

Detoxification of effluents with cyanide. application on a cyanide gossan mineral

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Abstract. The process of cyanidation is employed to extract the gold and silver components from minerals. As a result of this procedure, the production of effluents and solid waste occurs, wherein the presence of free cyanide is observed as the most hazardous form. The application of degrading processes can facilitate the transformation of cyanides in solution into forms that are less hazardous. The aim of this study is to investigate the degradation of cyanide effluents using either sodium hypochlorite or ozone. The primary purpose is to identify the optimal conditions for the degradation of total cyanide while ensuring the absence of any other pollutants. The cyanidation process will be implemented under optimal conditions for the purpose of recovering gold and silver from Gossan ore. The gossan ore sourced from Rio Tinto in Huelva, Spain, finds application in the detoxification of cyanide effluents. Characterization techniques are employed to identify the predominant elements present in the ore, namely iron (25.0%) and silicon (21.2%). The process of cyanide breakdown with ozone treatment yields carbonates, which are significantly more ecologically sustainable in comparison to cyanates formed by hypochlorite. Nevertheless, the utilization of ozone in mining is limited due to some disadvantages, namely its exorbitant cost and excessive consumption.

1 Introduction

When cyanide-containing effluents and solid waste are dumped into the environment without being cleaned up health are significant concerns. The cyanidation process utilized for the extraction of gold and silver results in the generation of effluents and solid waste that contain numerous pollutants, notably cyanide.

Peru holds a significant position among global mining nations, boasting substantial metallurgical prospects for several metals like copper, gold, silver, iron, lead, and others. These resources play a crucial role in the socioeconomic framework of the country. Mining is indeed a lucrative endeavour that generates economic prosperity. However, it is imperative to acknowledge that the adverse consequences it engenders, particularly in terms of global environmental contamination, are of grave concern [1]. Mining is an industrial practice that utilizes a substantial quantity of cyanide. The cyanidation process has been widely recognized as the predominant method employed for the extraction of gold and silver from minerals since the late nineteenth century [2].

The analysis of cyanide types holds significant importance in determining the most suitable procedure for detoxification [3]. The method employed for the

first, it goes beyond the ability of natural systems or soil to heal itself because it changes their properties and causes a lot of pollution and environmental damage. The destruction of ecosystems and its impact on population

determination of CN⁻ concentrations exceeding 5 mg/L in the specimen is Standard Methods 4500-CN-D, in accordance with ASTM D-2036-91 [4]. It is postulated that the pace at which silver and gold dissolve is dependent on the degree of concentration of sodium cyanide (NaCN) and the alkalinity of the solution. Hence, it is imperative to undertake a comprehensive treatment of both effluents and solid waste that are produced during the cyanide process. Cyanide may be oxidized to cyanate (CNO), a less toxic compound, with the help of a strong oxidizing agent like, ozone, hypochlorite, or hydrogen peroxide.

2 Materials

2.1 Gossan sample

Gossan, also known as "iron mounts," refers to exposed rock formations that were initially composed of sulphides and have undergone a process of supergene alteration. This alteration involves the physical and chemical

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transformations resulting from the influence of many forces, including rain, wind, sun radiation, and groundwater. The initial sulphides, which primarily consist of iron oxides, underwent changes that are responsible for the reddish physical appearance of gossan [5].

2.2 Mineral characterization techniques

Table 1 below shows the main mineral characterization techniques.

Table 1. Main techniques of mineral characterization.

Characterization techniques	Foundation
Fluorescence by X-rays (XRF)	Chemical make-up in general
(PCI) Emission Spectrometry	Composition of the elements
The X-ray diffraction (XRD)	Composition of the elements
ROM = Reflected Optical Microscope.	Composition of minerals, grain size, and structure
Scanner electron microscopy (SEM)	Chemical makeup, grain size, and grain appearance

3 Results

The experimental findings conducted in this study are reported as follows: The present study focuses on the characterization of the Gossan mineral, the degradation of cyanide using sodium hypochlorite and ozone, the leaching of gossan ore through cyanidation, the detoxification of effluents and solid waste produced during the cyanidation process, and the mass balance analysis of the process, specifically in relation to the behaviour of gold and silver.

3.1 Gossan ore description

3.1.1 Analysis of chemicals

This page presents the findings of the chemical characterisation analysis:

X-ray fluorescence (XRF) is a spectroscopic technique that utilizes the emission of characteristic X-rays from a material when it is exposed to high-energy X-rays, or gamma Table 2 displays the proportions of various components detected in the Gossan sample. The predominant elements identified in the sample are (Fe) and (Si), while the certain minorities, present in concentrations ranging from 2% to 0.1%, include Al, Pb, Ba, As, K, Mg, Ti, Ca, Sb, Cu, and Sn. Traces of elements constituting less than 0.1% by weight are taken into consideration [6].

Table 2. Proportion of the various elements found in the Gossan sample.

Element	%Weight	Element	ppm	Element	ppm
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Al	1.68	Zr	188	Mn	40.00
As	0.70	Zn	150	W	25.40
Ba	1.20	Hg	154	Sc	26.30
Ca	0.25	Ag	67.50	Cd	5.30
Cu	0.10	Sr	58.80	Ta	4.50
Fe	25.00	Na	400	I	57.10
K	0.44	Cr	110	Mo	24.20
Mg	0.43	V	79.20	TI	9.30
Pb	1.60	Bi	173	Rb	27.90
Sb	0.20	Y	59.80	Br	4.60
Si	21.20	P	200	La	40.20
Sn	0.10	Se	57.20	Ga	3.00
Ti	0.25	Ce	77.40	Nb	7.20

Table 3 presents the proportions of predominant, subordinate, and residual constituents detected in the specimen through the employment of the Particle Induced X-ray Emission (PIXE) technique. The predominant element observed is iron (Fe), while lead (Pb), arsenic (As), sulphur (S), barium (Ba), aluminium (Al), and calcium (Ca) are present as minor constituents. Other elements are categorized as trace elements [6].

Table 3. proportions of predominant

Element	%Weight	Element	ppm	Element	ppm
Al	0.349	Na	219	Sr	17.8
As	0.62	Cu	504	Cd	112
Ba	0.396	Mg	324	V	34
Ca	0.294	Mn	182	Au	9.6
Fe	21.6	K	846	Zn	162
Pb	1.57	Si	588	Ti	129
S	0.545	Sb	457	Ag	51.6

The insoluble residue, obtained following treatment with aqua regia, exhibited a composition of 50%. It comprises silica (quartz) as well as some silicates, perhaps comprising iron (Fe). The primary distinctions between the outcomes acquired through X-ray fluorescence (XRF) and inductively coupled plasma (ICP) analysis are as follows.

3.1.2 Characterization of minerals

The findings of the mineralogical characterization techniques, namely X-ray diffraction (XRD), reflected optical microscopy (ROM), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX), are reported.

The utilization of scanning electron microscopy (SEM) in conjunction with X-ray energy dispersive analysis (EDX) When scanning electron microscopy was combined with energy-dispersive X-ray spectroscopy (SEM/EDX), the main particles found were quartz, barite, silicates, jarosite, and iron oxides. Figure 1 and Figure 2 depicts the particles that were found through the utilization of scanning electron microscopy (SEM). Conversely, Figure 3 and Figure 4 presents the energy-dispersive X-ray (EDX) diagrams, which illustrate distinct chemical species. The results acquired from SEM/EDX analysis corroborate the findings obtained through other techniques like XRD and optical microscopy.

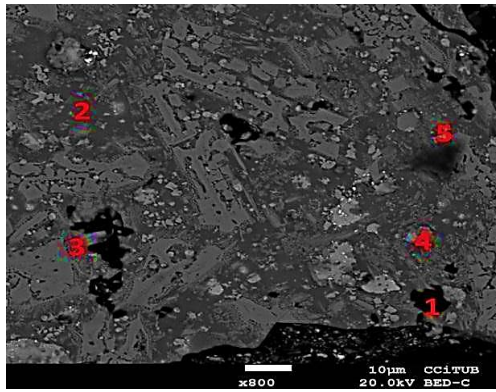


Figure 1. Particle size and morphology – backscattered electrons

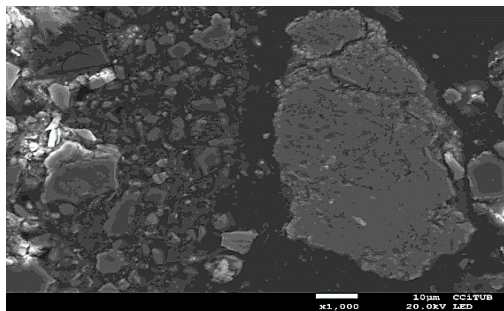


Figure 2. Goethite is a mineral that exhibits secondary electron emission.

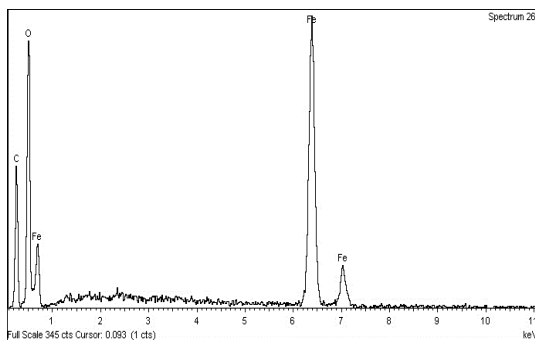


Figure 3. EDX Illustrations depicting many particles. (Goethite)

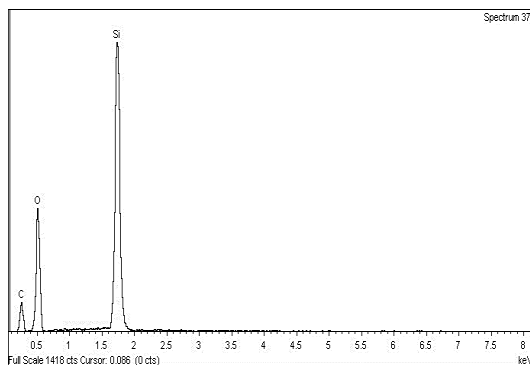


Figure 4. EDX Illustrations depicting many particles. (Quartz)

3.2 Study of cyanide breakdown using ozone and sodium hypochlorite

3.2.1 Cyanide reaction with sodium hypochlorite (NaClO)

The results obtained in the experiment conducted at room temperature with magnetic agitation are presented in Figure 5. The original sodium cyanide solution was subjected to the addition of a first millilitre of sodium hypochlorite solution. Following a reaction period of 5 minutes, a sample was extracted to facilitate the subsequent measurement of cyanides.

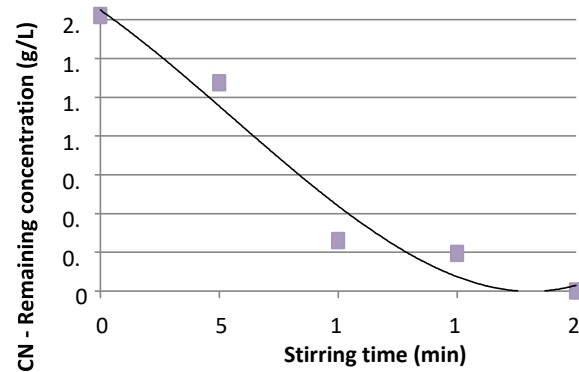


Figure 5. Evolution of cyanide oxidation using NaClO as an oxidant.

After leaving the experiment using 3 millilitres of sodium hypochlorite solution (47.4 grams of active chlorine per liter) for an hour, the findings reported in Figure 5 showed that the amount of degradation was more than 99%. As a direct result of this, it is feasible to ascertain the stoichiometry of this reaction. It is necessary to have 3.5 moles of active chlorine for every mole of cyanide. This outcome is consistent with what Smith found in his investigation [7].

3.3 Leaching of Gossan ore by cyanidation

3.3.1 Cyanidation experiment

Presents the temporal variation of the cyanide concentration observed in the conducted experiment. After a period of 10 hours of agitation, the concentration of cyanide exhibits a decline, reaching a final concentration of 1.57 g/L CN⁻. Furthermore, after the recovery of gold and silver by the precipitation of zinc, the resultant concentration of cyanide was determined to be 1.47 grams per liter of CN⁻. The findings shown in Figure 6 correspond to the data provided in Table 4.

Table 4. Cyanide degradation in cyanidation leaching

Time (Hours)	CN ⁻ remaining concentration (g/L)	% CN ⁻ not degraded
0	2.16	100
1	2.11	97.7
2	2.01	93.2
4	1.96	90.9
6	1.76	81.8
8	1.62	75.0

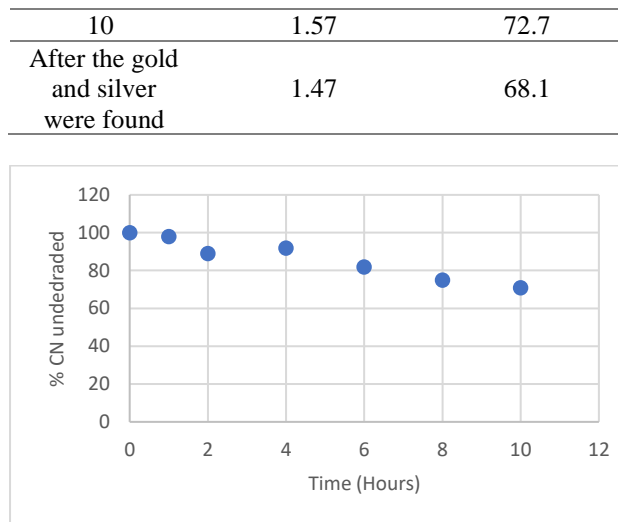


Figure 6. Cyanide degradation in cyanidation leaching

3.3.2 Recovery of gold and silver

After separating the liquid by sedimentation, zinc powder (1 g) and lead nitrate (0.1 g) were added, and the mixture was agitated. The activation of the zinc surface by lead nitrate antecedent to the precipitation of noble metals. Gold, silver, and copper precipitate readily from a solution, as shown in Table 5. The Zn is added to the solution, resulting in 277 ppm of Zn.

Table 5. Before and After Precipitation

Elements	Before precipitation (ppm)	After precipitation (ppm)
Zn	0.320	277.00
Fe	1.240	0.63
Cu	5.980	4.16
Au	1.220	<0.100
Ag	10.900	<0.500

3.4 Cyanidation effluents and solid waste detoxification.

3.4.1 Cyanide detox using (NaClO)

3.4.1.1 Effluent detoxification

The findings of the experiment involving the addition of sodium hypochlorite and subsequent degradation of cyanide are shown in Table 6, demonstrating a degradation efficiency of 99%.

Table 6. Effluent detoxification using (NaClO) as an oxidant.

Stirring time (min)	Vol. Add NaClO	Equivalent amount of Cl ₂ (mg)	CN ⁻ Remaining	CN ⁻ degraded (%)
0	0	0	1.47	0
15	2.20	34.7	0.03	99

(ml)	concentration (g/L)
0	0
15	99

3.4.1.2 Detoxification of solid waste

The ultimate concentration of cyanide in the pulp, as shown in Table 8, was determined to be 1.26 g/L CN⁻. According to the data shown in Table 7, the concentration of cyanides exhibited a reduction after the introduction of 1.80 ml of (NaClO) throughout a 15-minute period of agitation. The extent of cyanide decomposition exceeded 98%. The decontaminated material is transported away from the slag heap.

Table 7. (NaClO)-oxidized solid waste detoxicate

Stirring time (min)	Vol. Add NaClO (mL)	Equivalent amount of Cl ₂ (mg)	CN ⁻ Remaining concentration (g/L)	CN ⁻ degraded (%)
0	0	0	1.26	0
15	1.80	28.4	0.04	>98

4 Discussion

The discovered minority species include barite, goethite, hematite, beudantite, and jarosite [6]. The degree of deterioration exceeded 99%. Therefore, it is feasible to ascertain the stoichiometry of the reaction. A stoichiometric ratio of 3.5 moles of active chlorine per mole of cyanide is necessary. This finding aligns with the results found in a previous study [7]. Therefore, a molar ratio of 2 moles of ozone to 1 mole of cyanide is required. These findings align with the results reported by Ametller [8]. A solid substance was generated because of the oxidation process. The identification of the substance as calcium carbonate was verified using X-ray diffraction (XRD) analysis. This observation illustrates the formation of carbonates during the procedure.

5 Conclusion

The predominant constituents of Gossan ore are iron and silicon, while a smaller proportion consists of aluminum, lead, barium, arsenic, potassium, magnesium, titanium, calcium, antimony, copper, and tin. Elements that are present in quantities less than 0.1% by weight are often referred to as trace elements. The first Gossan ore exhibits a silver content of 87.4 grams per metric ton (g/t) and a gold content of 2.00 g/t. The predominant mineralogical constituents found in Gossan ore are quartz, barite, goethite, hematite, beudantite, and jarosite. The existence of these species is confirmed using MOR and SEM-EDX techniques. The use of sodium hypochlorite or ozone-oxygen for oxidation procedures applied to effluents and wastes produced during the cyanidation of Gossan ore results in degradation levels of 99%, hence reducing the cyanide concentration to less than 0.030 g/L.

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