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Scenarios for Sustainable Management of a Solid Release from a Hydrometallurgical Zinc Treatment in the Democratic Republic of Congo

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Abstract: The treatment of zinc ores at the UZK (Kolwezi Zinc Factory), in the DRC (Democratic Republic of Congo), has generated a deposit of solid releases rich in recoverable metals, but presented an environmental risk given the conditions of its storage. The results of chemical analyses by X-ray fluorescence have shown the presence of base metals recoverable in significant proportions in these releases, which contain on average 17% zinc and 3.5% copper. In addition, X-ray diffraction analyses have identified the main minerals: franklinite, willemite and sphalerite. The environmental risks are real, because the results of the availability tests for leaching have revealed significant zinc and copper extraction rates for a liquid to solid ratio of 100 and those of landfill compliances show that although under European Directive 2003/33/EC, these discharges are dangerous and must be treated under conditions which respect the environment. Following an environmental risk assessment, two scenarios for reprocessing these discharges are envisaged and will be compared from a technical, economic and environmental point of view, including their feasibility in the context of the DRC. The two processes would be on the one hand a hot acid attack in two or three stages and on the other hand a mixed digestion-roasting treatment followed by leaching with water.

Key words: Deposit, leaching, environmental risks, reprocessing process, hydrometallurgy.

1. Introduction

Following an assessment of the environmental risks on solid releases from hydrometallurgical treatment of zinc sulphide ores [1], two sustainable management scenarios are considered in this study to help reduce these risks. Indeed, the environmental challenges linked to the storage of these discharges near the former Zinc Factory in Kolwezi are real, because in the dry season, for example, we witness significant wind erosion in the direction of the prevailing winds, transporting residues towards the factory and the surrounding inhabited areas with all the risks of pulmonary and ocular irritation. In the rainy season, the breakage of the dykes favors the flow of runoff towards the Musonoie river, thereby causing a disturbance in aquatic life [2] and a possible infiltration into the water table.

The strategic framework of the DRC (Democratic Republic of Congo) relating to the prevention and reduction of mining pollution, as defined in the Mining Code [3], is articulated on a certain number of elements, namely: ensuring sustainable development natural resources, prevents the generation of mining environmental liabilities such as those currently existing in the mining province of Katanga located in the Congolese Copperbelt, and promotes the reprocessing of mining residues polluting the environment when these still contain economic contents of metals (artificial deposits) [3-8]. Faced with the problem of generating environmental liabilities containing

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by-products rich in recoverable metals, and because of their polluting nature, two reprocessing methods will be compared, namely a hot acid attack in two or three stages and a treatment mixed digestion-roasting followed by leaching with water.

The purpose of this work is to make a judicious choice of method which will minimize the negative impact on the environment through appropriate management and treatment of effluents.

2. Material and Methods

The first step consisted in chemically and mineralogically characterizing the UZK (Kolwezi Zinc Factory) discharges and then in carrying out leaching tests with demineralized water in order to assess the release of soluble fractions.

The chemical analyses were carried out by X-ray fluorescence, using a Siemens SRS3000 device. The mineralogical analyses were performed by X-ray diffraction using a Siemens D500 diffractometer. Two series of demineralized water leaching tests were performed. In the first series of tests (five leaching availability tests with a liquid/solid ratio = 100) according to standard NEN 7343 [9], a mass equivalent to 3.5 g of rejects (dried and ground material, smaller particle size at 38 μm) is brought into contact with 350 mL of demineralized water and in the second series (five other landfill compliance tests [10], with a liquid/solid ratio = 2), a mass equivalent to 175 g rejects (dried unmilled material, particle size less than 4 mm) is brought into contact with 350 mL of demineralized water; the whole is mixed in a polypropylene bottle of 500 mL by a return shaker, at 20 °C ± 5 °C and for 24 h. The mixture is then filtered on a Millipore filter (0.45 μm) and the leachate analyzed by ICP-OES. The pH of the leachate is measured using the PHM 210 Metalab brand pH-meter (Radiometer).

3. Results and Discussion

The characteristics of the former UZK discharge tanks are known and the estimates of contained metals are comparable to those provided for certain deposits known in the literature [5-8, 11].

The results of chemical analyses by X-ray fluorescence testify the presence of recoverable base metals: 13% to 21% Zn, 2% to 5% Cu and other strategic metals [1].

Mineralogical analyses by X-ray diffraction have shown that zinc is mainly present in the form of franklinite ($ZnFe_2O_4$) [1, 11], which is thought to have formed during the roasting of blende concentrates. In this form, zinc is difficult to dissolve in sulfuric acid medium and is found almost entirely in leaching residues [12]. The results of the leach availability tests made it possible to highlight extraction rates (ratio expressed as a percentage of the leached quantity of an element over its initial quantity in the release before leaching) of zinc and copper significant for a liquid to solid ratio of 100.

The examination of Table 1 below shows that the extraction with demineralized water makes it possible to quantify the soluble fraction, that is to say the fraction of elements which are extremely mobile or adsorbed non-specifically in a residue and which dissolve during equilibration by stirring a suspension of residue in demineralized water. Certain metals see their solubility limited following the pH values of the leachate obtained; this is particularly the case with iron which is not detected in leaching solutions.

Directive 2003/33/EC, based on the leachability of waste, gives the acceptance limits for waste in landfills [10]. From Table 2, it can be seen that former UZK discharges cannot be accepted in a Class I landfill, the least demanding, without prior treatment, because they are dangerous according to this directive. The leached amounts of copper and zinc far exceed the limits. Although the directive does not mention cobalt, it nevertheless constitutes an environmental problem in the Congolese context because of its presence in almostthe entire Congolese Copperbelt [1, 4, 10]. This information sufficiently demonstrates the need to consider scenarios for the appropriate management of

Table 1 Element extraction rate (L/S = 100).

Wording	Element extraction rate (%)				
	Zn	Cu	Pb	Co	Ba
Basin 1	2.5	4.1	0.2	---	0.4
Basin 2	9.1	7.6	0.3	---	0.2
Basin 3	3.1	3.2	0.3	1.2	0.4
Basin 4	0.6	0.7	0.1	0.7	0.4
Basin 5	5.3	4.3	0.7	1	1.8

Table 2 Amount of leached constituents per kg of release compared to landfill acceptance limit under Directive 2003/33/EC.

Wording	mg/kg					Element	Acceptance limit in landfills Liquid/solid = 2 mg/kg Class		
	Zn	Cu	Co	Pb	Ba		I	II	III
Basin 1	3,444	685	5.5	2.7	0.05				
Basin 2	13,119	184	6.4	2	0.05	Ba	100	30	7
Basin 3	6,503	560	2.9	----	0.05	Cu	50	25	0.9
Basin 4	964	107	0.7	----	0.04	Pb	25	5	0.2
Basin 5	7,783	481	1.5	2.8	0.04	Zn	90	25	2

the environmental liabilities of the Former Zinc Plant in Kolwezi.

3.1 Sustainable Management Scenarios Applicable to UZK Discharges

3.1.1 Hot Acid Leaching

The zinc concentrates produced are preferably treated hydrometallurgically, the thermal process having largely given way for energy and environmental reasons. More specifically, hydrometallurgy in a sulfuric acid environment has taken the lead [13]. Basic hydrometallurgy is still exploratory and has only one industrial application [14].

The bio-hydrometallurgy of zinc ores is a potentially interesting alternative for the treatment of poor sulphide ores. The hot acid leaching process [13] is used primarily to leach zinc ferrites. Dissolving ferrites is generally a slow process which sometimes requires the addition of concentrated sulfuric acid. The temperature must be maintained near 90 °C and the concentration of H_2SO_4 can be higher than 100 g/L. The leaching is then carried out against the current with, between each step, a solid/liquid separation by decantation. The solutions from the hot acid attack stages, which are particularly rich in iron, are subject to a specific precipitation treatment. The sludge produced represents the ultimate waste of the process. They are not recoverable and must be stored under economically and environmentally acceptable conditions. Indeed, for each ton of zinc produced, we can consider that 1 to 3 tons of iron jarosite will be produced and will have to be stored sustainably [13]. Iron is precipitated as goethite FeO(OH) or hematite Fe_2O_3. In the goethite process, precipitation occurs around 90 °C. Obtaining hematite requires working under pressure (in an autoclave) and at high temperature (180 to 220 °C). For the goethite process (also called “Old Mountain process”), the iron is reduced beforehand to ferrous iron by the addition of non-roasted concentrate, rich in blende (ZnS). The concentrate must be carefully selected to minimize the intake of insoluble zinc ferrites.

The solid residue from this iron reduction stage contains unreacted concentrate and sulfur and is recycled by roasting. In the second step, the solution is partially neutralized by adding calcine and the solid residue obtained recycled under hot acid attack. In the third step, the iron is precipitated in the form of goethite at a pH of about 2.8 to 3 and in the presence of air. The pH during precipitation is maintained by adding calcine. The jarosite process is by far the most common. Jarosites are a family of amorphous or crystalline compounds that are basic iron sulfates. The general composition of a jarosite is $MFe_3(SO_4)_2(OH)_6$, M representing a metallic, alkaline cation or the hydronium ion. The jarofix process [15] developed in recentyears, introduces an additional step. The sludge is mixed with predetermined amounts of Portland cement and lime. The process allows better fixation of heavy metals in mine tailings. The hot acid leaching leads to a solution containing zinc, copper, cadmium and iron ions and a solid residue where valuable metals such as lead, germanium, gallium and silver are concentrated.

3.1.2 Mixed Digestion-Roasting Process Followed by Leaching with Water

The sulfuric acid digestion technique, applied to the reprocessing of former UZK waste, is a three-step process [11, 15]. It allows a selective dissolution of metals (zinc, copper and cadmium), while leaving iron in the form of hematite, a compound insoluble in water. The first step consists of digestion using sulfuric acid; its goal being the sulfation of the maximum of oxidized compounds, in particular ferrites. During this stage, the following compounds: oxides, hydroxides, ferrites are converted into hydrated sulfates. The consumption of acid is 1 metric ton of sulfuric acid per metric ton of waste. In the second step, the digestion product obtained is subjected to roasting at around 770 °C, to selectively decompose iron sulphate into ferric oxide insoluble in water; the sulfates of the metals Zn, Cu, Cd remain soluble. The water treatment of the toasted product, which constitutes the third step, leads to a solution containing zinc, copper and cadmium ions and a solid residue formed mainly of hematite, of lead sulphate, in which the following metals are concentrated: germanium, gallium and silver. The zinc sulfate solution could be treated by solvent extraction before being subjected to electrolysis for the recovery of zinc in metallic form. Roasting gases, rich in SO_2, are used for the manufacture of recirculated sulfuric acid, thereby significantly reducing the consumption of fresh acid.

3.1.3 Comparison between These Two Processes

Technologically, the hot acid leaching process is widely applied industrially [13, 16]. It sometimes uses an addition of concentrated sulfuric acid and requires working at a relatively high temperature (90 to 95 °C) causing vapor management (mixture of water and acid); the solutions produced, rich in iron, must be subjected to specific precipitation (jarosite, goethite or hematite), the hematite form requiring working in an autoclave (high temperature and pressure). The mixed digestion-roasting process is still at the laboratory stage and requires a pilot study before its industrial application. He is selective; because the metals: copper, zinc and cadmium are leached with a yield of around 99%, in while iron is found almost entirely in leaching residues in the form of hematite, which is the ultimate stable form for long storage in the environment. The roasting produces SO_2 gas from which sulfuric acid is made and reused in the process, thereby significantly reducing the consumption of fresh acid. There are no stages of precipitation of the iron, because at the time of roasting the decomposition of the sulfates formed in digestion is done selectively. The leaching working temperature is relatively low (40 °C) and avoids the management of vapors.

With regard to the respective environmental impacts, in both cases we face new challenges. The chemical and mechanical stability of the rejected sludge must be guaranteed in the long term and therefore we must work in the direction of reducing the volume of the rejects and allow their storage in solid form after thorough dewatering and possible solidification with binders of the cement type [16]. The only water to be managed is that linked to runoff and drainage of sludge during drying. The metallurgical transformation of the rejects should make it possible to obtain stable final forms.

With regard to their economic costs, it will be noted that the mixed digestion-roasting process has no iron precipitation steps and that the production of sulfuric acid contributes more than 50% in the acid supply. Overall, according to initial estimates, the conversion rate of SO_2 to H_2SO_4 is almost maximum with the modern technique of DCDC (Double Contact and Double Conversion) used today for the manufacture of sulfuric acid.

Considering the recent conversion of UZK installations to a Copper Factory, the reprocessing of UZK rejections will have to be integrated into a new zinc production chain, which could be developed near the Kipushi zinc mine, about 300 km from the railway iron southeast of Kolwezi. The comparison can be pursued quantitatively using a few software, notably ASPEN+, which will allow refining the forecast costs and the quantities recovered and rejected.

4. Conclusion

This study highlighted the fact that solid discharges from the former Kolwezi Zinc Plant are dangerous with regard to European Directive 2003/33/EC. The reprocessing of this environmental liability is necessary not only in order to recover the valuable metals contained therein, but also to clean up the environment, this being reinforced by the DRC's Mining Code. The two sustainable management scenarios, hot acid leaching process and that of digestion-roasting followed by water leaching, incorporate an environmental approach compatible with current standards.

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