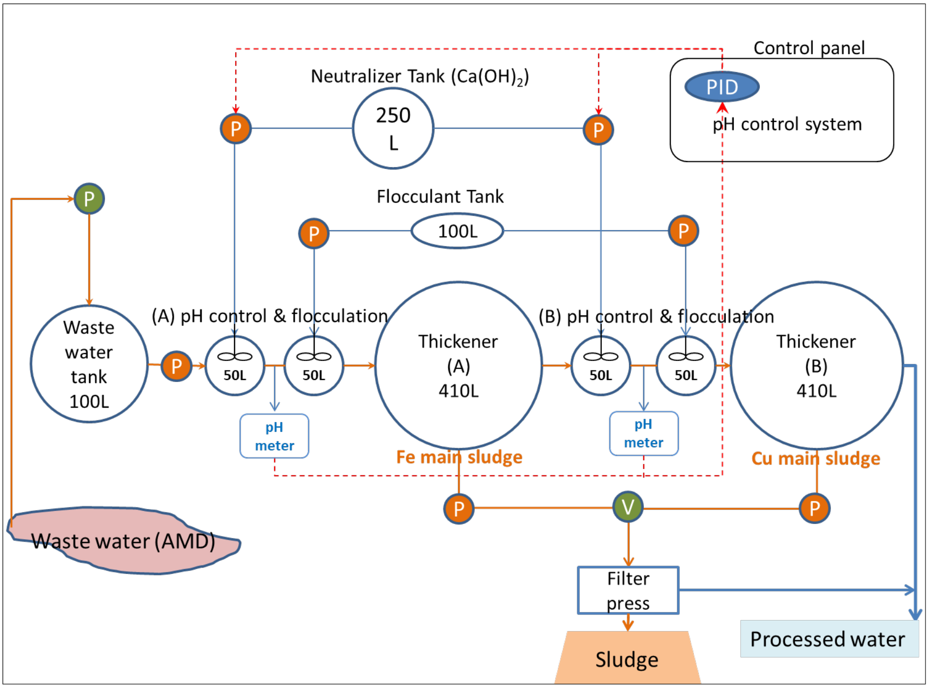

***Figure 1** Two step neutralization process diagram*

Figure 2 *Two step neutralization process experiment equipment installed in storage house.*

Experiment method

Based on samplings and chemical analysis of various AMD in Bor area, three AMD sites, which are more influential to the environment, were selected for the experiment to confirm the effectiveness of AMD treatment to improve the river environment and the possibility to recover the metals contained in the AMD. Figure 3-A shows the effluent water from overburden dump site of open-pit operation named "Saraka Stream". Figure 3-B shows waste water from underground mining operation named "Underground Waste Water. Figure 3-C shows the seepage water from mixture of mine waste materials named "Robule Lake".

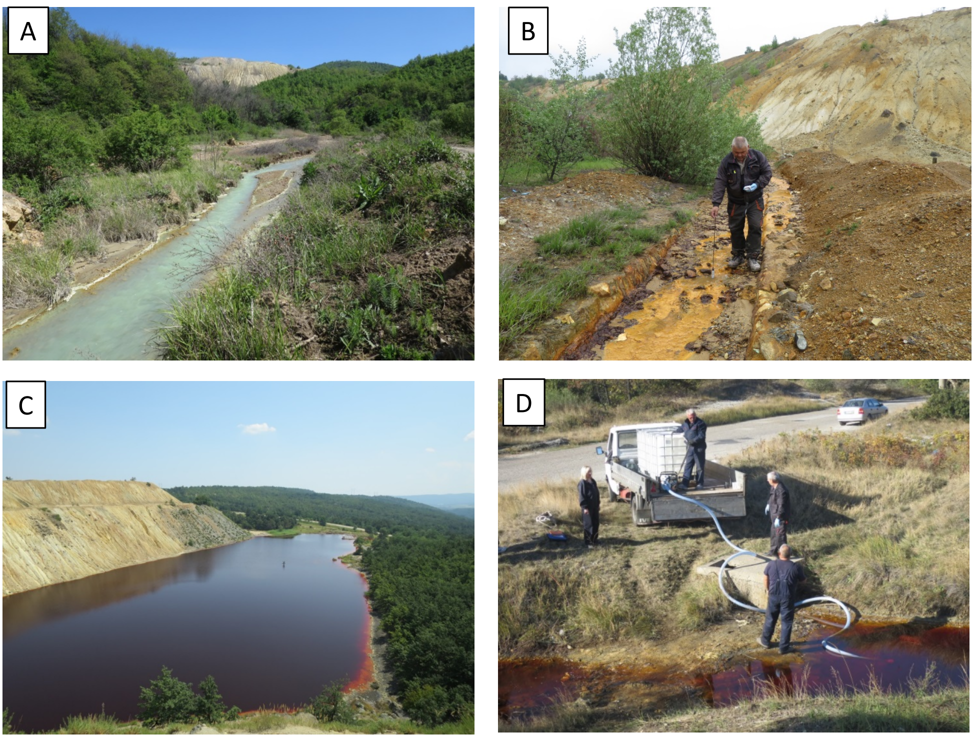

Figure 3 *A: Acid mine drainage at P-2 (Saraka Stream), B: Acid mine drainage at P-3 (Underground waste water), C: Acid mine drainage at P-11(Robule Lake), D: Sampling for experiment at P-11 (Robule Lake)*

Industrial hydrated lime ($Ca(OH)_2$) was used for the neutralizer, which is produced a local lime stone mine. ACCOFLOC@ A-95, which is produced in Japan and imported to Serbia, was used for flocculation in both steps. Lime milk density is 2.5% and flocculant density is 0.05%.

Figure 3-D shows sampling for the experiment. AMD of each site was pumped up to two plastic containers just before the experiment starts to avoid chemical changes by oxidation and transported by truck to the storage house installed the experiment equipment. Approximately 1.8 m^3 AMD samples for each three sites were used for the experiments. Flow rate of the experiment was set at 5.0L/min. It took approximately 6 hours for each experiment. pH was set 4.0 at the 1st step and 7.0 at the 2nd step by PID.

Results

Results of the chemical analysis of each AMD is shown in Table 1. It is understandable that the water color of P-2 is pale greenish as Figure 3 shows. It is because of pH 4.6 which is relatively high. Besides, iron and aluminum content is very low compared to others. Details should be investigated more, however it is thought that as the original AMD comes down by mixing with a river water through lime stone area, most of the iron and aluminum in the original AMD was removed along the stream. It can be said that P-3 and P-11 is almost same low pH value and higher content Cu and Fe. Mn should be noticed for all three AMD.

Results of the chemical analysis of Cu, Fe-total, Mn, As, Co and Ni of processed water and removal rate of metals of P-2 sample is shown in Table 2, results of P-3 sample is shown in Table 3, and results of P-11 sample is shown in Table 4. In case of P-2, only one step at pH 7.0 is applied, because the pH of P-2 is more than 4.0.

These results show that Fe and Cu can be removed separately by controlling pH at 4.0 and 7.0. Co and Ni behavior is similar to Cu behavior. It was not removed much at pH 4.0 but most of them are removed at pH 7.0. It is understandable considering the solubility product of these metals, and some amount of adsorption and/or precipitation phenomenon together with Fe sludge precipitation.

In case of Mn, removal rate at pH 7.0 are relatively low, such as 65.2% in P-2, 83.6 % in P-3, 57.5 % in P-11. At the 2nd step Cu, Total Fe-total and As are less than the limit value of the standard in both Serbia and Japan. However, it is necessary to lower the content of Mn to meet the effluent standard or limit value of water quality of Serbia.

Metal contents in the sludge generated by neutralization process of P-2, P-3 and P-11 are shown in Table 5, Table 6 and Table 7 respectively. Sludge was dried in Convection Ovens at temperature 40+ degree centigrade and analyzed by ICPAES for Cu, Fe, Mn, and by ICPMS for As, Co, Ni. These results suggest that Cu, Co and Ni in AMD can possibly recoverable in the sludge separately from Fe concentrated sludge generated by controlling pH conditions. The highest Cu content in the generated sludge was 7.8% at pH 7 from 75.11mg/L Cu contained AMD with comparably high content of Cobalt and Nickel. Highest Fe content in the sludge was 33.5% at pH 4 from 391.2mg/L Fe contained AMD. As behavior is more concordant with Fe.

Conclusions

The experiment results suggest that the two-step pH control neutralization and precipitation method is effective and practical to recover iron and copper separately in the sludge generated along the process and is reliable in processing the water quality to the requited levels.

Sludge recovered from three AMD samples at pH 7 contains at least 1% copper with some amount of molybdenum and nickel. It is possibly recyclable considering that average Cu grade of the ore produced in this area is less than 0.5%.

The experiment equipment, which was developed this time, is useful to carry out researches to know the relationship between metal contents in sludge and AMD characteristics in a practical way.

It should be considered more whether this process will be practical and metal recycling from the sludge is economical.

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Table 1 Chemical analysis of AMD samples at P-2, P-3, P-11.

Sample	pH	Cu	Fe - total	Mn	As	Co	Ni	Pb	Zn	Cd	Al	Ca	Mg
		mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	mg/L	µg/L	mg/L	mg/L	mg/L
P-2	4.60	75.1	0.3	16.8	3.3	1121.1	280.1	0.2	3.5	21.6	71.0	529.7	226.2
P-3	2.67	187.1	506.6	20.5	290.1	654.0	1530.7	3.7	8.6	87.6	328.5	435.1	313.6
P-11	2.84	38.3	391.2	69.2	9.8	865.3	427.5	<2.1	14.0	44.8	200.3	407.6	853.6
		ICP AES	ICP AES	ICP AES	ICP MS	ICP MS	ICP MS	ICP MS	ICP AES	ICP MS	ICP AES	ICP AES	ICP AES

Table 2 Chemical analysis of processed water and removal rate of metals of P-2 sample, and the Limit value of Serbia and Effluent standard in Japan.

P-2	Cu (mg/L)	Fe-total (mg/L)	Mn (mg/L)	As (µg/L)	Co(µg/L)	Ni (µg/L)
Start pH4.6	75.11	0.26	16.77	3.30	1121.10	280.10
1st step (pH7)	0.21	0.07	5.83	<1.0	100.50	49.20
Removal rate at 1st step (%)	99.7	75.3	65.2	100	91.0	82.4
Limit Value (Class V)-Serbia	1.0	2.0	1.0	100.0		
Effluent standard - Japan	3.0	10.0	10.0	100.0		

Table 3 Chemical analysis of processed water and removal rate of metals of P-3 sample .

P-3	Cu (mg/L)	Fe-total (mg/L)	Mn (mg/L)	As (µg/L)	Co(µg/L)	Ni (µg/L)
Start pH 2.67	187.07	506.58	20.46	0.29	653.97	1530.70
1st step (pH 4)	180.57	97.95	22.28	0.01	632.23	1363.30
2nd step (pH 7)	0.30	0.19	11.37	0.00	42.57	91.46
Removal rate at 1st step (%)	3.5	80.7	-8.9	96.9	3.3	10.9
Removal rate at 2nd step (%)	99.2	100.0	83.6	100.0	95.1	78.6

Table 4 Chemical analysis of processed water and removal rate of metals of P-11 sample.

P-11	Cu (mg/L)	Fe-total (mg/L)	Mn (mg/L)	As (µg/L)	Co(µg/L)	Ni (µg/L)
Start Ph 2.84	38.3	391.2	69.2	9.8	865.3	427.5
1st step (pH 4)	40.3	8.3	74.2	<2.1	909.0	428.4
2nd step (pH 7)	0.31	0.044	29.4	<2.1	134.1	79.1
Removal rate at 1st step (%)	-5.2	97.9	-7.3	100	-5.1	-0.2
Removal rate at 2nd step (%)	99.2	100.0	57.5	100	84.5	81.5

Table 5 Metal contents in the sludge generated by neutralization process of P-2 .

P-2 Sludge	Cu(%)	Fe(%)	Mn(%)	As(ppm)	Co(ppm)	Ni(ppm)
pH 7.0	7.8	3	0.76	6.4	628.8	145.7

Table 6 Metal contents in the sludge generated by neutralization process of P-3 .

P-3 Sludge	Cu(%)	Fe(%)	Mn(%)	As(ppm)	Co(ppm)	Ni(ppm)
pH4.0 (3.8)	0.41	22.43	0.01	131.26	12.57	64.99
pH7.0 (7.0)	3.89	3.55	0.44	5.97	186.38	377.49

Table 7 Metal contents in the sludge generated by neutralization process of P-11 .

P-11 Sludge	Cu(%)	Fe(%)	Mn(%)	As(ppm)	Co(ppm)	Ni(ppm)
pH4.0 (3.8)	0.15	33.52	0.26	24.44	8.85	6.51
pH7.0 (7.0)	1.24	0.47	1.67	14.50	373.55	188.61

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