

Article

Evaluation of the Efficiency of Using an Oxidizer in the Leaching Process of Gold-Containing Concentrate

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Abstract: This article presents the results of cyanide leaching of gold-containing concentrate using the trichloro cyanuric acid (TCCA) oxidizer. Gold-containing concentrate was obtained from a gold tailings sample from a gold recovery factory (GRF) in one of the deposits of Kazakhstan that have not previously been studied for concentrability. According to X-ray phase analysis and energy dispersive spectrometry (DSM) data, the main compounds in the tailings sample under study are pyrite FeS_2 , quartz SiO_2 , calcite CaCO_3 , albite $\text{NaAlSi}_3\text{O}_8$, muscovite $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_8$, dolomite $\text{CaMg}(\text{CO}_3)_2$, and oxidized iron compounds. Microscopic studies of the concentrate have established the presence of ultrafine gold with sizes from Au 0.9 to 10.2 μm in pyrite. Obtaining the gold-containing concentrate with a gold content of 15.95 g/t is possible according to the enrichment scheme, which includes centrifugal separation, classification according to the fineness class -0.05 mm, additional grinding of hydrocyclone sands to a fineness of 90.0–95.0% of the class finer than 0.050 mm, and control centrifugal separation. Since pyrite in technogenic raw materials is the main gold-containing mineral, this paper presents studies on the oxidizability of pyrite with the TCCA oxidizer. The results of studies on the oxidation of pyrite using the TCCA oxidizer show the products of its hydrolysis oxidize pyrite with the formation of various iron compounds on its surface. Pretreatment of gold-containing concentrate with oxidizer TCCA for 3 h before the cyanidation process (20 h) allows for an increase in the recovery of gold in the solution by 5.8%.

Keywords: stale tailings of a processing factory; grinding; centrifugal separation; pyrite; gold; redox potential; thermodynamic analysis; extraction



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1. Introduction

Over the past decades, there has been a significant depletion of rich ore reserves. As a result, it has become necessary to search for and introduce new methods of producing metals from non-traditional sources of raw materials. Stale tailings of processing plants, dumps of off-balance sheets, and substandard ores are a source of expansion of the mineral resource base. In the industrially developed countries of the world, the level of use of industrial waste reaches 70–80%. For Kazakhstan, which produces a significant share of mineral products and has a strong mining potential, the problem of industrial waste disposal is of paramount importance. The low-level use of man-made raw materials in the republic is explained by the lack of technology and equipment for processing many types of waste. An important circumstance is that the cost of commercial products from industrial waste is usually lower than from ores of mineral deposits extracted by traditional methods. The advantage of man-made dumps is the readiness of the product directly for processing (ores have already been lifted from the subsurface, washed, and disintegrated). Another

equally important aspect of the “thin gold” problem is that a huge number of man-made dumps accumulated over many decades are becoming profitable due to new technological opportunities and rising gold prices. Therefore, the development of technologies for processing gold-containing technogenic raw materials is an urgent task for the gold mining industry. The progress in improving methods for extracting useful components allows us to consider man-made dumps as a very attractive source of raw materials [1–3]. Man-made dumps can often compete in terms of content and reserves with newly discovered deposits today. Involvement in the processing of these wastes will not only allow obtaining additional products but also reduce environmental damage to the environment.

In [4], the possibility of obtaining gold and iron concentrate from gold-containing tailings by performing successive operations such as reduction roasting, mechanical activation, leaching, and magnetic separation is shown.

The effect of short-term mechanical activation of gold extraction mill tailings on the sulfide floatability was studied [5,6]. Flotation of finely ground tailings under the optimal reagent regime allowed the increase in the recovery of gold in concentrate from 29.0 to 45.4% with the residual metal content in the waste at the level of 0.2–0.3 g/t.

The authors of [7] present the results of tests on the concentrability of gold-containing tailings of the Mazove mine (Zimbabwe) with a gold content of 1.1 g/t. The processing technology includes the processes of flotation and grinding of flotation concentrate to a fineness of less than 25 microns, which ensures the opening of gold and subsequent sorption cyanidation.

Gravity enrichment has become widespread due to its advantages over other methods of processing mineral raw materials, which include its cheapness, environmental safety, separation of minerals without changing their properties, and a wide range of fineness of separated mineral particles. In the practice of processing gold-containing ores, centrifugal separators are widely used, in which the separation of minerals occurs under the action of centrifugal accelerations that are tens and hundreds of times greater than the acceleration of gravity. The use of centrifugal separators made it possible to significantly reduce the size limit of the separated minerals to 0.02 mm [8].

Positive results of using centrifugal separators have been obtained in the processing of gold-containing ores from placer and indigenous deposits, current and stale tailings from processing plants, tantalum-niobium, hematite, chromium ores, ilmenite-zircon sands, and coal slurries [9–14].

A significant part of the gold in the concentrate is finely interspersed and associated with pyrite and arsenopyrite, which makes it difficult to directly cyanide the enrichment products. Processing of persistent gold-containing raw materials is carried out according to technologies based on the use of pre-oxidative roasting, autoclave and bacterial oxidation, and ultrafine grinding with subsequent cyanidation [15–19]. The most common method of opening fine gold associated with pyrite and arsenopyrite and implemented in the practice of processing resistant gold-containing raw materials is oxidative roasting [20,21]. In the pre-oxidation process, a porous structure of mineral complexes is formed, which promotes the penetration of cyanide solutions. Technologies for processing resistant gold-containing ores under the “roasting-cyanidation” scheme are implemented at enterprises in Canada, South Africa, the USA, Australia, and other countries [15]. The method of oxidative roasting is most widely used in the processing of refractory ores, but it has the following main disadvantages: high production costs and serious environmental pollution with a large amount of sulfur and arsenic oxides.

The process of bacterial leaching in relation to gold-containing raw materials has become widespread in world practice in the form of a chemical bio-oxidation of resistant gold-containing concentrates. The preliminary bacterial treatment of gold-containing raw materials ensures the opening of sulfides and improves the recovery of gold into solution during cyanidation [22–26].

Currently, there are about 20 plants successfully operating in the world for processing persistent gold-containing concentrates in Australia, South Africa, Peru, Ghana, China, Kazakhstan, Uzbekistan, Russia, and other countries [27].

Biotechnologies can be applied to high arsenic gold-containing concentrates. Bacterial oxidative leaching is an inexpensive and environmentally friendly process for releasing gold from the sulfide matrix. Gold recovery during cyanidation of concentrate ground to a fineness of -30 microns was 55.3% after 48 h of cyanidation. The use of pre-biooxidation of gold-containing concentrate for 2 days allowed us to dissolve 90% of the gold [13]. The disadvantages of the process are the long oxidation cycle and high requirements for the technological equipment used in the leaching process.

The autoclave method of oxidative decomposition of sulfide minerals is known and implemented in the practice of processing persistent gold-containing ores. Water pulp containing sulfides is heated in an autoclave to a temperature of $180\text{--}280$ °C at an oxygen pressure exceeding the vapor pressure. Gold and silver remain an insoluble residue from which they can be extracted by cyanidation or other hydrometallurgical methods. The technology of autoclave oxidation–cyanidation makes it possible to extract up to 97% of gold from concentrates [28].

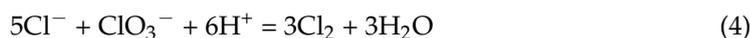
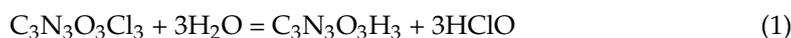
Processing of polymetallic gold-containing concentrates by autoclave oxidation makes it possible to simultaneously extract non-ferrous metals into marketable products [28–30].

The use of oxidative leaching at atmospheric pressure can significantly reduce capital costs in contrast to technologies such as oxidative roasting, autoclave, or bacterial leaching. The oxidizer of sulfide minerals is oxygen. Oxygen is supplied using supersonic ejector devices that provide a high rate of mass transfer of oxygen in the reactor. When sulfides are oxidized, a large amount of heat is released, so the operating temperature is close to the boiling point of the pulp ($90\text{--}95$ °C). At such operating temperatures, according to theoretical data, leaching occurs in two stages. In the first step, the sulfide mineral (SM) is oxidized to soluble sulfate and elemental sulfur.

There are many studies on the chemical oxidation of gold-containing pyrite and arsenopyrite sulfides using oxidizing agents [31].

There is little information in the literature about the use of organic chlorides for opening gold from iron sulfides. Trichlorocyanuric acid (TCCA) is an organic molecule of chlorinated isocyanate with the chemical formula: $\text{C}_3\text{N}_3\text{O}_3\text{Cl}_3$.

Based on extensive research, trichlorocyanuric acid (TCCA), a cyclic organic chloride containing three chlorines [32,33], can make up for the lack of inorganic chlorides. TCCA is hydrolyzed to form HClO, HClO dissociates to form ClO^- , Cl_2 , and O_2 are also formed as a result of subsequent reactions, as shown in the Equations (2)–(5) [34–38]. All four types are oxidizing agents, among which HClO is the most active.



In accordance with Equations (6) and (7) [17], the distribution of the main hydrolysis products from TCCA in an aqueous solution at various pH values was revealed. As can be seen from Figure 1, when the pH value is greater than 7.5, the predominant hydrolysis products are ClO^- ; when the pH value is from 3.5 to 7.5, the main type is HClO; and when the pH value is less than 3.5, Cl_2 acts as the main oxidizing agent. Among them, HClO has the highest redox potential and the strongest oxidizing capacity.

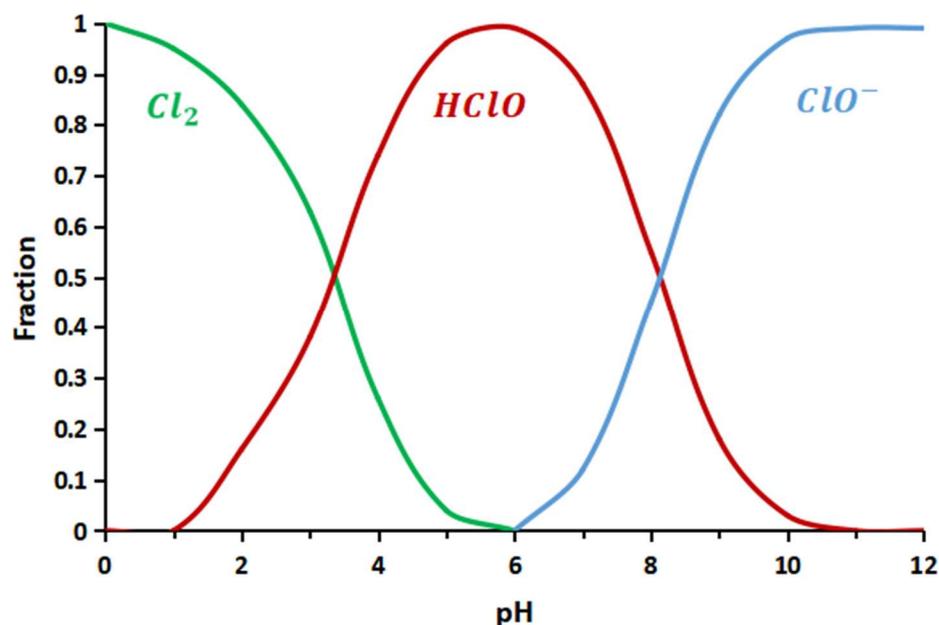


Figure 1. Distribution of the main types of hydrolysis products from TCCA at different pH values.

The aim of this work is to develop an effective method for pre-opening gold by oxidizing the sulfide part of the concentrate with trichlorocyanuric acid, followed by cyanidation. Since pyrite in a gold-containing concentrate is the main gold-containing mineral, this paper presents studies on the oxidation of pyrite with trichlorocyanuric acid.

2. Materials and Methods

Our studies were performed to develop technological solutions for the recovery of gold from mature tailings at one of the gold recovery factories (GRF) in Kazakhstan. Mature flotation tailings are a product with a gold content of up to 1.23 g/t. Studies on the oxidation of pyrite using trichloroisocyanuric acid were carried out. Research has been carried out on the oxidation of pyrite using trichloroisocyanuric acid. The following methods were used during our studies: X-ray fluorescent elemental analysis (wave-dispersive combined spectrometer Axios “PANalytical” (Eindhoven, Holland)); X-ray diffraction analysis (diffractometer “D8-ADVANCE” Bruker Elemental GmbH (Berlin, Germany)); electron microscopic analysis (microprobe analyzer JEOL “JEOLJXA-8230” (Tokyo, Japan)); and fire assay with AAS finish (NSAM 497-XC method). The spectra of solutions were obtained on an “Avatar IR-Fourier spectrometer 370” in the spectral range of 4000–500 cm⁻¹ from capillary layers in KRS-5 windows.

For research, an average sample for studying physical and chemical properties and samples for technological research were selected from the sample of the initial dump tailings. To conduct research, a medium sample was selected from a sample of the original dump tailings to study the physicochemical properties and a sample for technological re-research.

Experiments on gravity enrichment were performed on the Knelson “KS-MD3” laboratory centrifugal separator (Savona, Canada). Technological parameters of raw material enrichment on a centrifugal separator: weight of the suspension—500 g; the size of the initial material—90–95% of the class $-0.05 + 0$ mm; and the flow rate of diluent water—4.0 L/min; acceleration of the centrifugal field—90 m/s².

Oxidation of pyrite monomineral with a solution of trichloroisocyanuric acid depending on the mixing time and TCCA concentration was carried out according to the functional scheme shown in Figure 2.

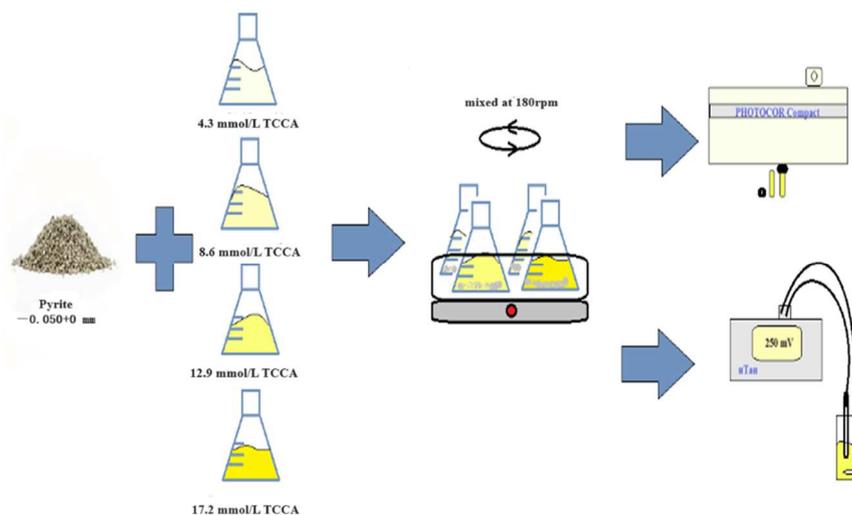


Figure 2. Measurement of the zeta potential and redox potential.

The zeta potentials of a pyrite monomineral with a size of $-0.050 + 0$ mm before and after interaction with TCCA were determined using Photocor Compact zeta potential and particle size—PhotocorAnalyzer. A total of 1 g of pyrite was added to 50 mL of an aqueous solution with concentrations of 4.3; 8.6; 12.9; and 17.2 mmol/L TCCA. Samples of a 50 mL mineral pulp solution were filtered through a filter paper using yellow tape. To control the pH, a solution with a concentration of 0.05 M NaOH or 0.05 M H₂SO₄ was used. With constant mixing of the samples for 180 min, the kinetics of the zeta potential change was measured as a function of the TCCA concentration at 20 °C.

The ζ -potential of the system was measured at 20 °C using a Photocor analyzer “COMPACT” (Moscow, Russia). The device was equipped with a laser with a wavelength of 657 nm/36 MW, and the measurements were carried out in round vials with an internal diameter of 14.8 mm. The correlation function for each sample was obtained by averaging 10 curves, each of which was obtained over 30 s.

The redox potential (ROP) of a $-0.050 + 0$ mm pyrite system with different TCCA concentrations was controlled using a combined Pt/Ag-AgCl ROP electrode in an ETHANE pH/ionomer. The ROP kinetics of the samples was measured every 10 min for 3 h at 20 °C.

It is known that due to the formation of different chlorine compounds during the hydrolysis of trichlorocyanuric acids, the oxidation of the process at different pH differs. So, at a pH closer to 1, atomic chlorine is released, which is a strong oxidizer, and at a pH of 5–7, the release of free chlorine is insignificant and requires a long oxidation time. Oxidation was carried out for 5 h, until the complete consumption of the chlorine compound (with sampling to determine the potential sampling time: 3 to 5 h), since the remaining chlorine in the pulp will interfere with the process of further cyanide leaching.

3. Results and Discussion

The material composition of the ore was studied. Studies on the concentrability of gold-containing tailings using a centrifugal separator Knelson were carried out.

To determine the phase composition of the flotation tailings sample, X-ray phase analysis (XRD) was performed in Figure 3. According to the X-ray diffraction analysis, the following minerals were determined in the sample: quartz, sericite, chlorite, feldspar, muscovite, and sulfides (Table 1).

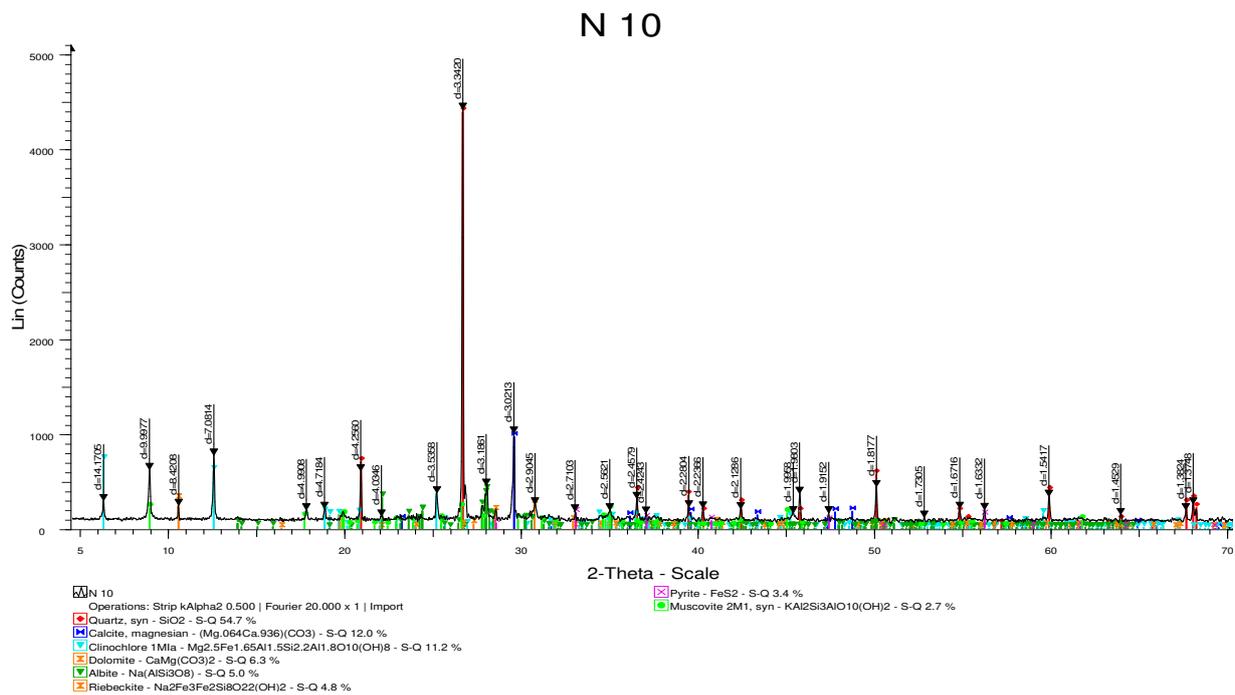


Figure 3. Results of XRD of the initial ore.

Table 1. X-ray diffraction analysis of the initial ore.

Compound Name	Formula	Content, %
Quartz, syn	SiO ₂	54.7
Calcite, magnesian	(Mg _{0.064} Ca _{0.936})(CO ₃)	12.0
Clinocllore 1M1a	Mg _{2.5} Fe _{1.65} Al _{1.5} Si _{2.2} Al _{1.8} O ₁₀ (OH) ₈	11.2
Dolomite	CaMg(CO ₃) ₂	6.3
Albite	Na(AlSi ₃ O ₈)	5.0
Riebeckite	Na ₂ Fe ₃ Fe ₂ Si ₈ O ₂₂ (OH) ₂	4.8
Pyrite	FeS ₂	3.4
Muscovite 2M1, syn	KAl ₂ Si ₃ AlO ₁₀ (OH) ₂	2.7

To determine the phase composition of the flotation tailings sample, X-ray phase analysis (XRP) was performed. According to the X-ray phase analysis, the following minerals were determined in the sample: quartz, sericite, chlorite, feldspar, muscovite, and sulfides (Table 1).

The results of the X-ray fluorescence analysis of stale GRF tails, shown in Table 2, were obtained using an Axios X-ray fluorescence wave dispersion spectrometer manufactured by Panalytical (Eindhoven, Holland). The spectrograms were processed using Super Q software (Omnian 37).

Table 2. Results of the X-ray fluorescence analysis of gold recovery plant tailings.

Chemical Element	Content, %	Chemical Element	Content, %
O	47.195	Cr	0.037
Na	1.976	Mn	0.091
Mg	2.131	Fe	5.293
Al	8.022	Co	0.013
Si	28.273	Ni	0.013
P	0.055	Cu	0.004
S	0.527	Zn	0.013
Cl	0.064	Sr	0.014
K	0.993	Zr	0.005
Ca	4.908	Pb	0.018
Ti	0.355		

Analysis of the distribution of gold by size class indicates that the main gold is distributed by size class +0.2; −0.2 + 0.1; −0.1 + 0.07; −0.07 + 0.05 mm. For example, in the +0.2 mm fineness class, the gold content was 4.0 g/t, with a yield of 9.4%, and up to 30.57% of gold is concentrated in it. In size classes −0.2 + 0.1; 0.1 + 0.07; −0.07 + 0.05 mm, the gold content is 1.3 g/t, 1.25 g/t, and 1.32 g/t, respectively. In the class of −0.05 + 0 mm, 21.27% of gold is concentrated, while the output is 44.36% with a content of 0.59 g/t.

The products of sieve analysis of the stale tailings sample were studied on a JEOL “JEOLJXA-8230” (Tokyo, Japan). Samples were placed on a double-sided adhesive electrically conductive carbon tape from NISSHIN EM Co., Ltd. (Tokyo, Japan). The results of energy dispersive spectrometry (DPS analysis) “from an area” of the fineness class −0.071 + 0.05 mm (with an increase of ×100) are shown in Figure 4, which allows us to estimate the concentration of elements on the surface, Au was 18.58 ms% or 3.71 mol%. Most of the SEM images were taken in the backscattered electron mode (COMRO), which minimizes resolution degradation and provides better images of such powders compared to the secondary image observation mode (SEI). During the DSP analysis, a beam current of about 10 nA was selected, which corresponds to a sufficient data accumulation rate.

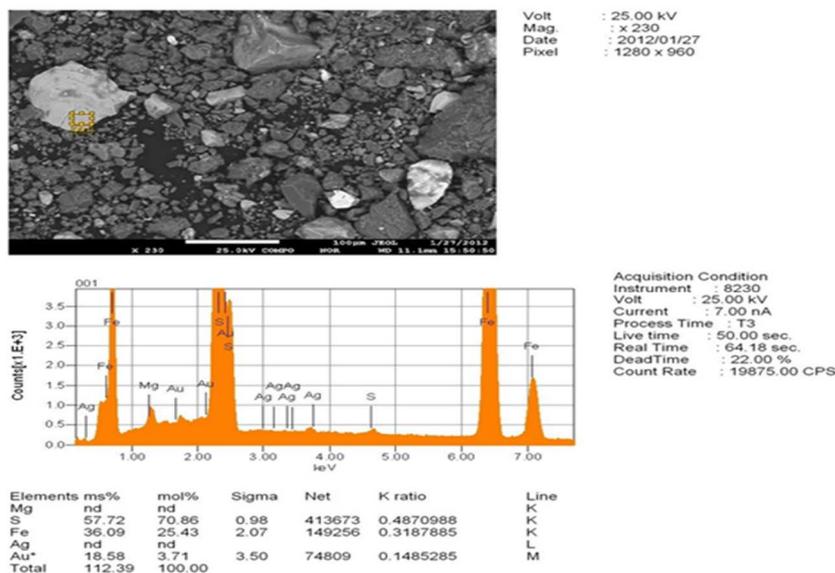


Figure 4. Results of DSP analysis of pyrite.

Microscopic studies on the surface ($m = 8\text{--}10\text{ g}$, $d = 25\text{ mm}$) revealed the presence of free-form gold grains, ranging in size from $\text{Au } 0.9$ to $0.2\text{ }\mu\text{m}$ Au-ultrafine and fine gold (Figure 5). The shape of gold particles is diverse: elongated, isometric, ellipsoid, spongy, spherical, scaly with a developed surface, and lamellar with uneven contours. The surface of the particles is clean, smooth, rough, or bumpy.

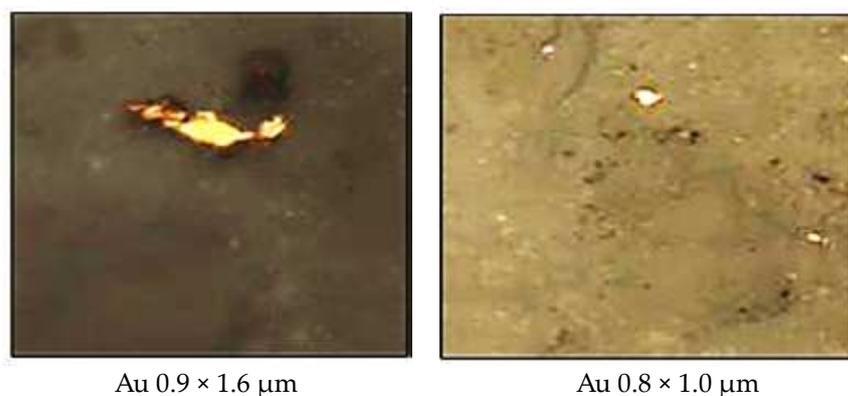


Figure 5. Free gold particles in polystyrene.

The presence of oxidized iron compounds in the studied sample of mature tailings of a gold extraction plant indicates that the sulfide minerals (pyrite and chalcopyrite) present in the tailings were oxidized to form iron oxides, hydroxides, sulfates, and carbonates as a result of prolonged exposure to climatic conditions.

Oxidation of pyrite. To find out the possibility of gold-containing pyrite disclosure using an organic chlorine-containing reagent TCCA, depending on the time of the process and its concentration, we conducted preliminary studies of its interaction with monomineral pyrite. The zeta potential in the shear plane provides important information necessary for analyzing electrostatic interactions between particles, suspension stability, and particle adsorption on mineral surfaces.

To assess the state of the surface of sulfide minerals and the electrostatic component of the interaction forces between particles, the electrokinetic potential was measured. Figure 6 shows the zeta potential of pyrite as a function of pH.

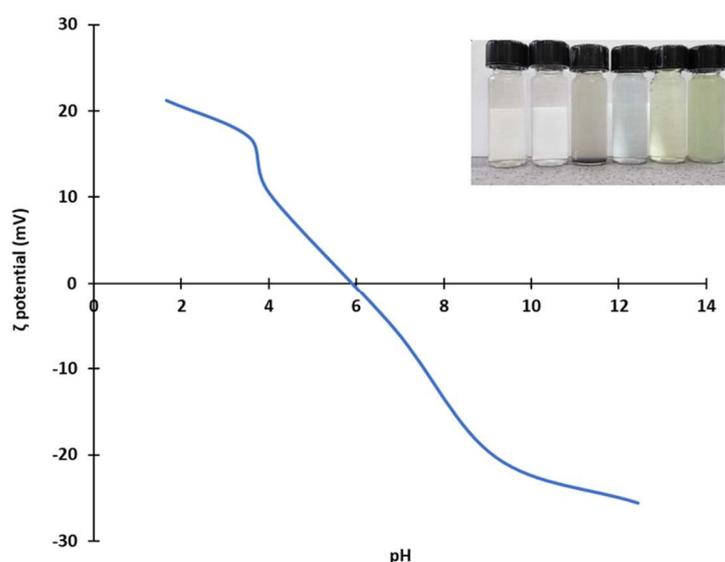


Figure 6. ζ -potential of pyrite as a function of pH.

With increasing pH in neutral and alkaline media, pyrite has a negative electrokinetic potential, varying from zero to -25 mV (Figure 5). Pyrite has a high negative charge

under alkaline conditions and becomes positively charged at $\text{pH} < 6$. With increasing pH values, the absolute value of the zeta potential gradually increased. This is consistent with experimental data in the literature [39].

The histogram (Figure 7) shows the effect of TCCA concentration on the pyrite zeta potential. The concentration of TCCA has a significant effect on the zeta potential. As the concentration of trichloroisocyanuric acid increases in the solution, a large number of iron compound ions are formed and, accordingly, the zeta potential value becomes positive. This means that the reaction of pyrite and trichloroisocyanuric acid produces Fe^{2+} , FeO^+ , and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, which are adsorbed on the surface of the mineral pyrite. On the other hand, as mentioned above, films consisting of goethite and hematite can form on the surface of pyrite, which also charge the surface of pyrite in a positive charge. However, these films can be dissolved in a solution of one of the products of TCCA hydrolysis, namely in HCl solution by the following Reactions (8) and (9):

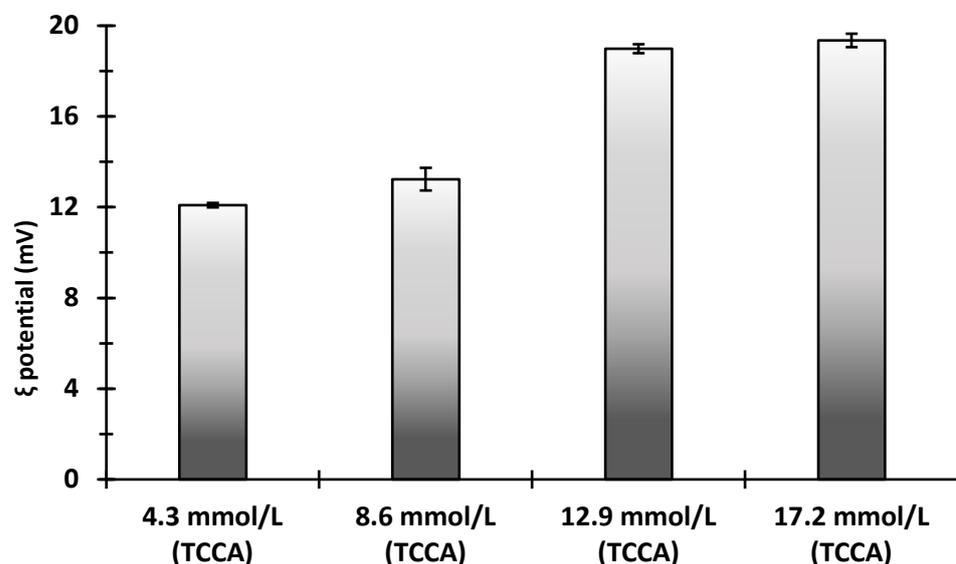
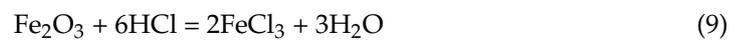


Figure 7. Influence of TCCA concentration on the zeta potential of pyrite.

Figure 8 shows changes in the electrokinetic potential depending on the concentration of the TCCA solution, where it is shown that with an increase in the concentration of TCCA, the value of the ξ -potential increases in the positive direction. This is due to the oxidation reaction of pyrite with the products of hydrolysis of TCCA, namely hypochlorous acid (HClO), which is more formed when TCCA is decomposed by water (see Reactions (1)–(5)). Consequently, as mentioned above, a large amount of iron (II, III) ions is formed.

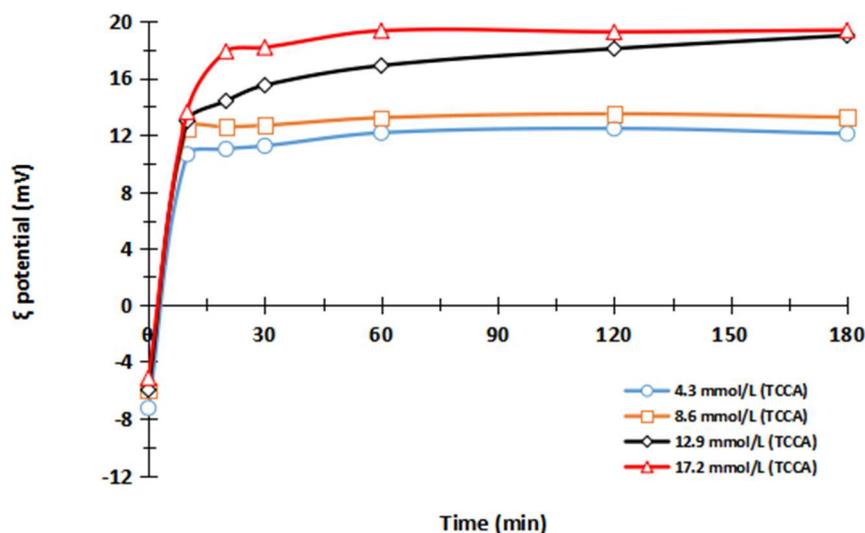
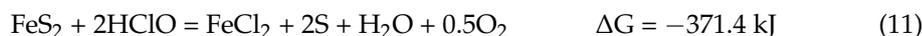


Figure 8. Kinetics of zeta potential change as a function of TCCA concentration.

Thermodynamic analysis. It is known that when a dry TCCA powder is added to an aqueous solution, the hydrolysis reaction proceeds according to Equation (1). Then various chlorine compounds are formed as a result of redox disproportionation reactions (see Equations (2)–(5)). As is known (5)–(7), hypochlorous acid (HClO) is mainly formed—concentration of 2–2.5 g/L at pH 6 for 3–5 h, the following reactions can occur without air purging:



According to the Gibbs energy value calculated using a computer program HSC Chemistry 8, it can be judged that the Reaction (10) is mainly taking place. At the same time, hydrochloric acid reacting with iron oxides (hematite, goethite) can form iron (II, III) cations, increasing the ξ —potential in the positive direction, as indicated above.

Measurements were carried out using IR spectroscopy to determine the potential mechanism by which TCCA is adsorbed on mineral surfaces (Figure 9). To investigate the mechanism of TCCA with pyrite, the IR spectra of a pure pyrite sample and a pyrite–TCCA sample were determined to understand the nature of the interaction.

In the TCCA IR spectrum, the absorption peak at 3346 cm^{-1} was attributed to $-\text{OH}$. The absorption peaks at 1641 and 1323 cm^{-1} were assigned to the carboxylic carbonyl group, respectively. The absorption peaks at 1623 and 1440 cm^{-1} were attributed to the aromatic ring with a double bond. Absorption peaks between 1100 and 1000 cm^{-1} were attributed to C–O deformation. The results of IR spectroscopy are consistent with previous results of TCCA characterization [34]. The spectrum shows automatic correction of the baseline and automatic smoothing in the range of 1000 – 950 cm^{-1} . The information obtained indicates that TCCA molecules contain a large number of OH^- , C–O, which can bind to mineral surfaces and enhance the hydrophilicity of mineral particles. The presence of a band in the spectrum corresponding to the oscillation of the sulfate ion at a wavenumber of 916 cm^{-1} indicates the coordination of the metal sulfate ion. In the IR spectrum of pyrite, the band at 1085 cm^{-1} was attributed to the vibration of stretching of single bonds.

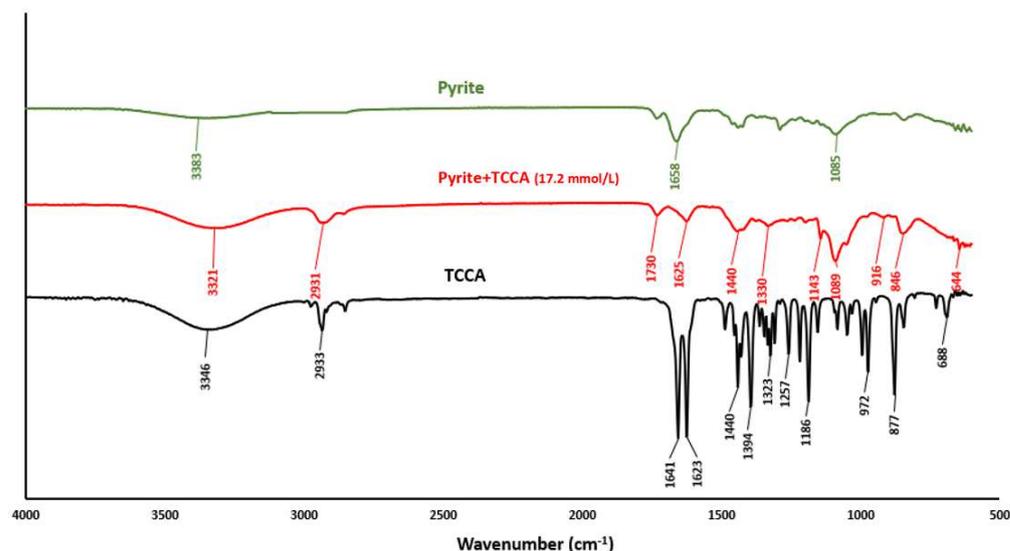
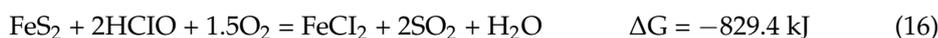
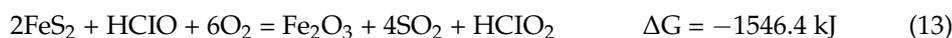
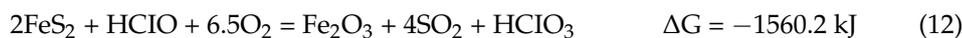


Figure 9. IR spectra of pyrite before and after TCCA treatment.

To determine which of the above reactions are more likely to occur, we performed thermodynamic calculations using a well-known computer program HSC Chemistry 8, which showed the following results: when pyrite is oxidized using HClO and air oxygen, reactions occur very easily (12), (13) and (17), (18). These calculated reactions are confirmed by IR spectroscopic data.



Pyrite oxidation is known as an electrochemical process. The histogram (Figure 10) shows the effect of TCCA concentration on the pyrite redox potential. However, pyrite is inert, and an aqueous solution of pyrite has a low ROP of about 100–130 mV. In the oxidation process, it can be detected only at ROP above 200 mV [4]. The redox potential mainly depends on the activity of iron ions, which means that pyrite will oxidize faster if there is a higher percentage of iron ions in the solution.

The redox potential also changes in the same way as the electrokinetic potential changes, which are shown in Figure 11.

With an increase in the concentration of the TCCA solution, the ROP of the system increases accordingly, leading to greater oxidation of pyrite. The optimal oxidation time of pyrite is 60 min.

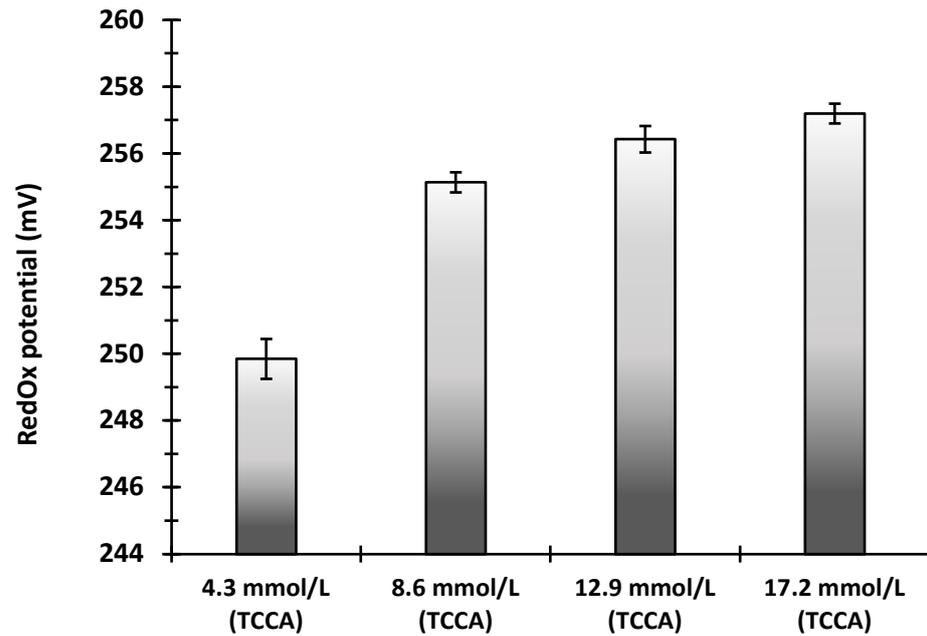


Figure 10. Effect of TCCA concentration on the redox potential of pyrite.

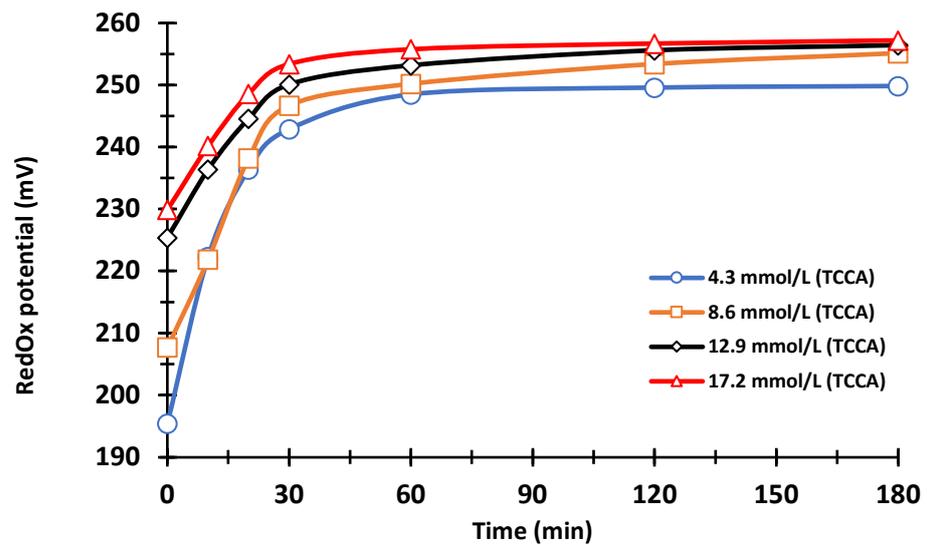


Figure 11. Kinetics of changes in ROP as a function of TCCA concentration.

Thus, the results of studies on the oxidation of pyrite using the TCCA oxidizer show that the products of its hydrolysis oxidize pyrite to produce various iron compounds.

Large-scale laboratory tests on the enrichment of initial gold-containing tailings in a centrifugal separator were carried out according to the scheme shown in Figure 12. The first stage of centrifugal separation was carried out at the initial fineness, then the tailings of the first centrifugal separation were further ground to a fineness of 90–95% less than $-0.05 + 0$ mm (Figure 13).

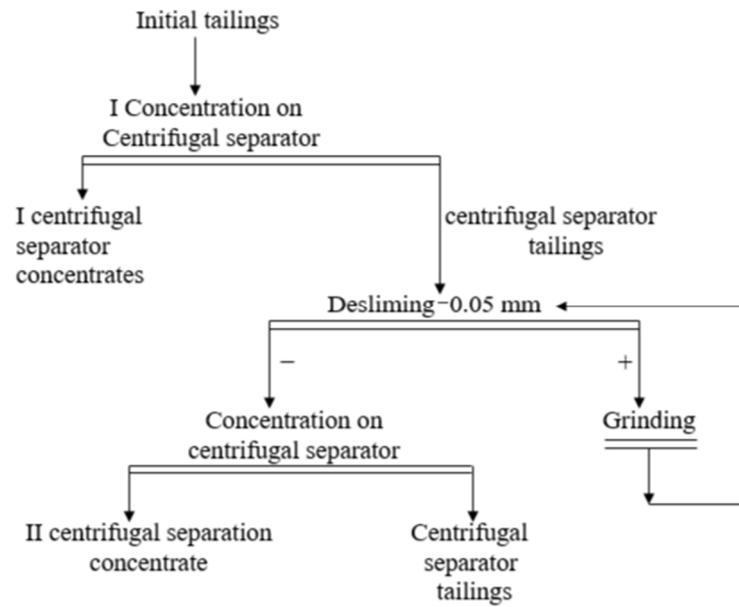


Figure 12. Scheme of enrichment of stale mill tailings using a centrifugal separator.



Figure 13. Knelson KS-MD 3 centrifugal concentrator and the gravitational enrichment process.

Centrifugal separation was carried out at a cone rotation speed of 750 min^{-1} and a turbulizing water flow rate of 6.0 L/min , acceleration of the gravitational fall of 90 G .

The results of stage enrichment of stale tailings on a centrifugal separator Knelson are presented in Table 3.

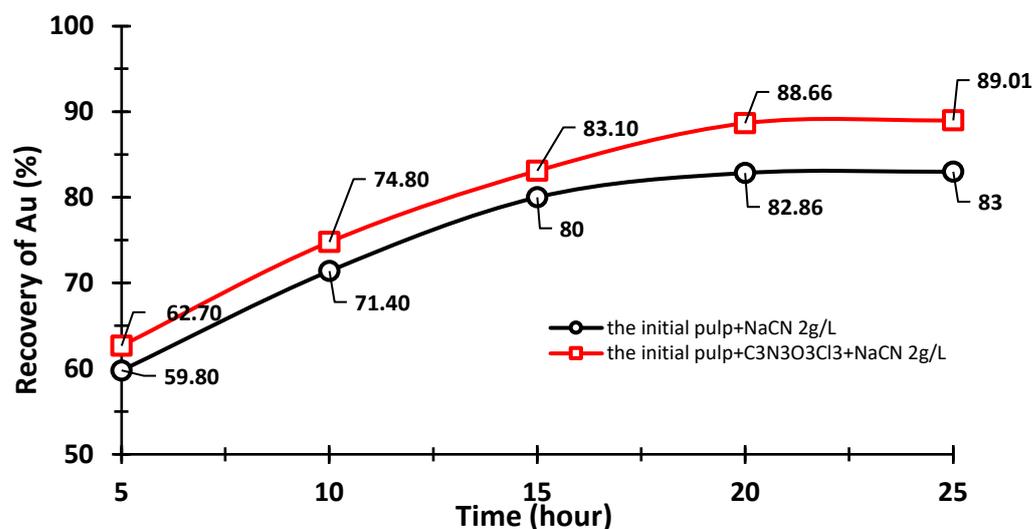
Table 3. Results of stage enrichment of stale tailings in a centrifugal separator.

Products	Yield, %	Gold Content, g/t	Gold Recovery, %
I centrifugal separator concentrates	3.22	17.1	43.33
II centrifugal separation concentrate	3.19	14.8	37.39
Combined ash concentrate	6.41	15.95	80.72
Centrifugal separator tailings	93.61	0.26	19.28
Initial tailings	100.0	1.263	100.0

The results of the experiments show that the enrichment of stale tailings of GRE in a centrifugal separator makes it possible to obtain a combined gold-containing concentrate with a gold content of 15.95 g/t, with a yield of 6.41%. Gold losses with flotation tailings are 19.28%.

Obtaining dump tailings with a gold content of 0.264 g/t is possible according to the enrichment scheme, which includes centrifugal separation, classification according to the fineness class -0.05 mm, additional grinding of hydrocyclone sands to a fineness of 90.0–95.0% of the class finer than -0.05 mm, and control centrifugal separation. The resulting gold-containing concentrate with a gold content of 15.95 g/t is suitable for further processing by the hydrometallurgical method.

Cyanidation of the obtained gold-containing concentrate was preceded by pre-oxidation of sulfides using TCCA for 3 h at a concentration of 2 g/L. The results of leaching the gold-containing concentrate are shown in Figure 14 as a function of the cyanidation time.

**Figure 14.** Dependence of gold extraction into solution on cyanidation time.

From the results obtained, it follows that pretreatment of gold-containing concentrate with an oxidizer TCCA for 3 h before the cyanidation process (20 h) allows for an increase in the recovery of gold in the solution by 5.8%.

In this paper, the oxidation of pyrite in TCCA solution is studied by the redox potential and zeta potential and thermodynamic analysis of the reactions. The results of studies on the oxidation of pyrite using the TCCA oxidizer show that the products of its hydrolysis oxidize pyrite produce various iron compounds and thereby contribute to the intensification of the cyanidation process of gold-containing concentrate.

Sulfate ions in the solution were analyzed by complex titration. A total of 1 g of monomineral was mixed with TCCA (17.2 mmol/L), and then an aliquot was taken and titrated with EDTA. The amount of sulfate ions was 3.22 mmol/L at the initial TCCA. After interaction with monomineral, its amount increased by 16.12 mmol/L, that is, the

presence of 12.90 mmol/L sulfate ions in the total solution is explained by the oxidation of the monomineral surface.

4. Conclusions

The conclusions of this study are as follows:

- Chemical oxidation of pyrite occurs mainly in an acidic and slightly alkaline environment. Pyrite has a high negative charge under alkaline conditions and becomes positively charged at $\text{pH} < 6$. With an increase in pH in neutral and alkaline media, pyrite has a negative electrokinetic potential, varying from zero to -25 mV.
- The results of studies on the oxidation of pyrite using the TCCA oxidizer show that the products of its hydrolysis oxidize pyrite with the formation of various iron compounds on its surface.
- The results of the experiments show that the enrichment of stale tailings of GRF in a centrifugal separator allows you to get a combined gold-containing concentrate with a gold content of 15.95 g/t, with a yield of 6.39%, which, not being conditioned, allows you to cyanide a relatively small mass of it, which as a result reduces the operating costs for processing gold-containing concentrate. Gold recovery in Knelson's concentrate was 80.72%.
- It was found that pretreatment of gold-containing concentrate with TCCA and subsequent leaching in cyanide solutions can increase the recovery of gold in solution by 5.8%.

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References

1. Master Plan for the Development of the Mining and Metallurgical Industry of the Republic of Kazakhstan Until 2030. Available online: <https://kapital.kz/economic/4765/v-rk-razrabotayut-master-plan-razvitiya-gorno-metallurgicheskogo-kompleksa.html> (accessed on 4 December 2023).
2. Kenzhaliyev, B.; Surkova, T.; Yessimova, D.; Baltabekova, Z.; Abikak, Y.; Abdikerim, B.; Dosymbayeva, Z. Extraction of noble metals from pyrite cinders. *Chemengineering* **2023**, *7*, 14. [CrossRef]
3. Toktar, G.; Magomedov, D.R.; Koizhanova, A.K.; Abdyladaev, N.N.; Bakraeva, A.N. Extraction of gold from low-sulfide gold-containing ores by beneficiating method using a pressure generator for pulp microaeration. *Kompleks. Ispol'zovanie Miner. Syr'â/Complex. Use Miner. Resour./Miner. Shikisattardy Keshendi Paid.* **2023**, *325*, 62–71. [CrossRef]
4. Zhang, L.; Jiang, T.; Guo, X.-Y.; Tian, Q.-H.; Zhong, S.-P.; Dong, L.; Qin, H.; Liu, Z.-W.; Makuza, B. Sustainable processing of gold cyanide tailings: Reduction roasting, mechanical activation, non-cyanide leaching, and magnetic separation. *Hydrometallurgy* **2023**, *217*, 106028. [CrossRef]
5. Bragin, V.I.; Burdakova, E.A.; Kondrateva, A.A.; Plotnikova, A.A.; Baksheeva, I.I. Dressability of old gold-containing tailings by flotation. *J. Min. Sci.* **2019**, *54*, 663–670. [CrossRef]
6. Chang, C.S.; Yusoff, A.H.; Mohamed, C.A.R.; Liu, S.F.; Shoparwe, N.F.; Husain, N.A.; Azlan, M.N. Geochemistry of Rare Earth Elements in Pahang River Sediment, Malaysia. *Kompleks. Ispol'zovanie Miner. Syr'â/Complex. Use Miner. Resour./Miner. Shikisattardy Keshendi Paid.* **2024**, *331*, 42–50. [CrossRef]
7. Bantshi, A.M.; Makuise, P. Extraction of gold from sands and slimes tailings dump from Mazowe mine, Zimbabwe. In *Proceedings of the 3rd Pan American Materials Congress*; Springer: Berlin/Heidelberg, Germany, 2017; pp. 507–517. [CrossRef]
8. Chen, Q.; Yang, H.-Y.; Tong, L.-L.; Niu, H.-Q.; Zhang, F.-S.; Chen, G.-M. Research and application of a Knelson concentrator: A review. *Miner. Eng.* **2020**, *152*, 106339. [CrossRef]

9. Guney, A.; Önal, G.; Atmaca, T. New aspect of chromite gravity tailings re-processing. *Miner. Eng.* **2001**, *14*, 1527–1530. [[CrossRef](#)]
10. Sen, S. Gold recovery by KC from grinding circuit of Bergama CIP plant. *Rem. Rev. Esc. Minas* **2010**, *63*, 539–545. [[CrossRef](#)]
11. Uslu, T.; Sahinoglu, E.; Yavuz, M. Desulphurization and deashing of oxidized fine coal by Knelson concentrator. *Fuel Process. Technol.* **2012**, *101*, 94–100. [[CrossRef](#)]
12. Kökkılıç, O.; Langlois, R.; Waters, K.E. A design of experiments investigation into dry separation using a Knelson concentrator. *Miner. Eng.* **2015**, *72*, 73–86. [[CrossRef](#)]
13. Abbruzzese, S.; Ubaldini, F.; Veglio, L.; Toro, L. Preparatory bioleaching to the conventional cyanidation of arsenical gold ores. *Miner. Eng.* **1994**, *7*, 49–60. [[CrossRef](#)]
14. Kenzhaliyev, B.K. Innovative Technologies Providing Enhancement of Non-Ferrous, Precious, Rare and Rare Earth Metals Extraction. *Kompleks. Ispol'zovanie Miner. Syr'â/Complex. Use Miner. Resour./Miner. Shikisattardý Keshendi Paid.* **2019**, *310*, 64–75. [[CrossRef](#)]
15. Lodeyshchikov, V.V. *Technology for Extracting Gold and Silver from Refractory Ores*; OJSC “Irgiredmet”: Irkutsk, Russia, 1999; p. 452.
16. Hapid, A.; Zullaikah, S.; Kawigraha, A.; Sudiyanto, Y.; Nareswari, R.B.; Quitain, A.T. Oxidation of sulfide mineral and metal extraction analysis in the microwave-assisted roasting pretreatment of refractory gold ore. *Arab. J. Chem.* **2024**, *17*, 105447. [[CrossRef](#)]
17. Watling, H. Microbiological Advances in Biohydrometallurgy. *Minerals* **2016**, *6*, 49. [[CrossRef](#)]
18. Fomchenko, N.V.; Muravyov, M.I.; Kondrateva, T.F. Two-stage bacterial–chemical oxidation of refractory gold-containing sulfidic concentrates. *Hydrometallurgy* **2010**, *101*, 28–34. [[CrossRef](#)]
19. Koizhanova, A.K.; Toktar, G.; Banks Craig, E.; Magomedov, D.R.; Kubaizhanov, A.A. Research of hydrometallurgical method of leaching gold from flotation tails with using bio-oxidation. *Kompleks. Ispol'zovanie Miner. Syr'â/Complex. Use Miner. Resour. /Miner. Shikisattardý Keshendi Paid.* **2020**, *314*, 28–39. [[CrossRef](#)]
20. Amaya, D.; Bernal, S.; Garnica, M.; Reslen, R.; Correa, R. Improved roasting of some colombian gold ores. *Rev. Dyna* **2013**, *80*, 70–77.
21. Karimova, L.M.; Oleinikova, T.O.; Mansurov, B.E.; Saganbek, S. Oxidizing roasting and cyanidation for the processing of refractory gold concentrates. *Obogashchenie Rud.* **2023**, *3*, 10–15. [[CrossRef](#)]
22. Boduen, A.; Zalesov, M.; Melamud, V.; Grigorieva, V.; Bulaev, A. Combined Bacterial and Pressure Oxidation for Processing High-Sulfur Refractory Gold Concentrate. *Processes* **2023**, *11*, 3062. [[CrossRef](#)]
23. Johnson, D.B. The Evolution, Current Status, and Future Prospects of Using Biotechnologies in the Mineral Extraction and Metal Recovery Sectors. *Minerals* **2018**, *8*, 343. [[CrossRef](#)]
24. Nestor, D.; Valdivia, U.; Chaves, A.P. Mechanisms of bioleaching of a refractory mineral of gold with *Thiobacillus ferrooxidans*. *Int. J. Miner. Process.* **2001**, *62*, 187–198. [[CrossRef](#)]
25. Van Aswegen, P.C.; Van Niekerk, J.; Olivier, W. The BIOX process for the treatment of refractory gold concentrate. In *Biomining*; Rawlings, D.E., Johnson, B.D., Eds.; Springer: Berlin/Heidelberg, Germany, 2007; pp. 1–35. [[CrossRef](#)]
26. Mahmoud, A.; Cezac, P.; Hoadley, A.F.A.; Contaminea, F.; D'Hugues, P. A review of sulfide minerals microbially assisted leaching in stirred tank reactors. *Int. Biodeterior. Biodegrad.* **2017**, *119*, 118–146. [[CrossRef](#)]
27. Sedelnikova, G.V. Comparison of autoclave and bacterial leaching. *Gold Technol.* **2014**, *2*, 110–115.
28. Soto-Urbe, J.C.; Valenzuela-Garcia, J.L.; Salazar-Campoy, M.M.; Parga-Torres, J.R.; Tiburcio-Munive, G.; Encinas-Romero, M.A.; Vazquez-Vazquez, V.M. Gold extraction from a refractory sulfide concentrate by simultaneous pressure leaching/oxidation. *Minerals* **2023**, *13*, 116. [[CrossRef](#)]
29. Adewuyi, S.O.; Ahmed, H.A.M.; Ahmed, H.M.A. Methods of ore pretreatment for comminution energy reduction. *Minerals* **2020**, *10*, 423. [[CrossRef](#)]
30. Valenzuela, A.; Valenzuela, J.L.; Parga, J.R. Effect of pretreatment of sulfide refractory concentrate with sodium hypochlorite, followed by extraction of gold by pressure cyanidation, on gold removal. *Adv. Chem. Eng. Sci.* **2013**, *3*, 7. [[CrossRef](#)]
31. Feng, F.; Sun, Y.X.; Rui, J.Y.; Yu, L.; Liu, J.M.; Zhang, N.; Zhao, M.X.; Wei, L.W.; Lu, C.S.; Zhao, J.; et al. Study of the “Oxidation-complexation” coordination composite ionic liquid system for dissolving precious metals. *Appl. Sci.* **2020**, *10*, 3625. [[CrossRef](#)]
32. Puvvada, G.V.K.; Murthy, D.S.R. Selective precious metals leaching from a chalcopyrite concentrate using chloride/hypochlorite media. *Hydrometallurgy* **2000**, *58*, 185–191. [[CrossRef](#)]
33. Basu, N.; Maity, S.K.; Chaudhury, A.; Ghosh, R. Trichloroisocyanuric acid (TCCA): an efficient green reagent for activation of thioglycosides toward hydrolysis. *Carbohydr. Res.* **2013**, *369*, 10–13. [[CrossRef](#)]
34. Samusev, A.L.; Tomskaya, E.S. Modern methods for intensifying the process of leaching gold from refractory mineral raw materials. *Min. Inf. Anal. Bull.* **2015**, *8*, 100–105.
35. Teut, A.O.; Kuimov, D.V.; Kosyanov, E.A. Extraction of gold from refractory sulfide ores using the electrochlorination method. In *Proceedings of the New Technologies for Enrichment and Complex Processing of Difficult-to-Enrich Natural and Technogenic Mineral Raw Materials*, Upper Pyshma, Russia, 10 October 2011.
36. Li, S.K.; Gu, G.H.; Qiu, G.Z.; Chen, Z.X. Flotation and electrochemical behaviors of chalcopyrite and pyrite in the presence of N-propyl-N0—Ethoxycarbonyl thiourea. *Trans. Nonferrous Met. Soc. China.* **2018**, *28*, 1241–1247. [[CrossRef](#)]
37. Feng, B.; Feng, Q.; Lu, Y. The effect of lizardite surface characteristics on pyrite flotation. *App. Surf. Sci.* **2012**, *259*, 153–158. [[CrossRef](#)]

-
38. Bicak, O.; Ekmekci, Z.; Bradshaw, D.J.; Harris, P.J. Adsorption of guar gum and CMC on pyrite. *Miner. Eng.* **2007**, *20*, 996–1002. [[CrossRef](#)]
 39. Cheng, W.; Deng, Z.; Tong, X.; Lu, T. Hydrophobic Agglomeration of Fine Pyrite Particles Induced by Flotation Reagents. *Minerals* **2020**, *10*, 801. [[CrossRef](#)]

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