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Thiosystem leach processes for precious metal ores and concentrates: a review

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Abstract

The reserves of precious metals are limited, and the availability of high grade and easy to process ores is rapidly decreasing. It therefore becomes an absolute necessity to shift to alternative processing techniques that are cheaper and more environmentally friendly. Thiosystems leaching of precious metals is being proposed as a possible alternative to leaching with cyanide. The thio-techniques have advantages over traditional leaching, such as reduced hindrance from foreign cations and lower harmful effects on the environment. However, these techniques exhibit relatively high reagent utilisation in the extraction of precious metals, and this limits their industrial application. It is therefore imperative to understand the nature of decomposition reactions of these reagents under practical leaching conditions in order to reduce their consumption and encourage their use in industry. On that account, this paper reviews the thiosystem leach processes for precious metal ores and concentrates, drawing parallels with thiosystem gold leaching processes.

Keywords

Gold, leaching, thiosystem, low-grade deposits, PGMs

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Introduction

The traditional leaching technique for the extraction of most valuable or precious metals including platinum group metals (PGMs) for over 100 years is cyanidation. This owes to its affordability, robustness and high leaching efficiencies, as proven during gold extraction. There has been, however, a significant shift from leaching with traditional reagents to alternative lixiviants such as thiourea, thiosulphate and thiocyanate mainly because of the toxicity of the prevailing cyanide technique. Also, these alternative lixiviants have promising high dissolution rates, which may consequently result in reduced capital expenditure and energy requirements due to the reduced size of leaching tanks.[1] Gold forms many compounds with these alternative lixiviants although some of them are still yet to be tested on an industrial scale. The aim of the review is therefore to provide a clear picture of precious metals leaching using the aforementioned lixiviants, and where no information is available on PGMs and silver, the gold leaching process will be discussed. The paper also includes future development trends for thiosystem leach processes.

Valuable metals such as platinum (Pt), gold (Au) and silver (Ag) are highly valuable and widely used in many industrial applications owing to exceptional properties such as catalytic behaviour, conductivity of electricity and resistance to corrosion. They are mainly used in catalysis and manufacture of electronic components and this utilises over 90% of the valuable metals. Precious metals are highly demanded in the manufacturing of jewellery because of their colour and beauty.[2] PGMs are the mainly used in catalysis in the automobile industry, refining of oil and pharmacy consumables.[3]

The thiosulphate process is a potential non-toxic alternative to conventional cyanidation that presents undesirable environmental and safety aspects. This is due to the fact that thiosulphate leaching allows for a decreasing impedance from foreign cations and thus reduce adverse effects to the environment. Thiosulphate solution solubilises precious metals, forming stable complexes over an extended range of pH and Eh values. The disintegration of oxides of iron, silicates, silica and carbonates, which are unwanted minerals in ores of precious metals, is hindered by the presence of ammonia in thiosystems. It has been shown that in thiosulphate leaching processes, copper (II) ions are essential for the oxidation of metals in solution. However,

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successful commercialisation of thiosulphate leaching system has not been successful owing to the high consumption of thiosulphate and the intricate chemistry of the leaching process, as a result of the occurrence of ammonia and thiosulphate which are complexing ligands, thiosulphate stability in solution, and the reduction- oxidation of the Cu(II)–Cu(I) couple.[4]

Gold generally forms cationic complexes as it dissolves in acidic thiourea solutions. Thiourea extraction/ leaching can be carried out in a media that is acidic, an important feature that enables the use of oxidising salts such as soluble ferric salts.[5,6] The extraction under acidic conditions is very fast, and up to 99% leaching of gold at pH 1.4 of the solution is feasible in 10 to 15 min.[7] A solution pH of between 1 and 2 and Fe^{3+} and Tu concentrations of 0.2% and 0.1 to 1% respectively is required under practical leaching conditions of gold.[8] In addition, research has shown that thiourea can form leachable compounds with both palladium and platinum.[9–12] Despite all this, the thiourea leaching of precious metals has not been clearly established in industry, mainly due to the excessive reagent consumption owing to its rapid decomposition.

Thiocyanate has been proven an alternative lixiviant to gold extraction and can extract valuable metals in solutions with pH less than 7.[13,14] Kriek[15] showed that platinum and palladium can form complexes with thiocyanate ions in solution. Hamáček and Havel[16] also proved that Pt and Palladium (Pd) and platinum (Pt) thiocyanate compounds are more stable than chloro-complexes, indicating that thiocyanate can be a potential lixiviant for PGMs. In a case where no data from thiocyanate lixiviant experiments is available, a plot of Pt in different oxidation states and a plot of log Pd in different oxidation states are used to approximate Pd and Pt values[17]

In view of limited, concise studies on the application and mechanisms of these alternative lixiviants in the leaching of valuable metals, in particular PGMs, this research seeks to piece together concepts from the available literature on the subject in order to highlight the opportunities and challenges in a bid to encourage more research work in the use of the alternative lixiviants, in particular the thiosystem leaching processes.[3]

Thiosystem leaching processes

Thiosystem leaching reagents include thiocyanate (SCN-), thiourea ($CS(NH_2)_2$) and thiosulphate ($Na_2S_2O_3$). The thiosystems form stable complexes with precious metals, mainly gold, which have been shown to be sufficiently stable. The success of thiosystems in the gold leaching presents a great potential in the leaching of PGMs, as it is most likely that similar mechanisms will be at play, drawing from the parallel of cyanide leaching of gold and PGMs.

Thiosystem leaching principles and mechanisms will be discussed with reference to gold leaching due to the lack of similar information on the leaching of PGMs. The conventional cyanidation technique for gold extraction has been investigated to a great extent and successfully implemented an industrial scale for more than 100 years. The extraction of gold using cyanide has been the favoured technique, although there is need for pretreatment of refractory ores mainly because of the relatively good recovery rates, reduced operating costs and easiness of the technique. However, the process has some drawbacks, such uneconomic consumption of reagents,[8] retarded oxygen solubility in water resulting in poor reaction kinetics and environmental issues.[18] As a result, this has stirred up interest among researchers to find alternative leaching agents with lower toxicity, improved economics, that pose less adverse effects to the environment, that can be successfully applied to complex ores, in addition to increased leaching rates. Thiosystem leaching reagents have emerged as a potential alternative to cyanide as these reagents meet most of the desired attributes. They have reduced adverse effects on the environment as compared to the cyanidation. An added advantage in the application of these reagents is that the extraction technique can be successfully carried out in solution pH below 7, hence the applicability of soluble ferric salts and copper chloride as oxidising compounds.[19]

Despite all this, Figure 1 shows that the thiosystem leaching reagents have high oxidising potentials. This consequently leads to increased consumption of reagents due to oxidation of the reagents. There is therefore a need to carefully monitor leaching conditions.

Thiourea ($Cs(NH_2)_2$) leach processes

Gold extraction using thiourea as a lixiviant is a promising alternative leaching technique to the conventional cyanidation process because of reduced adverse effects to the environment, increased extraction rates and the purportedly reduced impedance from base metals compared to the cyanidation process.[8]

Figure 2 shows the basic flowsheet of thiourea leaching system for gold dissolution. The overall process reaction is given by equation (1), and ferrous ion (Fe^{3+}) is employed as an oxidising agent to attain the oxidative extraction of gold with thiourea as a lixiviant.

$$Au + 2CS(NH_2)_2 + Fe^{+3} \rightarrow Au\ [CS(NH_2)_2]^{2+} + Fe^{+2} \quad (1)$$

In practice, the thiourea leaching process of gold is performed at Thiourea solution concentrations of 0.13 M (10 glL), ferrous ion concentrations of between 0 and 9×10^{-2} M (0 to 5 glL), pH less than 2 and potential values between 400 and 450 mV (SHE)are ideal for practical operating conditions. Oxidative decomposition of thiourea into formamidine disulphide ($NH_2(NH)CSSC(NH)NH_2$) can occur at elevated potentials which disintegrates into elemental sulphur (S^o) and cyanamide (NH_2CN). Thiourea also disintegrates into hydrogen sulphide (H_2S) and urea (NH_2CONH_2) by acid hydrolysis. Unwanted species during gold leaching are elemental sulphur and hydrogen, as both species are believed to limit extraction by surface inactivation and H_2S causes gold precipitation.[8] Figure 3

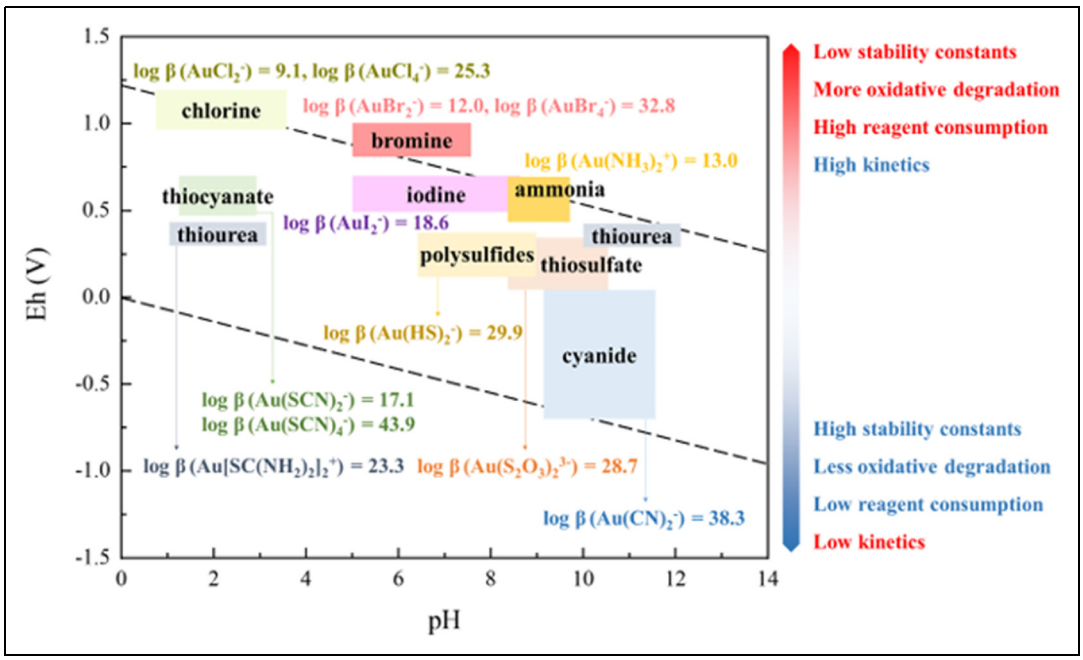

Figure 1. Alternative gold leaching solutions Eh- pH diagram.[41]

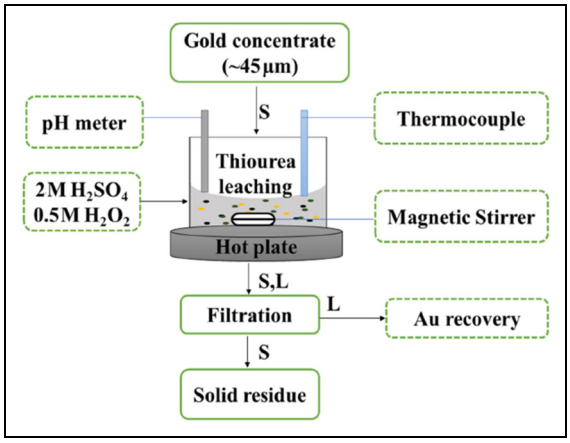

Figure 2. Flowsheet of Thiourea leaching process.[17]

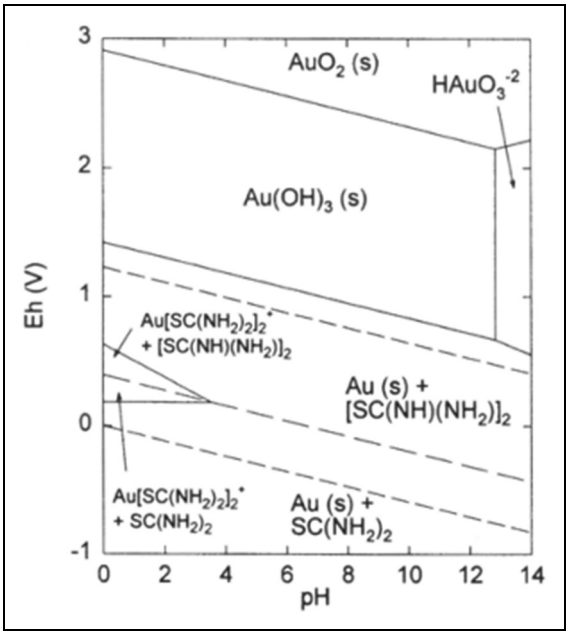

Figure 3. Au- thiourea-H_20 process Eh- pH diagram at 25°C.[19]

is the Eh-pH diagram for the Au-thiourea-H_20 system at an average temperature of 25°C, an assumed activity of 10.5 for all disintegrated gold compounds and activity of 1.5 × 10.1 for formamidine disulphide and thiourea.[20]

Although thiourea (TU) is a potential alternative lixiviant for extraction of valuable metals due to reduced adverse effects to the environment compared to cyanide, its high consumption significantly limits its industrial application. Research work done thus far has established that the uneconomic consumption of thiourea during extraction is caused by oxidation disintegration by the oxidants and attachment of mineral elements from the source materials. However, the disintegration phenomena of the thiourea by mineral elements have not been proven experimentally. The main challenge for researchers therefore remains to limit the disintegration of the lixiviant for increased availability of the compounds critical for extraction. A study carried out to determine how the presence of pyrite affects the stability of the thiourea lixiviant process for refractory gold extraction showed that an increase in pyrite concentration greatly reduces the stability of the thiourea extraction process with 0.3 g/L addition of pyrite resulting in 96% disintegration of thiourea. It was concluded from the investigations that sulphides, such as arsenopyrite and pyrite, should be removed from complex gold ores for increased gold extraction and reduced price of the reagents.[21]

Oxalate and citrate can be utilised as additives to increase thiourea extraction of gold from a gold ore. Results of

research work showed that in the presence of the additives, thiourea consumption is lowered significantly whilst increasing gold extraction to levels that match the cyanidation technique. This owes to the ability of the additives to form compounds that can combine with the ferrous (Fe^{3+}) ion resulting in $Fe(ox)+/Fe(ox)^{2-}$ and $Fe_2(cit)_2(OH)_2^{2-}$ compounds that significantly reduces the solution potential and stabilises the ferrous ion, hence lowering uptake of thiourea. The research therefore provided a platform for the use of additives such as citrate to improve the thiourea extraction process and can be further improved to enhance gold extraction from complex ores. However, further research work needs to be done for verification of the applicability of the leaching technology on other precious metals, such as PGMs.[22]

Other researchers have recommended the use of water or diluted acid solutions for washing and the presence of stabilising agents like cysteine, SO_2, Na_2SO_3, and $Na_2S_2O_5$ for improved gold leaching kinetics and economic consumption of the thiourea lixiviant.[23]

Toxicity and environmental issues associated with thiourea. Researchers have contradicting views on thiourea toxicity, with some suggesting that thiourea has low acute toxicity as it has been scientifically proven to be a carcinogen for rats and in other cases fish. However, thiourea has been employed for a number of years in thyroid disease control and is therefore considered to be non-cancer causing in humans.[5] Kuzugudenli and Kantar[24] on the other hand indicated that the lixiviant is a potential thyroid poison for humans, and considered as potentially cancer causing where exposure is expected and is therefore a harmful lixiviant.

Thiosulphate ($Na_2S_2O_3$) leach processes

Thiosulphate leaching has been widely recommended for precious metals extraction as a substitute to the cyanide leaching technique because of minimal toxic effects to the environment. It has reduced corrosive effect to processing equipment, cost effectiveness (ammonium thiosulphate is cheaper compared to sodium cyanide, US$ 130/tonne ammonium thiosulphate vs. US$1 800/tonne sodium cyanide) and required specificity.[4,25–30] In addition, $S_2O_3^{2-}$ successfully combines with Pd^{2+} and Pt^{2+} resulting in compounds of $Pd(S2O3)_4^{6-}$ and $Pt(S2O3)_4^{6-}$, making it a potential extractant of PGMs.[31,32]

Nevertheless, very little or no information on the thiosulphate leaching processes of PGMs is available. This review is therefore aimed at provoking more research and focus on adopting thiosulphate leaching processes for PGMs leaching in industry.

The occurrence of compounds such as thiosulphate, ammonia and the Cu^{2+}/Cu^{+} reduction- oxidation couple in the form of ligands and the possible thiosulphate disintegration behaviour that results in build-up of extra products of sulphur for example tetrathionate makes the chemistry of the ammonia-thiosulphate system very complicated. Equation (2) represents the reduction-oxidation reaction of the cuprous-cupric compound in the ammonia reaction solution.[33]

$$Cu(NH_3)_4^{2+} + 3S_20_3^{2-} + e^- = Cu(S_20_3)_5^- + 4NH_3 \quad (2)$$

This results in oxidative dissolution and complex ion formation in thiosulphate extraction of valuable metals. Figure 4 is a schematic representation of the catalysed reaction of thiosulphate extraction with copper ions present as oxidising agents.[33–35]

Equation (3) shows the important role played by the ions of copper that occur as tetraamine complex, in the oxidative reaction of gold from the metal to the gold ions.

$$Au + 5S_20_{2-} + Cu(NH_3)_4^{2+} = Au(S_20_3)_{3-} + 4NH_3 + Cu(S_20_3)_3^{5-} \quad (3)$$

Gold solubilises as a stable anionic complex in solutions of ammonia thiosulphate and gold extraction occurs at relatively high dissolution rates.[36,37] Figure 5 shows the tendency of thiosulfate to decompose in ammoniacal solution into intermediate products, such as $S_4O_6^{2-}$, $S_3O_6^{2-}$, and SO_3^{2-}.

Gold, palladium and lead Eh-pH illustrations in NH_3–$S_2O_3^{2-}$–water media are represented in Figures 6–8 modified using Microsoft Word from.[38]

As indicated in Figures 6–8, thermodynamic data shows that palladium and gold is successfully extracted in ammonia thiosulphate solutions. Figure 6(a) indicates that the most occurring compounds of gold in solutions with pH greater than 7 are $Au(NH_3)^{2+}$ or $Au(S_2O_3)_2^{3-}$ and this is in agreement with the data shown in the Eh-pH illustration of Au-Ammonia-$S_2O_3^{2-}$water media in literature.[39]

Although research has shown that thiosulphate extraction is a feasible replacement to cyanide extraction, its commercial application is limited due to the uneconomic use of the lixiviant and the challenges faced in adsorption of the precious metals from the leach liquor. This necessitates the need for continued research since the lixiviant is not stable, and it can disintegrate or reduce to S^0, S^-, and $S_3^{-2}S_2^{3-}$. The compounds accumulate on metal surface, reducing its disintegration. Also, in the absence of Cu(II) ions and ammonia the reaction kinetics are slow.[40]

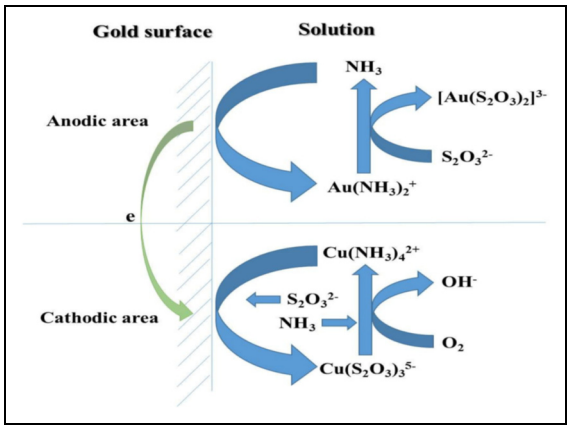

Figure 4. Schematic diagram of the catalysed reaction route of thiosulphate extraction.[35]

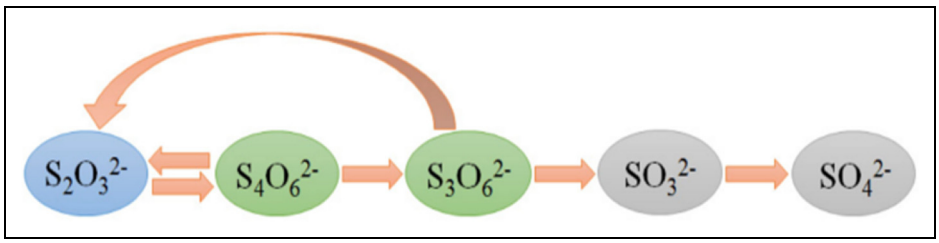

Figure 5. Simplified route of thiosulphate decomposition.[35]

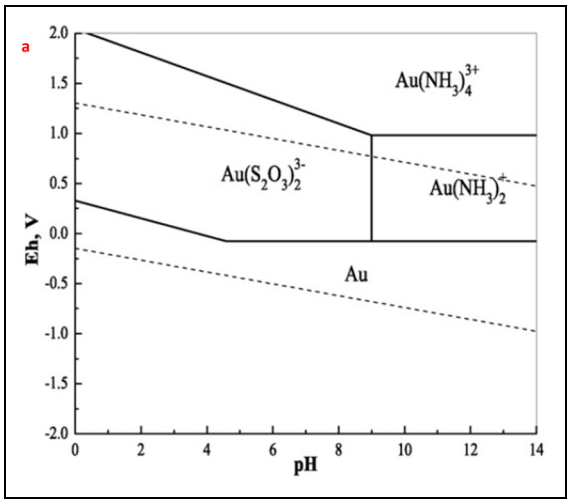

Figure 6. Eh-pH illustration for Gold–Ammonia–$S_2O_3^{2-}$–water media.[38]

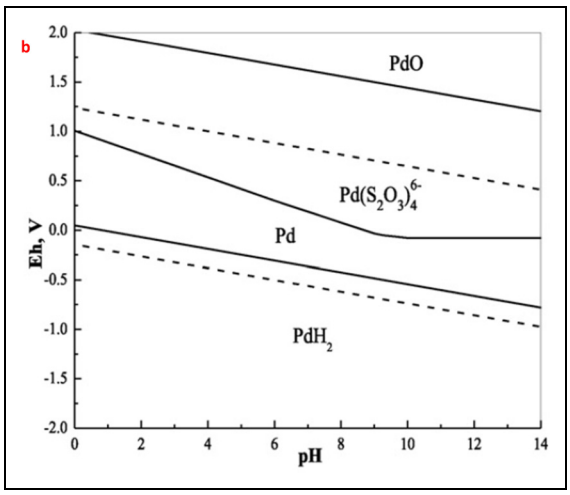

Figure 7. Eh-pH illustration for Pd–Ammonia–$S_2O_3^{2-}$ water media.[38]

A study conducted on ammoniacal thiosulphate extraction of oxidised sulphide concentrate of gold under pressure showed that high Au extraction (89%) can be achieved in 6 h with thiosulphate solution concentration of 0.2 M, ammonia (NH_3) solution concentration of 0.2 M and Cu solution concentration of 0.1 g/L. Leaching experiments results showed that gold concentrate oxidised under pressure was successfully extracted in ammonia thiosulphate lixiviant with reduced consumption of the reagent. The research also proves that the uneconomic use of the lixiviant during extraction that has hindered commercial application can be reduced by extraction of oxidised sulphide concentrates of gold under pressure. Reduced lixiviant uptake is also a good indication that it can be re-used after gold recovery and solid–liquid separation process.[4]

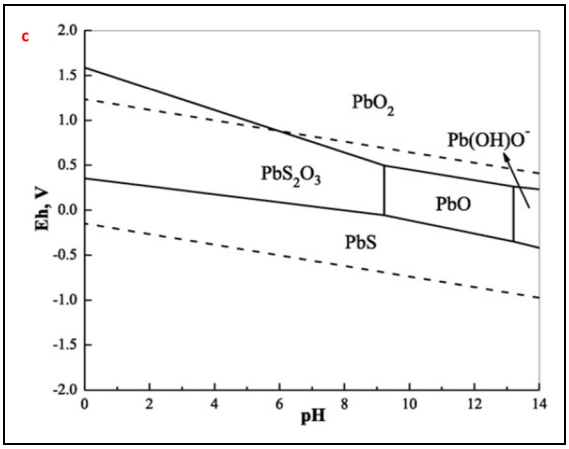

Figure 8. Eh-pH illustration for Pb–Ammonia–$S_2O_3^{2-}$ water media.[38]

Barrick Gold Corporation developed a commercial thiosulfate system free of ammonia at the Goldstrike, Nevada, United States of America. It was however discovered that the accumulation of sulphur due to the decomposition of thiosulphate on the surface of gold inactivates gold dissolution. This results in reduced gold dissolution and high reagent consumption. Changes in ore feed are necessary to ensure thiosulphate system stability.[41]

Toxicity and environmental issues associated with Thiosulphate. Thiosulphate is used to reduce the poisonous effects of arsenic and cyanide. The lixiviant is also used in the treatment of ringworm which is a skin disease caused by parasites.[42] The application of ammonium thiosulphate as a fertiliser has been successfully carried out for more than 100 years in soils that have low sulphur content. The useful application as a fertiliser and reduced adverse effects to the environment results in thiosulphate having distinct advantages over the conventional cyanidation technique.

Thiocyanate (SCN) leach processes

Thiocyanate leaching of gold has been studied fairly extensively.[13,43–48] Figure 9 is a graphical representation of the gold thiocyanate leaching system.

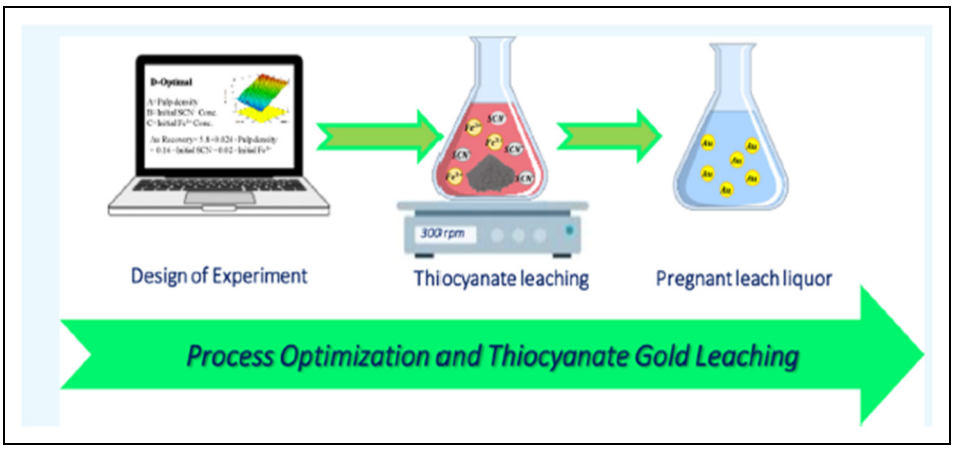

Figure 9. An illustration of gold leaching using thiocyanate.[13]

The lixiviant thiocyanate is thermodynamically unstable and can be oxidised when applied during leaching and oxidation with the potentials necessary for gold extraction as shown by equations (4) and (5).[49]

$$Au + 2SCN^- + Fe^{3+} = Au(SCN)_2^- + Fe^{2+} \quad (4)$$

$$Au + 4SCN^- + 3Fe^{3+} = Au(SCN)_4^- + 3Fe^{2+} \quad (5)$$

The intermediates, trithiocyanate $(SCN)_3$ and thiocyanogen $(SCN)_2$ are also not thermodynamaically stable as their hydrolysed during extraction. Cyanic acid (HCN) that is produced when ammonium ions and carbonate are hydrolysed is stable thermodynamically under the gold extraction potentials.[13,49,50]

Ferric sulphate is employed as an oxidising agent for gold extraction in acidic thiocyanate solution. As expected, oxidation of thiocyanate by ferrous ion occurs in thiocyanate solutions with pH lower than 7, in a scenario that thiocyanate oxidation half-cell potential is lower than the half-cell potentials values given. Also, a value of 0.44 V or 0.68 V is expected as the standard potential for the Fe (III)–SCN/Fe (II)–SCN compound given a reaction between the ferric/ferrous ion and thiocyanate and taking into account the ferric–SCN compound chosen.[49]

Figure 10 shows the Eh-pH illustration for the Gold-Thiocyanate-Water reaction at a temperature of 25°C, with an assumed activity of 10^{-5} for gold species in solution and thiocyanate activity of 10^{-1}.

The conclusion by researchers that oxidative decomposition of thiocyanate by ferrous ion is the highest contributing factor in the uneconomic use of the lixiviant is therefore not surprising. Nevertheless, not many researchers have looked at the reduction oxidation reaction rates for thiocyanate and ferric ion couple. John[51] have carried out laboratory test works and availed experimental results for the thiocyanate and ferric ion reaction but the mechanism of oxidative decomposition of thiocyanate using ferrous ions is not yet clear. Previous researchers[6,44] observed a decrease in the gold extraction rate and dissolution potential of thiocyanate–ferric sulphate solution under pH conditions less than 7 with increasing reaction time. It is assumed that

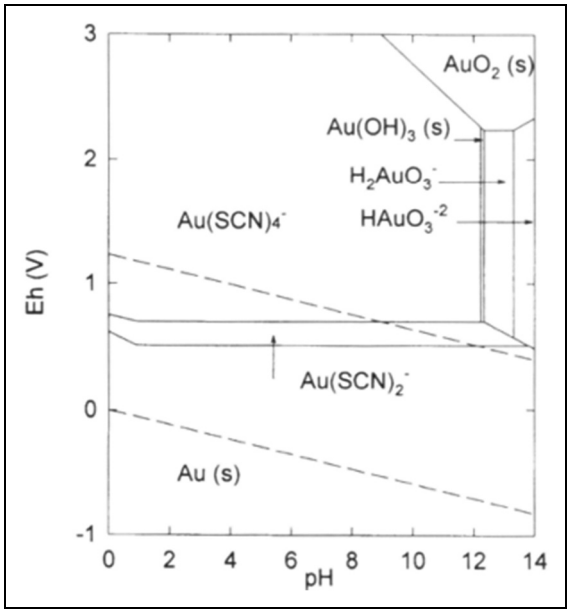

Figure 10. Gold-Thiocyanate-Water reaction Eh- pH illustration at 25°C.[19]

this this trend is originating from the chemical composition of the solution and the formation of compounds between the ferrous ion and thiocyanate and also the accumulation of ferric ion as a result of oxidation reduction reaction of the reagents.

Thiocyanate is one of the lixiviants that has been proposed as a substitute to cyanide in gold extraction although a lot of research work still needs to be done. It has reduced adverse effects to the environment compared to cyanide and presents very good leaching kinetics.[52]

The major obstacle in the commercialisation of the thiocyanate gold extraction technique is the high oxidation -reduction potential than the one necessary for the gold cyanidation technique. In contrast with the need to lower the reduction- oxidation potential by eliminating oxidising agents in the adsorption of gold from the leach liquor, ferrous oxidising ion is needed in gold extraction. Molarity ratio which should lie between 2 and 20 oxidising

agents to lixiviant is crucial in the oxidation behaviour of gold. Gold extraction with thiocyanate is a chemical reaction that is electrochemically controlled under acidic conditions between pH 1.5 and 2.5 and a potential of 600–700 mV. An interesting observation of the process is that soluble ferrous ion, an oxidant can be utilised in the technique since it is thermodynamically stable at pH conditions less than 7. Thiocyanate therefore deserves special attention as a promising substitute for cyanidation at industrial levels. Research has also proved economic use of the reagent compared to other thiosystem reagents. It has also been substantiated that thiocyanate is more stable than thiourea.[53]

Li et al.[54] proposed a new MnO_2-assisted thiocyanate extraction method as a substitute to the conventional cyanidation technique. The complex gold sample was pre-treated by roasting and assayed 54.4 g/t gold with the dominant mineral compounds being quartz and iron oxide. As part of the new system, gold extraction in terms of association of gold with other minerals, thermodynamic behaviour, extraction kinetics and optimum operating conditions was studied utilising cyclic extraction protocols. Extraction conditions that were determined in the experiments carried out were 1.20 mol/L thiocyanate solution, 4.00 mmol/L manganese oxide, pH of 1.00, 4 mL/g liquid-to-solid ratio, and 24 h extraction time, achieving 94.8% extraction of gold. Gold extraction of 99.4% from the leach liquor was successfully attained through precipitation of zinc. A cyclic process together with addition of lixiviant to reduce reagent use achieved reduced lixiviant consumption of 75% without compromising gold extraction kinetics. The results lead to the conclusion that this novel gold extraction process can achieve the desired recovery rates economically and can be applied in processing of complex gold ores under acidic conditions.[54]

Toxicity and environmental issues associated with Thiocyanate. The stability of thiocyanate in an acidic environment makes it a promising substitute to the conventional cyanidation technique in the extraction of valuable metals. Thiocyanate toxicity needs to be considered when looking at its potential use in extraction. Research has shown that the lixiviant occurs naturally and exists as an unharmful compound in food products. Natural foods that contain thiocyanate include beets, cabbage, cauliflower and milk. The Cruciferae family of plants is an important source of the lixiviant in animal foods.[50]

In mammals, the adverse effects of the lixiviant is considerably reduced, as it has been proven scientifically that an adult needs to take in a substantial amount of the lixiviant in the form of potassium thiocyanate for it to be considered poisonous. Also, the lixiviant is a lot less harmful than the conventional cyanide reagent and more easily handled for test animals, as shown by the safety health and environment data sheets. The lixiviant can be degraded by microorganisms commonly found in land and water. However, further research is needed in a bid to develop the thiocyanate lixiviant system for valuable metals, in particular PGMs extraction, to meet the environmental regulations and successful commercialisation of the process.[50,55]

Summary

The substitution of the conventional cyanidation technique with thiosystem leaching reagents is possible if limitations such as consumption of large amounts of reagents and thermodynamically unstable behaviour are addressed. Researchers need to be more innovative and come up with acid resistant equipment that is relatively cheap in order to encourage industry to adopt the reagents which have proved to be environmentally sustainable compared to cyanide.

Future development trends for Thiosystem leach processes

Despite the research interest on thiosystem leaching reagents most of the lixiviants are still under development

Table 1. A summary of the advantages and disadvantages of thiosystem leach processes highlighting their toxicity.

Thiosystem reagent	Advantages	Disadvantages
Thiourea	Fast leaching kinetics lasting between 4 and 6 h. Limited amount of ions that interfer with the extraction process. The lixiviant can be successfully employed to treat refractory ores.	The reagent is not economic due to consumption of large amounts during extraction. The process is capital intensive as equipment resistant to corrosion is required. It is a potential cancer causing lixiviant.
Thiocyanate	Reasonably high extraction rate.	Thiocyanate is not stable thermodynamically, it readily oxidises to ammonium, carbonates and sulfates. Relatively high consumption of lixiviant. Considerably less harmful than the conventional cyanide reagent and more easily handled for test animals. Corrosion resistant equipment required.
Thiosulfate	The lixiviant is environmentally friendly and fairly priced. Fast leaching kinetics and can take 5 to 10 h. Extraction occurs at non-acidic conditions. Effective in treatment of complex ores.	Can be easily oxidized in the presence of oxidizing agents and there is high reagent consumption. Recovery of precious metals from leach liquor is not easy.

and this has affected commercialisation of the reagents. Research done thus far has shown that the system is complicated and unsteady. There is need therefore to come up with robust process flow sheets for the processing of precious metals, novel thiosystem processes that present minimal reagent degradation, recycling of reagents, control of impurities that can be applied to a broad range of precious metals ores and research on additives and oxidants that discourage passivation in gold processing. Also, disposal of wastes in an environmentally sustainable manner should be considered during design. Advanced technologies such as stirred leaching, pressure and high temperature autoclave leaching should be considered focussing on practical applications and fundamental aspects to promote the complete dissolution of the metals. Table 1 shows the toxicity effects of thiourea, thiocyanate and thiosulphate leaching systems.

Conclusion

In the recent years, there has been a lot of research on alternative leaching systems for precious metal extraction from ores and concentrates. Thiosystem leaching approaches that include thiosulphate, thiourea and thiocyanate have been considered. This review has highlighted the information deficient spaces that warrant further research. The areas include kinetics of the thiosystem-PGMs lixiviant system, high reagent consumption and stability of thiosystem reagents. Thiosulphate as a leaching reagent is nontoxic and fairly priced. Despite higher recovery rates that can be attained by thiosulphate extraction of gold, its major drawback is the uneconomic consumption of lixiviants, resulting in high operating costs. Thiourea extraction of gold has also gained momentum because of its high gold extraction rates, reduced cost and reduced environmental impact as compared to cyanide. However, it is unfortunate to note that practical application of thiourea extraction of gold and PGMs leaching systems has not gained enough attention, therefore further research is crucial. The thiocyanate leaching process's toxicity is much less than that of cyanide. However, the leaching process has some potential problems, such as high reagent consumption, a disadvantage that should be compared to the advantage of potential reuse of the lixiviant from the spent leach liquor. This shows that continued research on the thiocyanate extraction process is essential as an interesting substitute system for the recovery of precious metals, in particular PGMs.

In conclusion, the thiosystem leaching processes of gold and, in rare cases, PGMs reported in the literature have shown that the leaching processes have not been adopted industrially mainly due to high reagent consumption. Continued research is therefore required on leaching under low reagent concentrations. While challenges still remain to be overcome, in order for the thiosystem leaching reagents to meet three crucial categories for an effective substitute lixiviant: reduced price, reduced adverse effects, and potential for commercialisation. Research on these reagents should be encouraged, as the thiosystem leaching approaches have significant extraction efficiencies and reduced harmful effects to the environment in the leaching of gold, PGMs and other precious metals from their ores and concentrates.

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References

1. Syed S. Recovery of gold from secondary sources—A review. *Hydrometallurgy* 2012; 115-116: 30–51.
2. Otsuki A, Chen Y and Zhao Y. Characterisation and beneficiation of complex ores for sustainable use of mineral resources: refractory gold ore beneficiation as an example. *Soc Mater Eng Resour Jpn* 2014; 20: 126–135.
3. Ding Y, Zhang S, Liu B, et al. Recovery of precious metals from electronic waste and spent catalysts: a review. *Resour Conserv Recycl* 2019; 141: 284–298.
4. Lampinen M, Laari A and Turunen I. Ammoniacal thiosulfate leaching of pressure oxidized sulfide gold concentrate with low reagent consumption. *Hydrometallurgy* 2015; 151: 1–9.
5. Li J and Miller JD. A review of gold leaching in acid thiourea solutions. *Miner Process Extr Metall Rev* 2006; 27: 177–214.
6. Munoz G and Miller J. Noncyanide leaching of an auriferous pyrite ore from Ecuador. *Min Metall Explor* 2000; 17: 198–204.
7. Prasad M, Mensah-Biney R and Pizarro R. Modern trends in gold processing—overview. *Miner Eng* 1991; 4: 1257–1277.
8. Sparrow GJ and Woodcock JT. Cyanide and other lixiviant leaching systems for gold with some practical applications. *Miner Process Extr Metall Rev* 1995; 14: 193–247.
9. Dunne R, Levier M, Acar S, et al. Keynote address: Newmont's contribution to gold technology. In: *World gold conference*, p.221, 2009.
10. Green B, Smit DMC, Maumela H, et al. Leaching and recovery of platinum group metals from UG-2 concentrates. *J South Afr Inst Min Metall* 2004; 104: 323–331.
11. Schoeman E, Bradshaw S, Akdogan G, et al. The recovery of platinum, palladium, and gold from a cyanide heap solution, with use of ion exchange resins. In: *Proceedings of The 5th International Platinum Conference "A Catalyst for Change"*. The South African Institute of Mining & Metallurgy, pp.729–742, 2013.

12. Tatarnikov A, Sokolskaya I, Shneerson YM, et al. Treatment of platinum flotation products. *Platinum Met Rev* 2004; 48: 125–132.
13. Azizitorghabeh A, Mahandra H, Ramsay J, et al. Gold leaching from an oxide ore using thiocyanate as a lixiviant: process optimization and kinetics. *ACS Omega* 2021; 6: 17183–17193.
14. Li J, Wan R, LeVier K, et al. Thiocyanate process chemistry for gold recovery. In: Young CA, Taylor PR, Anderson CG, Choi Y (eds) *Hydrometallurgy 2008, Proceedings of the sixth international symposium, Phoenix, AZ, USA*, pp.824–836, 2008.
15. Kriek R. Leaching of selected PGMs: a thermodynamic and electrochemical study employing less aggressive lixiviants. *Thesis*, 2008.
16. Hamáček J and Havel J. Determination of platinum (II, IV) and palladium (II) as thiocyanate complexes by capillary zone electrophoresis: analysis of carboplatin and similar drugs. *J Chromatogr A* 1999; 834: 321–327.
17. Munganyinka JP, Habinshuti JB, Komadja GC, et al. Optimization of gold dissolution parameters in acidified thiourea leaching solution with hydrogen peroxide as an oxidant: implications of roasting pretreatment technology. *Metals* 2022; 12. doi:10.3390/met12101567
18. Kroschwitz JI, Howe-Grant M, Kirk RE, et al. *Encyclopedia of chemical technology*. Repository Universitas Perintis Indonesia: John Wiley & Sons, 1996.
19. Muñoz GA and Miller JD. Noncyanide leaching of an auriferous pyrite ore from Ecuado. *Miner Metall Process* 2000; 17: 198–204.
20. Lacoste-Bouchet P, Deschênes G and Ghali E. Thiourea leaching of a copper-gold ore using statistical design. *Hydrometallurgy* 1998; 47: 189–203.
21. Qin H, Guo X-Y, Tian Q-H, et al. Recovery of gold from refractory gold ores: effect of pyrite on the stability of the thiourea leaching system. *Int J Miner Metall Mater* 2021; 28: 956–964.
22. Li K, Li Q, Zhang Y, et al. Improved thiourea leaching of gold from a gold ore using additives. *Hydrometallurgy* 2023; 222. doi:10.1016/j.hydromet.2023.106204
23. Ahmed MR, Mohammed HS, El-Feky MG, et al. Gold leaching using thiourea from uranium tailing material, gabal el-missikat, central eastern desert, Egypt. *J Sustainable Metall* 2020; 6: 599–611.
24. Kuzugudenli ÖE and Kantar Ç. Alternates to gold recovery by cyanide leaching. *Erciyes Üniversitesi Fen Bilimleri Enstitüsü Dergisi* 1999; 15: 119–127.
25. Aazami M, Lapidus G and Azadeh A. The effect of solution parameters on the thiosulfate leaching of Zarshouran refractory gold ore. *Int J Miner Process* 2014; 131: 43–50.
26. Puente-Siller D, Fuentes-Aceituno J and Nava-Alonso F. A kinetic–thermodynamic study of silver leaching in thiosulfate–copper–ammonia–EDTA solutions. *Hydrometallurgy* 2013; 134: 124–131.
27. Wang J, Faraji F, Ramsay J, et al. A review of biocyanidation as a sustainable route for gold recovery from primary and secondary low-grade resources. *J Cleaner Prod* 2021; 296. doi:10.1016/j.jclepro.2021.126457
28. Xu B, Yang Y, Li Q, et al. Stage leaching of a complex polymetallic sulfide concentrate: focus on the extraction of Ag and Au. *Hydrometallurgy* 2016; 159: 87–94.
29. Yang Y-B, Zhang X, Bin X, et al. Effect of arsenopyrite on thiosulfate leaching of gold. *Trans Nonferrous Met Soc China* 2015; 25: 3454–3460.
30. Yu H, Zi F, Hu X, et al. The copper–ethanediamine–thiosulphate leaching of gold ore containing limonite with cetyltrimethyl ammonium bromide as the synergist. *Hydrometallurgy* 2014; 150: 178–183.
31. Mpinga C, Eksteen J, Aldrich C, et al. Direct leach approaches to platinum group metal (PGM) ores and concentrates: a review. *Minerals Engineering* 2015; 78: 93–113.
32. Zhang S. *Oxidation of refractory gold concentrates and simultaneous dissolution of gold in aerated alkaline solutions*. Doctoral Dissertation, Extactive Metallurgy, Murdoch University, Western Australia, 2004.
33. Abbruzzese C, Fornari P, Massidda R, et al. Thiosulphate leaching for gold hydrometallurgy. *Hydrometallurgy* 1995; 39: 265–276.
34. Mohamed HMA. Improved recovery of gold and silver from thiosulfate solution on activated carbon in presence of ammonium persulfate. *Physicochem Probl Miner Process* 2019; 5: 1271–1285.
35. Xu B, Kong W, Li Q, et al. A review of thiosulfate leaching of gold: focus on thiosulfate consumption and gold recovery from pregnant solution. *Metals* 2017; 7. doi:10.3390/met7060222
36. Seisko S, Lampinen M, Aromaa J, et al. Kinetics and mechanisms of gold dissolution by ferric chloride leaching. *Miner Eng* 2018; 115: 131–141.
37. Birich A, Stopic S and Friedrich B. Kinetic investigation and dissolution behavior of cyanide alternative gold leaching reagents. *Sci Rep* 2019; 9: 7191.
38. Xu B, Yang Y, Li Q, et al. Thiosulfate leaching of Au, Ag and Pd from a high Sn, Pb and Sb bearing decopperized anode slime. *Hydrometallurgy* 2016; 164: 278–287.
39. Xia C. *Associated sulfide minerals in thiosulfate leaching of gold: problems and solutions*. Doctoral thesis, Department of Mining, Queen's University, Kingston Ontario Canada, 2008.
40. Roldán-Contreras E, Salinas-Rodríguez E, Hernández-Ávila J, et al. Leaching of Silver and Gold Contained in a Sedimentary Ore, Using Sodium Thiosulfate; A Preliminary Kinetic Study. *Metals* 2020; 10. doi:10.3390/met10020159
41. Aylmore MG. Alternative lixiviants to cyanide for leaching gold ores. In: *Gold Ore Processing*, pp.447–484, 2016.
42. Muir DM and Aylmore MG. Thiosulfate leaching of gold–a review. *Miner Eng* 2000; 14: 135–174.
43. Barbosa O and Monhemius A. Thermochemistry of thiocyanate systems for leaching gold and silver ores. In: *Precious Metals'89*, pp.307–339, 1989.
44. Barbosa-Filho O and Monhemius AJ. Leaching of gold in thiocyanate solutions -Part 3: rates and mechanism of gold dissolution. *Trans Inst Min Metall Sect C* 1994; 103: C117–C125.
45. Barbosa-Filho O and Monhemius A. Leaching of gold in thiocyanate solutions. Pt. 1: chemistry and thermodynamics. *Trans Inst Min Metall Sect C Miner Process Extr Metall* 1994; 103: C105.
46. Barbosa-Filho O and Monhemius A. Iodide—thiocyanate leaching system for gold. In: *Hydrometallurgy'94: Papers presented at the international symposium 'Hydrometallurgy'94' organized by the Institution of Mining and Metallurgy and the Society of Chemical Industry, and held in Cambridge, England, from 11 to 15 July, 1994*. Springer, pp.425–440, 1994.
47. Broadhurst J and Du Perez J. A thermodynamic study of the dissolution of gold in an acidic aqueous thiocyanate medium using iron (III) sulphate as an oxidant. *Hydrometallurgy* 1993; 32: 317–344.

48. Fleming C. A process for the simultaneous recovery of gold and uranium from South African ores. In: *Gold 100: proceedings of the international conference on gold. V. 2*, 1986.
49. Li J, Safarzadeh MS, Moats MS, et al. Thiocyanate hydrometallurgy for the recovery of goldPart III: thiocyanate stability. *Hydrometallurgy* 2012; 113-114: 19–24.
50. Li J, Safarzadeh MS, Moats MS, et al. Thiocyanate hydrometallurgy for the recovery of gold. Part V: process alternatives for solution concentration and purification. *Hydrometallurgy* 2012; 113-114: 31–38.
51. Monhemius J and Barbosa-Filho O. Leaching of gold in thiocyanate solutions -Part 2: redox process in iron (III)-thiocyanate solutions. *Trans. Inst. Min. Metall., Sect. C* 1994; 103: C111–C116.
52. Azizitorghabeh A, Wang J, Ramsay JA, et al. A review of thiocyanate gold leaching – Chemistry, thermodynamics, kinetics and processing. *Miner Eng* 2021; 160: 106689.
53. Azizitorghabeh A, Wang J, Ramsay JA, et al. A review of thiocyanate gold leaching – Chemistry, thermodynamics, kinetics and processing. *Miner Eng* 2021; 160. doi:10.1016/j.mineng.2020.106689
54. Li W, Liu B, Wu J, et al. Gold recovery from roasted refractory gold concentrate through cyclic extraction using MnO2-assisted thiocyanate leaching and cementation with zinc powder. *Hydrometallurgy* 2024; 228. doi:10.1016/j.hydromet.2024.106359
55. Oulego P, Collado S, Garrido L, et al. Wet oxidation of real coke wastewater containing high thiocyanate concentration. *J Environ Manage* 2013; 132C: 16–23.