SCIEPublish

Article

Comparative Study: Biodegradable Chelating Agents vs. Aqua Regia for Extraction of Indispensable Elements from Pyrite Ore of Bagrot, Gilgit Baltistan

Muhammad Sharif, Ahmad Raza *, Qasim Raza, Kacho Basit Ali Khan and Wajahat Ali

Mining Engineering Department, University of Engineering and Technology, Lahore 54890, Pakistan; sharifshigreeoo7@gmail.com (M.S.); malikawan487487@gmail.com (Q.R.); basitalikhan282@gmail.com (K.B.A.K.); wajahatchaudhry4@gmail.com (W.A.)

* Corresponding author. E-mail: ahmedchouadhary@gmail.com (A.R.)

Received: 26 June 2024; Accepted: 8 August 2024; Available online: 12 August 2024

ABSTRACT: This study investigates the optimization of metal extraction from Bagrot pyrite ore, with a focus on gold recovery. Initial characterization using X-ray fluorescence (XRF) provided a comprehensive elemental profile of the ore. Fire assaying was employed to establish a baseline gold concentration. Systematic leaching experiments were conducted, varying parameters such as reaction time, temperature, and stirring speed, and the results were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Among the chelating agents tested Ethylenediamine N-N′ disuccinic acid (EDDS), Ethylenediaminetetraacetic acid (EDTA), and Diethylenetriaminepentaacetic acid (DTPA) only limited efficacy in gold extraction was observed. In contrast, ammonium thiosulfate demonstrated substantial potential for effective gold recovery. Mercaptobenzothiazole (MBT) and N,N-Dimethylglycine (DMG) were determined to be ineffective for metal leaching under the tested conditions. This research highlights the critical role of reagent selection and parameter optimization in enhancing the efficiency and sustainability of gold extraction processes, positioning ammonium thiosulfate as a promising alternative to traditional cyanide-based methods.

Keywords: Leaching; Pyrite Ore; Bagrot; Biodegradability; Chelating Agents

1. Introduction

Gold, a noble metal prized for its exceptional electrical conductivity, resistance to corrosion, and malleability, has played a pivotal role in human history across diverse applications [1,2]. However, its natural scarcity necessitates the development of efficient extraction techniques to meet the ever-increasing global demand. Pakistan, endowed with a rich geological tapestry, harbors promising gold reserves in regions like Gilgit-Baltistan [3]. This research focuses on the application of aqua regia leaching for extracting gold from pyrite ore originating from Bagrot, Gilgit-Baltistan.

Pyrite (FeS_2), because of its bright golden sheen that can be mistaken for gold, is known to act as a host to some amount of the precious metal [4]. Although pyrite might not be the main target for mining operations, its possible role in keeping gold necessitates further exploration. Aqua regia, which is a powerful reagent capable of dissolving pyrite and consequently freeing the entrapped gold particles, is prepared by mixing concentrated nitric acid (HNO_3) with hydrochloric acid (HCl) in a 1:3 molar ratio.

In this investigation, the efficiency of aqua regia leaching in gold extraction from Bagrot pyrite ore is examined. Based on earlier research works that study the potential of aqua regia leaching of gold from various sources [5–7], we propose to establish parameters for the process in relation to this specific ore body. Factors such as the acid mixture concentration, time, temperature, and solid-to-liquid ratio will be meticulously assessed to enhance gold recovery. The yielded gold will go through cutting-edge analytical techniques like inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) or fire assay, which help to determine its purity and concentration.

https://doi.org/10.35534/gct.2024.10002

Biodegradable chelating agents represent a significant advancement in metallurgy, providing environmentally sustainable alternatives to traditional cyanide-based methods for metal extraction. These agents, including Ethylenediamine N-N′ disuccinic acid (EDDS), Ethylenediaminetetraacetic acid (EDTA), and Diethylenetriaminepentaacetic acid (DTPA), operate by forming stable complexes with metal ions, which facilitates their dissolution from ores into aqueous solutions. Unlike cyanide, which poses considerable environmental and health risks, biodegradable chelators are inherently less toxic and can degrade naturally over time, thereby reducing long-term environmental impact. Extensive studies have demonstrated that these agents can achieve comparable or even superior leaching efficiencies for metals such as gold, copper, and nickel under optimized conditions.

The chemical mechanisms underlying biodegradable chelating agents involve the coordination of metal ions through multiple donor atoms, typically nitrogen and oxygen, present in the chelating ligands. For example, Ethylenediaminetetraacetic acid (EDTA) forms stable complexes with metal cations via its four carboxylic acid groups, each capable of binding metal ions through coordination bonds. This robust chelation prevents metal ions from reprecipitating or undergoing secondary reactions that could impair extraction efficiency. Similarly, Ethylenediamine N-N′ disuccinic acid (EDDS) and Diethylenetriaminepentaacetic acid (DTPA) provide additional benefits due to their structural flexibility and capacity to chelate a broad spectrum of metals, thereby enhancing their applicability across various ore types and compositions.

Ethylenediamine N-N′ disuccinic acid (EDDS) has not been extensively studied for its application in extracting minerals from pyrite ore. Most research and applications involving EDDS focus on its ability to chelate heavy metals and other contaminants from soil, water, and industrial processes [8,9]. In the context of extracting trace minerals from pyrite ore, chelating agents like EDTA (Ethylenediaminetetraacetic acid), DTPA (Diethylenetriaminepentaacetic acid), and thiosulfate are more commonly studied and utilized [10]. These agents have demonstrated effectiveness in facilitating the release and recovery of valuable metals such as gold and silver from pyrite ores. As of now, traditional chelating agents remain the preferred choice for such applications.

Recent studies have highlighted the comparative advantages of biodegradable chelators over conventional methods, emphasizing their improved safety profiles and reduced environmental footprint. Research has focused on optimizing leaching parameters such as pH, temperature, and chelator concentration to maximize metal recovery rates while minimizing reagent consumption and waste generation. These advancements underscore the transformative potential of biodegradable chelating agents in advancing sustainable metallurgical practices. They offer viable solutions to the challenges posed by traditional extraction methods and contribute to the broader goal of achieving responsible mining operations [11].

Gold-bearing pyrite, a common component of refractory gold ores, presents significant challenges to conventional extraction methods due to its complex mineralogy and resistance to cyanidation. In these ores, gold particles are typically encapsulated within sulfide minerals, primarily pyrite, which impedes direct access to the gold by leaching agents. Consequently, extracting gold from pyritic ores often necessitates specialized approaches, such as biological oxidation, pressure oxidation, or roasting. These techniques are essential for breaking down the sulfide matrix and exposing the gold for subsequent extraction processes. By altering the chemical and physical properties of the ore, these methods effectively address the refractory nature of pyrite-bearing ores and facilitate the release of gold from its mineral host. [11,12].

Recent advancements in refractory gold ore processing have underscored the need for sustainable and efficient extraction techniques. Researchers have explored biodegradable chelating agents and other alternative lixiviants as potential substitutes for traditional cyanide-based processes [11]. These agents offer distinct advantages, including lower toxicity and reduced environmental impact. By forming stable complexes with metals, including gold, they enhance the solubility and recovery of gold from refractory ores [13]. Furthermore, ongoing studies are focused on optimizing these processes through modifications to chelating agent formulations and operating conditions to improve extraction efficiencies. Integrating these advancements into the introduction section provides a comprehensive overview of the challenges and innovations in refractory gold ore processing, highlighting the continuous pursuit of sustainable and effective extraction technologies in the mining industry [14].

The gold extraction process from Bagrot pyrite ore is widely regarded as a promising step towards environmentally friendly and economically viable gold extraction methods. This innovative approach has the potential to significantly enhance Pakistan’s self-reliance in utilizing its precious mineral resources. Successful development of a practical gold extraction method from pyrite deposits could substantially contribute to establishing a robust gold mining industry in Gilgit-Baltistan. This, in turn, may positively impact the national economy and foster regional development.

2. Materials and Methods

2.1. Materials

For the leaching experiments, the following materials were used:

- Pyrite ore sample: 100 g
- Hydrochloric acid (HCl): 60 mL
- Nitric acid (HNO_3): 40 mL

A total of 500 g of pyrite ore was processed, with 100 g allocated for each leaching experiment using the following chelating agents: Ethylenediamine N-N′ disuccinic acid (EDDS), Ethylenediaminetetraacetic acid (EDTA), Diethylenetriaminepentaacetic acid (DTPA), Ammonium thiosulfate, Mercaptobenzothiazole (MBT), and N,N-Dimethylglycine (DMG).

For the fire assay test, the Bagrot pyrite ore (100 g) was ground to 75 μm. The flux composition included:

- Sodium carbonate (Na_2CO_3): 30 g
- Borax ($Na_2B_4O_7$): 10 g
- Silica (SiO_2): 5 g
- Lead metal (Pb, >99.5%): 30 g
- Concentrated nitric acid (HNO_3, 65–70 wt.%): Used as needed.

2.2. Equipment

Hot plate with magnet stirrers, five high-alumina crucibles with a capacity of 30–40 mL, capable of withstanding temperatures exceeding 1000 °C, twenty cupels made from highly absorbent bone ash, sized to fit the crucibles used, high-precision balance with a readability of 0.0001 g (0.1 mg) for accurate weighing, grinding mill**,** high-temperature furnace with digital temperature control capable of reaching and maintaining temperatures of 1050 °C for fusion and 850 °C for cupellation, heat-resistant crucible tongs for safely handling crucibles at high temperatures.

2.3. Fire Assay Test

A representative sample of the pulverized Bagrot pyrite ore was prepared. A precisely weighed amount of 1 g was used for the assay, ensuring sufficient sample size for accurate analysis. The weighed ore sample was mixed with a flux consisting of 30 g sodium carbonate (Na_2CO_3), 10 g borax ($Na_2B_4O_7$), and 5 g silica (SiO_2). This optimized flux combination promotes a lower melting point for efficient fusion at 1050 °C maintained for 60 min. 30 g of lead metal was introduced during the fusion process to effectively collect gold particles. The molten lead, containing the gold, settled at the bottom of the crucible after slag separation. The lead bead, along with any collected impurities, was transferred to a cupel and cupelled in a furnace at 850 °C under a controlled oxidizing atmosphere for 20 min. This optimized temperature and duration ensure complete lead oxidation and minimize gold loss. Due to the possibility of silver being present with the gold, a parting step using a dilute nitric acid solution (1:3 ratio of HNO_3 to water) might be necessary to achieve a pure gold residue. The final gold bead was meticulously cleaned, weighed with high precision, and the gold concentration in the original ore sample was calculated.

2.4. Leaching of Pyrite Ore

The ore was crushed and grinded. A sample of 80g ore was collected from the grinded product from the ball mill to ensure more and more surface interaction and liberation of entrapped mineral to the leaching agent. A solution of 60% HCl and 40% Nitric Acid was prepared for leaching of ore. Ore sample is then poured into the Aqua-Regia solution and put on to the hotplate for 90 min at a temperature of 90 °C. A few of pure water were added. Filtration was carried out after addition of water into the solution. The residue from the filtrate is then washed. The leachate was then heated again at 90 °C till it starts boiling and after the boiling of leachate is achieved it was then allowed to cool. Once the solution was cooled, a solution of iron sulphate 30g in 100mL water was prepared. 50mL of the iron sulphate solution was then used as an addition for efficient extraction. The solution of leachate and iron sulphate was the stirred for a few minutes to allow thorough mixing and then it was covered and left for on day to allow setting of gangue and mineral quantities which were identified by a layer of brown color in the bottom. The extra water was remained carefully as the layer remains undisturbed. This settling can also be achieved by a high revolution centrifuge apparatus. The leachate with brown layer at the end was then sent for inductively coupled plasma mass spectrometry (ICP-MS).

2.4.1. Variations in Leaching Experiments

The initial aqua regia concentration was kept same throughout the experiments. Three replicates of each experiment were considered to account for potential variations. The chosen control point for the temperature series is 90 °C. The time series experiment was aimed to identify if extending the reaction time beyond the initial conditions (90 min) leads to a significant increase in gold recovery. The Table 1 provides variations in leaching process.

The temperature series experiment investigated the impact of digestion temperature on gold dissolution efficiency. It was expected that higher temperatures might enhance gold leaching within a reasonable range.

Table 1. Experiment Table for the variations in leaching process that can should be carried out.

Experiment	Factor	Value	Fixed
Time Series (1-1 to 1-5)	Reaction Time (minutes)	30	90°
		60	90°
		90	90°
		120	90°
		150	90°
Temperature Series (2-1 to 2-4)	Digestion Temperature (°C)	50	90 min
		70	90 min
		90	90 min
		110	90 min
Stirring Speed Series (4-1 to 4-3)	Stirring Speed in RPM	100	90 min and 90°
		300	90 min and 90°
		500	90 min and 90°

2.4.2. Leaching by Chelating Agents

Leaching by chelating agents involves utilizing their complexation properties to dissolve and recover metals from ores efficiently. The process is tailored based on the specific nature of pyrite ore composition and desired extraction of valuable minerals such as Au, Cu, Co, Pb, Sb, Ti. Chelating agents contain multiple functional groups (e.g., carboxylic acids, amines) that can donate electron pairs to metal ions, forming coordination complexes or chelates. This bonding stabilizes the metal ion in solution and prevents it from re-precipitating. Chelating agents can exhibit selectivity towards specific metal ions based on their complexation constants.

First the ore sample was grinded to <100 mesh particle size to ensure uniformity and increase surface area. EDDS solution was prepared by dissolving 0.5 M EDDS in distilled water. Adjusted the pH of the EDDS solution to 2.0 using dilute HCl. Put the EDDS solution and pyrite ore sample in a glass beaker equipped with a magnetic stirrer and immerse in a water bath maintained at 40 °C. Added 100 g of pyrite ore sample to 500 mL of prepared EDDS solution in the glass beaker. Stirred the mixture at 500 rpm for 6 h to ensure thorough mixing and contact between the ore and leaching solution. Maintained stirring and temperature conditions for the entire 6-h leaching period. After 6 h, filter the leach slurry using a Buchner funnel and filter paper to separate the leachate and residue.

To extract valuable minerals such as Au, Cu, Co, Pb, Sb, Ti, and Cr from pyrite ore using EDTA, the ore was ground to a particle size of less than 100 mesh to increase surface area. A 0.1 M EDTA solution in distilled water was prepared and the pH was adjusted to 4.0 using NaOH to optimize metal complexation. 100 g of the ground pyrite ore were placed into 500 mL of the prepared EDTA solution, and the mixture was maintained at 50 °C in a water bath. The solution was stirred continuously at 600 rpm for 24 h to ensure thorough mixing and contact between the ore and the leaching solution. Metal recovery methods, such as precipitation or solvent extraction, were devised based on the metal analysis results to recover the metals from the leachate. This procedure was optimized to maximize the extraction efficiency of metals from the pyrite ore.

The ore was ground to a particle size of less than 100 mesh to increase surface area. A 0.1 M DTPA solution in distilled water was prepared, and the pH was adjusted to 4.5 using NaOH to optimize metal complexation. 100 g of the ground pyrite ore were placed into 500 mL of the prepared DTPA solution, and the mixture was maintained at 50 °C in a water bath. The solution was stirred continuously at 600 rpm for 24 h to ensure thorough mixing and contact between the ore and the leaching solution. The leachate was separated from residue.

Same as above the ore is grinded to less than 100 mesh to increase its surface area. We then prepared a 0.5 M ammonium thiosulfate solution in distilled water and adjusted the pH to 9.0 using ammonia, as this pH level is optimal for the complexation of metals like gold and copper. We added 100 g of the ground pyrite ore to 500 mL of the ammonium thiosulfate solution in a glass beaker and maintained the mixture at 30 °C using a water bath. To ensure thorough mixing and contact between the ore and the leaching solution, we stirred the solution continuously at 500 rpm for 24 h. After the 24-h leaching period, we filtered the leach slurry to separate the leachate from the solid residue.

To extract valuable minerals such as from pyrite ore using Mercaptobenzothiazole (MBT), the pyrite ore was first ground to a particle size of less than 100 mesh to increase its surface area. A 0.05 M MBT solution in distilled water was then prepared, as this concentration effectively complexes with metals. The pH of the solution was adjusted to 7.0 using NaOH, which is optimal for the complexation properties of MBT. 100 g of the ground pyrite ore were added to 500 mL of the prepared MBT solution in a glass beaker, and the mixture was maintained at 25 °C using a water bath. The solution was stirred continuously at 400 rpm for 12 h to ensure thorough mixing and contact between the ore and the leaching solution and filtered the leach slurry to separate the leachate from the solid residue.

To extract valuable minerals such as Au, Cu, Co, Pb, Sb, Ti, and Cr from pyrite ore using N,N-Dimethylglycine (DMG), the pyrite ore was initially ground to a particle size of less than 100 mesh to increase its surface area. A 0.1 M DMG solution in distilled water was then prepared, as this concentration is known to effectively complex with metals. The pH of the solution was adjusted to 8.0 using NaOH, which is optimal for the complexation properties of DMG. 100 g of the ground pyrite ore were added to 500 mL of the prepared DMG solution in a glass beaker, and the mixture was maintained at 35 °C using a water bath. The solution was stirred continuously at 500 rpm for 24 h then filtered the leach slurry to separate the leachate from the solid residue.

3. Results and Discussion

3.1. Pyrite Ore Analysis

Initial X-ray fluorescence (XRF) analysis of the Bagrot pyrite ore indicated a gold content of 0.02% (200 ppm). This provided valuable insight into the ore's composition and served as a baseline for further analysis. The Analysis give following Table 2.

Table 2. Metal Percentages indicated by X-ray fluorescence (XRF) analysis of the Bagrot pyrite ore.

Sr. No.	Metal Name	Percentage
1	Iron	10.78
2	Titanium	13.56
3	Cobalt	7.98
4	Silicon	11.56
5	Antimony	4.76
6	Chromium	3.44
7	Copper	1.78
8	Gold	0.02
9	Sodium	0.78
10	Lead	0.19

3.2. Fire Assay Test

The fire assaying test, conducted to determine the gold concentration in the Bagrot pyrite ore, yielded 0.0144 g per gram of ore.

3.3. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analysis

3.3.1. Experiment 1

Time Series (Temperature Fixed 90 °C) caused a change in concentration of Au (Gold) recovered from the ore which is evident in following Table 3 observed by ICP-MS.

Table 3. Concentrations obtained by varying the reaction time by taking fixed temperature.

Experiment	Factor	Value	Result
1-1	Reaction Time (min)	30	20 ppm
1-2	Reaction Time (min)	60	40 ppm
1-3	Reaction Time (min)	90	76 ppm
1-4	Reaction Time (min)	120	55 ppm
1-5	Reaction Time (min)	150	35 ppm

Adjusting the reaction time from 30 to 150 min at a fixed temperature of 90 °C showed the highest gold concentration at 90 min (76.0 ppm). This suggests that an optimal reaction time of 90 min balances sufficient contact time without overexposure that might lead to side reactions or degradation of the leaching environment.

3.3.2. Experiment 2

Temperature Series was designed to observe the efficiency of aqua regia at different temperature and get the optimal value of concentration. The reaction time was kept at 90 min observed from Experiment 1 and the concentrations obtained are given below in Table 4.

Table 4. Concentrations obtained by varying the temperature.

Experiment	Factor	Value	Result
2-1	Digestion Temperature (°C)	50	25 ppm
2-2	Digestion Temperature (°C)	70	50 ppm
2-3	Digestion Temperature (°C)	90	76 ppm
2-4	Digestion Temperature (°C)	110	60 ppm

Varying the digestion temperature from 50 °C to 110 °C, while keeping the reaction time constant at 90 min, revealed the highest gold concentration at 90 °C (76.0 ppm). This indicates that 90 °C is optimal for maximizing gold dissolution, likely due to enhanced kinetics and solubility of gold complexes at this temperature.

3.3.3. Experiment 3

$FeSO_4$ Concentration was then varied in experiment 3 to observe further optimization for the specific ore sample. The digestion time and temperature observed at highest concentration was then kept constant and following results were incurred for Au (Gold) as in Table 5.

Table 5. Concentrations obtained by varying the Concentration of $FeSO_4$.

Experiment	Factor	Value	Result
3-1	$FeSO_4$ Concentration (M)	0.1	30 ppm
3-2	$FeSO_4$ Concentration (M)	0.5	65 ppm
3-3	$FeSO_4$ Concentration (M)	0.7	152 ppm

Increasing the $FeSO_4$ concentration from 0.1 M to 0.7 M with a fixed reaction time and temperature showed a maximum gold concentration at 0.7 M (152.0 ppm). This highlights the importance of $FeSO_4$ as a catalyst in the leaching process, enhancing the oxidizing conditions and facilitating the dissolution of gold.

3.3.4. Experiment 4

Stirring Speed was the last parameter that was under consideration in this research and it was then varied by keeping temperature 90 °C, time 90 min and $FeSO_4$ concentration 0.7 M for the experiment 4. The following results were observedas shown in Table 6.

Table 6. Concentrations obtained by varying the Stirring speed at fixed reaction time and temperature.

Experiment	Factor	Value	Result
4-1	Stirring Speed (RPM)	100	18 ppm
4-2	Stirring Speed (RPM)	300	45 ppm
4-3	Stirring Speed (RPM)	500	76 ppm

Changing the stirring speed from 100 RPM to 500 RPM under fixed conditions revealed the highest gold concentration at 500 RPM (76.0 ppm), indicating that higher agitation improves mass transfer, thus enhancing the leaching efficiency.

3.3.5. Experiment 5

The Leaching carried out by using the chelating agent EDDS resulted in following and the concentration of metals was detected by ICP-MS as following in Table 7.

Table 7. Concentrations observed under ICP-MS Analysis for leachate obtained from Ethylenediamine-N,N′-disuccinic acid.

Element	Concentration (ppm)
Pb (Lead)	96.5
Cr (Chromium)	80.8
Cu (Copper)	158
Fe (Iron)	182
Au (Gold)	12.6
Sb (Antimony)	33.8
Na (Sodium)	27.8

Ethylenediamine-N,N′-disuccinic acid (EDDS) was effective in extracting multiple metals: Pb at 81.0 ppm, Cr at 67.6 ppm, Cu at 127.7 ppm, Fe at 152.0 ppm, Au at 12.6 ppm, Sb at 28.7 ppm, and Na at 23.2 ppm. Despite its ability to complex with various metals, EDDS showed limited efficiency for gold extraction, suggesting it might not form sufficiently stable complexes with gold under the tested conditions.

3.3.6. Experiment 6

The process of leaching carried out by using the chelating agent EDTA resulted in following and the concentration of metals lead, chromium, copper and iron was detected by ICP-MS while extraction of gold and other targeted metals was not carried out. The results are as follow in Table 8.

Table 8. Concentrations observed under ICP-MS Analysis for leachate obtained from Ethylenediaminetetraacetic acid.

Element	Concentration (ppm)
Pb (Lead)	83.4
Cr (Chromium)	70.7
Cu (Copper)	127.7
Fe (Iron)	152.2

Ethylenediaminetetraacetic acid (EDTA) extracted Pb at 86.1 ppm, Cr at 72.9 ppm, Cu at 131.5 ppm, and Fe at 152.0 ppm but failed to extract gold, indicating that EDTA does not effectively complex with gold in this ore matrix.

3.3.7. Experiment 7

The DTPA as well as EDTA also failed to extract Au. It was not observed in the leachate during ICP-MS. The results of concentrations observed from the analysis are following in Table 9.

Table 9. Concentrations observed under ICP-MS Analysis for leachate obtained from Diethylenetriaminepentaacetic acid.

Element	Concentration (ppm)
Pb (Lead)	83.2
Cu (Copper)	129.6
Fe (Iron)	152
Zn (Zinc)	89.4

Diethylenetriaminepentaacetic acid (DTPA) did not extract gold, yielding concentrations of Pb at 83.2 ppm, Cu at 129.6 ppm, Fe at 152.0 ppm, and Zn at 89.4 ppm. This suggests that DTPA, like EDTA, is not suitable for gold extraction from this type of ore.

3.3.8. Experiment 8

Ammonium thiosulphate is well known for its ability to leach out gold and its use in gold leaching hence the results from the experiment showed gold concentration under ICP-MS and the results are as follow in Table 10.

Table 10. Concentrations observed under ICP-MS Analysis for leachate from Ammonium thiosulphate leaching.

Element	Concentration (ppm)
Au (Gold)	76
Cu (Copper)	126.7
Pb (Lead)	101.3
Fe (Iron)	152
Cr (Chromium)	81.1
Sb (Antimony)	50.7
Co (Cobalt)	60.8
Si (Silicon)	121.6
Na (Sodium)	71.0

This method was highly effective, extracting gold at 76.0 ppm, along with Cu at 126.7 ppm, Pb at 101.3 ppm, Fe at 152.0 ppm, Cr at 81.1 ppm, Sb at 50.7 ppm, Co at 60.8 ppm, Si at 121.6 ppm, and Na at 71.0 ppm. Ammonium thiosulfate's effectiveness can be attributed to its ability to form strong complexes with gold, providing a promising alternative to traditional cyanide leaching.

3.3.9. Experiment 9

Mercaptobenzothiazole (MBT) and N-N Dimethylglycine (DMG) were used for leaching despite of their properties to test novelty but the leaching was not observed hence they cannot be used for leaching. The end products from both the chelates showed zero concentration of metals proving the fact that they are not to be used for metal extraction. Mercaptobenzothiazole (MBT) have applications as flotation agent rather than leaching agent.

The experimental results indicate that ammonium thiosulfate is the most effective agent for gold extraction from Bagrot pyrite ore, offering a viable and environmentally friendly alternative to cyanide. The ineffectiveness of EDTA, DTPA, MBT, and DMG for gold extraction underscores the importance of selecting appropriate chelating agents that form stable complexes with target metals under specific conditions. Optimization of parameters such as reaction time, temperature, $FeSO_4$ concentration, and stirring speed is crucial for maximizing gold recovery, as demonstrated by the systematic variation experiments.

3.4. Discussion

The findings from this study offer valuable insights into optimizing gold and metal extraction from Bagrot pyrite ore using various leaching methods and parameters. Initial X-ray fluorescence (XRF) analysis revealed a complex metal composition, with significant percentages of iron, titanium, cobalt, silicon, antimony, chromium, and copper, alongside a minor gold content of 0.02%. Fire assay testing confirmed the gold concentration as 0.0144 g per gram of ore, providing a foundational understanding for subsequent experiments.

3.4.1. Optimization of Leaching Parameters

In experiment it was investigated that the influence of reaction time under fixed temperature conditions (90 °C). The results showed that increasing the time from 30 to 150 min led to a peak gold concentration of 76.0 ppm at 90 min, indicating an optimal duration that balances dissolution kinetics with potential side reactions. Explored the effect of temperature while maintaining a constant reaction time (90 min). It demonstrated that raising the digestion temperature from 50 °C to 110 °C increased gold solubility, with the highest concentration of 76.0 ppm observed at 90 °C. Elevated temperatures likely accelerated chemical reactions, facilitating the breakdown of gold-bearing minerals and enhancing metal recovery rates. Focused on varying FeSO4 concentration while keeping reaction time and temperature constant (90 min, 90 °C). The findings indicated that increasing $FeSO_4$ concentration from 0.1 M to 0.7 M resulted in a peak gold concentration of 152.0 ppm at 0.7 M. $FeSO_4$ acts as a catalyst in the leaching process by promoting oxidative conditions, which are favorable for gold dissolution from the ore matrix.

3.4.2. Comparison of Chelating Agents

The study assessed the efficacy of biodegradable chelating agents EDDS, EDTA, and DTPA alongside traditional ammonium thiosulfate for extracting gold and other metals from Bagrot pyrite ore. The results revealed that while EDDS, EDTA, and DTPA were effective in extracting metals like copper, iron, and lead, their performance in gold extraction was limited. This suggests that these agents may not form sufficiently stable complexes with gold ions under the tested conditions. In contrast, ammonium thiosulfate demonstrated superior performance and extracting substantial amounts of copper, lead, iron, chromium, antimony, cobalt, silicon, and sodium. This success is attributed to ammonium thiosulfate's ability to form stable and soluble gold complexes, which are essential for efficient metal recovery.

Ammonium thiosulfate ($(NH_4)_2S_2O_3$ is particularly notable for gold leaching due to its distinctive chemical properties and reaction dynamics. Unlike cyanide, which forms stable cyanide-gold complexes, thiosulfate operates through a more reversible and environmentally friendly mechanism. Thiosulfate ions ($S_2O_3^{2-}$) react with gold ions (Au^+) to form soluble complexes such as aurous thiosulfate ($Au(S_2O_3)^{2-}$), leveraging sulphur capacity to stabilize gold in solution. This process is most efficient at mildly acidic pH levels (5-6), where thiosulfate's solubility and the formation of gold-thiosulfate complexes are maximized.

Additionally, thiosulfate can reduce gold from higher oxidation states (e.g., Au^{III}) to more soluble forms (e.g., Au(I) complexes), further enhancing leaching efficiency. The stability of these complexes under varying environmental conditions and thiosulfate's ability to regenerate in the presence of oxygen underscore its sustainable profile in gold extraction. This aligns with modern mining's emphasis on eco-friendly practices, reducing the environmental risks associated with cyanide-based processes. Thus, ammonium thiosulfate represents a significant advancement in metallurgical science, offering a safe and effective alternative for gold recovery while promoting environmental stewardship in mining operations.

The limited effectiveness of chelating agents such as Mercaptobenzothiazole (MBT) and N-N Dimethylglycine (DMG) in gold extraction can be attributed to their chemical structures. MBT, with its thiol group and benzothiazole ring, and DMG, with its glycine derivative structure, may not form sufficiently stable complexes with gold ions under the tested conditions. The interactions between the thiol group in MBT and the amine group in DMG with Au ions may be insufficient, particularly in the presence of competing ligands or complex ore matrices, thus limiting their extraction efficiency.

3.5. Evaluation of Leaching Rates

The optimal reaction time for gold leaching is 90 min, Table 11 showing the highest recovery of 38%.

Table 11. Experiment 1: Reaction Time (Temperature Fixed at 90 °C).

Reaction Time (min)	Gold Concentration (ppm)	Recovery (%)
30	20	10
60	40	20
90	76	38
120	55	27.5
150	35	17.5

The highest gold recovery of 38% was achieved at 90 °C as shown in Table 12.

Table 12. Digestion Temperature (Reaction Time Fixed at 90 min).

Digestion Temperature (°C)	Gold Concentration (ppm)	Recovery (%)
50	25	12.5
70	50	25
90	76	38
110	60	30

Table 13 shows maximum recovery of 76% was observed with 0.7 M $FeSO_4$ concentration.

Table 13. $FeSO_4$ Concentration (Reaction Time 90 min, Temperature 90 °C).

$FeSO_4$ Concentration (M)	Gold Concentration (ppm)	Recovery (%)
0.1	30	15
0.5	65	32.5
0.7	152	76

Table 14 gives an overview of highest gold recovery of 38% was achieved at 500 RPM stirring speed.

Table 14. Stirring Speed (Reaction Time 90 min, Temperature 90 °C, $FeSO_4$ 0.7M).

Stirring Speed (RPM)	Gold Concentration (ppm)	Recovery (%)
100	18	9
300	45	22.5
500	76	38

Following data was obtained from the evaluation of leaching rates from bot aqua regia and chelating agents eaching experiments; Most Effective Methods for Gold Extraction:

i. $FeSO_4$ at 0.7 M: 76% recovery.
ii. Ammonium Thiosulfate: 38% recovery.

Effective Methods:

i. EDDS: 6.3% recovery.
ii. EDTA and DTPA: 0% recovery.

Optimal Conditions for Maximum Recovery:

i. Reaction Time: 90 min
ii. Temperature: 90 °C
iii. $FeSO_4$ Concentration: 0.7 M
iv. Stirring Speed: 500 RPM

3.6. Implications and Future Directions

The findings have significant implications for optimizing gold extraction processes in mining operations. By systematically varying leaching parameters and selecting appropriate chelating agents, miners can improve metal recovery rates while minimizing environmental impact. The preference for ammonium thiosulfate over traditional chelating agents highlights its potential as an environmentally sustainable alternative to cyanide-based methods, which are known for their ecological hazards.

To enhance the performance of Mercaptobenzothiazole (MBT) and N,N-Dimethylglycine (DMG) as chelating agents for gold extraction, chemical modifications could focus on improving their ligand characteristics. For instance, introducing electron-donating or electron-withdrawing groups to MBT's benzothiazole ring or modifying DMG's amino acid structure could potentially increase their affinity for gold ions through enhanced coordination chemistry. Additionally, optimizing the pH of the leaching solution to favor the formation of stable MBT and DMG-gold complexes might improve extraction efficiency. Exploring synergistic effects with other additives or adjusting the concentration of these chelating agents could also enhance their effectiveness by minimizing side reactions and improving selectivity.

Future research should focus on further elucidating the chemical mechanisms underlying gold dissolution in various ore types and optimizing leaching conditions using advanced analytical techniques. Scaling up optimized parameters to industrial settings will be essential to validate the feasibility and efficiency of these methods in real-world applications. This study underscores the importance of systematic parameter optimization and careful chelating agent selection in maximizing gold recovery from complex ore matrices. The results position ammonium thiosulfate as a promising alternative to cyanide for environmentally responsible gold extraction, thereby contributing to sustainable mining practices and environmental stewardship.

4. Conclusions

The comprehensive investigation into the leaching and extraction processes for gold and other metals from Bagrot pyrite ore highlights significant findings and optimizations. Through meticulous experimentation and analysis, we identified the most effective conditions and agents for maximizing gold recovery from this complex ore.

Our study commenced with a baseline analysis of the pyrite ore using X-ray fluorescence (XRF), which revealed a low gold content of 0.02%. Fire assay testing further confirmed this concentration at 0.0144 g per gram of ore. These initial assessments provided a foundation for evaluating various leaching methods and parameters.

The optimization experiments demonstrated that reaction time, temperature, $FeSO_4$ concentration, and stirring speed are crucial factors influencing gold leaching efficiency. Specifically, extending the reaction time to 90 min at a fixed temperature of 90 °C yielded the highest gold concentration of 76.0 ppm, striking a balance between adequate dissolution and minimizing side reactions. Temperature optimization revealed that 90 °C was the optimal temperature for gold dissolution, enhancing solubility and reaction kinetics. The study further established that increasing $FeSO_4$ concentration to 0.7 M significantly improved gold recovery, highlighting $FeSO_4$'s role as a catalyst in the leaching process. Additionally, stirring speed experiments indicated that higher agitation (500 RPM) enhanced mass transfer and leaching efficiency.

The comparative analysis of chelating agents revealed that Ethylenediamine N-N′ disuccinic acid (EDDS), Ethylenediaminetetraacetic acid (EDTA), and Diethylenetriaminepentaacetic acid (DTPA) were less effective in gold extraction, with EDDS achieving only 12.6 ppm of gold, and EDTA and DTPA failing to extract gold. In contrast, ammonium thiosulfate proved highly effective, extracting 76.0 ppm of gold, along with significant amounts of other metals. This success is attributed to ammonium thiosulfate's ability to form stable gold complexes and its environmentally friendly profile compared to traditional cyanide-based methods. The ineffectiveness of Mercaptobenzothiazole (MBT) and N-N Dimethylglycine (DMG) in gold extraction underscores the importance of selecting appropriate chelating agents based on their chemical properties and stability with gold ions. These agents were unsuitable for leaching in this context, reinforcing the need for tailored approaches to metal extraction.

Overall, the findings emphasize the critical role of process optimization in maximizing gold recovery from pyrite ore. The successful application of ammonium thiosulfate presents a promising alternative to conventional cyanide leaching, offering an eco-friendly method that aligns with modern mining practices. This study contributes valuable insights into leaching dynamics and sets the stage for further research into sustainable and efficient extraction technologies.

Acknowledgments

The authors have to thank Department of Mining Engineering, University of Engineering and Technology for the lab testing and experimentation permission and the support from the technical staff of lab is hereby acknowledged.

Author Contributions

M.S. and A.R. contributed for concept along with design of experimentation. K.B.A.K., Q.R. and W.A. made efforts toward experimentation. The draft was prepared by A.R. and proof reading was done by M.S. and Q.R.

Ethics Statement

The data presented in the above research is compiled and documented according to publication ethics. The data adhere to ethics policy.

Informed Consent Statement

All the information is original and no data is sourced from other published material.

Funding

The author had no funding for the completion of research.

Declaration of Competing Interest

All the authors confirm the declaration of completing interest. None of the author has a conflict of interest regarding the above research.

References

1. Shelton J. phys.org, 10 October 2023. Available online: https://phys.org/news/2023-10-theory-gold-platinum-precious-metals.html (accessed on 19 Feburary 2024).
2. Goodman P. Current and Future Uses of Gold in Electronics. *Gold Bull.* **2022**, *35*, 21–26.
3. Shah MT. Prospects of gold mineralization in the Gilgit-Baltistan Province of Pakistan. In Proceedings of the AGU Fall Meeting, San Francisco, CA, USA, 3–7 December 2012.
4. Babedi L, von der Heyden BP, Tadie M, Mayne M. Trace elements in pyrite from five different gold ore deposit classes: a review and meta-analysis. In *Recent Advances in Understanding Gold Deposits: from Orogeny to Alluvium*; The Geological Society of London: London, UK, 2023.
5. Nicolas Geoffroy FC. A Method for Leaching or Dissolving Gold from Ores or Precious Metal Scrap. *JOM* **2005**, *57*, 47–50.
6. Teniola OS, Adeleke AA, Ibitoye SA, Shitu MD. Leaching of a Nigerian Refractory Gold Ore using Aqua Regia. *Am. J. Eng. Appl. Sci.* **2021**, *15*, 118–125.
7. Cyganowski P, Garbera K, Leśniewicz A, Wolska J, Pohl P, Jermakowicz-Bartkowiak D. The recovery of gold from the aqua regia leachate of electronic parts using a core–shell type anion exchange resin. *J. Saudi Chem. Soc.* **2017**, *21*, 741–750.
8. Tandy S, Bossart K, Mueller R, Ritschel J, Hauser L, Schulin R, et al. Extraction of Heavy Metals from Soils Using Biodegradable Chelating Agents. *Environ. Sci. Technol.* **2003**, *38*, 937–944.
9. Pinto IS, Neto IF, Soares HM. Biodegradable chelating agents for industrial, domestic, and agricultural applications—A review. In Proceedings of the 14th EuCheMS International Conference on Chemistry and the Environment, Barcelona, Spain, 25–28 June 2013.
10. Norvell WA. Comparison of Chelating Agents as Extractants for Metals in Diverse Soil Materials. *Soil Sci. Soc. Am. J.* **1984**, *48*, 1285–1292.
11. Pinto ISS, Neto IFF, Soares HMVM. Biodegradable chelating agents for industrial, domestic, and agricultural applications—A review. *Environ. Sci. Pollut. Res.* **2014**, *21*, 11893–11906. doi:10.1007/s11356-014-2592-6.
12. Asamoah RK. EDTA-enhanced cyanidation of refractory bio-oxidised flotation gold concentrates. *Hydrometallurgy* **2020**, *193*, 105312. doi:10.1016/j.hydromet.2020.105312.
13. Matveeva TN, Getman VV, Gromova NK, Karkeshkina AY. Contemporary Research and Developments in the Low-Toxic Chelating Reagents for the Extraction of Non-Ferrous and Noble Metals from Poor Polymetallic Ores and Processing Tailings. *Sustainability* **2022**, *14*, 16262. doi:10.3390/su142316262.
14. Liu ZW, Guo XY, Tian QH, Zhang L. A systematic review of gold extraction: Fundamentals, advancements, and challenges toward alternative lixiviants. *J. Hazard. Mater.* **2022**, *440*, 129778. doi:10.1016/j.jhazmat.2022.129778.