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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 $CaSO_4.2H_2O$. 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, itis 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 toa 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 potential and mineralogical composition, guide in the choice of the method of its recovery.

2. Materials and methods

2.1 Materiel

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/cm^3 and its Finesse Blaine is 523 m^2/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 grinding finesse 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 $CaSO_4.2H_2O$ 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 Dectector 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 kVA device of Simultaneous Thermal Analysis STA-NETZSCH 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 H_2O (20.93% wt.) of the gypsum containing ~100% wt. de $CaSO_4.2H_2O$ [21, 22].

$\% \; CaSO_4.2H_2O = Total\ mass\ loss\ (\%)/20,93$ 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 SO_3. The H_2O 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 SO_3 and H_2O 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 (Ultra-pure Gypsum) would indicate its low $CaSO_4.2H_2O$ content.

Table 1: Chemical Composition of Gypsum (HGW)

Chemical composition of gypsum in % wt.										
CaO	SO_3	Fe_2O_3	SrO_2	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	TiO_2	PF
25.13±1.00	46.87±2.00	0,31	0,03	0,08	0,20	0,7	0,13	0,02	0,02	22.83±1.00

Table 2: Chemical composition of natural gypsum compared to ultra pur ous gypsum [23]

	Natural Gypsum (Zaleschiki, Ukraine) NG	***UPG***
SO_3	46,00	46,50
CO_2	0,28	-
CaO	32,36	32,57
H_2O	20,82	20,93
Insoluble	0,16	-

In addition to CaO, SO_3 and H_2O, 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** -NFU 44-041 [5, 8]
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

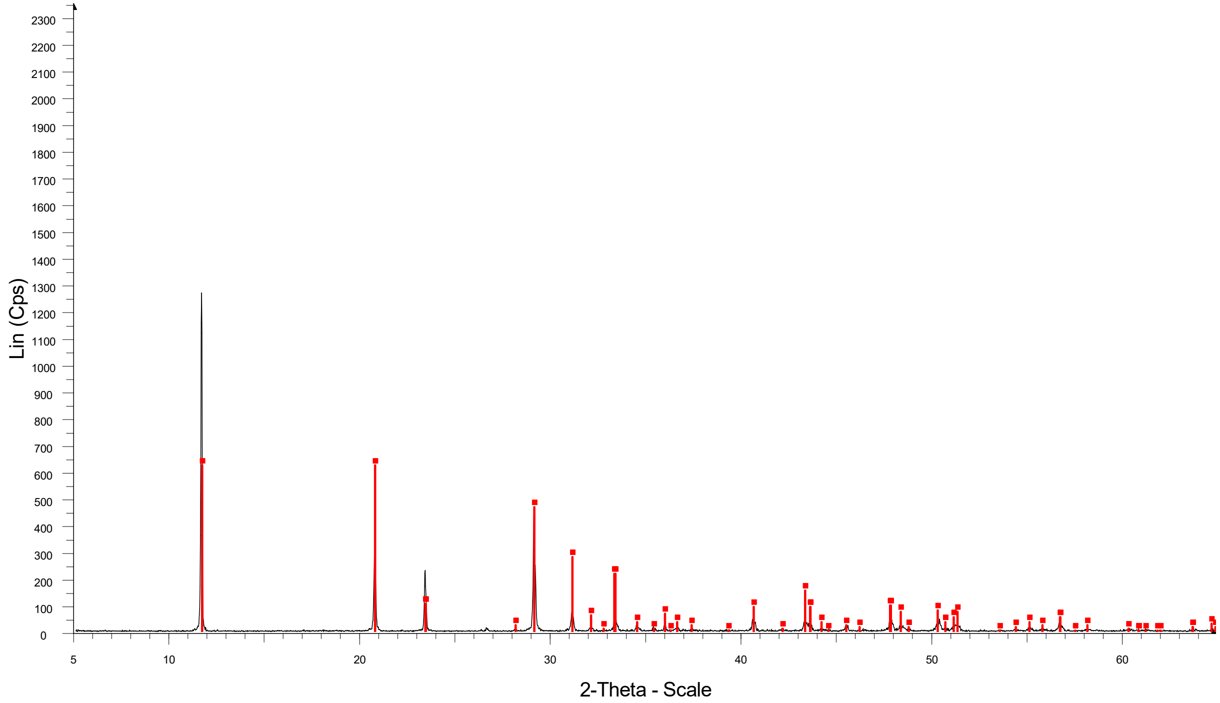
The table 3 shows that, like the Pb, all other MTE contained in the HGW have their concentration above the limits tolerated in the soil [5, 8]. So to assess the multi-element contamination of HGW, we will use the concept of a soil pollution index (IP) introduced in many studies [4, 6].This index, calculated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

$$IP = (Ni/50 + Zn/300 + Co/50 + Pb/100 + Mn/3000)/5$$

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 to 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 $CaSO_4.2H_2O$ 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 $CaSO_4.2H_2O$. In SEM (fig.2), this gypsum crystallizes in the form of small acicular needles. Like this phase ($CaSO_4.2H_2O$), 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.



Gypse metalurgique Lubumbashi - Step: 0.020 ° - Step time: 1.2 s - Anode: Cu - WL1: 1.5406 - Generator kV: 40 kV - Generator mA: 40 mA - Divergence slit: V6 - Company: ULB Matières et Matériaux - Creation: 2/10/2006 1
00-033-0311 (*) - Gypsum, syn - CaSO4·2H2O - Monoclinic - a 6.28450 - b 15.20790 - c 5.67760 - alpha 90.000 - beta 114.090 - gamma 90.000 - Base-centered - C2/c (15) - 4 - 495.371

Fig. 1: X-ray diffractogram of hydrometallurgical gypsum (HGW)

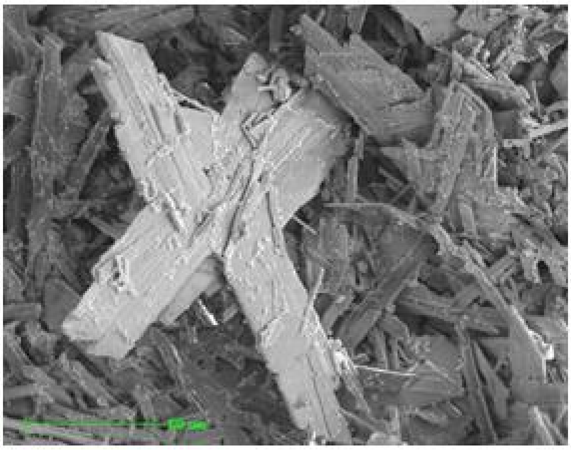


Figure 2: Micrograph of a fresh gypsum break

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 νOH to (stretching band) and δOH (bending mode) of H_2O crystallization. Two peaks at $668\ cm^{-1}$ and $597\ cm^{-1}$characterize the vibration of $\delta S - O$ the $CaSO_4.2H_2O$. However, the stretching band ($\nu S - O$) 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 $CaSO_4.2H_2O$ 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.

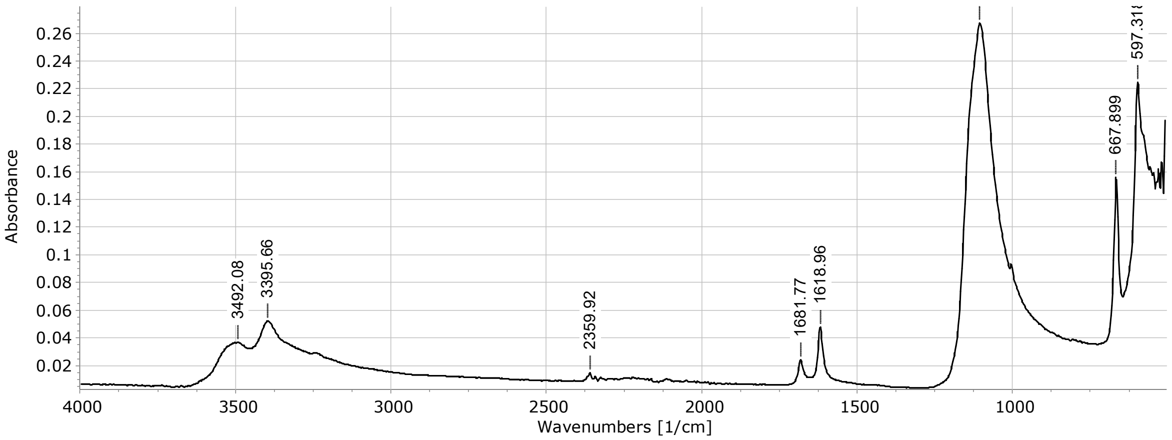


Figure 3: Spectre IRTF of the HGW sample

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 $CaSO_4.2H_2O$ in $CaSO_4.1/2\,H_2O$ (reaction 1) which involves the departure of 1.5 moles of H_2O 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 $CaSO_4.1/2\,H_2O$ in $CaSO_4$ (fig.5). Complete dehydration occurs above 250°C (fig.6) which gives $CaSO_4$ (soluble anhydrite III: $CaSO_4.\varepsilon H_2O$ where $0.06 < \varepsilon < 0.11$)) [22, 26]. As for the maximum dehydration, it occurs at about 200°C. As suggested [29], this region also corresponds to the dehydroxylation of $Co(OH)_2$ (3).

$$CaSO_4.2H_2O \rightarrow CaSO_4.1/2\,H_2O + 3/2\,H_2O \quad (1)$$
$$CaSO_4.1/2\,H_2O \rightarrow CaSO_4 + 1/2\,H_2O \quad (2)$$
$$Co(OH)_2 \rightarrow CoO + H_2O \quad (3)$$

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 $CaSO_4.1/2\,H_2O$ in $CaSO_4$ 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 ($CaSO_4.\varepsilon H_2O$) [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 Co_2O_3 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].

$$2MnOOH_{(s)} \rightarrow Mn_2O_{3\,(s)} + H_2O \quad (5)$$

The $MnOOH$, whose number of oxidation of Mn is 1.5 would come from the partial oxidation of the ions Mn^{2+}in the presence of oxygen from the air [31]. Being $MnOOH$ unstable, it partially oxidizes in the presence of air by giving MnO_2 ($Mn(IV)$) (reaction6) [31]. It is the presence of this phase in the HGW that gives it its black appearance. To verify the presence of MnO_2, 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 Mn^{2+}ions (colorless) (reaction7).

$$4Mn^{2+}{}_{(aq)} + O_{2(aq)}6H_2O \rightleftharpoons 4\,MnOOH_{(s)} + 8H^{+}{}_{(aq)} \quad (6)$$
$$MnO_{2(s)} + 2H_2O + 2Fe^{2+}_{(aq)} \rightleftharpoons Mn^{2+}_{(aq)} + 4OH^- + 2Fe^{3+}_{(aq)} \quad (7)$$

3.4 Possible cement plant valuation

A grade of ~ 84% wt. in $CaSO_4.2H_2O$ 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.

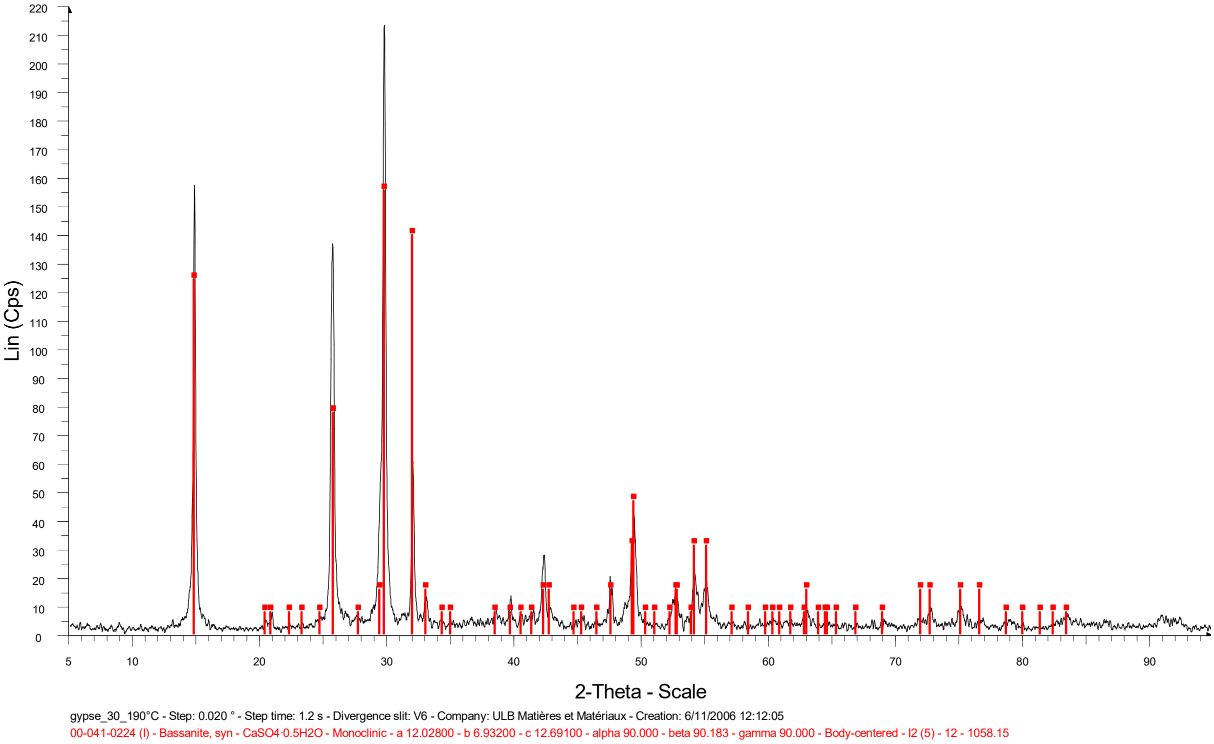


Fig. 4: HGW X-ray Diffractogram treated thermally at 190°C.

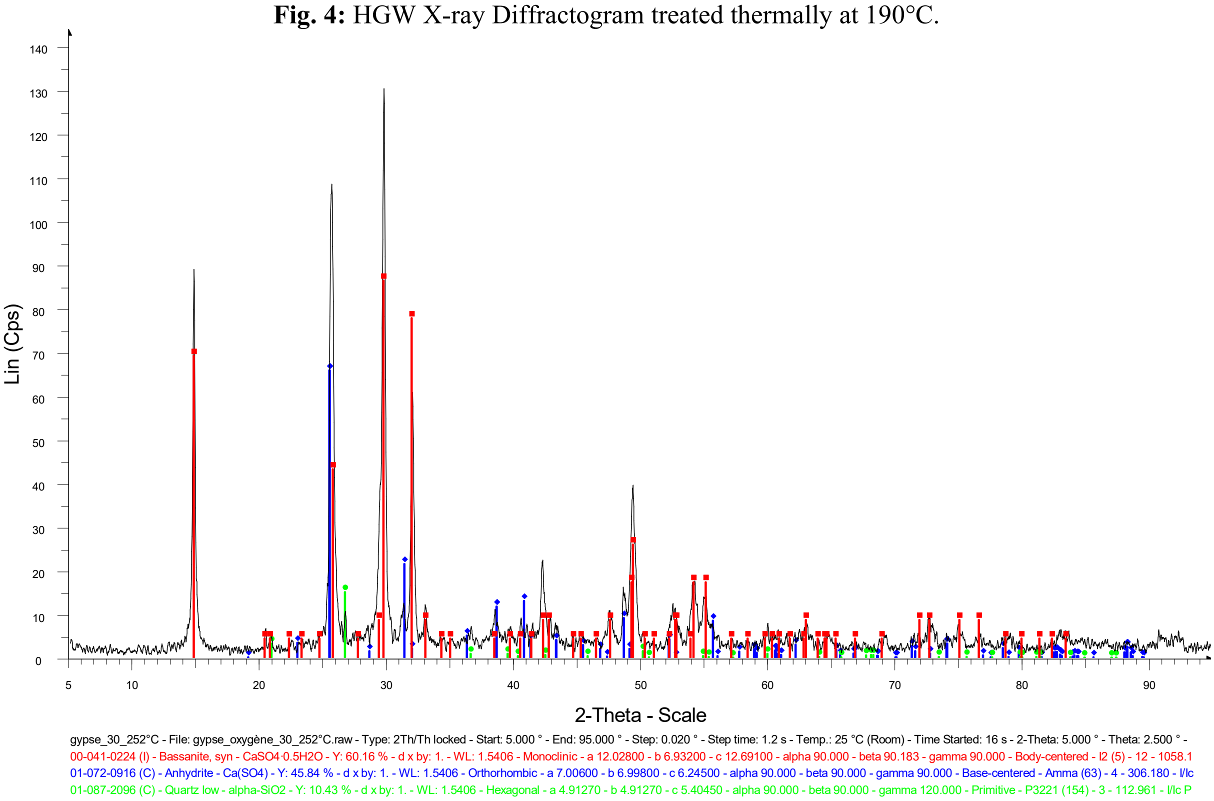


Fig. 5: HGW X-ray Diffractogram processed thermally between 190 and 250 degrees Celsius.

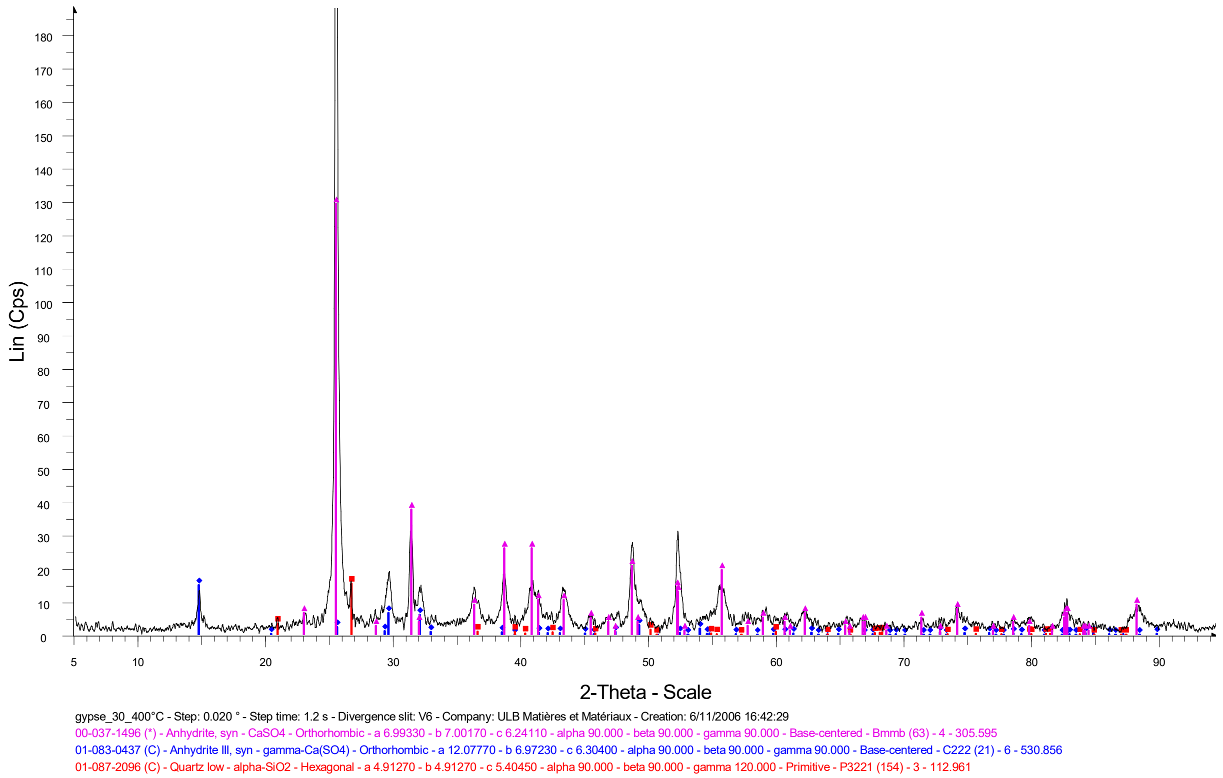


Fig. 6: HGW X-ray Diffractogram treated thermally at a temperature of 250 degrees Celsius

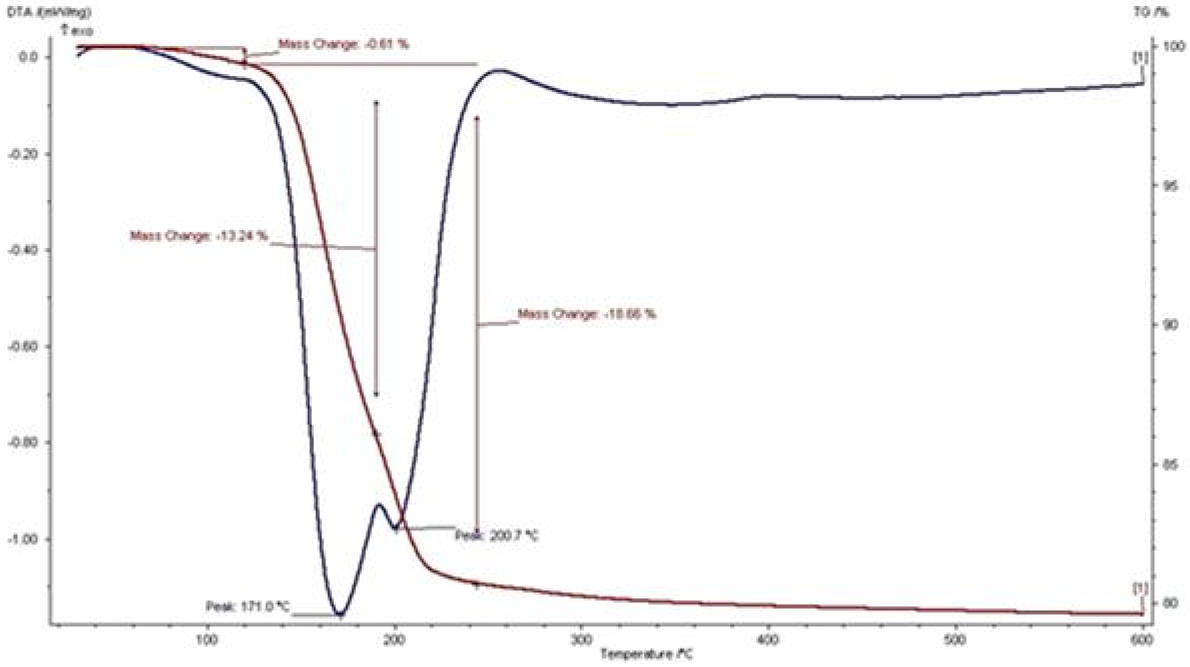


Fig. 7: Thermograms of DTA (blue) and TG (red) of hydrometallurgical gypsum

4. Conclusion

HGW mining releases consist mainly of CaO and SO_2. 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, $CaSO_4.2H_2O$ with a grade of approximately 84% wt. Other probable mineralogical phases are MnO_2 and $Co(OH)_2$. Due to its high $CaSO_4.2H_2O$ 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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References

[1] Shengo, M.L., et al., *A review of the beneficiation of copper-cobalt-bearing minerals in the Democratic Republic of Congo.* Journal of Sustainable Mining, 2019. **18**(4): p. 226-246.
[2] E. Umpula, J.-C.A., *Transparency of Mining Revenues in DRC: Case of Katanga Province*. 2012, Action Against Impunity for Human Rights (ACIDH): Lubumbashi.
[3] Crowson, P., *The copper industry 1945–1975.* Resources Policy, 2007. **32**(1): p. 1-18.
[4] Chon, H.-T., J.-S. Ahn, and M.C. Jung, *Seasonal Variations and Chemical Forms of Heavy Metals in Soils and Dusts from the Satellite Cities of Seoul, Korea.* Environmental Geochemistry and Health, 1998. **20**(2): p. 77-86.
[5] Baize, D., *Total "heavy levels" in The French soils, the general results of the ASPITET programme.*INRA 2000 Environment Mail.**39:**39-54.
[6] Jung, M.C., *Heavy Metal Contamination of Soils and Waters in and Around the Imcheon Au-Ag Mine, Korea.* Applied Geochemistry, 2001. **16**(11): p. 1369-1375.
[7] Buteau, S., *Validation of the B and C criteria for manganese in soils, on the basis of the protection of human health,*I.N.D.S.P.D. QUEBEC, Editor. 2012: Quebec 59.
[8] AFNOR, *Standards Collection:* Soil Quality. , A.F.d. Standardization, Editor. 1999: Paris.
[9] International, S.-L., *Study on the Restoration of Copper and Cobalt Mines. Democratic Republic of Congo.* 2003, World Bank. 229.
[10] Kayembe-Kitenge, T., et al., *Congenital Malformations and Trace Metals: A Case-Control Study from Lubumbashi, DR Congo.* ISEE Conference Abstracts, 2018. **2018**.
[11] Nkulu, C., et al., *Sustainability of artisanal mining of cobalt in DR Congo.* Nature Sustainability, 2018. **1**.
[12] Kayembe-Kitenge, T., et al., *Respiratory Health and Urinary Trace Metals among Artisanal Stone-crushers: a Cross-sectional Study in Lubumbashi, DR Congo.* 2019. PA2823.
[13] Kayembe-Kitenge, T., et al., *Holoprosencephaly: A case series from an area with high mining-related pollution.* Birth Defects Research, 2019. **111**.
[14] Richard-A-Mutshimbe Mukendi, C.L.N.B., Clarence-A-Kaut Mukeng, Jules Thaba Moyambe Ngwe, Albert Ntambwe-A-Nkoy Mwembo, Prosper Muenze Kayamba Kalenga, *Human Exhibition of Metal Trace Elements and Semen Alteration: Study conducted in mining areas of Upper Katanga in the Democratic Republic of Congo.*The Pan African Medical Journal, 2018.**35.**.
[15] Obadia, P., et al., *Erectile dysfunction and mining-related jobs: an explorative study in Lubumbashi, Democratic Republic of Congo.* Occupational and Environmental Medicine, 2019. **77**: p. oemed-2019.
[16] Stranges S, M.J., Natarajan R, et al., *Effects of long-term selenium supplementation on the incidence of type 2 diabetes: a randomized trial.* Ann Intern Med., 2007. **147(4)**: p. 217–223.
[17] Sen A, H.N., Senut MC, et al., *Multigenerational epigenetic inheritance in humans: DNA methylation changes associated with maternal exposure to lead can be transmitted to the grandchildren.* Sci Rep., 2015. **2015(5)**: p. 14466.
[18] Li Z, D.T., Pröschel C, Noble M., *Chemically diverse toxicants converge on Fyn and c-Cbl to disrupt precursor cell function.* PLoS Biol 2007. **5** p. 35.
[19] Kitobo, W.S., *Decontamination and recovery of the katanga sulphur mining discharges "Case of the taillings of the Old Kipushi Concentrator"*, in *Faculty of Applied Sciences* 2009, University of Liège Belgium. p. 276.
[20] Ngenda Banka, R., *Waste Recovery Study of Kolwezi Zinc Plants, Democratic Republic of Congo,*in *Faculty of Applied Sciences - Materials and Materials.*2010, Free University of Brussels Brussels.
[21] Földvári, M., *Handbook of thermogravimetric system of minerals and its use in geological practice*, ed. G. MAROS. Vol. 213. 2011, BUDAPEST: Geological Institute of Hungary 180.
[22] Geraldo, R.H., et al., *Gypsum plaster waste recycling: A potential environmental and industrial solution.* Journal of Cleaner Production, 2017. **164**: p. 288-300.
[23] John W. Anthony, R.A.B., Kenneth W. Bladh, and Monte C. Nichols, *Handbook of Mineralogy*. Vol. VA 2003, Chantilly, USA: Mineralogical Society of America, Chantilly. 20151-1110.
[24] Salvadori, B., et al., *Evaluation of Gypsum and Calcium Oxalates in Deteriorated Mural Paintings by Quantitative FTIR Spectroscopy.* Spectroscopy Letters, 2003. **36**(5-6): p. 501-513.
[25] F., F. and P. T. , *Fourrier's Infrared Transformed Spectrometry (IRTF) An interesting method for the characterization of cements.*Bulletin of the Laboratories of Bridges and Roads, 2001.**230:**77-88.
[26] Engbrecht, D.C. and D.A. Hirschfeld, *Thermal analysis of calcium sulfate dihydrate sources used to manufacture gypsum wallboard.* Thermochimica Acta, 2016. **639**: p. 173-185.
[27] Strydom, C.A. and J.H. Potgieter, *Dehydration behaviour of a natural gypsum and a phosphogypsum during milling.* Thermochimica Acta, 1999. **332**(1): p. 89-96.
[28] Marinkovic, S., A. Kostic-Pulek, and V. Manovic, *Differential thermal analysis and gypsum binders.* Journal of Mining and Metallurgy Section B Metallurgy, 2001. **37**: p. 77-87.
[29] Kim, S.W.e.a., *γ-ray Radiation Induced Synthesis and Characterization of α-Cobalt Hydroxide Nanoparticles.* Bulletin of the Korean Chemical Society, 2010. **31**(4): p. 910–914.
[30] *Handbook of thermal analysis and calorimetry.* Applications to inorganic and miscellaneous materials, ed. P.K. Gallagher. Vol. 2. 2003. 942

[31] Morgan, J.J., *Kinetics of reaction between O2 and Mn(II) species in aqueous solutions.* Geochimica et Cosmochimica Acta, 2005. **69**(1): p. 35-48.

[32] Deja, J., *Immobilization of Cr6+, Cd2+, Zn2+ and Pb2+ in alkali-activated slag binders.* Cement and Concrete Research, 2002. **32**(12): p. 1971-1979.

[33] Giergiczny, Z. and A. Król, *Immobilization of heavy metals (Pb, Cu, Cr, Zn, Cd, Mn) in the mineral additions containing concrete composites.* Journal of Hazardous Materials, 2008. **160**(2): p. 247-255.