Mining Waste from the Cobalt Circuits of the Hydrometallurgical Plants of Shituru (DR Congo), a Potential Mineral Source for the Cement Industry in DR Congo

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Abstract: The Democratic Republic of Congo, one of the countries full of huge deposits of copper and cobalt ores, is also one of the countries with significant impact unrecycled mining releases whose negative impact on the environment is being felt on the environment and the people living along the shoreline. This article discusses the characterization of mining waste from the cobalt circuit of copper and cobalt ores (HGW), one of the wastes that presents one of the most complex management problems in the region. This characterization should serve as a guide in the choice of the method of its valuation. To characterize this waste, the following techniques were used: XRF, XRD, FTIR, SEM and DTA-TGA. The results showed that HGW has an extremely high pollution index (IP) and near 85 % wt. of CaSO₄.2H₂O. The presence of this phase in this waste makes it possible to consider its valuation in cement plant as a setting regulator.

Keywords: Characterization, mining waste, setting regulator, cement

1. Introduction

The Democratic Republic of Congo (DRC), one of the richest mineral deposits in the world of Cu, derives most of its income from the mining sector. It is its south western region (formerly Katanga province), particularly rich in copper and cobalt mineral resources (Cu-Co) [1] that is home to about 5% of the world's Cu and more than half in Co. Since 2012, the country has become the leading African producer of Cu, with an estimated annual production of 900,000 tons [2]. At the time when the UMHK (High Katanga Mining Union) was created and then renamed General of Careers and Mines (Gécamines) [3], its production in Cu and Co came mainly from the operations of the hydrometallurgical plants of Shituru and Luilu [3]. Over the years, this production has generated huge quantities of solid residues, not yet valued and containing heavy metals such as Cu, Co, Ni, Cr, Mn, Fe, Zn, Ag, Pb, Cd, As, etc. at concentrations above the required limits [4-8]. Some of this waste, stored for decades in retention ponds, reveals health risks to surrounding populations, soil, plants, and water. To date, its estimated to be thousands of tones, and the Congolese state has not yet put in place a national politics of their management. Lack of it, they are dispersed either by air (wind) or by chemical (leaching by rainwater). Leaching as a result, these elements see infiltration into the ground, or they end up in the air. The impact of these phenomena on ant nature is the contamination of the entire ecosystem around. According to a report by the World Bank on the restoration of mines in the DRC [9], the various sites housing these releases should be restored in order to reduce the pollution they generate. Recent studies [10-14] on the health risks associated with exposure to heavy metals from surrounding of populations show a perfect correlation between heavy metals of these wastes and the pathologies manifested by the populations of these areas. Among the most commonly recorded pathologies in areas at risk are respiratory diseases, congenital malformation (holoprosencephaly) and semen alteration [10-15] (Other unstudied health problems, such as cancer, diabetes, and lower IQ (intellectual quotient) could also be associated with the same elements contained in this waste [16-18]. And yet, given their quantity, this waste could constitute, if it is managed efficiently significant potential sources of metals such as Cu, Co and Zn [19, 20], or be recovery in cement works or in the design of other materials. This article looks at mining waste from the cobalt circuit of the Shituru plants of Gécamines (HGW) obtained by an electrochemical process after leaching with sulphuric acid from the base ores. This waste, stored in a full tailings park since 1986, represents one of the most complex environmental issues in the region. As it is filled, the residues from the metallurgical process flow on it and are dumped directly downstream of this park without any sedimentation. These acid residues (pH-5.9) end several kilometres downstream of the surrounding rivers (Likasi, Buluo and Panda) and fall further into the Lufira and Tshangalele Lake where it has been noted the deterioration of the fish flesh and the disappearance of some aquatic species. To eliminate and/or limit this pollution, it has been proposed to restore this waste park whose area is worth 51ha (hectares) for an amount between 6.0 and 12.0 million U.S. dollars [9]. However, this solution is not efficient, because it will always leave this waste intact. It is therefore necessary to find another method, simple and less costly that can lead to eliminate this HGW from nature and stabilize their ETMs. In order to respond to this concern, this study aims to study HWG discharges in order to characterize their pollution

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potential and mineralogical composition, guide in the choice of the method of its recovery.

2. Materials and methods

2.1 Material

Hydrometallurgical gypsum is a black paste when it is released from the cobalt circuit. Dry, it is black and tender to the touch. Its density determined from a helium pycnometer is 2.33 g/cm³ and its Finesse Blaine is 523 m²/Kg.

2.2 Site studied

2.2.1 Methods

To characterize HG, we used the following analytical techniques: the helium pycnometer and the Blaine, which were used to determine the density and grading fineness of the sample. X-ray Fluorescence (XRF), X-Ray Diffractometry (XRD), Scanning Electron Microscopy (MEB) and Thermal Analysis (AT) were used to determine the chemical composition, mineral composition, morphology of crystallized phases and HG dehydration mechanism, respectively. Using thermal analyses (Thermogravimetric Analyses (TG)), we were able to measure the amount of crystallization water of CaSO₄·2H₂O contained in the GH sample, to further evaluate its content. With differential Thermal Analysis (DTA), we have been able to highlight the forms in which certain mineralogical phases not identified by the XRD are present in the HG. The pycnometer used was micromeritic AccuPyc II 1340 and the permeabilimeter used was manual air Hz-3808. The XRF device used was a Siemens SRS 3000 and the diffractometer was a Bruker-Siemens D5000. The diffractometer was equipped with a generator with a Cu-Kα radiation tube, operating at 40 kV and 40 mA, a graphite front monochromator and a General Area Detector Diffraction System (GADDS) detection system. The analysis was carried out directly on powder in the angular area between 5 and 65° 2θ. The MEB used was a JEOL JSM-6340F. The micrographs presented in this work were performed in secondary electron mode and an acceleration voltage was set at 20 kV device of Simultaneous Thermal Analysis STA-NETSCH 449 PC. The analyses using this technique were conducted in an oxygen atmosphere to identify phases that were likely to undergo oxidation and under the atmosphere of nitrogen for the determination of the crystallization water content. The temperature rise rate was set at 10°C/min in a temperature range of 25 to à 600°C.

With regard to the gypsum content determination, we used the equation (1), based on the total mass loss of H₂O (20.93% wt.) of the gypsum containing ~100% wt. de CaSO₄·2H₂O [21, 22].

% CaSO₄·2H₂O = Total mass loss (%)/20.93  Equation 1.1

3. Results

3.1 Chemical composition

The analysis of the results in Table 1 indicates that around 72% wt. of HG are made up of CaO and SO₃. The H₂O content, determined by the loss of mass, by thermogravimetric analysis at 250°C, under a nitrogen atmosphere, corresponds to ~23% wt. Like the CaO content, this chemical composition is similar in its SO₃ and H₂O content to high purity natural gypsum and ultrapure laboratory gypsum [23]. The CaO content of HGW is nearly 7% wt. compared to NG (Natural Gypsum) and UPG (Ultrapure Gypsum) would indicate its low CaSO₄·2H₂O content.

<table>
<thead>
<tr>
<th>Table 1: Chemical Composition of Gypsum (HGW)</th>
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<tbody>
<tr>
<td>Chemical composition of gypsum in % wt.</td>
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<tr>
<td>CaO</td>
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<tr>
<td>25.13±1.00</td>
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<tr>
<th>Table 2: Chemical composition of natural gypsum compared to ultra purous gypsum [23]</th>
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<tr>
<td>SO₃</td>
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<tr>
<td>CO₂</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>H₂O</td>
</tr>
<tr>
<td>Insoluble</td>
</tr>
</tbody>
</table>

In addition to CaO, SO₃ and H₂O, GH contain Mn and Co at respective concentrations of 1.5 et 1.3 % wt. In addition, HGW also contains Ni, Zn and Pb at concentrations above the standards of certain soil-contaminating elements. Like Mn, considered essential trace element for animals, plants and humans, this element becomes toxic in high doses. However, the criterion that defines its tolerable limit concentration in soil is not well defined in DR Congo and literature and depends on one country to another. Since the dominant route of exposure is the inhalation of dust from contaminated soil, a value of 3000 ppm proposed by [7] was selected for our discussions. The standards for the other elements mentioned above are taken up with the concentrations of these elements in Table 3.

| Table 3: Chemical composition in minor elements (expressed as oxides) |
|-----------------------------|-------------------|------------------|
| ETM | Concentration in ppm | AFNOR Standards |
| Or | 314.0 ± 16 | 50 ppm |
| Zn | 723.1 ± 32 | 300 ppm |
| Co | 12662.1 ±80 | 50 ppm |
| Pb | 92.83 ± 5 | 100 ppm |
| Mn | 14792.1 ± 620 | 3000 ppm |

The table 3 shows that, like the Pb, all other MTE contained in the HGW have their concentration above the limits tolerated in the soil [5, 8]. So to assess the multi-element contamination of HGW, we will use the concept of a soil pollution index (IP) introduced in many studies [4, 6].
index, calculated from the average of the reports of metal concentrations in soil samples against the limit values, is defined as follows [4]:

\[
IP = \frac{(Ni/50 + Zn/300 + Co/50 + Pb/100 + Mn/3000)}{5}
\]

The calculated value of this IP is 53.6. This extremely high value underlines the extremely harmful character of HGW releases abandoned for years without any rehabilitation of the site that abounds them. HGW are therefore a source of contamination by the environment and the local population, as confirmed by some studies [10-14]. HGW discharge is dangerous mainly because of two phenomena that affect them cyclically during the year: (1) during the dry season, HGW, tenders are in the form of dust, their fine particles are carried away (air leaching) by the wind and are transported to kilometers from the site where they are stored. Using this process, they are regularly inhaled by the surrounding populations. In the presence of rain, these fine particles are washed away, and if the physical and chemical conditions permit them, they are leached, resulting in the release of their ETMs which can be found on all the paths of rainwater and therefore in areas expected to release.

3.2 X-ray and SEM diffraction

Figure 1 reveals the presence of a single crystalline phase in the HGW sample and corresponding to \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) which crystallizes in the same system as a natural gypsum (monoclinic system). The comparison of its DRX spectrum to that of natural gypsum (spectrum in blue) shows a perfect and complete overlay of all its stripes to that of natural gypsum. The shape and position of these rays define a good crystallization of \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \). In SEM (fig.2), this gypsum crystallizes in the form of small acicular needles. Like this phase (\( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)), DRX has not been able to detect other mineralogical phases despite the presence of cobalt (Co) and manganese (Mn) in significant proportions. Based on the process of obtaining cobalt by hydrometallurgy, it would appear that these two elements are present in amorphous forms not identifiable by this technique.

3.3 FTIR- DTA&TG-XRD

Figure 3 gives HGW’s FTIR spectrum. Analysis of this spectrum indicates the presence of two doublets (3492 – 3396 cm\(^{-1}\), 1682 – 1619 cm\(^{-1}\)) linked respectively \( \nu\text{OH} \) to (stretching band) and \( \delta\text{OH} \) (bending mode) of \( \text{H}_2\text{O} \) crystallization. Two peaks at 668 cm\(^{-1}\) and 597 cm\(^{-1}\) characterize the vibration of \( \delta\text{S} – \text{O} \) the \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \). However, the stretching band (\( \nu\text{S} – \text{O} \)) that should appear in two peaks are absent on the spectrum and appear in single one around 1107 cm\(^{-1}\). The low intensity of the two bands reveals that the content in \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) of the HGW does not very high as in a natural gypsum [24, 25]. Apart from gypsum, FTIR was unable to identify the Co and Mn compounds through their respective vibrations.

**Figure 1:** X-ray diffractogram of hydrometallurgical gypsum (HG)

**Figure 2:** Micrograph of a fresh gypsum break
DTA-TG thermograms are shown in Figure 4. This figure derives from the existence of four distinct endotherms located respectively in temperature intervals of 60-110°C, 115-190°C, 190-250°C and 250-380°C. An exotherm around 410°C was also observed. These transformations correspond to a specific chemical and/or physical phenomenon [21, 26-28]. Endotherm reactions were identified at the different temperatures characteristic of the ATD curve shown in figure 3. The first endothermic valley characterizes the loss of adsorbed water and its value corresponds to 0.61% wt [26]. The second endothermic valley located at 170°C is the most intense. It defines the first structural transformation of the CaSO₄.2H₂O in CaSO₄.1/2H₂O (reaction 1) which involves the departure of 1.5 moles of H₂O crystallization (fig.4). This phenomenon leads to a loss of mass of 13.24% wt. The maximum temperature of dehydration of the gypsum depends on its heating speed, the impurities it contains, the working atmosphere and its fine grinding [21, 22, 26, 27]. As for its mass loss in this region, it has been shown to correspond to 75% wt. of its total mass [21, 22]. The third endotherm is related to partial dehydration of the CaSO₄.1/2H₂O in CaSO₄ (fig.5). Complete dehydration occurs above 250°C (fig.6) which gives CaSO₄ (soluble anhydrite III: CaSO₄. eH₂O where 0.06 < ε < 0.11) [22, 26]. As for the maximum dehydration, it occurs at about 200°C. As suggested [29], this region also corresponds to the dehydration of Co(OH)₂ (3).

\[
\begin{align*}
\text{CaSO}_4.2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4.1/2\text{H}_2\text{O} + 3/2\text{H}_2\text{O} & (1) \\
\text{CaSO}_4.1/2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4 + 1/2\text{H}_2\text{O} & (2) \\
\text{Co(OH)}_2 & \rightarrow \text{CoO} + \text{H}_2\text{O} & (3)
\end{align*}
\]

The TG diagram indicates that the two chemical reactions that occur between 190-250°C are accompanied by a total weight loss of 5.42%. Assuming that about 75% wt.de weight is associated with Eq.1. Based on reactions (1) and (2), it follows that the mass loss associated with dehydration from CaSO₄.1/2H₂O in CaSO₄ for HGW is 4.41 % wt. We therefore infer from equation 1 that the gypsum content of HGW is 84.3% wt.

The remaining 1.01% wt. would be the mass loss associated with dehydroxylation of Co(OH)₂ and anhydrite III (CaSO₄.eH₂O) [22]. Based on these results, we can therefore say that Co(OH)₂ would be amorphous in the HGW sample, hence its absence on the DRX diagram. The CoO formed during dehydroxylation oxidizes at around 410°C to give as Co₂O₃ indicated by the exotherm on the DTA curve [30]. In the temperature range of 250-380°C, we are witnessing another loss of mass. It is mainly related to the dehydroxylation (reaction 5) of the manganite (MnOOH) that would be present in the HGW [21].

\[
2\text{MnOOH} \rightarrow \text{Mn}_2\text{O}_3(s) + \text{H}_2\text{O} \quad (5)
\]

The MnOOH, whose number of oxidation of Mn is 1.5 would come from the partial oxidation of the ions Mn²⁺ in the presence of oxygen from the air [31]. Being MnOOH unstable, it partially oxidizes in the presence of air by giving MnO₂ (Mn(IV)) (reaction6) [31]. It is the presence of this phase in the HGW that gives it its black appearance. To verify the presence of MnO₂, we treated the black HGW with an iron ion solution (II); which resulted in a white material; result of the reduction in Mn (+IV) in Mn²⁺ions (colorless) (reaction7).

\[
4\text{Mn}^{2+}(aq) + 0.2(\text{aq})6\text{H}_2\text{O} \rightarrow 4\text{MnOOH} + 8\text{H}^+(aq) \quad (6) \\
\text{MnO}_2(s) + 2\text{H}_2\text{O} + 2\text{Fe}^{3+}(aq) \rightarrow \text{Mn}^{2+}(aq) + 4\text{OH}^- + 2\text{Fe}^{3+}(aq) \quad (7)
\]

3.4 Possible cement plant valuation

A grade of ~ 84% wt. in CaSO₄.2H₂O from HGW reveals that it is a potential mineral source that can be used to completely replace natural gypsum used as a set regulator in cement. Such a prospect may, on the one hand, make it possible to decrease the ETM concentrations of HGW and reduce their pollution index. Optimization of the HGW content in the cement is then necessary, as it will optimize short-term mechanical properties of the HGW cement. On the other hand, the stabilization of ETM (Co, Mn, Ni, Pb and Zn) in the cement matrices during the hydration of HGW cement [32, 33]. However, the influence of Co and Mn on the hydration of HGW cement, its impact on the mechanical properties and its durability will need to be investigated. A study of the leaching of ETMs contained in HGW mortars / or concretes should also be the subject of an in-depth study in order to
confirm the “stabilization” of Mn, Co, Ni, Pb and Zn by the cement matrix.

Fig. 4: HGW X-ray Diffractogram treated thermally at 190°C.

Fig. 5: HGW X-ray Diffractogram processed thermally between 190 and 250 degrees Celsius.
4. Conclusion

HGW mining releases consist mainly of CaO and SO₂. They are accompanied by Mn, Co, Zn, Pb and Ni at concentrations that exceed the required limits. The IP pollution index of these HGWs is around 54, which shows that they are a source of contamination by the environmentally heavy and the population surrounding the storage site of these minerals’ releases. Analyses by XRD, MEB, FTIR and DTA-TG revealed that HGW consists of a main mineral phase, CaSO₄·2H₂O with a grade of approximately 84% wt. Other probable mineralogical phases are MnO₂ and Co(OH)₂. Due to its high CaSO₄·2H₂O content, the HGW can be used to completely cement replace natural gypsum, used as a setting regulator in cement. This replacement can only be made possible if the ETM it contains can stabilized in the cement matrix and would not negatively impact the performance of the cement.
5. Thanks

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