A new approach to recover dissolved metals in AMD by two-step pH control on the neutralization method

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Abstract A new approach is proposed to recover iron and copper separately by controlling the pH using a two-step neutralization process. Iron sludge and copper sludge can be recovered separately. It is expected that copper sludge will dissolve in sulfuric acid to feed to solvent extraction process or feed directly to an existing copper smelter. Effluents from wastes and river water samplings were carried out several times from 2015 and three point's AMDs were selected to treat and recover the metals in Bor mine area in Serbia. The experiment results suggested the proposed process is promising.

Key words AMD, neutralization, metal recovery, copper mine, pH control

Introduction

AMD treatment is a serious matter for mining industry especially for mines that have been abandoned or operating long-term. Substances such as accumulated waste materials, flotation tailings and underground cavities generate AMD which contains various metal elements. Such AMD should be treated by removing the contained hazardous metals before they flow out of the mine area. However, the cost for such treatment has long been a heavy burden on the mining industry.

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. 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, 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, S.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. There exists flotation tailings, waste rocks and AMD with relatively high content of copper in the mine area(N.Masuda et al. 2012). In this research, a new approach is proposed to treat the AMD effectively by recovering toxic but valuable metals.

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Methods

Sampling and chemical analysis

Fig. shows a schematic map of the river system in the Bor area, explaining the mine facilities along the river which may be affecting the water quality. P-[number] s are the sampling points of the river water. The 11 bold numbers (red) are the sampling points in this research. Other points (black) were sampled in previous research. Previous research has shown that the water in these 11 sampling points contain copper exceeding 10mg/L. Points of the P-[number] in boxes were selected as target AMD for this research to treat and recover copper and iron. The river flows from left to right and up to River Danube, shown at the upper right corner.

Tab.1 shows the example results of chemical analysis of the 11 points samples, taken in August 2016. Samples were collected and analysed four times in 2016. The pH and metal contents differ each time, depending on the time of sampling; however, the tendency is clear that the water with higher content of metals always derived from the same sampling points.

P-1 is the most up-stream sampling point in Veriki Krivelj River, and the sampled water is not contaminated. P-2 is the branch of the Veriki Krivelj River, located down-stream of over burden damp site. The over burden contains oxidized copper minerals as well as pyrite. This suggests that the seepage water from the dump contains copper. Tab.1 shows that more than 90mg/L of copper and 30mg/t of iron are contained at this specific point. P-3 is a sample of pumped-up water from the underground mine operation site, which also flow down to Veriki Krivelj River. It is low in pH and contains more than 100mg/L of copper, 361mg/L of iron, 23mg/L of manganese and more than 0.1mg/L of arsenic. P-6-1 is very low in pH and the highest content of iron, copper, zinc and arsenic in all the sampling points. However, all this water runs down from the metallurgical plants, such as smelter and refinery of the mine, and flows down to Bor River. It is possible that the plants release the waste water directly into the drainage channel without any treatment in their operation. P-11 also has higher content of metals; more than 500mg/L of iron, 50mg/L of copper, and the content

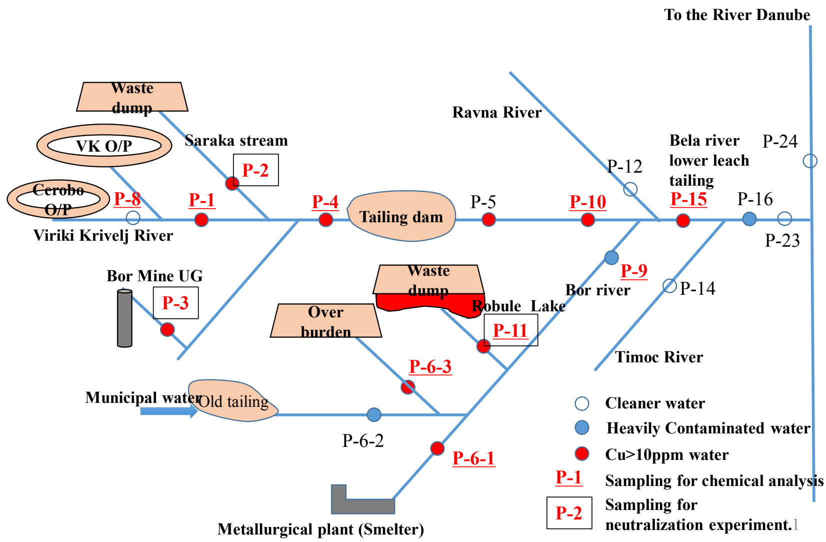

***Figure 1** Schematic map of the river system in Bor area*

of manganese is exceptionally high, exceeding 100mg/L. P-11 water is sampled from a flow from a lake formed by seepage and underground water from waste dump site that consist of waste rocks, flotation tailings, and low grade ores accumulated from the beginning of the mine operation.

Table 1 Results of the chemical analysis of water samples in August in 2016 (mg/L for metals)

Sample	pH	Al	Cr	Mn	T-Fe	Ni	Cu	Zn	As	Pb	Cd
P-1	6.78	0.3	0.00	2.0	<0.007	0.0	0.0	0.0	0.00	0.00	0.00
P-2	4.46	59.1	0.00	13.8	34.0	0.3	92.6	1.4	0.00	0.00	0.01
P-3	2.89	240.7	0.02	23.4	361.1	1.0	111.7	9.2	0.16	0.01	0.12
P-4	3.77	44.8	0.00	8.8	39.2	0.2	33.0	1.7	0.01	0.00	0.02
P-6-1	1.77	331.0	0.17	18.6	1,633.0	10.4	457.4	50.8	82.75	0.31	2.75
P-6-3	5.24	10.7	0.00	21.2	38.6	0.2	5.3	5.9	0.05	0.00	0.01
P-8	7.10	0.1	0.00	0.2	0.0	0.0	0.1	0.0	0.01	0.00	0.00
P-9	3.08	31.7	0.01	6.8	66.7	1.4	61.9	5.4	0.08	0.51	0.15
P-10	6.04	3.3	0.00	6.2	3.0	0.1	3.6	0.5	0.00	0.00	0.00
P-11	2.79	292.6	0.01	100.8	537.6	1.0	50.9	21.8	0.02	0.00	0.06
P-15	4.37	18.0	0.00	5.2	36.8	0.6	30.1	2.7	0.01	0.21	0.06
		ICP-AES	ICP-MS	ICP-AES	ICP-AES	ICP-MS	ICP-AES	ICP-AES	ICP-AES	ICP-MS	ICP-AES
											(mg/L)

Tab.2 shows the water quality standards in Japan and Serbia. The criteria are not same, but the target water quality after the treatment in the present research will be considered based on these standards.

Manganese at P-2, P-3, P-4, P-6-1, P-6-3, P-11 and P-15, Total Fe (T-Fe) at P-3, P-6-1 and P-11, copper at P-2, P-3, P-4, P-6-1, P-6-3, P-9, P-11 and P-15, exceeds the standard on municipality water. P-6-1 water is over the standard for other metals. P-9 water may be affected by P-6-1 water quality and is over the standard.

Table 2 *Water quality standard in Japan and Serbia*

	pH	Cr	Mn	T-Fe	Ni	Cu	Zn	As	Se	Cd	Pb
Effluent standard of Japan	5.8-8.6	2	10	10		3	2	0.1	0.1	0.03	0.1
Serbia (Class V)*	6.5-8.5	0.25	1	2		1	5	0.1			
Serbia (Water for Irrigation)	6.5-8.5	0.5			0.1	0.1	1	0.05		0.01	0.1
Serbia municipality water		1	5	200	1	2	2	0.2		0.1	0.2
*Surface waters that belong to this class have not be used for any purpose.											mg/L

Fig.2 shows the Fe^{2+} content and the ratio (%) of total Fe by month in 2016 at the sampling points of P-2, P-3 and P-11. The Fe^{2+} ratio is relatively low at all points. Fig.3 shows the Fe^{2+} ratio (%) in total Fe by month (2016) by the time of the year.

Proposed approach

Sulphide method, Ion exchange method, Neutralization and precipitation method are considered to be applicable to recover metals from AMD. In general, the Sulphide method has some difficulty to handle the reagent of hydrogen sulphide and the Ion exchange method may cause higher content of iron solution instead of recovering copper. In this research, the Neutralization and precipitation method is proposed as a simpler and more cost effective method to treat and recover iron and copper metals in AMD (N.Masuda et al. 2008). The idea is to recover iron at around pH 4 and copper at around pH 8 by controlling pH value. To confirm this idea, neutralization experiments using artificial AMD were carried out. Characteristics of the artificial AMD (50mg/L of Fe(II)(50%) + Fe(III)(50%), 140mg/L of Cu and 250mg/L of Al) were prepared and pH values were controlled at pH 4 and pH 8 starting at pH 2.57 with sulfuric acid. A portion of the result is shown in Fig.2. The result suggests that the ferrous iron can be precipitated at pH 4 and almost all the copper iron is precipitated at pH 8. However, the ferric iron is not precipitated at pH 4.

Fig.3 shows the Fe2+ content and the ratio (%) of total Fe by month in 2016 at the sampling points of P-2, P-3 and P-11. The Fe2+ ratio is relatively low at these points. This indicates the new approach to recover Fe and Cu separately by neutralization and precipitation method from AMD in Bor area is considered possible and practical.

Results of neutralization and precipitation experiment

Neutralization experiments using real AMD were conducted on samples P-2, P-3 and P-11, in August 2016. One litre of AMD samples were provided to each batch of experiment. The water qualities are shown in Tab.1.

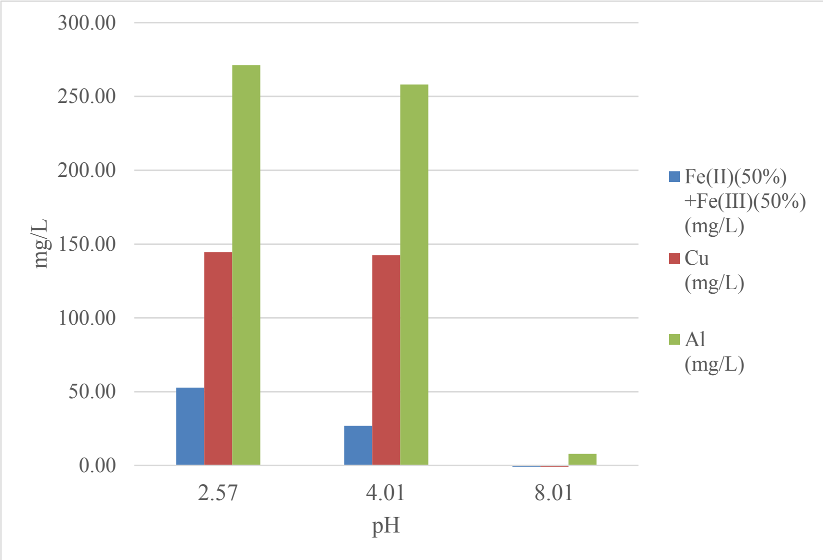

***Figure 2** Neutralization experiment result using artificial AMD*

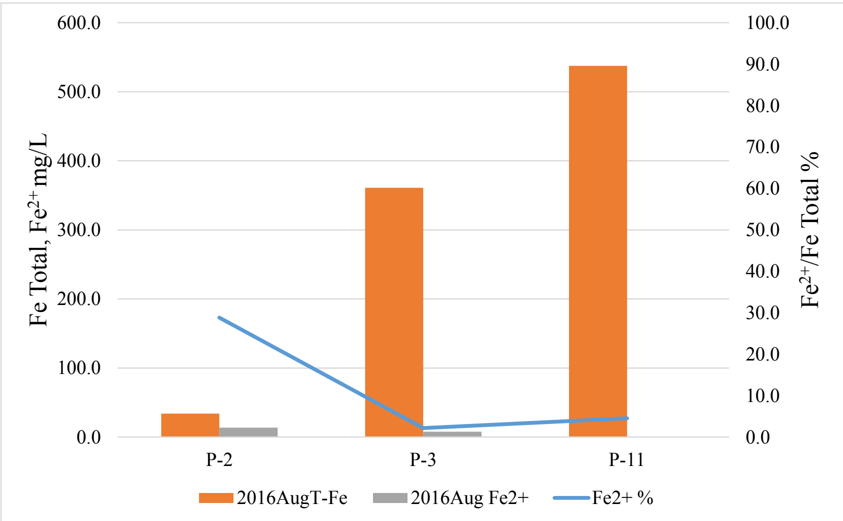

***Figure 3** Fe2+ content and the ratio (%) of Total Fe by month 2016*

Experiment results are shown in Tab.3 for P-2, Tab.4 for P-3, and in Tab.5 for P-11. In Tab.3, the starting pH value is pH 4.2 and neutralized up to pH 8. Almost all Fe and Cu were removed, whereas only about a half of Mn remained in outflow. In Tab.4, 99.67% of Fe was removed at pH 4, but only 0.68% of Cu was removed. However, almost 100% of Cu was removed between pH 4 and pH 8. Tab.5 shows similar results as Tab.4.

These data clearly shows that Fe and Cu are recoverable separately in pH 4 sludge and pH 8 sludge, respectively. Manganese was removed at approximately 50% between pH 4 and pH 8 in all the samples. However, manganese content needs to be even lower to meet the Serbian standard of municipal waste water quality.

***Table 3** Results of neutralization experiment on sample P-2*

Sample	pH	Al	Cr	Mn	T-Fe	Ni	Cu	Zn	As	Pb	Cd
P-2	4.2	59.094	0.000	13.8	34.0	0.269	92.6	1.4	0.004	0.001	0.015
P-2 pH 8	8.0	0.353	0.000	7.1	0.007	0.003	0.021	0.005	0.001	0.000	0.001
Reduction rate at pH4 (%)		-	-	-	-	-	-	-	-	-	-
Reduction rate at pH4-8 (%)		99.40	-	48.28	99.98	98.80	99.98	99.65	67.17	66.02	90.40
											mg/L

***Table 4** Results of neutralization experiment on sample P-3*

Sample	pH	Al	Cr	Mn	T-Fe	Ni	Cu	Zn	As	Pb	Cd
P-3	3.0	240.737	0.016	23.4	361.1	0.981	111.7	9.2	0.160	0.007	0.118
P-3 pH 4	4.1	240.697	0.004	22.2	1.2	0.944	110.9	8.7	0.005	0.006	0.138
P-3 pH 8	8.0	0.261	0.001	10.6	0.007	0.006	0.014	0.014	0.001	0.000	0.012
Reduction rate at pH4 (%)		0.02	75.77	5.15	99.67	3.76	0.68	5.79	96.71	13.80	0.00
Reduction rate at pH4-8 (%)		99.87	15.73	49.64	0.33	95.60	99.31	94.06	2.38	84.22	100.00
											mg/L

***Table 5** Results of neutralization experiment on sample P-11*

Sample	pH	Al	Cr	Mn	T-Fe	Ni	Cu	Zn	As	Pb	Cd
P-11	2.9	292.644	0.007	100.8	537.6	1.005	50.9	21.8	0.016	0.004	0.061
P-11 pH 4	4.0	262.236	0.006	96.2	0.97	1.034	47.8	16.5	0.007	0.004	0.073
P-11 pH 8	8.0	0.375	0.006	46.1	0.007	0.005	0.008	0.024	0.002	0.000	0.010
Reduction rate at pH4 (%)		10.39	4.75	4.62	99.82	0.00	6.03	24.41	58.09	0.00	0.00
Reduction rate at pH4-8 (%)		89.48	13.73	49.68	0.18	100.00	93.96	75.48	31.19	100.00	100.00
											mg/L

Two-step pH control site experiment equipment

Various experiments in the laboratory indicated the two-step pH control process is effective to recover Fe and Cu separately and to process AMD in Bor area to meet the water quality standard. A new continuous experiment equipment was developed based on these experiment data. The new equipment was designed and manufactured in Japan, transported to the Mining and Metallurgy Institute Bor, and installed in a storehouse in the Institute.

The process capacity of the equipment is 2 – 5 L/min AMD and it is capable to use in the field with continuous operation. The equipment consists of 7 units with a filter press to de-water the sludge. It is separable and can be transported to an experiment site in the field by truck.

A test operation was carried out and the designed capacity was satisfied. An actual AMD sampled at P-11 was used for the test operation. Approximately 2 m^3 of AMD was fed to the equipment, and the pH level was set at pH 4 and pH 8. Flow rate of the process varied according to the test configuration.

Sludge, recovered on the newly developed two-step pH control experiment equipment, was analysed. Preliminary results are shown in Tab. 6. The results indicate that the sludge is clearly separated into two; one rich in iron and the other rich in copper. The concentration of Cu 1.1% in the sludge at pH 8 is comparable to the copper ore in other copper mines around the world. The copper content of 0.29% in the sludge at pH 4 is reduced and it is possible to move to the sludge at pH 8 by optimizing the two-step pH value and controlling the pH more carefully. As is distributed in the sludge at pH 4 and 8.

Table 6 *Preliminary results of sludge analysis*

Element	pH 4	pH 8	
Fe (%)	23.43	1.32	ICP-AES
Cu (%)	0.29	1.1	ICP-AES
As (mg/kg)	12	8	ICP-MS

Conclusions

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

It was expected the copper concentration in the sludge recovered by the proposed process will be comparable to present-day copper ore in other operating mines around the world.

To optimize the two-step, pH is important to increase recovery ratio of copper at the second step. Laboratory experiments play an important role in finding the optimum conditions, which may vary by AMD quality, and site by site.

More precise and practical data will be acquired and confirmed by continuous experiments using the newly developed on-site experiment equipment.

Water sampling and analyses will continue to investigate whether water quality changes by factors such as season, weather and mine operation conditions.

Manganese reduction process should be considered on top of this two-step pH control process.

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