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Impact of effluents from a copper-cobalt processing plant in the environment

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ABSTRACT

The new concentrator of Kipushi (NCK) in Katanga province is located in the southeast of the Democratic Republic of the Congo. This processing plant produces a concentrate of copper and cobalt, and it also generates a large amount of effluents equivalent to 2,500 m³/h. The complex nature of these effluent has become a threat to human lives, vegetation, as well as to freshwater resources in the surrounding areas. During this investigation, it was found that NCK effluents have high turbidity and high levels of sulphates compared with EPA standards. These sulphates originate from acid mine water used as one of the components for the flotation process. Also, high chlorides compared with EPA standards and hardness levels due to high concentrations of calcium and magnesium were recorded. Furthermore, the effluents contain heavy metals such as zinc, copper, cobalt, lead, ion, cadmium, and arsenic. Water used during flotation and downstream processes to produce copper and cobalt concentrates was a mixture of raw water from Kamalenge pond and acid mine water from Kipushi mine in a volume ratio of 70/30 respectively. However, it was found that the mine water is the major contributor to the effluent contamination.

Key words | effluents, environment, mine water, pollution, remediation

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INTRODUCTION

The new concentrator of Kipushi (NCK) is a joint venture between the state-owned mining company named GECAMINES and private company EGMF Malta Forrest. The operation is focused on recovering copper and cobalt by flotation. Cobalt is the most important metal needed by the investors (GECAMINES and EGMF) because of its market value. The mineral/ore from Luswishi contains 1.4% to 1.6% of cobalt, and after flotation cobalt is at 12% and copper 14% (Katchong 2002). The mineral undergoes a series of unit processes including milling, flotation, classification, filtration, settling, and drying. The unit processes require large amounts of water and flotation reagents such as sodium silicate and ammonium sulphates in order to recover more cobalt. Water used for the flotation is a mixture of mine water (70%) from Kipushi

mine and water from Kamalenge pond (30%) both situated in the vicinity. Subsequently, large quantities of effluents are generated on a daily basis from the plant operating for 24 hours with an estimated flow rate of $2,500 \text{ m}^3/\text{h}$.

Concerning the origin, pathway and evacuation of effluents towards reception points, the overflows from the settling process, including the overflows from flotation cells, is mixed with wastewater from daily cleaning operations and laboratory wastes. This mixture generates the final NCK effluent. It is therefore channeled by a piping system to the Katapula drain. This drain already contains mine water from the old concentrator. Therefore, a highly polluted effluent is generated from this mixture. Because Katapula drain is short in length (less than a 1 km), NCK

doi: 10.2166/ws.2018.074

effluent with high turbidity flows over a large area of about 3 km² in a very disorderly manner toward Dam III. In this area, the vegetation and soil are in an advanced state of deterioration due to the damaging effects of the contaminated effluent from NCK. From Dam III, NCK effluent flows toward Kipushi River. Furthermore, water from Kaniemesha River (KANI) flows into Kipushi River which ends with high flow into Kafubu River. Kafubu River also collects water from Kamalenge River (KAMAL) and Kampemba River (KAMP).

The NCK effluents pathway is illustrated by the scheme presented as follows:



Regarding the ecological situation of the residential site closer to NCK, solid particles have settled in the Kipushi River over a long period of time (more than 20 years) and the river is filled by solid particles with no more aquatic life in the river. This river is regularly loaded with a continuous flow of NCK effluents and it might disappear unless proper treatment is undertaken. Consequently, solids overflowing from the river have formed a larger desert zone estimated at 9 km² named 'tailings' closer to the residential area opposite the old concentrator site. Almost 2 km of Kipushi River has disappeared because the area is filled with solid particles from the OCK and NCK effluents. Agricultural activities practiced in the area a few years ago are no longer undertaken because of the significant pollution of the rivers and soil. During the dry season, serious air pollution takes place especially in windy times. Consequently, health issues occur in communities because of the presence of heavy

metals in the tailings (Benzaazoua et al. 2000). Table 1 shows the average composition of solid particles from the tailings where dams are situated. These solids are certainly absorbed by the population during the dry season when the weather is windy. The presence of arsenic (As), cadmium (Cd), and other heavy metals such as copper (Cu), zinc (Zn), and lead (Pb) though in low concentration can be harmful to the population as they are accumulated in the tailings.

The objective of this work is to identify the main cause of NCK effluents being harmful to the residential areas, rivers, vegetation, and soil closer to the plant.

MATERIALS AND METHODS

Sampling points (sites)

Based on the objectives of this study samples were collected from various sites where the effluents were in contact with reception points such as vegetation, soil, and surface waters. The following sampling sites are indicated in Figure 1.

Designation of sampling points

- Effluent from mineral processing plant (discharge point): site A, made up with NCK effluent.
- Katapula drain: site B, combination of mine water from Kipushi mine and NCK effluent from site A.
- Dam III: site C, at this point the effluent is a combination of effluent from sites A and B.
- Kipushi River: site D, this site receives the mixed effluent from sites A, B and C.

Table 1 | Average composition of solid particles from tailings (Dams I, II, III)

	Cu [%]	Zn [%]	Fe [%]	Pb [%]	Cd [ppm]	As [%]	SiO ₂ [%]	MgO [%]
Dam I	0.58	2.38	4.92	0.10	176	0.11	31.3	7.10
Dam II	0.35	2.80	6.72	0.09	178	0.13	40.94	9.24
Dam III	0.32	2.18	5.52	0.09	168	0.09	40.18	6.90

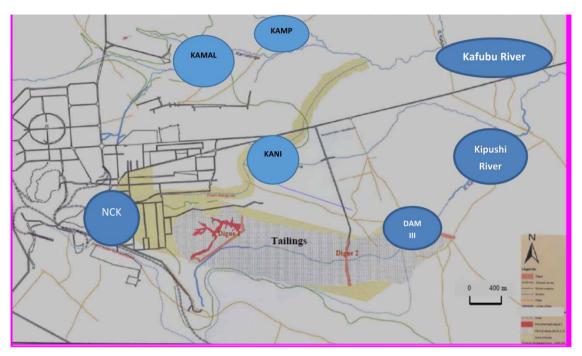


Figure 1 | Map of the main sampling points.

Kafubu River: site E, this represents the last receiving effluent point, made up of all the mixed effluent from the previous sites.

Sampling conditions and characterization

Samples were taken in polyethylene bottles and were kept in a cold room at 4 °C; temperature and pH were measured on site during sampling. The following parameters were chosen for testing using absorption spectrophotometry: Ca, Mg, Na, Cu, Zn, Cd, Fe, Co, Ni. Chlorides were determined by precipitation with the Mohr method using chromate ions as an indicator and silver nitrate as standard solution. Sulphates were measured using the gravimetric method for the precipitation of the insoluble sulphates using barium perchlorate. Effluent total hardness was performed by a complexometric titration using EDTA solution. Total suspended solids test was undertaken according to the standard methods (APHA 1998). Complete alkalimetric titration (TAC) and alkalimetric titration (TA) were determined by the titrimetric method using HCl 0.02N with phenolphthalein.

Frequency of sampling

Sampling was done once every 10 days within a month for water samples used in flotation. Mine water samples were collected once every week. Effluent from sites A, B, C, D, and E were collected every 10 days within a month. For sludge and plants on various sites, samples were collected also once every 10 days. Results were generated in triplicate and averages were determined by EXCEL with standard deviations.

RESULTS AND DISCUSSION

Suspended solids

Effluents generated from the processing plant have high turbidity. This is displayed by the presence of high amounts of suspended solids found in the effluents as recorded in Table 2. Effluents from sites A and B have the highest concentrations of suspended solids. This is due to gangue removal during the flotation process aiming to get the maximum cobalt concentrate. The gangue is made up of 58% SiO₂ to which minerals such as Ca, Mg, Fe, Cu, Mn, and Ni are

Table 2 | NCK effluent recorded data from various sites (averages for 1st, 2nd and 3rd round sampling)

	Site A		Site B		Site C		Site D		Site E						
Parameter	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Co (mg/L)	0.26	0.03	0.62	0.75	1.76	0.09	0.13	0.12	0.11	0.11	0.08	0.09	0.14	0.07	0.07
Cu (mg/L)	1.48	0.34	2.19	3.66	6.06	0.18	0.18	0.23	0.27	0.20	0.09	0.10	0.20	0.19	0.21
Zn (mg/L)	0.17	0.07	0.30	0.14	0.12	0.56	0.13	0.11	0.18	0.38	0.18	0.55	0.11	0.31	0.18
Fe (mg/L)	0.84	0.12	1.74	0.77	0.60	0.09	0.11	0.16	0.10	0.30	0.13	0.11	0.20	0.01	0.23
Pb (mg/L)	0.23	0.01	0.08	0.05	0.01	0	0.01	0.02	0	0.31	0.05	0	0.01	0.01	0
Mn (mg/L)	0.08	0.01	0.13	0.15	0.26	0.05	0.20	0.26	0.27	0.04	0.02	0.01	0.06	0.08	0.08
Cd (mg/L)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	5.3	0.01
Ca (mg/L)	154	150	60.9	145.5	132.3	107	70.0	55.6	60.3	62.1	48.2	65.8	30.0	0.08	29.8
Mg (mg/L)	231	228	126	157.5	137.3	132.5	121.8	111.8	118.3	116.0	94.8	112.3	34.2	27.9	45.2
Ni (mg/L)	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01
Na (mg/L)	647	656	658	660.5	662.5	667.2	211.0	218	220	196	185	190	4.0	30.9	5
SO_4^{-2} (mg/L)	390	396	483.2	284	387	404	346.6	296.4	228.8	286.4	251	228.31	0.01	0.01	0.01
pH	9.2	9.95	9.62	10	9	7.59	7.46	7.91	7.06	7.10	7.4	7.15	7.7	7.63	7.14
Cl ⁻ (mg/L)	57	183	42	401.86	377.57	245.09	211.56	216.38	207.55	191.75	189.89	181	15.43	15.46	15.46
TA	2.2	27.4	38	3.5	4	2.4	0	1.8	0	0	0	19.2	0	1.4	0
TAC	39	89.8	78	22	26	28	21.6	24.2	22.4	19.8	19.2	78.8	14.8	15.6	15.6
Total hardness	68.04	68	45.36	32.40	51.84	58.32	53.46	43.74	44.06	40.50	40.50	45	21.06	22.68	27.54
Conductivity (µS/cm)	1,444.2	1,480	1,552	1,300	1,308	1,420	1,776	1,770	1,788	1,562	1,560	1,574	542	544	543
Suspended solids (mg/L)	127,000	159,000	27,000	9,665	10,500	10,060	26.11	23.02	28.1	18.18	14.18	16.1	8.40	8.20	10.11

TAC: complete alkalimetric titration, TA: alkalimetric titration.

attached. Solid particles mainly originating from the gangue are slowly decanted in sites C and D. Definitely, sites C, D, and E still have small amounts of suspended solids.

Calcium, magnesium, and hardness

Hardness is found to be high at sites A, B, C, and D as presented in Table 2. However, it is low at site E. Hardness is more inclined to magnesium than calcium as reflected in Table 3. This is explained by the fact that water used for flotation has high levels of magnesium compared with calcium. Mine water could be the major contributor to this problem because of its proportion in the mixture regarding water used for the flotation process. Furthermore, Table 4 presents the concentrations of calcium and magnesium, and it is clearly observed that hardness is more inclined to magnesium than calcium. Another reason making the hardness more magnesium-based is that the ore treated at NCK has high concentrations of magnesium compared with calcium (0.36% of CaO and 13.11% MgO) (Katchong 2002).

Table 3 | Average values for characterization of water used for flotation and downstream processes

Parameter	Results (1st round of sampling)	Results (2nd round of sampling)	Results (3rd round of sampling)
Co [mg/L]	0.04 ± 0.005	0.03 ± 0.001	0.05 ± 0.0045
Cu [mg/L]	0.09 ± 0.0002	0.09 ± 0.0002	0.1 ± 0.0015
Zn [mg/L]	0.24 ± 0.01	2.60 ± 0.002	3.83 ± 0.004
Fe [mg/L]	0.13 ± 0.01	0.11 ± 0.01	0.16 ± 0.00002
Pb [mg/L]	0.01 ± 0.0001	0.01 ± 0.001	0
Mn [mg/L]	0.03 ± 0.0001	0.02 ± 0.0018	0.08 ± 0.0004
Cd [mg/L]	0.02 ± 0.0001	0.05 ± 0.002	0.03 ± 0.0002
Ca [mg/L]	66.5 ± 3	57.8 ± 3.5	70 ± 5.5
Mg [mg/L]	106 ± 4	84.8 ± 6.2	103.8 ± 3.8
Ni [mg/L]	0.01 ± 0.0001	0.01 ± 0.001	0.01 ± 0.001
Na [mg/L]	74 ± 3	41 ± 3.5	36 ± 2.8
$\mathrm{SO_4^{2-}}$ [mg/L]	142 ± 8	71.6 ± 4.2	126.8 ± 6
pH	8.43	7.52	7.36
Cl ⁻	147.67 ± 4.2	99.4 ± 6.2	97.15 ± 5.8
TA [°F]	3.8 ± 0.0003	2.2 ± 0.02	1.8 ± 0.0018
TAC [°F]	19 ± 0.6	20.4 ± 1.8	19.2 ± 1.7
Total hardness [°F]	46.98 ± 2	24.38 ± 1.9	43.74 ± 3.8
Conductivity (µS/cm)	1,055	1,008	1,002

Table 4 | Mine water

Parameter	Results (1st round of sampling)	Results (2nd round of sampling)
Co [mg/L]	0.01 ± 0.001	0.02 ± 0.00018
Cu [mg/L]	0.04 ± 0.001	$0.06\ \pm0.0012$
Fe [mg/L]	0.04 ± 0.001	0.05 ± 0.001
Zn [mg/L]	1.94 ± 0.02	1.16 ± 0.017
Pb [mg/L]	0.17 ± 0.002	0.13 ± 0.0017
Mn [mg/L]	0.05 ± 0.004	0.02 ± 0.0016
Cd [mg/L]	0.04 ± 0.001	0.02 ± 0.0018
Ca [mg/L]	106.5 ± 6.02	111.3 ± 7.1
Mg [mg/L]	137.0 ± 7	145.0 ± 7.8
Ni [mg/L]	$0.01 \ \pm 0.001$	0.01 ± 0.0001
SO ₄ [mg/L]	$120.2\ \pm 4$	205 ± 14
pH	4.27	4.21
Cl ⁻ [mg/L]	291.46 ± 18	278.21 ± 16
TA [°F]	5 ± 0.45	3.8 ± 0.27
TAC [°F]	30 ± 2	29.6 ± 1.9
Total hardness [°F]	64.80 ± 5	61.56 ± 4.5
Conductivity [µS/cm]	1,580	1,620

pH and alkalinity

Analyzing the data generated in Table 2, effluent from sites A and B are alkaline with a pH ranging from 7 to 9. However, for sites C, D, and E, pH tends towards alkalinity. The effluent alkalinity is due to the fact that flotation takes place in an alkaline environment to avoid the decomposition of NaHS, a reactant used during the flotation process. In some instances lime is used to regulate the pH but for NCK the pulp pH is always between 7 and 10. Therefore, the use of lime for effluent pH regulation is not needed. TAC and TA represent the concentration of Ca and Mg bound to bicarbonates. The concentrations of TAC and TA expressed in French degree (°F) are strong indicators showing that effluents for all sites might contain bicarbonate ions. These bicarbonate ions originate from the gangue. Knowing that bicarbonate ions are alkaline, therefore, pH values recorded will be basic rather than acidic. Most pH values are within the range for EPA standards, which is between 6.5 and 8.5, except for site A.

Conductivity and mineralization

From the data recorded in Table 2, it is observed that effluents from sites A, B, C, and D are highly loaded with dissolved compounds making them very mineralized. Consequently, the conductivity is high. This is due to the addition of reactants during the flotation process. However, the nature of the ore and its gangue contribute to high mineralization and consequently lead to high conductivity. The same data show that conductivity exceeds 1,500 µS/cm. This could be the cause of plants-growth inhibition, vegetation destruction and any other environmental concern recorded in the surroundings (Bejan & Bunce 2015). Analyzing the conductivity data, it is noticed that effluents from sites A, B, C, and D are highly mineralized compared with site E. As a result, the conductivity at these sites is higher. The other major contributor of high conductivity is mine water, which is a large quantity of the water used for flotation. Also, conductivity at site E is the lowest compared with other sites as recorded. This is due to the river's high flow and volume of water that dilute the effluents discharged into it. As a result, the related mineralization decreases as well as the conductivity at site E.

Sodium

This is a regular element found in water and wastewater. Its origin in NCK effluents can be traced through the use of flotation reactants such as NaHS and Na₂SiO₃ and the water used for the flotation process. Sodium does not impact directly on effluent contamination but contributes more toward the increase of conductivity (WHO 2008).

Chlorides

Chloride ions are always found in water as is the case for sodium. However, in the current case with recorded values in Table 2 they were found in high concentrations at site B (Katapula drain) compared with the EPA and WHO acceptable limit equivalent to 250 mg/L (Natarajan et al. 2005; WHO 2008). This is due to the fact that effluents from Katapula drain are mixed with mine water which has a high concentration in chlorides, but on site E their concentration is lower due to the dilution taking place in the Kafubu River. These ions contribute to the mineralization of effluents and consequently increasing the conductivity. The origin of these chloride ions could be mine water (Table 4) in which they reach more than the 250 mg/L considered as the normal limit for discharge.

Sulphates

Sulphate concentrations are very high at sites A, B, C, and D as recorded in Table 2. However, in most cases they remained higher compared with the EPA acceptable limits of 250 mg/L and 480 mg/L for plants and vegetation (Natarajan et al. 2005; Asensio et al. 2013; Hao et al. 2014; Bejan & Bunce 2015). This situation regarding sulphate presence in effluents is explained by:

- oxidation of sulfur ions by air injected in flotation cells;
- the presence of NH₄SO₄ in the flotation process used as a reactant for flotation;
- the presence of SO₄ ions in the water used for flotation, which comes mainly from mine water.

Copper

The main focus during the process is to recover cobalt out of the ore. Therefore, copper will remain at high concentration in the effluents based on the selectivity process undertaken during flotation. Table 2 shows that most values are superior to 1 mg/L, which is beyond the acceptable EPA limit and also beyond the acceptable limit for aquatic life. It is possible that mine water could have contributed slightly to the presence of copper in the NCK effluents because of low concentrations of copper in mine water (Asensio et al. 2013; Simate & Ndlovu 2014).

Cobalt

Cobalt remained in the effluents though it is supposed to be totally removed from the ore during the flotation process. However, its concentration as shown in Table 2 is very low in most cases because it has been taken from the ore during the flotation process.

Zinc

This element is not found in the ore treated at NCK, however, it is found in mine water. As a result, zinc appears in the effluents. The concentration of zinc recorded in Table 2 is less than 5 mg/L, which is the EPA limit and also the limit for aquatic life (Asensio et al. 2013).

Lead, cadmium, nickel

Table 2 shows that these are trace elements in the effluents. They are not found in the main ore processed at NCK. However, their origin could be mine water because they are found in low concentrations in acid mine water as recorded in Table 4 (Asensio et al. 2013).

PROBABLE REASONS FOR SOIL CONTAMINATION FROM EFFLUENTS IN THE ENVIRONMENT

High amounts of sludge were found in the effluents especially at sites A and B as indicated in Table 2. The sludge fills the receiving points such as rivers and soil, and affects the vegetation on the effluent pathway. To solve this issue there is a need for solidification and sludge stabilization before the sludge reaches these receiving points (Asensio et al. 2013; Demers et al. 2015). It is observed from the data recorded in Table 5 that magnesium in sludge is in higher concentrations. This element can be very beneficial for plants in allowing them to absorb phosphorus but it prevents plants from absorbing potassium, which is a key element for plant growth. This has caused growth inhibition for plants, weakening of plant roots and chlorosis on the effluent pathway. Also, the analysis of data recorded in Table 5 shows that sulphate concentrations in the sludge are very high. The origin of sulphates has been discussed earlier. However, they cause many problems for the surrounding plants and vegetation that are close to the effluent pathway. These problems include the death of cells for plants, inhibition of plant growth, falling of leaves, and change of color for plant leaves (Asensio et al. 2013; Bolan et al. 2014). There are limited options to be undertaken in order to control acid and sulphate generation from mine wastes (Dhal et al. 2013; Perreault 2013; Demers et al. 2015).

REMEDIATION PLAN: SUMMARY

The treatment should take into consideration all aspects related to management of mine wastes whether solids or liquids, and this should include the challenges and various opportunities that can be explored to reuse the waste

Table 5 | Characterization of sludge from the effluents and plants (flora) intake in the affected environment close to NCK (1st, 2nd and 3rd round samplings)

	Results (1st round	of sampling)	Results (2nd round	of sampling)	Results (3rd round of sampling)		
Parameter	Sludge	Plant (flora)	Sludge	Plant (flora)	Sludge	Plant (flora)	
Co [mg/kg]	3.0 ± 0.22	5.3 ± 0.4	2.9 ± 0.18	1.6 ± 0.2	2.6 ± 0.3	3.2 ± 0.19	
Cu [mg/kg]	6.6 ± 0.58	17.4 ± 2	4.5 ± 0.35	20 ± 2	3.4 ± 0.2	4 ± 0.38	
Fe [mg/kg]	20 ± 0.17	38.8 ± 2	23.7 ± 1.9	40.2 ± 3	19.2 ± 1.6	19.4 ± 1.7	
Zn [mg/kg]	0.9 ± 0.06	1.7 ± 0.2	0.2 ± 0.018	0.1 ± 0.01	0.1 ± 0.01	0.7 ± 0.038	
Pb [mg/kg]	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0	0	
Mn [mg/kg]	0.7 ± 0.04	1.2 ± 0.02	0.5 ± 0.03	1.1 ± 0.1	0.4 ± 0.02	1.3 ± 0.1	
Cd [mg/kg]	1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0	0	
Ca [mg/kg]	8.8 ± 0.66	12.5 ± 1.5	2.7 ± 0.29	8.4 ± 0.6	2.4 ± 0.12	2.4 ± 0.12	
Mg [mg/kg]	$1{,}263\pm19$	121.2 ± 9	$1{,}545\pm15$	111.8 ± 7	123.5 ± 8	140.5 ± 9	
Ni [mg/kg]	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0	0	
Na [mg/kg]	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	
SO ₄ [mg/kg]	385 ± 23	370 ± 21	383 ± 22	355 ± 18	408 ± 19	396 ± 28	

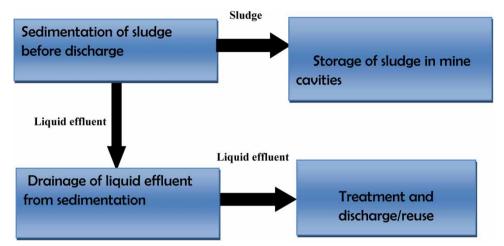


Figure 2 | Suggested scheme for the remediation plan.

(Hughes et al. 2013; Hughes & Gray 2013a, 2013b; Rose 2013; Strosnider et al. 2013; Simate & Ndlovu 2014). Figure 2 presents a summarized plan to manage the issue of pollution due to NCK effluents in the environment. This plan includes sedimentation of sludge, storage of sludge in mine cavities, drainage of effluent from the sedimentation process and its treatment for reuse (Hughes et al. 2013; Hughes & Gray 2013a; Rose 2013; Simate & Ndlovu 2014; Demers et al. 2015; Uster et al. 2015; Parbhakar-Fox & Lottermoser 2015). This scheme aims to minimize the harmful environmental impacts of NCK effluents.

CONCLUSION

The control of effluents generated from the NCK has revealed the following facts:

- · Effluents generated from the NCK are highly contaminated by inorganic substances coming from the ore, the mine water used in the flotation process, and the use of reactants during the flotation process.
- These effluents, after being discharged from the processing plant, contaminate the soil, the vegetation, and surface waters from surrounding rivers along their pathway from the discharge point to the receiving points of Katapula drain, Dam III, Kipushi River, and Kafubu River.
- Vegetation is destroyed because the management and discharging of effluents is not properly done, and also

because of sulphates, chlorides, and other minerals such as magnesium, sodium, calcium, and other heavy metals in the discharged waste. These elements or compounds may be in higher concentrations, therefore, causing high levels of conductivity and high mineralization or high amounts of soluble substances in the effluents.

- Calcium and magnesium cause high hardness, the biggest contribution of hardness being magnesium.
- High suspended solids in the effluent at the discharge point causes soil and surrounding river pollution.

To minimize the effects of NCK effluents, the treatment of mine water is suggested before using it for any process. The implementation of the remediation plan suggested in this study can be useful in this regard.

ACKNOWLEDGEMENTS

Thanks to the NCK management for support.

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First received 4 August 2017; accepted in revised form 29 March 2018. Available online 17 April 2018