

Characterization and Assessment of Cyanide and Trace Metal Behavior in Gold Mine Tailings Water

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Abstract

The mining industry constitutes a major economic sector, supporting development while generating significant environmental challenges. Indeed, it produces large quantities of residues from ore processing that are stored in dedicated basins called tailings storage facilities (TSF). These residues also contain various types of trace metal elements and cyanides that can be released into the environment. In this context, the aim of this work is to analyze and characterize the water quality in the TSF of the Sabodala mine and, on the other hand, to identify the hydrogeochemical phenomena that condition the behavior of pollutants. Samples were collected monthly (between 2022 and 2025) at two points (tailings discharge and decant water), and various physico-chemical parameters (pH, sulfates, cyanides and trace metal elements (As, Sb, Cd and Ni)) were analyzed. From this work, it emerges that: The waters of the tailings storage facility overall have a neutral to alkaline pH, with an average of 9.88 in raw tailings and a lower average of 7.98 in decant water. The higher sulfate concentrations in the decant water reflect a gradual oxidation of sulfides, which locally contributes to a decrease in pH. A strong decrease in cyanide contents is observed between the raw tailings and the decant water, suggesting significant degradation or dilution in the TSF enclosure. Trace metal elements show contrasting behaviors. Arsenic has high and highly variable concentrations in the raw tailings, but is significantly lower in the settling water, indicating a partial migration to the liquid phase. Cadmium, weakly present in both matrices, appears very little mobile. Nickel, although more concen-

trated in the tailings, migrates only weakly towards water. Conversely, antimony shows a more marked mobility, with contents in water sometimes higher than those measured in the raw tailings. Various physico-chemical processes such as oxidation, precipitation, volatilization and photodegradation are responsible for the behavior of the parameters studied, making the risk to surrounding surface and groundwater low.

Keywords

Tailings Storage Facility, Water Quality, Cyanides, Trace Metal Elements

1. Introduction

Mineral resources are vital natural resources for human societal development [1]. They provide an important material foundation for society development and national security [2]. However, the mining processes generate a large amount of tailings, which is about 2 - 12 times the metal extracted from the ore [3]. Indeed, the operation of a mine produces mainly two types of solid waste: sterile rock and mining residues (tailings). Sterile rock represents the fraction of rock without great economic value resulting from the blasting of the source rock. The sterile rock is generally transported by truck and stacked in waste-rock dumps. The tailings that result from concentrator ore processing [4] are deposited in special infrastructures called Tailings Storage Facilities (Tailings Storage Impoundment) for their safe and controlled containment, avoiding leaks and any contact with the environment. Tailings storage facilities (TSFs), which are reservoirs designed to contain mine tailings, represent some of the most hazardous infrastructures in the mining industry and have been responsible for severe environmental and structural damages in recent years [5]. From the plant, mine tailings are transported in pipelines and are discharged from the crest of the dam and the perimeter of the tailings facility at different discharge points, also known as spigots [6]. In this place, a natural phenomenon called sedimentation occurs, which consists of the solid-liquid separation of the deposited tailings. In this way, a supernatant process water (decant water) pond is formed in the TSF, which must be adequately managed and controlled [7]. The waters of the supernatant pond, also known as process waters (waters that have come into contact with mine tailings), usually have a turquoise green color; this is due to the presence of high concentrations of metallic elements (e.g., Cu, Mo, Cd, As, Pb, Mn, and Fe, among others), nonmetallic elements (e.g., sulfates, nitrates, chlorides, and ammonium, among others), and chemical reagents (e.g., copper sulfate, sodium cyanide, sodium ethyl xanthate, pine oil tar, fatty acid soaps, collectors, dithiophosphates, foaming agents, flocculants, and lime, among others) [8]. The behavior of pollutants in the chemistry of mine tailings and water is complex and diverse. It varies according to mineralogy and ore processing, as well as environmental conditions governed by complex hydrogeochemical reactions. Likewise, mine tailings and water frequently face social

and environmental controversy, considering the risk for surrounding hydro-systems by directly penetrating through surface runoff and/or groundwater recharge [9]. In Russia, the study by [10] confirmed that the long-term operation of the tailings leads to contamination of groundwater and surface water. Characterization of tailings and water quality through tailings dams and the infiltration and/or runoff of waters outside the structure represents a significant challenge that the mining industry must address. In the Sabodala gold mining site operated by the company Endeavour, the tailings generated by operations are stored in a tailings storage facility very close to surface water reservoirs used for multiple purposes. In addition, the groundwater in the area is used by communities. In this context, the aim of this work is to analyze and characterize the water quality in the TSF and, on the other hand, to identify the hydrogeochemical phenomena that condition the behavior of pollutants in the tailings impoundment of Sabodala Gold Mine.

2. Materials and Methods

2.1. Study Area

Located in the southeast of Senegal, at a distance of 700 kilometers from Dakar, the Sabodala mine is situated within the Mako greenstone belt, which constitutes the western part of the Birimian gold-bearing province. From an administrative point of view, it is located in the commune of Sabodala, within the department of Saraya and the region of Kédougou (**Figure 1**). The study site is the Tailings Storage Facility (or TSF1), an upstream construction structure that covers approximately 0.38 km², located to the northwest of the treatment plant that was commissioned in March 2009. It comprises:

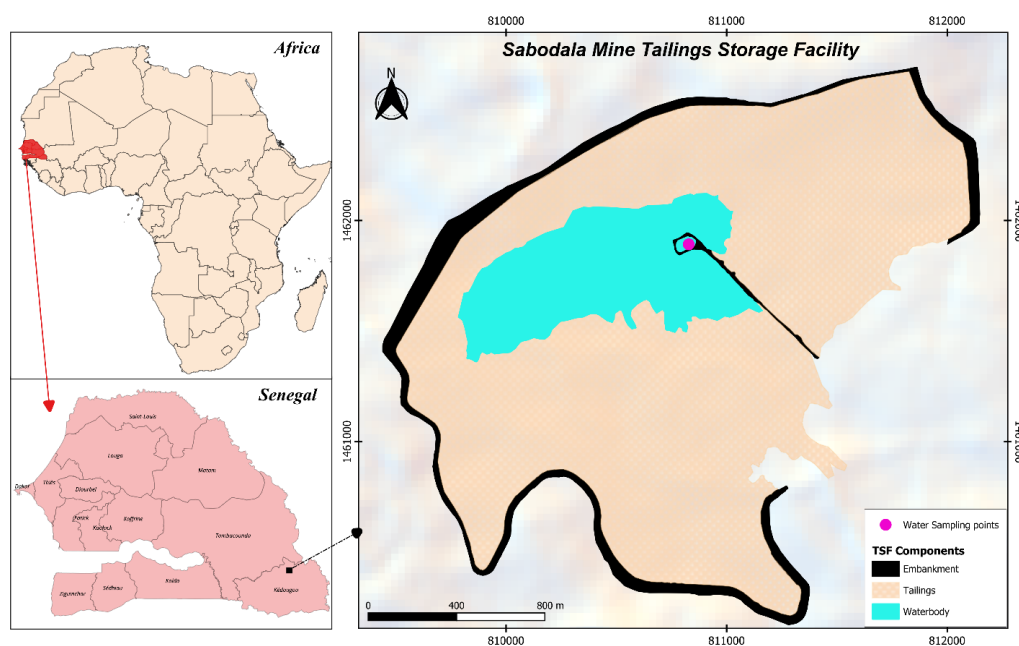


Figure 1. Location of the study area.

Embankments:

- 1) A western embankment, originally built in 2008.
- 2) Eastern embankment was originally built in 2010.
- 3) A south embankment, originally built in 2006.
- 4) A southwest embankment (connecting the south to the west embankment).

The embankments were raised at different times throughout the operating period. Following the last raising of the dike in 2021, the maximum storage capacity reached 48.8 million m³, of which 35 million m³ were already occupied by the tailings in February 2024 [11].

Impoundment: which stores the tailings and whose foundation is made of compacted laterite, greatly reducing the risk of infiltration.

Decantation pond in the middle of the TSF, collecting supernatant water from the solid-liquid separation of residues.

2.2. Tailings and Water Sampling and Analysis

The sampling of TSF waters is carried out each month on the SGO site at two points: The raw tailings (corresponding to the liquid phase of the slurry), sampled at the exit of the treatment plant towards the tailings dam; and the supernatant water sampled at the pond, which has residue corresponding to the settled water returned and reused at the plant (see diagram in **Figure 2** below).

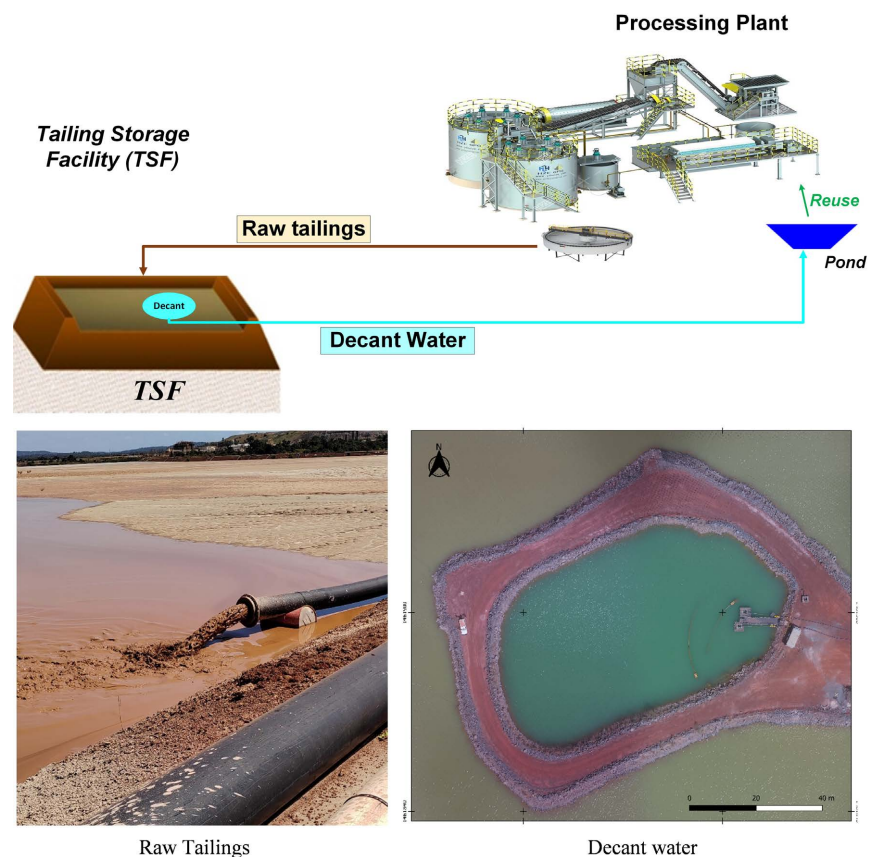


Figure 2. Schematic representation of discharges and water recovery at SGO.

The equipment used includes: sampling bottles, ice cubes for storing samples, etc. Once the samples are collected, they are stored in containers to stabilize the temperature below 10°C until they are sent to the ALS laboratory in Prague (Czech Republic), where analyses are carried out. In this laboratory, the water quality parameters are determined by inductively coupled plasma atomic emission spectrometry (ICP-MS), and stoichiometric calculations of the concentration of compounds are carried out from measured values, following their internal process CZ_SOP_D06_04_001, standardized and certified by US EPA 200.7, ČSN EN ISO 11885.

A statistical analysis of the data for the series in question was carried out using the XLSTAT software. A comparison with the relevant standards for each type of water was made (see annex).

3. Results

Below are the results of the discharge and settling water measurements from 2022 to 2025.

3.1. pH and Sulfates

The pH values of the waters of the Sabodala tailings pond are neutral to alkaline, with the following values (Figure 3).

- 1) Raw tailings: between 8.99 and 10.5, with an average of 9.88.
- 2) Decant water: between 7.23 and 8.46, with an average of 7.98.

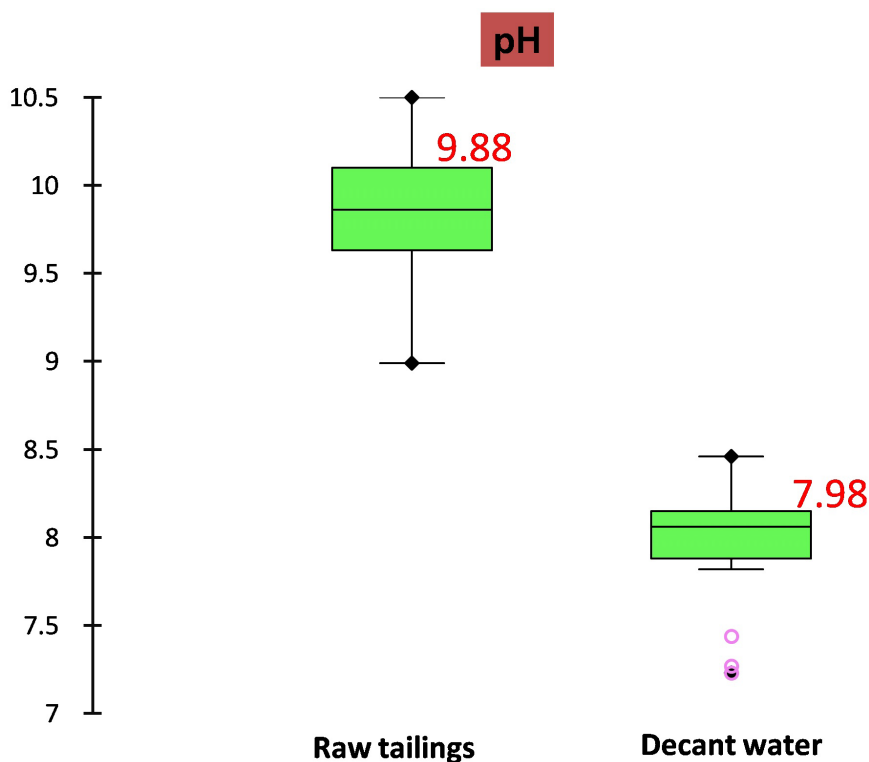


Figure 3. Box diagrams of pH in tailings and decant water.

According to [12], neutral pH is the result of a relative poverty of residual sulfide and a relative abundance of carbonates such as calcite, ferrodolomite, and silicates such as muscovite, chlorite, etc., in mine waste [13]. At the plant, during ore processing, lime (CaO or Ca(OH)) is added before unloading the residues into the TSF. Beyond the operational aspect (facilitating gold recovery), this addition of lime buffers the pH of the rejects, hence the high values recorded in the raw tailings. The pH of raw discharge water is higher than the pH of the decantation pond. Indeed, in the residue park, oxidation of the sulfides contained in the discharges occurs following the reaction in Equation (1).



This reaction releases hydrogen ions (H^+), thereby lowering the pH.

Figure 4 below illustrates the evolution of sulphate levels in tailings and settling water. It is noted that the sulphate resulting from oxidation is more abundant in settling waters than in raw waste waters, thus confirming the effect of sulphide oxidation in lowering pH. **Figure 4** below shows the repartition of sulphates in raw tailings and decant water.

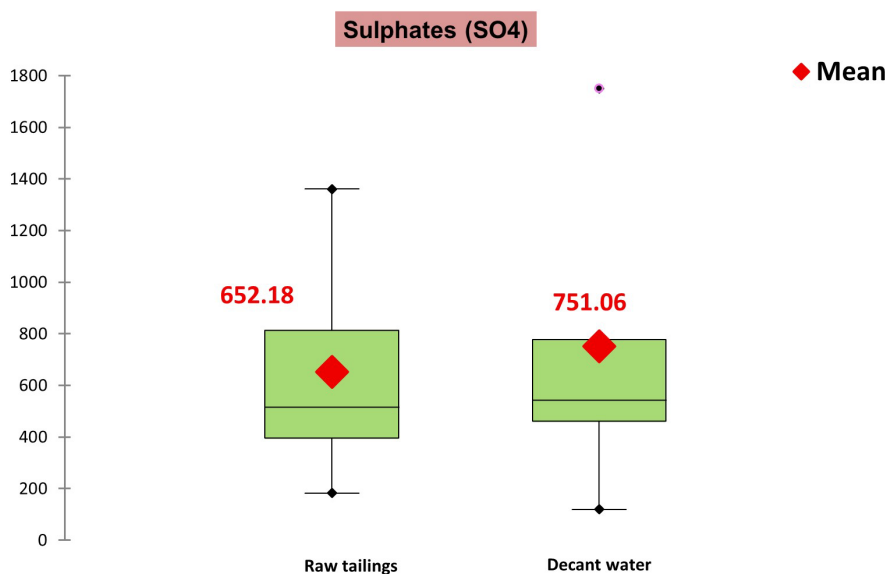


Figure 4. Box diagrams of sulfates (SO_4) in tailings and decant water.

3.2. Cyanides

Cyanides are a group of toxic recalcitrant compounds that contain the cyano ion ($\text{C}\equiv\text{N}$), used for silver and gold leaching in a process named cyanidation [14]. Approximately 90% of gold is extracted by cyanidation [15]. Thus, the gold industry is one of the largest consumers of cyanide due to the high affinity of the substance for gold. In the majority of gold leaching cases, cyanide is transported to the mining site as solid sodium cyanide (NaCN). Once used, it is found in the residues in several chemical forms. In the mine tailings and decant waters of Sabodala, three forms of cyanides were analyzed:

1) Free Cyanide: The uncomplexed cyanide ion (CN^-) and gaseous or aqueous hydrogen cyanide (HCN).

2) Weak Acid Dissociable (WAD) Cyanide: These are cyanide species liberated at moderate pH (pH 4.5), such as aqueous HCN and CN^- , the majority of Cu, Cd, Ni, Zn, and Ag complexes, and other metal cyanide complexes having similar low dissociation constants.

3) Total Cyanide: A measurement of cyanide concentration that includes all free cyanide, all WAD cyanide complexes, and all strong metal cyanides, including ferro-cyanide $\text{Fe}(\text{CN})_6^{4-}$, ferri-cyanide $\text{Fe}(\text{CN})_6^{3-}$, and portions of hexacyanocobaltate $\text{Co}(\text{CN})_6^{3-}$ and those of gold and platinum. Only the related or derived compounds cyanate (CNO^-) and thiocyanate (SCN^-) are excluded from the definition of total cyanide [16].

Figure 5 illustrates the different forms of cyanides generally found in tailings.

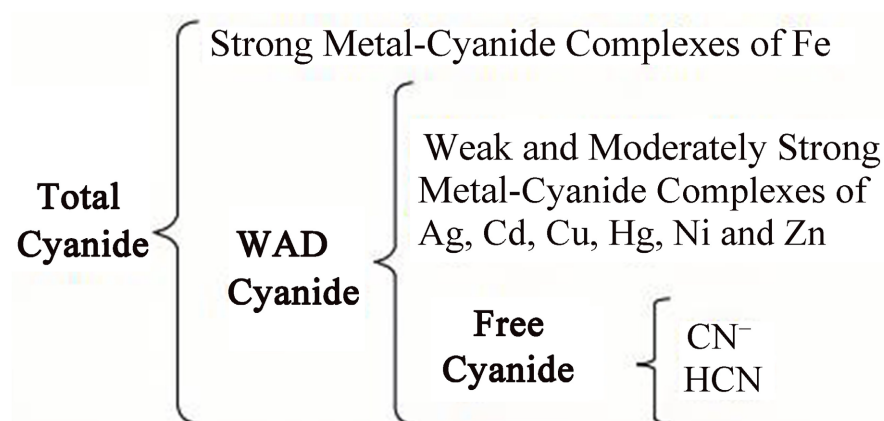


Figure 5. Different forms of cyanides [17].

The following results were obtained:

1) Total cyanides: The raw tailings have contents ranging from 60.3 mg/L to 121 mg/L, with a median value equal to 92.05 mg/L and an average of 95.72 mg/L. For decant water, the contents vary between 0.017 mg/L and 5.29 mg/L, with a median value equal to 0.31 mg/L and an average of 0.964 mg/L.

2) Free cyanides: The raw tailings have contents ranging from 52 mg/L to 116 mg/L, with a median value of 83.5 mg/L and a mean of 85.3 mg/L. For decant water, the contents vary between 0.012 mg/L and 4.11 mg/L, with a median value equal to 0.21 mg/L and an average of 0.85 mg/L.

3) WAD Cyanide: The raw tailings have contents ranging from 64.5 mg/L to 115 mg/L, with a median value of 87.6 mg/L and an average of 89.319 mg/L. For decant water, the contents vary between 0.014 mg/L and 4.52 mg/L, with a median value equal to 0.28 mg/L and an average of 0.89 mg/L.

Figure 6 presents the results of the different forms of cyanides in the raw tailings and in the decant water.

In the decant waters, the total cyanide contents are on average higher than the maximum admissible content, 0.2 mg/l according to the Senegalese standard for

discharge [18] and 1 mg/l according to IFC guidelines [19]. In the raw discharges, cyanide levels are higher than the standards; therefore, these waters must never be released into the environment. However, considering the large difference in contents between raw tailings and decant water without any engineering process, it is clear that a natural neutralization or degradation phenomenon occurs. The cyanide degradation efficiency (DE) calculated using Equation (2) for the analyzed series (2022 to 2025), degradation rates ranged from 93.78% to 100%, with an average of 98.73%.

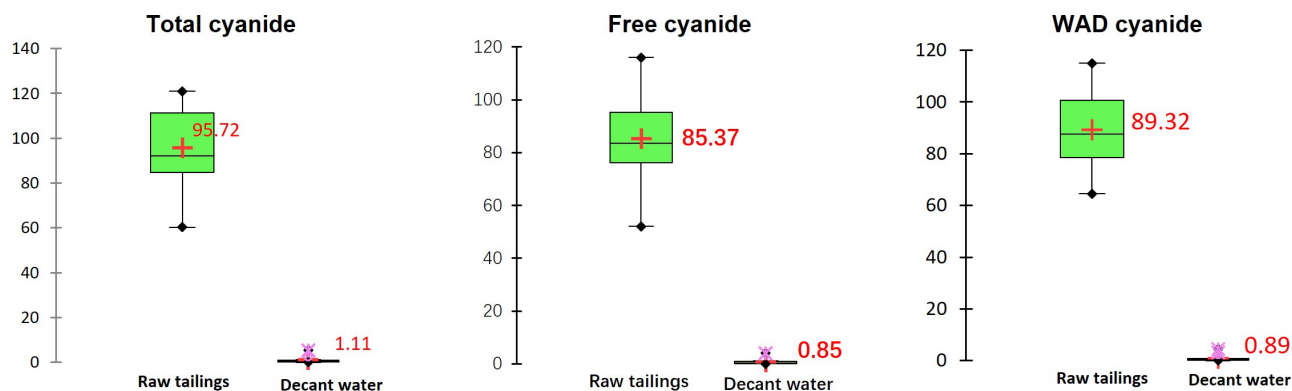


Figure 6. Cyanide results in tailings and decant waters.

$$DE = \frac{[\text{Conc}(\text{Raw tailings}) - \text{Conc}(\text{decant water})]}{\text{Conc}(\text{Raw tailings})} \quad (2)$$

3.2.1. Natural Cyanide Removal Mechanisms

For the removal of cyanide from the effluent of the gold plant, various approaches, ranging from natural degradation in tailings impoundment (natural attenuation in surface ponds) to highly sophisticated plant applications, have been developed [20]. In many countries, natural degradation in tailings ponds has been the most commonly used treatment method in most mills. Several authors have studied the natural attenuation of cyanides in effluents and soil [21], and several studies were done in mine tailings from gold extraction plants.

Similar to our findings, a study conducted on Australian sites reported that concentrations of several tens of mg/L of weak acid dissociable (WAD) and free cyanides decrease over time during the storage of cyanide residues. The concentrations of cyanide-metal complexes also decline, though at a slower rate, as a result of natural degradation processes [22] cited by [23]. They have the advantages of low cost and simple treatment, and do not generate secondary pollution, so they are very suitable for large-scale treatment of cyanide residues even if it is advisable to size them in such a way that natural degradation processes are facilitated. Natural degradation mechanisms include: volatilization, photolysis, chemical oxidation, biological oxidation, hydrolysis, and other cyanide reactions induced by air, light, and natural biology. Among the mechanisms listed, volatilization of hydrogen cyanide (HCN) from solution represents the primary natural attenuation pro-

cess in most surface ponds, such as tailings ponds. This pathway accounts for the removal of more than 90% of free cyanide. In addition, photolysis is believed to play a role in cyanide degradation within catchment areas [24].

3.2.2. Volatilization

Volatilization is known to be one of the main attenuation mechanisms for cyanide from tailing storage facilities [25]. This process primarily affects free cyanide.

Free cyanide is the sum of the cyanide ion (CN^-) and hydrocyanic acid (HCN) species released into an aqueous solution by the dissolution and dissociation of cyanide compounds (Mudder, 1991). These two species coexist in solution, their relative proportions depending on pH and temperature. The relationship between solution pH and the ratio of CN^- to HCN is illustrated in **Figure 7**. Below a pH of 7.0, all free cyanide is present as HCN in the toxic gaseous state [17], and above 11, almost all the hydrogen cyanide will be dissociated [25]. The reaction between the cyanide ion and a water molecule results in the formation of hydrogen cyanide (HCN), as shown in Equation (3) and Equation (4).



$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}, \quad pK_a = 9.21 \text{ at } 25^\circ\text{C} \quad (4)$$

At $\text{pH} < 9.2$, cyanide exists as a volatile HCN gas, which can escape into the atmosphere.

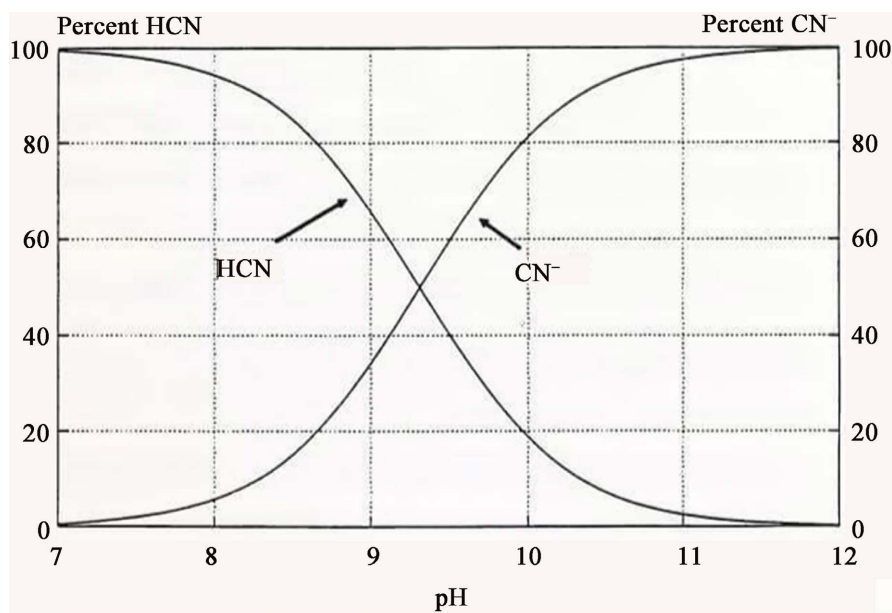


Figure 7. Relationship between HCN/ CN^- and pH.

The rate of volatilization of HCN in the residue park depends on the pH value of the residues and also on the prevailing atmospheric conditions [26]. In general, the following processes also accelerate volatilization:

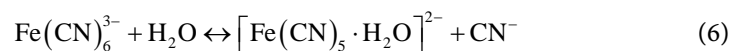
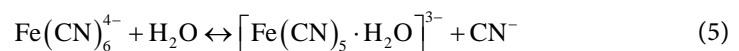
- 1) Low Ph.
- 2) High temperature.
- 3) Shallow water depth.

Furthermore, UV radiation and aeration promote gas exchange and the loss of HCN.

Thus, in the studied TSF, volatilization can be considered one of the main natural mechanisms for cyanide attenuation, due to the relatively rapid diffusion of hydrogen cyanide in the air and the low pH of the tailing solution. In fact, when entering the tailing dams, the raw tailings' pH is substantially equal to 10, but with time, the pH of the decant water tailing solution drops to 7.8 as a result of certain environmental interactions [25]. These include dilution effects due to rainfall, which has a natural pH of 5 - 8 and can decrease the tailing solution pH down to < 9, and oxidation of sulfur species, thus reducing the solution pH.

3.2.3. Degradation by Ultraviolet (UV) Photolysis

Photolysis is a natural degradation mechanism of cyanide in tailings storage facilities (TSFs), and is less dominant than volatilization. It contributes to cyanide breakdown when sunlight interacts with metal-cyanide species in slurries. According to [25], when tailings solutions are exposed to ultraviolet irradiation, CN^- is released from ferrous and ferric cyanides through photochemical degradation, as indicated in Equation (5) and Equation (6), and by the formation of iron precipitates, such as Prussian blue in acidic solutions, or ferric hydroxide in basic solutions [27]. Many metal-cyanide complex ions are relatively stable in aqueous solution in the absence of ultraviolet and visible light. However, under certain conditions, photodecomposition, with subsequent release of cyanide ions, will occur.



Ultraviolet (UV) and visible radiation cause complex iron cyanides to decompose, particularly in the presence of dissolved oxygen (Burdick and Lipschuetz, 1950). pH, temperature, and cyanide concentration all have a variable effect on the photolysis reaction of both iron-cyanide complexes (ferro- and ferri-). The lower the concentration of the iron complex ion, the faster the rate of photodegradation (Broderius and Smith, 1980). The release of a cyanide ion from the complex causes an increase in free cyanide present in the solution during daylight hours. Photodegradation occurs naturally in any pond or shallow lagoon where light can penetrate. Factors such as turbidity, color, depth, and many other parameters will condition the light penetration and affect the impact of photodegradation in a specific water body. Factors that improve photolysis also improve HCN removal. This will promote the volatilization of hydrogen cyanide (HCN) by increasing the exposed surface area and mass transfer rate (Ecological Analysts Inc. 1979).

3.2.4. Dilution from Rainfall

Rainfall plays a significant role in reducing cyanide content within tailings storage facilities by diluting cyanide through the large volumes of water entering the dam, lowering the pH since rainwater is typically acidic ($\text{pH} < 6$), and percolating through the tailings where it transports cyanide to deeper layers, facilitating the formation of stable complexes that decrease free cyanide availability and resist dissociation [28] [29].

3.3. Trace Metal Elements

The statistical analysis of data on trace metal elements (As, Ni, Cd, Sb) over the period 2022-2025 is presented in **Figure 8** below. It is noted:

3.3.1. Arsenic

In the raw residue from the plant, concentrations range between 0.044 mg/L and a very high maximum (9.470 mg/L), which gives a fairly high average of 1.528 mg/L. In the decant waters of the TSF, the rates are more modest, varying between 0.001 and 0.735 mg/L for a mean value of 0.182 mg/L. This strong variance between tailings and supernatant water shows that arsenic partially migrates towards water, but that a large part is precipitated or even trapped in the solid residue.

3.3.2. Cadmium

It is generally recorded that very low concentrations varying between 0.001 and 0.007 mg/L are present for raw tailings and between 0 and 0.001 for decant water, which shows that cadmium is weakly present in the tailings of the Sabodala mine. However, it must be recognized that the variance between the two points also indicates low mobility towards supernatant water and therefore poses less risk to the environment.

3.3.3. Nickel

In the raw tailings, nickel values range from 0.465 mg/L to a maximum of 8.000 mg/L, with a mean value of 2.230 mg/L. In supernatant water, lower values are recorded (between 0.001 and 0.819 mg/L), with a mean of 0.231 mg/L. These values indicate that this element also migrates weakly in water.

3.3.4. Antimony

The raw tailings have contents between 0.036 and 5.690 for a median value equal to 0.237 mg/L. For decant water, the median is higher compared to other metals, with 0.658 mg/L. However, the measurements vary between 0 and 1.650 mg/L.

In tailings facilities, metals behave differently from other pollutants such as cyanides. Indeed, the TME do not generally degrade under the effect of environmental conditions but simply change form and sometimes become more dangerous. Mine tailings, once discharged into the park, can be subjected to numerous physical and biochemical processes that result in the mobilization and immobilization of trace elements in water and soil [30]. These processes determining the mobility of TMEs are: sorption, desorption, complexation, precipitation, dissolu-

tion, as well as advection and dispersion phenomena. The determination of TME mobility in soils can be done using several sequential extraction methods, including those developed by [31]-[33]. According to [34], the best-known sequential extraction scheme (Tessier *et al.*, 1979) consists of five steps in which trace elements are considered to be distributed among different soil fractions: (1) exchangeable, (2) bound to carbonate, (3) bound to Fe-Mn oxides, (4) bound to organic matter, and (5) residual. Using this approach of Tessier to analyze the speciation of heavy metals in the solid tailings of Sabodala, [11] determined the distribution of the four target metals (As, Sb, Ni, Cd) in the different fractions and thus calculated their mobility factor. The mobility order obtained as a result of this analysis was: Cd > Ni > As > Sb. However, according to [35], several factors influence and modify the mobility of TME, including pH, redox potential, temperature and humidity, and microbiological activity.

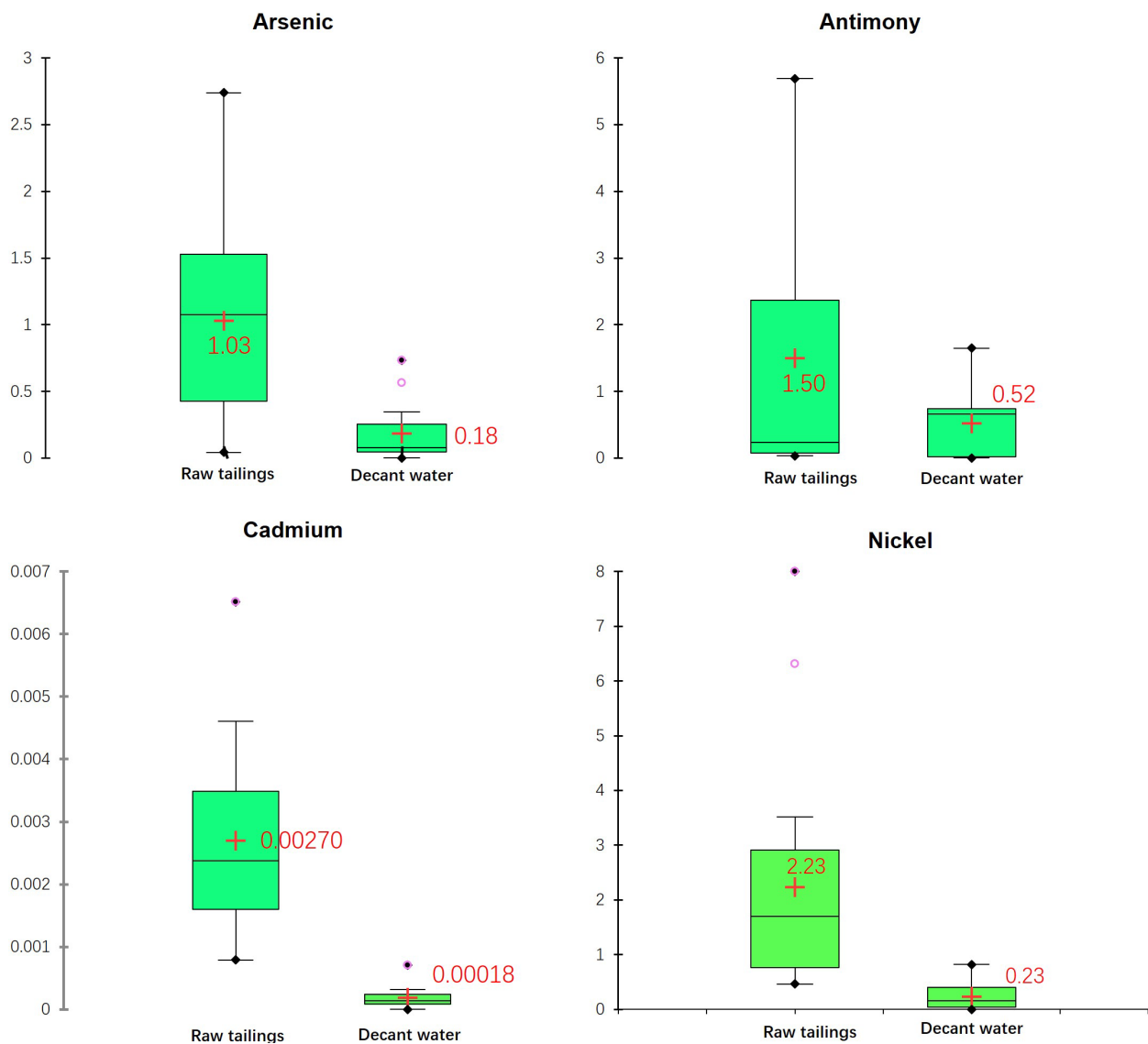


Figure 8. Trace metal elements in tailings and in decant water.

In the environment of the Sabodala TSF, these three factors influence their behavior: the pH is generally neutral to slightly alkaline (~7.9), the park is completely aerated (oxidant) and subjected to high temperatures, and the TME analyses are generally more favorable to precipitation in solid residues than to mobility towards supernatant water.

In fact, as previously observed by [28], when tailings are discharged from the spigot forming a deposition, the slurry flows towards the center of the TSF; fine particles flow into the central pond and precipitate to form sediments; metals are then adsorbed onto the sediments. Several factors influence the long-term behavior of metals:

- 1) The solubility of metallic trace elements decreases as pH increases.
- 2) Oxidative conditions lead to the retention of TME in soils through the precipitation process, while reducing conditions promote their mobility through the dissolution of complexes [36].
- 3) According to [37], under oxidizing conditions, arsenic can precipitate as scorodite and tooeleite. Antimony precipitates in the form of valentinite, senarmonite, and different sulfates (quandite, klebelsbergite, peretaite).

Microorganisms such as sulfate-reducing bacteria present can also have an effect on the behavior of ETM, especially through oxidation. However, for the case of Sabodala, a recent study by [38] showed that iron oxidation activities and the presence of sulfurous bacteria were not detected in the mine tailings. Thus, metals are found in higher concentrations in the tailings than in the overlying decant water mainly due to the phenomenon of precipitation that keeps them in the tailings (see Figure 9).

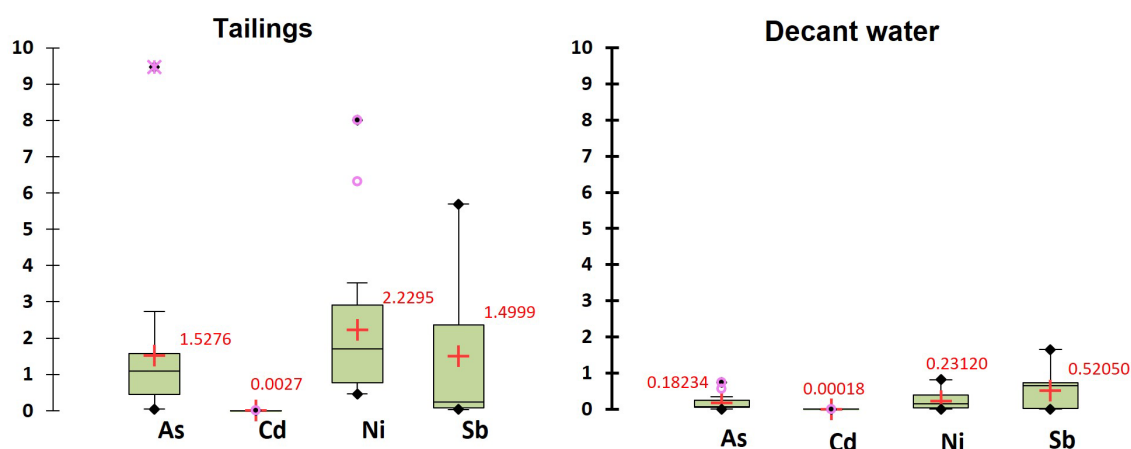


Figure 9. Box diagram of the heavy metal contents in the residues and in the decant water.

In summary, the following processes govern the behavior of the parameters studied in the tailings dam:

- 1) The oxidation of sulfides leads to the release of trace elements and hydrogen ions that contribute to lowering the pH in the park.
- 2) The precipitation of a large part of the TME in the residues.

- 3) The transfer of TMEs to the settling area with greater mobility of antimony.
- 4) A volatilization of free cyanides is favored by pH < 9.
- 5) Photodegradation of complex cyanides under the effect of solar UV.
- 6) Dilution and acidification effects of rainfall.

Figure 10 below gives an illustration of these phenomena.

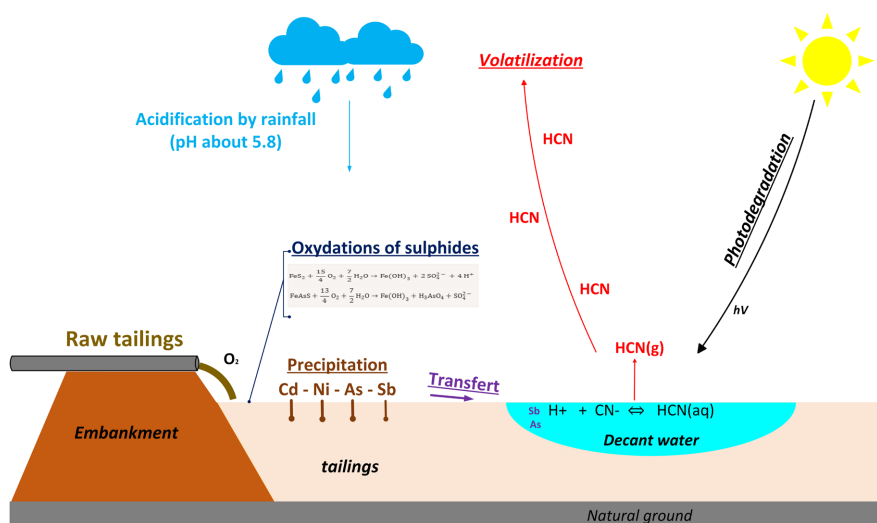


Figure 10. Illustration of hydrogeochemical phenomena in the Sabodala tailings dam.

4. Conclusions

The water quality characterization study allowed for the preparation of a precise inventory of the physico-chemical characteristics of the waters and tailings in the TSF of Sabodala. The raw tailings from the plant show an alkaline pH (~9.88), and high levels of cyanides and trace metal elements. On the other hand, in settling waters, the cyanide concentrations are very low, showing that natural degradation occurs. High degradation rates ranging from 93.78% to 100%, with an average of 98.73%, were recorded. Trace metal elements show contrasting behaviors. Arsenic has high and highly variable concentrations in the raw tailings, but significantly lower concentrations in the settling water, indicating partial migration to the liquid phase. Cadmium, weakly present in both matrices, appears to be very little mobile. Nickel, although more concentrated in the tailings, migrates only weakly towards water. Conversely, antimony shows a more marked mobility, with contents in water sometimes higher than those measured in the raw residues. pH values close to neutrality promote the precipitation of trace metal elements and allow the reduction of environmental impact, even if part of the TME is transferred into the waters.

On the other hand, the study also made it possible to appreciate the physical and hydrogeochemical phenomena that condition the behavior of the pollutants studied in the TSF. It appeared that the oxidation of sulfides and acidification by rainfall contribute to the lowering of pH, making possible the volatilization of species of free cyanides. Also, in this TSF, open on more than 380 hectares to the

effects of intense solar radiation, photodegradation is mainly used to eliminate complex cyanides. Moreover, the TME are slightly mobile towards settling waters and precipitate mainly in solid residues. In sum, this characterization provides a critical foundation for improving TSF management, underscoring the importance of appropriate sizing to promote volatilization, aeration, and sunlight exposure. It further highlights the role of rotational spigotting in achieving a more uniform distribution of tailings within the facility, thereby enhancing cyanide degradation and supporting the protection of aquatic ecosystems surrounding the Sabodala gold mining TSF.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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