

UNIVERSIDADE FEDERAL DE MINAS GERAIS

Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas

Dissertação de Mestrado

**“Lixiviação de Minério Oxidado de Ouro-Cobre  
com Tiosulfato de Amônio”**

Aluno: Cláudio Duque Araki

Orientadores: Virgínia Sampaio Teixeira Ciminelli  
Lino Rodrigues de Freitas

Maio/2004

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Cláudio Duque Araki

*LIXIVIAÇÃO DE MINÉRIO OXIDADO DE OURO-COBRE COM TIOSSULFATO DE  
AMÔNIO*

Dissertação de Mestrado apresentada ao Curso de Pós-Graduação em Engenharia Metalúrgica  
e de Minas da Universidade Federal de Minas Gerais

Área de Concentração: Tecnologia Mineral  
Orientadores: Virgínia Sampaio Teixeira Ciminelli  
Lino Rodrigues de Freitas

Belo Horizonte  
Escola de Engenharia da UFMG  
2004

*Aos meus pais, Norio e Laura*

## ***Agradecimentos***

De 2001 a 2004 eu tive o privilégio de cursar um dos mais bem conceituados cursos de pós-graduação que existem, e ainda sob a orientação da Virgínia Ciminelli e do Lino Freitas! Meus orientadores me proporcionaram uma oportunidade realmente única e muito rica, por isso eu agradeço muito, todos os seus esforços, conselhos, motivação e críticas. Também devo ao Professor Afonso Martins muitos bons conselhos e o contato inicial com meus orientadores.

Nesse período ainda tive a oportunidade de conviver e de contar com pessoas maravilhosas e geniais que me acolheram no grupo e dividiram comigo seus conhecimentos e experiências. Sem o apoio da Ilda, do João e da Cláudia eu não teria conseguido nem montar todo o aparato necessário para realizar os ensaios. Olívia, Sandro e Madalena, se não fosse por eles eu estaria até hoje pensando entre ensaios e análises, sem contar a metodologia de titulação de tiosulfato, que foi praticamente uma criação do Laboratório de Análises Químicas. Nelson, Christina e Cida, muito obrigado pelo apoio e pelas esticadas nos prazos para a entrega de documentos. Também agradeço muito a colaboração e o companheirismo dos colegas Eleonora, Mônica, Ana Cláudia, Luciana, Flávia, Henrique, Flávio, Paula, Anderson, Raquel, Fabiana, Valéria, Bocão, Buzanfa, Ricardo, Maurrem e Grazielle.

Por estarem sempre ao meu lado, pelo incentivo e pela inspiração, agradeço especialmente aos meus pais, Norio e Laura. Agradeço aos meus irmãos, Flávia, Rodrigo e Ana, por me aturarem e também o nosso amigo Jackson Lessa, que nos tornou fluentes em inglês. Priscila, obrigado por me dar motivação sempre que eu precisei. Arthur e Bárbara, muito obrigado pela mão, pé, braço e ombros que vocês me deram quando eu não dispunha dos meus próprios membros.

Agradeço também à Capes, à Companhia Vale do Rio Doce e todos que fizeram parte das equipes das minas do Igarapé Bahia, Almas e Caeté – especialmente ao Edson Cintho, Adilson, Cida, Antônio Celso, Cleon, Otoniel, Evilmar, Hildegundes, Marcus Galvão, Cláudio Coimbra e Coré – e todas as pessoas e instituições que tornaram possível a realização deste trabalho.

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## **Resumo**

O presente estudo teve como objetivo verificar, em escala de bancada, a aplicação da lixiviação amoniacal de ouro com tiosulfato a uma amostra de minério oxidado de ouro-cobre com elevado teor de cobre solúvel em cianeto (cerca de 0,1%). Os ensaios de lixiviação realizados visaram estabelecer os efeitos da relação  $[\text{NH}_3]/[\text{S}_2\text{O}_3^{2-}]$ , da concentração de cobre em solução, da adição de sulfito de sódio e da aeração da polpa na extração de metais (ouro e cobre) e no consumo de tiosulfato. Também foi estudada a adição estagiada de tiosulfato ao sistema.

Foi demonstrado que, para a amostra estudada, o emprego de tiosulfato permite obter extrações de ouro compatíveis com a cianetação e que o cobre presente no minério é suficiente para catalisar a dissolução de ouro – e também causar consumo excessivo de tiosulfato (33 a 101kg/t). Nenhuma alteração no sistema foi observada com a adição de sulfito de sódio. Concentrações de cobre inferiores a 100mg/L, obtidas através da pré-lixiviação do minério com ácido sulfúrico, reduziram sensivelmente o consumo de tiosulfato, porém, afetaram negativamente a cinética de extração de ouro.

Aumentando a relação  $[\text{NH}_3]/[\text{S}_2\text{O}_3^{2-}]$ , foi elevado o potencial de redox (Eh) da polpa, o que pode indicar uma elevação da concentração de  $\text{Cu}^{2+}$  em relação ao  $\text{Cu}^+$ . Já a lixiviação em atmosfera inerte, proporcionada pela injeção de nitrogênio, reduziu o Eh da polpa. Mas para qualquer uma dessas medidas não foram observados ganhos significativos no consumo de reagentes ou na extração de ouro em relação às condições centrais (reator aberto; 25°C; 1atm; 0,23mol/L  $\text{S}_2\text{O}_3^{2-}$ ; 0,67mol/L  $\text{NH}_3$ ), nas quais foi obtida uma extração de 90% do ouro contido. A adição estagiada visou realizar a lixiviação do minério em concentração de tiosulfato constante menor que a do experimento de controle (0,1mol/L), mas também não logrou êxito em combinar alta extração de ouro com baixo consumo de reagentes.



## ***Abstract***

The present study aimed to verify the application of ammoniacal thiosulfate leaching to a sample of an oxidized gold-copper ore with high cyanide soluble copper content (0.1%) in bench scale experiments. The leaching experiments carried out aimed at establishing the effects of  $[\text{NH}_3]/[\text{S}_2\text{O}_3^{2-}]$  ratio, copper concentration in solution, sulfite addition, and aeration of the slurry on metals extraction and thiosulfate consumption. Continuous thiosulfate addition, as an attempt to keep the concentration constant, was also experimented.

It was shown that, for this particular sample, the use of thiosulfate allows to extract as much gold as cyanidation, and that the copper available in the ore is enough to catalyze gold leaching – and also to cause excessive thiosulfate consumption (33 to 101kg/t). Copper concentrations below 100mg/L - obtained by leaching the ore with sulfuric acid prior to thiosulfate leaching – resulted in little gain in thiosulfate consumption, but with negative effects on gold dissolution kinetics.

Varying  $[\text{NH}_3]/[\text{S}_2\text{O}_3^{2-}]$  ratio raised slurry redox potential (Eh) that may indicate an increase in the  $[\text{Cu}^{2+}]/[\text{Cu}^+]$  ratio. Conversely, leaching in inert atmosphere, achieved by nitrogen injection, resulted in lower slurry Eh. However, none of these conditions resulted in increased gold extraction, or in lower thiosulfate consumption in comparison with standard conditions (open vessel; 25°C; 1atm; 0.23mol/L  $\text{S}_2\text{O}_3^{2-}$ ; 0.67mol/L  $\text{NH}_3$ ), in which 90% gold extraction was obtained. Continuous thiosulfate addition aimed to promote leaching at constant thiosulfate concentration but lower than in the control experiment (0,1mol/L), did not work as expected, since it did not result in high gold extraction and low thiosulfate consumption.

## 1. Introdução

A elevação do teor de cobre solúvel, devido à presença de minerais de cobre como a malaquita, azurita, cuprita e cobre nativo, é um dos problemas que surgem com o aprofundamento das cavas de minas de ouro e tem como origem o enriquecimento supergênico das porções superficiais de mineralizações epitermais de cobre-ouro (Fonseca *et al.*, 2000). O cobre solúvel eleva o consumo de cianeto, que cresce em 23 kg/t para cada 1% de cobre solúvel no minério, afetando a recuperação de ouro com efeitos negativos nos processos subsequentes à lixiviação.

Entre as alternativas de minimização do consumo de NaCN estão a adição de amônia e a reciclagem do cianeto através de resinas de troca iônica. A utilização de tiosulfato de amônio, em substituição ao cianeto, é outra opção de abordagem do problema do cobre solúvel. Na lixiviação com tiosulfato de amônio, os íons  $\text{Cu}^{2+}$  são necessários para catalisar a dissolução do ouro. O tiosulfato de amônio é um reagente não-tóxico e de custo unitário menor do que o do cianeto, sendo amplamente utilizado na piscicultura e na agricultura, onde auxilia a fixação do nitrogênio no solo. Porém, o tiosulfato degrada-se facilmente em meio aquoso e também reage com o cobre, o que pode levar a consumos não-econômicos de reagentes. Além disso, o complexo de ouro e tiosulfato não é adsorvido em carvão ativado, o que torna necessário utilizar resinas poliméricas de troca iônica ou cementação com cobre para recuperar o ouro.

A lixiviação de metais preciosos com tiosulfato é conhecida desde o final do século XIX, quando essa técnica era a maior concorrente da cianetação. O maior desenvolvimento da cianetação tornou este método de extração predominante nas operações industriais por mais de um século. Entretanto, o aumento da quantidade de minérios refratários e carbonosos, bem como as restrições ambientais ao uso do cianeto, fizeram renascer o interesse por outros reagentes. O tiosulfato destaca-se entre os reagentes alternativos pela alta estabilidade do seu complexo com ouro, por utilizar o cobre como catalisador e não se adsorver em matéria carbonosa, o que o torna vantajoso para o tratamento de minérios que apresentem o efeito “*preg-robbing*”, ou com elevado teor de cobre. As principais variáveis do processo são as concentrações de amônia, tiosulfato e  $\text{Cu}^{2+}$ , pH, temperatura e Eh. O mecanismo da dissolução é complexo e o cobre, além de oxidar o ouro, pode oxidar o tiosulfato, elevando o consumo de reagentes. Dessa forma, o uso industrial do tiosulfato de amônio como lixivante

de minérios de ouro tem apresentado como obstáculos principais o alto consumo de reagentes, em particular na presença de minerais de cobre, e a falta de métodos confiáveis de recuperação em polpa do ouro lixiviado. Ressalta-se que os limites superiores das concentrações de cobre solúvel, tiosulfato e amônia não são bem estabelecidos na literatura. Além disso, com base nas informações hoje disponíveis, pode-se afirmar que não há consenso sobre as concentrações ótimas de tiosulfato e amônia, em particular para minérios de ouro-cobre.

O presente trabalho tem como objetivo investigar a aplicação da lixiviação amoniacal com tiosulfato no processamento de um minério oxidado de Au-Cu. Os estudos foram conduzidos com uma amostra da mina do Igarapé Bahia, de propriedade da Companhia Vale do Rio Doce (CVRD). De forma mais específica, propõe-se estabelecer como as relações entre as concentrações dos principais reagentes – amônia,  $\text{Cu}^{2+}$  e tiosulfato – afetam a extração de ouro e a degradação do tiosulfato.

Espera-se que os resultados do presente estudo contribuam para uma melhor compreensão dos fenômenos envolvidos e, por conseguinte, para viabilizar o emprego dessa alternativa de processo para o tratamento de minérios de ouro-cobre. Observa-se que apesar do grande número de trabalhos sobre a lixiviação de ouro com tiosulfato, estes tratam principalmente da lixiviação de minérios carbonosos ou sulfetados, sendo raros aqueles voltados à extração de minérios oxidados de ouro-cobre, comuns em regiões tropicais. Além disto, diversos estudos foram realizados com soluções sintéticas e, portanto, sem a presença de eventuais contaminantes presentes nos minérios. De forma mais ampla, espera-se contribuir para o desenvolvimento de processos hidrometalúrgicos de menores riscos ocupacionais/ambientais, alternativos à cianetação, e que possibilitem o aproveitamento de depósitos de minérios de ouro com alto teor de minerais cianicidas.

## **2. Literature review**

Thiosulfate leaching of precious metals ores has been known since the XIX century, but, as many other processes based on alternative leachant, it was overcome by cyanidation. Due to the increasing number of deposits of refractory ores, and to the growing (sometimes unjustified) of environmental restrictions to cyanide utilization (De Voto and McNulty, 2000), research on processes based on alternative reagents has been stimulated. Among these alternative reagents, ammonium thiosulfate is the most promising one; its stability is the highest one, it is used under alkaline conditions, and is a non-toxic reagent. But the success of a process based on thiosulfate leaching relies on the balance of the main reagents of the system – ammonia, Cu (II), and thiosulfate – and on the control of the pH and Eh ranges.

Early works focused on pressure leaching with the use of high temperatures in order to avoid the formation of sulfur or sulfide layers on gold surface. Due to the high costs associated with those processes, recent works changed the focus to atmospheric leaching. The process, however, has still some limitations, which hinder its industrial application. Reducing the high reagent consumption and developing an in-pulp method to recover the gold from solutions – since the thiosulfate-gold complex cannot be adsorbed onto activated carbon – are the major challenges to be addressed.

The development of technologies based on thiosulfate leaching for treatment of precious metals began with the von Patera process (1858) that consisted in submitting the ore to a chloridizing roasting followed by thiosulfate leaching. This process was successfully employed for the treatment of silver-bearing sulfidic ores in South America prior to WWII (Aylmore and Muir, 2001; O'Malley, 2002). Nevertheless, the cyanidation process developed by MacArthur and the Forrest brothers overcame thiosulfate leaching as well as all other processes of gold extraction.

In 1970's the Newmont Gold Co. renewed the interest in thiosulfate leaching by investigating biooxidation followed by thiosulfate heap leaching for the treatment of carbonaceous gold ores; but the process was shown to be feasible only for high-grade ores (O'Malley, 2002). Gold recoveries of 65.2% were achieved in pilot tests with ammonium thiosulfate consumptions in the range of 5.2kg/t to 8.4kg/t (Wan and Brierley, 1997). As zinc cementation was found to be inefficient, the recovery of gold was carried out by copper cementation.

In the 80's, at La Colorada mine, in Sonora, Mexico, a pilot plant was operated using ammonium thiosulfate to leach tailings of an old cyanidation plant. The process consisted in leaching the tailings in agitated tanks with ammonium thiosulfate, and gold was recovered through copper cementation (Perez and Galaviz, 1987). However, due to corrosion of equipments caused by thiosulfate, the operation was interrupted.

As adsorption onto activated carbon cannot be employed for gold recovery directly from slurries, most of early works in the ammonium thiosulfate system concentrated in recovering gold by means of copper cementation. However, as copper cementation implies in costly steps of solid/liquid separation, more recent studies focused on ion exchange polymeric resins as an alternative to recover gold from slurries.

In summary, the renewed interest in thiosulfate leaching is due to the growing amount of refractory ores and to the environmental pressure against the use of cyanide. Several companies and research centers are currently working towards the development of technologies based on thiosulfate as a gold ore leachant.

### **2.1. Thermodynamics**

Thermodynamic studies are of great value to establish the most favorable conditions in the copper-ammonia-thiosulfate system, due to the complexity and interdependency between the many variables involved. Table II.1 indicates that the complex formed by gold and thiosulfate is the most stable among alternative lixivants, though less stable than the cyanide complex. The Pourbaix diagrams help to identify the stability areas of the desired species in the system. But thermodynamic data may be a source of conflict since small changes in the reported  $\Delta G_f^0$  for a given species may result in different diagrams.

By drawing two diagrams for the gold-ammonia-sulfur system with different values for thiosulfate  $\Delta G_f^0$ , Molleman and Dreisinger (2002) obtained different Eh-pH diagrams, suggesting different reaction mechanisms (Figures 2.1 and 2.2). According to the diagram of Figure 2.1, the complex  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  is stable in all pH range and there is no formation of a gold-ammonia complex. The diagram of Figure 2.2 indicates that the complex  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  is not stable in the pH range in which leaching is performed, but rather that the  $\text{Au}(\text{NH}_3)_2^+$  complex is the predominant species, a conclusion not supported by the experimental practice.

As copper is essential to achieve fast gold dissolution rates the stability of its complexes will be discussed, as well as the stability of metastable sulfur species.

Stability diagrams for the systems Cu-N-S-H<sub>2</sub>O and S-H<sub>2</sub>O were calculated using Outokumpu HSC Chemistry<sup>®</sup> for Windows software, version 3, considering room temperature, and pressure of 1 atm. Results are shown in Figures 2.3 and 2.4.

Figure 2.3 shows that the  $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$  complex has a quite narrow stability area while the complex  $\text{Cu}(\text{NH}_3)_4^{2+}$  has a much larger area of stability. This diagram also indicates that precipitation of copper oxide (CuO) may occur at pH 10. Thus, it would not be advisable to work beyond this pH. In Figure 2.4 the diagram shows that the thiosulfate meta-stability area, quite narrow, does not entirely correspond to the stability areas of the desired gold and copper complexes. In regions of stability of these gold and copper complexes thiosulfate is oxidized to sulfite. According to these observations the system should be operated at room temperature, 1 atm pressure, and pH ranging from 9 to 10 in order to have the complex  $\text{Cu}(\text{NH}_3)_4^{2+}$  available to oxidize gold.

**Table II.1 Stability constants of gold complexes (Aylmore and Muir, 2001b)**

Specie	Stability (log K)
$\text{Au}(\text{CN})_2^-$	38.30
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	28.00
	26.50
$\text{Au}(\text{NH}_3)_2^+$	26.00
	13.00
$\text{AuCl}_4^-$	25.60
$\text{Au}(\text{SCN})_2^-$	16.98
$\text{Au}(\text{SCN})_4^-$	10.00

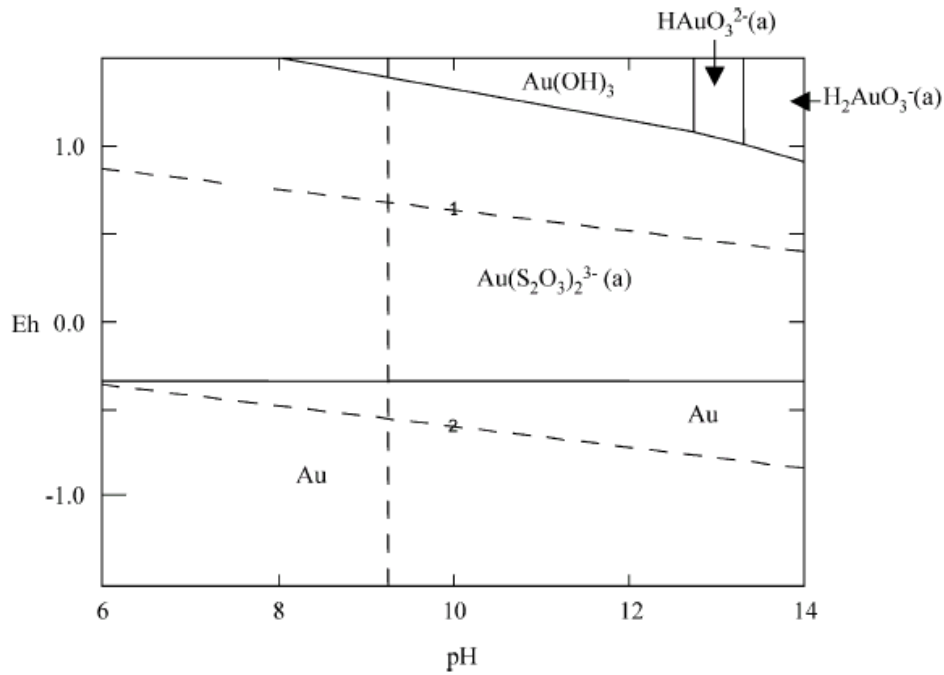


Figure 2.1 Eh-pH diagram of Au-S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-NH<sub>3</sub>-H<sub>2</sub>O system at 25°C for  $\Delta G_f^0(S_2O_3^{2-}) = -518.8 \text{ kJ/mol}$  (Molleman and Dreisinger, 2002, [Au] =  $2.5 \times 10^{-5} \text{ mol/L}$ , [N] = 0.4 mol/L, [S] = 0.4 mol/L)

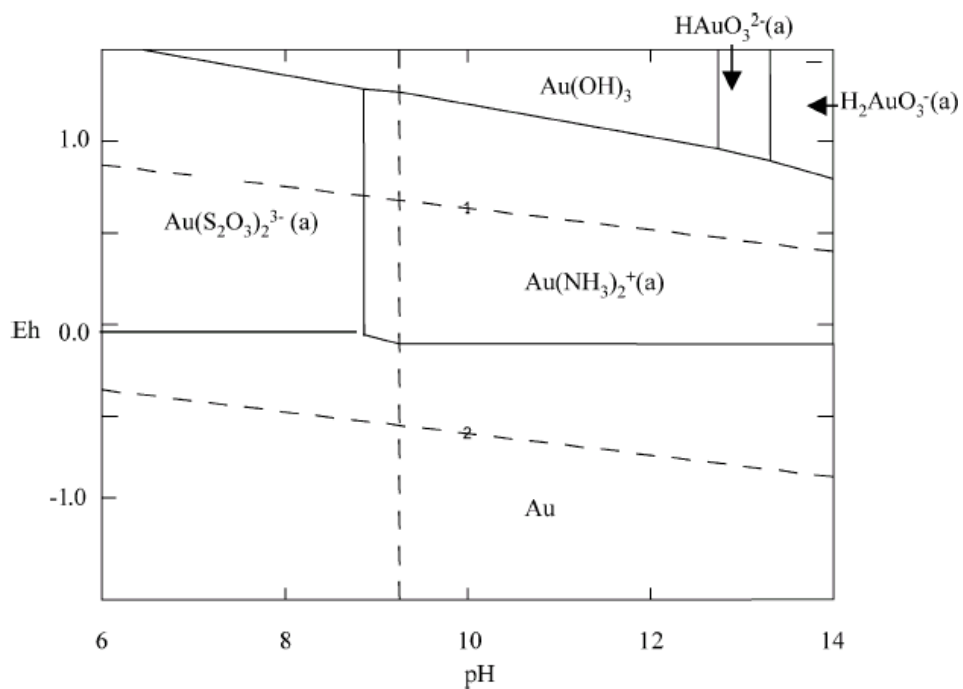


Figure 2.2 Eh-pH diagram of Au-S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-NH<sub>3</sub>-H<sub>2</sub>O system at 25°C for  $\Delta G_f^0(S_2O_3^{2-}) = -532.2 \text{ kJ/mol}$  (Molleman and Dreisinger, 2002, [Au] =  $2.5 \times 10^{-5} \text{ mol/L}$ , [N] = 0.4 mol/L, [S] = 0.4 mol/L)

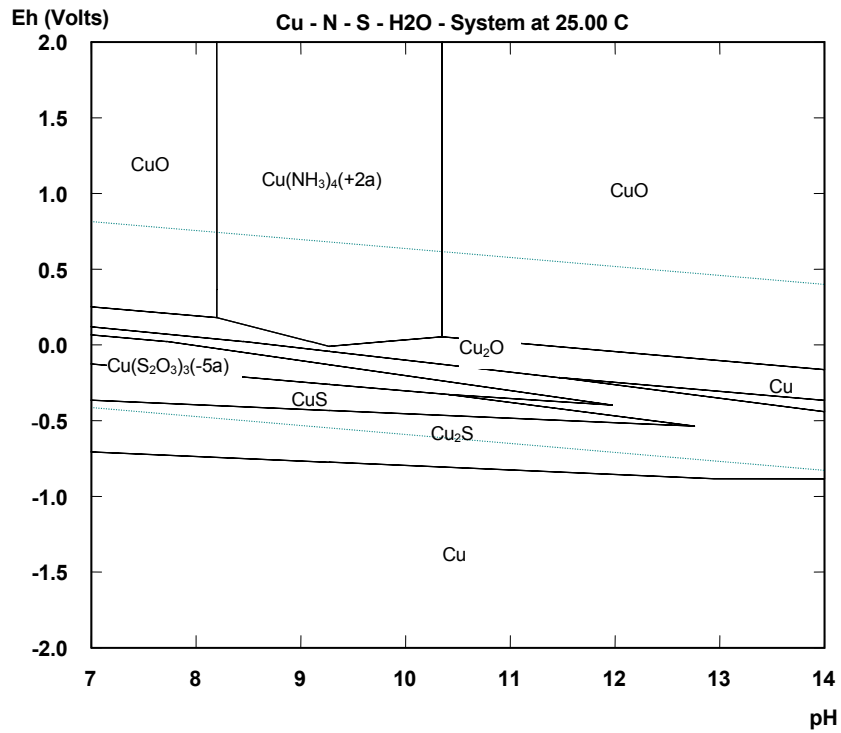


Figure 2.3 Eh-pH diagram of copper-ammonia-sulfur system (present study,  $[Cu] = 0.04\text{mol/L}$ ,  $[S] = 0.46\text{mol/L}$ ,  $[N] = 0.67\text{mol/L}$ )

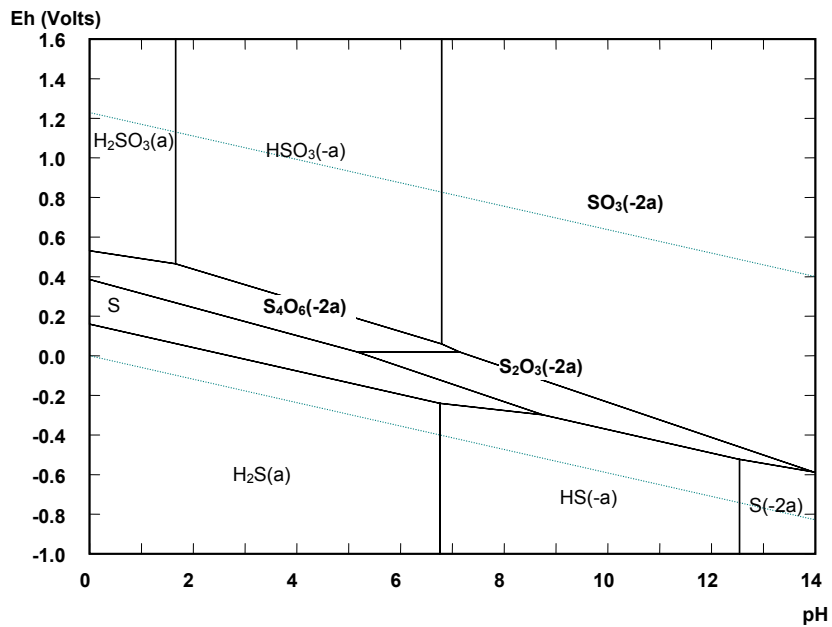


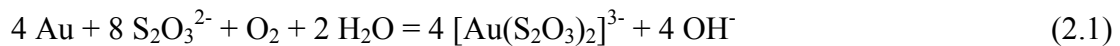
Figure 2.4 Eh-pH meta-stable diagram of sulfur-water system (present study,  $[S] = 0.23\text{mol/L}$ )



## 2.2. Reaction mechanism

Due to the relatively higher number of reagents and side reactions, gold thiosulfate leaching is far more complex than cyanidation. The main variables are thiosulfate, copper, ammonia and oxygen concentrations, in addition to pH, temperature and Eh.

Gold dissolution, in alkaline media and in the presence of thiosulfate and oxygen, may be described by the following equation:



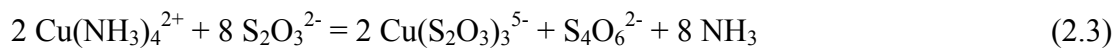
$\text{Cu}^{2+}$  ions are more soluble in water or aqueous ammonia solutions than oxygen. Therefore, the presence of  $\text{Cu}(\text{NH}_3)_4^{2+}$  catalyses the reaction, acting as a more efficient and soluble oxidant than oxygen. For the copper-ammonia system two mechanisms of gold dissolution are proposed. In the first one (Yen *et al.*, 2001)  $\text{Cu}^{2+}$  ions oxidize metallic gold to  $\text{Au}^+$ , which is complexed by ammonia and brought into solution where thiosulfate ions replace ammonia forming the  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  complex.  $\text{Cu}^+$  ions are then oxidized by oxygen to  $\text{Cu}^{2+}$  ions (Figure 2.5). In the second mechanism, shown in Figure 2.6, the gold-thiosulfate complex is formed without ammonia intervention (O'Malley, 2002); just after gold oxidation by copper ions, the  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  complex is formed.  $\text{Cu}^+$  ions are also complexed by thiosulfate and cupric ions are regenerated by oxygen and complexed by ammonia forming  $\text{Cu}(\text{NH}_3)_4^{2+}$ . Above pH 10 and in the absence of oxygen, cupric ions will also oxidize thiosulfate (Aylmore and Muir, 2001). Therefore, an adequate copper concentration is essential in order to achieve high Au extractions with low consumption of thiosulfate.

## 2.3. Effect of process variables

Ammonia is added to the system in order to stabilize  $\text{Cu}^{2+}$  ions, to hinder dissolution of gangue minerals, and to prevent passivation of gold surface. However, there is no consensus on its optimum concentration in the system. In several works it is stated that there is a limit to ammonia addition (Abbruzzese *et al.*, 1995; Jeffrey, 2000; Trindade *et al.*, 1998; Changlin *et al.*, 1992), as an excess of ammonia would reduce the thermodynamic stability areas of copper complexes and increase the stability area of copper oxides. However, O'Malley (2002) indicates that gold extraction is directly related to the ratio between ammonia and thiosulfate concentrations. By fixing the thiosulfate concentration at 0.05mol/L, gold extraction increased 50% when ammonia concentration was increased from 0.2mol/L to 0.8mol/L. Breuer and

Jeffrey (2001) also stated that high ammonia concentrations can speed up thiosulfate gold leaching. Ammonia may also affect the kinetics of thiosulfate oxidation by cupric ions. It is suggested that the  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex is stabilized by  $\text{OH}^-$  ions; thus at high pH, cupric ions would show a less oxidative performance, reducing thiosulfate consumption but also slowing down gold leaching.

Cupric ions have a catalytic effect on thiosulfate gold leaching, and if compared with gold oxidation by oxygen, copper may speed up gold dissolution by 18 to 20 times (equation 2.2). However, cupric ions can also oxidize thiosulfate ions to tetrathionate, increasing reagent consumption and hindering gold extraction (equation 2.3).



At low thiosulfate concentrations ( $< 0.01 \text{mol/L}$ ) gold dissolution is incomplete and downstream operations may be negatively affected. On the other hand, an excess of thiosulfate ( $> 1 \text{mol/L}$ ) does not improve the rate of gold extraction and may lead to excessive reagent consumption. A consequence of a high decomposition rate of thiosulfate is an increase in concentration of sulfur species noxious to the adsorption of gold-thiosulfate complex onto ion exchange resins (O'Malley, 2002).

According to the literature, the most favorable ranges for reagent concentration are between 50 and 100mg/L for cupric ions, 0.1 to 0.2mol/L for thiosulfate, and 0.2 to 0.4mol/L for ammonia (Molleman and Dreisinger, 2002). Table II.2 summarizes the levels of the main process variables, as proposed by various authors. Few of them tested thiosulfate for leaching oxide gold-copper or copper-gold ores. In most of them, only sulfidic ores were tested. In some cases, despite the high copper grade in the ore, cupric ions were added.

In order to prevent thiosulfate decomposition due to excess of cupric ions, complexing agents such as chelating agents and amino acids may be added to the system. Another option is to add reducing reagents to inhibit thiosulfate oxidation. Sulfite may avoid thiosulfate decomposition as well as the formation and precipitation of sulfides on gold's surface.



Investigating the efficacy of several additives on the stability of thiosulfate ions in ammoniacal leaching of gold with thiosulfate and cupric ions, Xia *et al* (2002) found that the use of EDTA or NTA provided the best results. Sulfite and sulfate additions were innocuous, while good results were obtained with glycine.

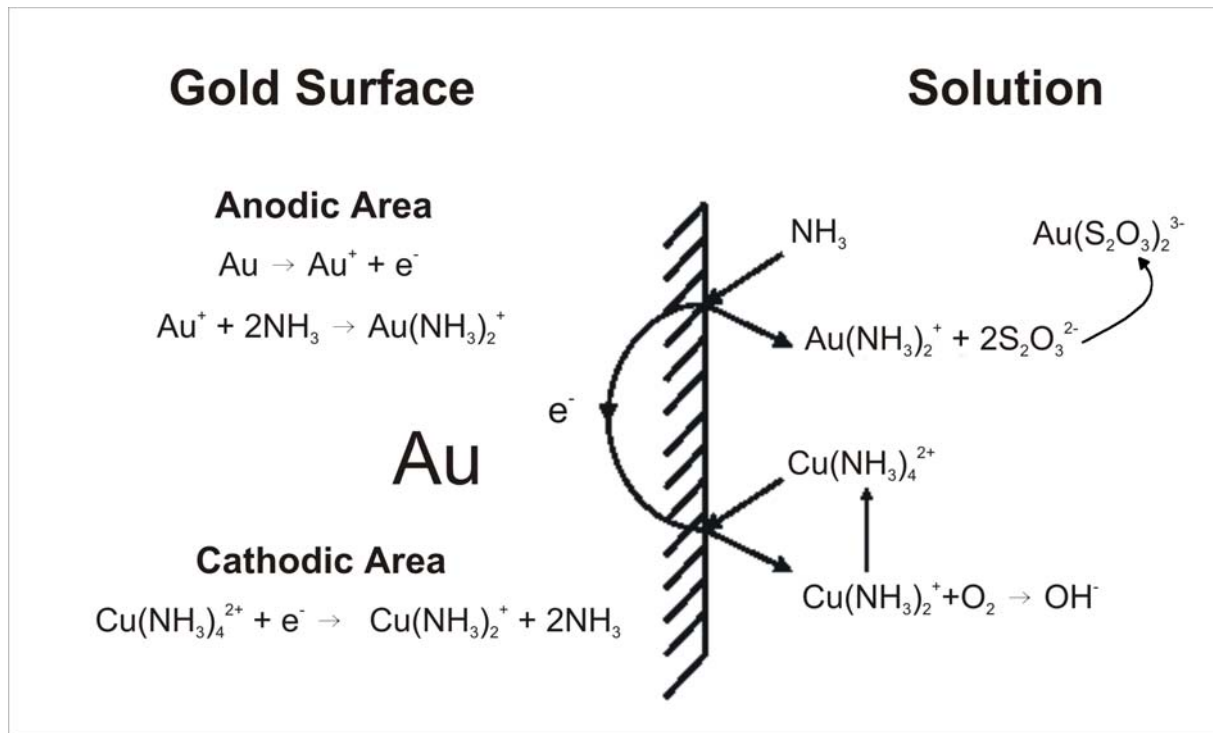
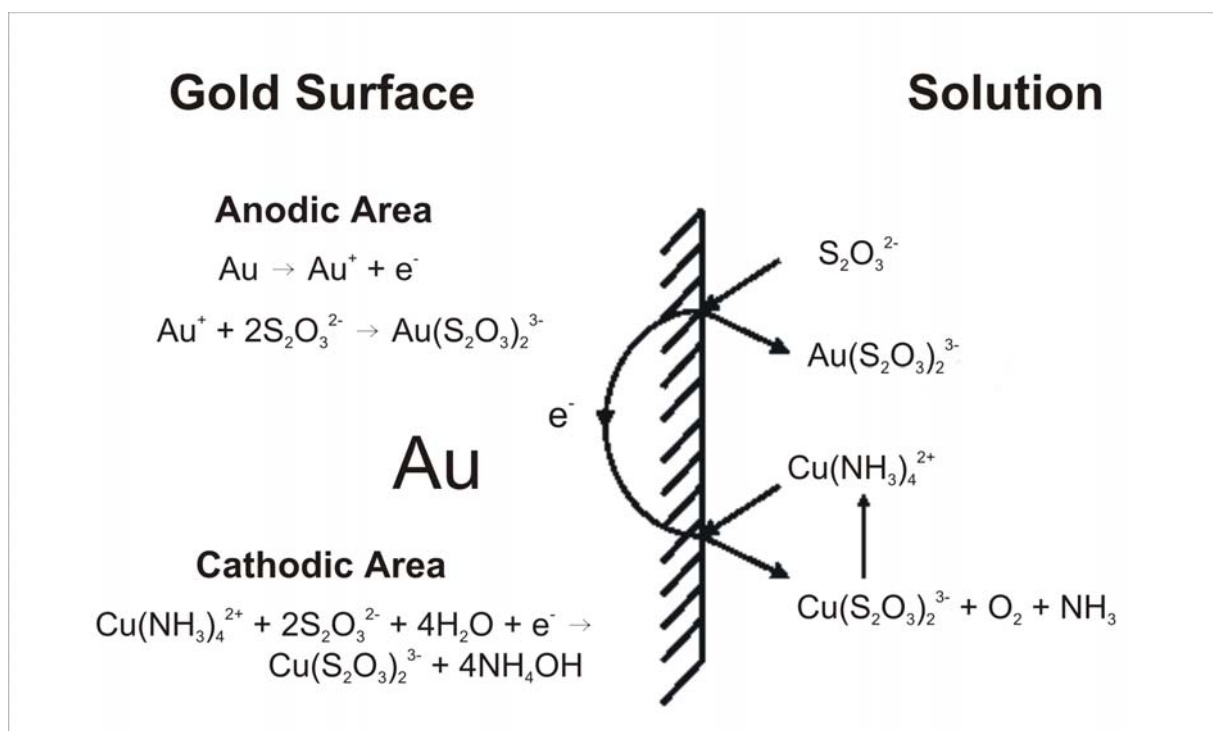
Figure 2.5 Dissolution mechanism proposed by Yen *et al* (2001)

Figure 2.6 Dissolution mechanism proposed by O'Malley (2002)

**Table II.2 Range of variables, as suggested in the literature to achieve maximum gold extraction**

Author	Gold extraction (%)	$S_2O_3^{2-}$ (mol/L)	$(NH_4)_2S_2O_3$ consumption (kg/t)	Copper grade (%)	$Cu^{2+}$ addition (mol/L)	$NH_4OH$ (mol/L)	Leaching time (h)	pH	Temperature ( $^{\circ}C$ )
Freitas et al., 2001	90.8	1.20	n/a	5.23	0.0000	0.44	24	n/a	25
Aylmore, 2001	90.0	0.80	74.0	n/a	0.0500	4.00	96	10.20	25
Langhans et al., 1992	83.0	0.20	0.4	n/a	0.0010	0.09	48	10.35	25
O'Malley, 2002	98.0	0.05	n/a	n/a	0.0003	0.80	48	9.50	25
Navarro et al., 2002	90.0	0.70	117.0	3.70	4.7kg/t	n/a	10	10.00	25
Molleman and Dreisinger, 2002	83.3	0.20	15.7	1.60	0.0000	0.00	24	10.00	35
Kononova et al., 2001	94.0	0.50	n/a	n/a	n/a	0.50	3	n/a	20 - 22
Zipperian and Raghavan, 1988	90.0	2.00	n/a	n/a	0.0940	4.10	3	10.00	50
Wan and Brierley, 1997 (heap leaching)	65.2	0.10	8.4	n/a	0.0005	0.10	2784	n/a	25

n/a – not available

#### **2.4. The effect of metallic ions**

The effect of manganese on the thiosulfate leaching of oxidized gold-copper ores is not well established. For this particular sample of oxidized ore from Igarapé Bahia mine there is a concern about the effect of manganese on the stability of thiosulfate in pulp, due to the high grade of manganese oxides in the ore. Apparently, manganese could oxidize thiosulfate as in the case of cupric ions. Other metallic ions, such as iron, cobalt, and nickel, might also play a role in this system. The presence of Pb or Zn ions is not a problem since they do not form complexes with ammonia that might affect ammoniacal gold leaching with thiosulfate (Feng and van Deventer, 2001).

The oxidation of thiosulfate by iron can be avoided by operating the system above pH 8. Below this pH value iron is dissolved reducing gold extraction (Aylmore and Muir, 2001b). Cobalt and nickel have also little effect over thiosulfate stability since only above room temperature it is possible to find moderate concentrations of these metallic ions in solution (Niinae *et al*, 1996; Aylmore and Muir, 2001b). Indeed, nickel could replace cupric ions as gold oxidant with advantages. Xia *et al* (2002) reported that the addition of nickel sulfate resulted in faster gold extraction and lower thiosulfate consumption in comparison to cupric ions. Niinae *et al* (1996) verified that thiosulfate and sulfite are able to extract only small amounts of manganese from ferromanganese nodules, and as pH rises extractions falls.

#### **2.5. Gold recovery**

Recovery of gold-thiosulfate complex directly from slurries is hindered by the impossibility of activated carbon to adsorb the complex. Therefore, this operation must be carried out through copper cementation, solvent extraction or adsorption onto ion exchange polymeric resins. However, copper cementation and solvent extraction demand clarified solutions, which implies in additional and costly operations of solid/liquid separation. Clarification is unnecessary when using ion exchange polymeric resins, which can be used in pulps such as activated carbon. These resins have a relatively higher unit cost compared to coconut shell activated carbon, but they also have advantages such as:

- Higher selectivity against calcium or magnesium (no acid washing);
- Elution may be carried out at room temperature

- Superior kinetics;
- Resins do not require the operation of thermal regeneration, as activated carbon does, resulting in smaller and less costly plants.

Ion exchange resins are mainly used in waste and water treatment, usually in a pH range of 5 to 8. At this range weak base resins are quite suitable to recover metal anions from solutions, and elution can be performed by a change in pH, since at higher pH values resins are not protonated. As gold thiosulfate leaching system operates above pH 9, strong base resins are more suitable to perform gold recovery (Kononova et al, 2001, Nicol and O'Malley, 2002, O'Malley, 2002, Zhang and Dreisinger, 2002a).

The poisoning of resins by thiosulfate degradation products, such as trithionate and tetrathionate, is another obstacle to the industrial use of this reagent since these ions may displace and compete with the gold-thiosulfate complex for the adsorption sites of the resins (O'Malley, 2002, Zhang and Dreisinger, 2002ab).

Zhang and Dreisinger (2002b) found that by raising the pH to values higher than 11 tetrathionate is converted to thiosulfate, favoring gold recovery from solutions. High ammonia concentration does not affect gold loading, but may hinder copper adsorption (Zhang and Dreisinger, 2002a). Thiocyanate, thiosulfate, nitrate salts, and sulfite may be employed as eluants.

### 3. Experimental

#### 3.1. Samples

The material utilized is a sample of an oxidized gold-copper ore rich in cyanide soluble copper ( $\text{Cu}_{\text{sol}}$ ) from Igarapé Bahia mine, northern Brazil, owned by CVRD. Chemical and mineralogical compositions of the samples, as informed by CVRD, are shown in Tables III.1 and III.2, respectively. This strongly oxidized gold-copper ore is mainly composed by goethite (39%), hematite (26%), and quartz (22%). Due to its high cyanide soluble copper content (0.1%  $\text{Cu}_{\text{sol}}$ ), if treated in conventional CIP process this ore may consume more than 2.3kg NaCN/t ore.  $\text{Cu}_{\text{sol}}$  concentration was determined by the so-called Red Dome procedure and is also shown in Table III.1. This procedure consists in adding 140mL of a solution containing 1% NaCN and 5% NaOH to 1 gram of sample pulverized to about 95% below 45 $\mu\text{m}$ . The leach is carried out for a period of 1 hour. The solids are filtered and the filtrate is transferred to a volumetric flask and the volume adjusted to 250mL. The pregnant solution was analyzed for copper by atomic absorption spectroscopy (Romayna, 2000).

**Table III.1 Chemical composition of the ore sample (Fujikawa, 2001)**

Element	Grade (%)
Fe	39.4
Si	9.40
Al	4.50
Mn	1.61
PF	8.0
Ti	0.44
Cu	0.54
$\text{Cu}_{\text{sol}}$	0.095
Au (g/t)	3.88
Ag (g/t)	20

Mineralogical composition was obtained by optical microscopy and X-ray diffraction analyses. Copper distribution (Table III.2) was determined by scanning electron microscopy. Copper was found in association with iron hydroxides, manganese oxides, and as copper



carbonate, which together bear 87% of the total amount of copper in the ore sample (Fujikawa, 2001).

**Table III.2 Copper distribution by minerals (Fujikawa, 2001)**

Minerals	Percentage of total copper (%)
Goethite (FeOOH)	43
Malaquite (Cu <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub> )	27
Mn oxides	17
Cuprite (Cu <sub>2</sub> O)	7
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	2
Chlorite ((Mg,Al,Fe) <sub>12</sub> (Si,Al) <sub>8</sub> .20(OH) <sub>16</sub> )	2
Tenorite (CuO)	1
Native copper (Cu)	~0.5
Digenite (Cu <sub>1.8</sub> S)	~0.5
Calcopirite (CuFeS <sub>2</sub> )	~0.5
Bornite (Cu <sub>5</sub> FeS <sub>4</sub> )	~0.5

### 3.2. Leaching tests

Leaching experiments were carried out in 2000mL open vessels under stirring and 33% solids at room temperature (Figure 3.1). Based on previous work with a sample from Igarapé Bahia mine (Freitas et al, 2001) thiosulfate concentrations were selected as 0.15mol/L and 0.23mol/L; ammonium thiosulfate was used as the source of thiosulfate. Ammonium hydroxide was added to the system to achieve total ammonia/ammonium concentrations ranging from 0.52mol/L to 0.67mol/L. Ammonia was added prior to thiosulfate addition in order to start copper extraction. Sulfite concentration was fixed in 0.05mol/L in some of the exploratory experiments. Experiments without sulfite were carried out in order to verify the effects of this reagent on both metal extraction and reagent consumption. The duration of these tests varied from 1h to 48h. Samples of leaching liquors were taken at the end of each experiment and solids were filtered, rinsed and dried. With the addition of ammonium thiosulfate pH remained around 9.2 and 9.5 with no need of adjustment.

Intensive leaching experiments with cyanide and thiosulfate were carried out for the sake of comparison. These experiments comprised two leaching steps of 24h each one. After the first step, solids were filtered and rinsed; a sample of the pregnant solution was taken for gold and copper analysis. Then a new leaching step was carried out with the same conditions employing the residue of the first step. At the end of the second leaching, solids are filtered, rinsed, and dried. Samples of residue and liquor were assayed for gold and copper analysis. Intensive cyanidation was carried out at 1%NaCN, and 5%NaOH. Intensive thiosulfate leaching employed 1mol/L thiosulfate and 2.44mol/L NH<sub>3</sub>/NH<sub>4</sub>.

The pretreatment parameters of the sulfuric acid leaching (Table III.3) were the same of a previous work with a similar ore sample (Cunha, 2002). These experiments were carried out in a 2000mL open vessel.

**TableIII.3 Parameters of sulfuric leaching pretreatment**

Variable	Settings
Temperature	25 and 60°C
Particle size distribution	-200 mesh Tyler
% Solids	40%
Sulfuric acid	98.5kg/t
Leaching time	15min

For experiments carried out in anoxic atmosphere tests were done in closed vessels. Prior to leaching, nitrogen was bubbled in slurries for 2h at the flow rate of 50mL/min, which was kept during the test time.

In all tests analytical grade reagents and distilled water were employed to reduce error sources.

It is important to point out that the ammoniacal thiosulfate liquors are not stable; as thiosulfate is consumed, copper may precipitate from solution. Thus, it is necessary to store liquor samples in amber glass flasks under refrigeration. Cyanide must also be added to the liquor in order to stabilize copper.

**Figure 3.1 Schematic diagram of the equipment set-up**

### **3.3. Analyses**

Gold and copper in solution were assayed by Atomic Absorption Spectroscopy (AAS), in a Perkin-Elmer AAnalyst 300 equipment. Solid residues were also assayed for gold (fire assay) and copper by ICP spectrometry.

Two techniques were used to determine thiosulfate concentration in the aqueous phase, iodine titration (Appendix 2) and High Pressure Liquid Chromatography (HPLC) in a Dionex DX 500 chromatographer equipped with ED 40 detector, and AG 12A and AS 12A columns. Titration is considered less reliable than chromatography. Chromatography has some distinct advantages over iodine titration: it is more accurate, operationally simpler, requires smaller volumes of solution (~2mL), and, depending on the column used, additional chemical species can be assayed.

Thiosulfate concentration remains unaltered for 3 days at room temperature, if stored in amber glass flasks.

## **4. Results and discussion**

### **4.1. Effect of thiosulfate concentration**

Despite the fact that plenty of information can be found in the literature on leaching of preg-robbing carbonaceous ores, sulfidic ores, and that several studies with synthetic solutions and materials were carried out showing that thiosulfate leaching of gold is catalyzed by cupric ions, little information is available about thiosulfate leaching of oxide gold-copper ores.

Thus, the first questions to be answered were (i) if the sample was amenable to ammoniacal thiosulfate leaching, (ii) if the extraction obtained was comparable to the one verified with cyanide leaching, and, finally, (iii) if the copper present in the ore would be enough to enhance leaching without using other sources of cupric ions. Once these questions were answered, it was necessary to establish to what level it was possible to reduce thiosulfate concentration maintaining a reasonable gold extraction.

The answers to some of these questions were readily available in the publication of Freitas and co-workers (2001). That work, in which similar ore samples were employed, clearly showed that no addition of cupric ions is necessary - the ore can provide even more copper than necessary to speed up gold dissolution. The authors employed thiosulfate concentrations ranging from 150 to 450kg Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>/t ore (0.4-1.2mol/L). Thiosulfate concentrations ranging from 0.15mol/L to 0.23mol/L were explored in our preliminary experiments and a comparison between cyanidation and thiosulfate leaching was also carried out.

Results of intensive leaching experiments with cyanide and thiosulfate are shown in Figure 4.1. Copper contents in solution for the first 24h of leaching are also displayed. The objective of these experiments was to compare the maximum possible gold extractions for both reagents. Both systems employed high reagent concentrations (1% NaCN and 690kg ATS/t ore) and extended leaching times (48 hours). The results clearly show that thiosulfate leaching can provide as efficient gold extractions as cyanidation (thiosulfate leaching achieved 92.7% and cyanidation achieved 93.6% gold extraction). One can observe that copper concentration in ammoniacal thiosulfate media is higher than in cyanide media, suggesting that copper could be more soluble in the first media. This is indeed a problem since copper acts as an oxidizer not only for gold, but also for thiosulfate, causing excessive reagent consumption and generation of polythionates, such as trithionate and tetrathionate,

which are detrimental to metal recovery by ion-exchange (O'Malley, 2002; Molleman and Dreisinger, 2002; Zhang and Dreisinger, 2002ab).

As an attempt to decrease copper dissolution, thiosulfate concentration was reduced. Two thiosulfate concentrations were tested: 0.23mol/L and 0.15mol/L. Sodium sulfite concentration was fixed in 0.05mol/L for both tests.

Lower copper and gold extractions were achieved for the initial thiosulfate concentration of 0.15mol/L (Figure 4.2). Thiosulfate consumption kinetics was found to be similar for both initial concentrations, as can be inferred from the shape of the graphics. Thiosulfate concentrations at the end of the experiments were approximately the same, regardless of the initial concentration. At this point, thiosulfate concentration was measured through an adapted iodometric titration methodology.

As the previous results, shown in Figure 4.2, did not indicate a condition to obtain low copper dissolution (by achieving copper concentration in slurry below 100mg/L) combined with high gold extraction (above 80%) the addition of ammonium thiosulfate (ATS) during leaching was tested (Figure 4.3). This test consisted in start leaching at 0.15mol/L and dosing thiosulfate concentration in pulp every 2h and bringing its concentration back to 0.15mol/L whenever it reaches 0.1mol/L. Gold extractions higher than 90% were achieved, but at the expense of high thiosulfate consumption (101.4kg/t).

Sulfite was supposed to enhance thiosulfate stability, thus reducing its consumption. However, comparing the two systems in Figure 4.4, one may conclude that there was no gain in thiosulfate consumption when sulfite was added to the system even though both copper concentration in solution and Eh were reduced. Due to this finding, sulfite was abandoned as a possible additive. The curve representing the system without sulfite addition became the reference for all subsequent experiments.

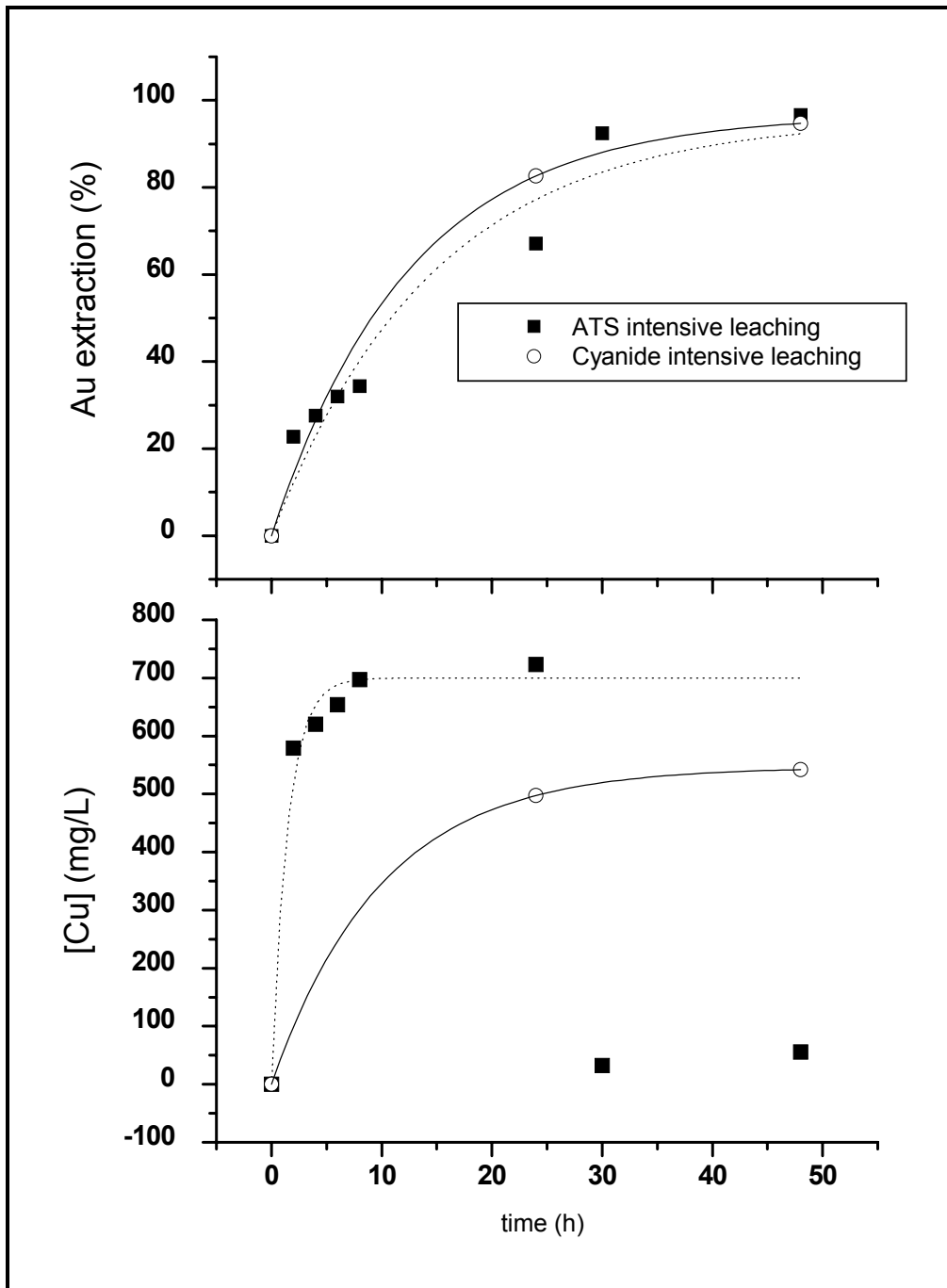


Figure 4.1 – Comparison between intensive cyanidation and intensive ammoniacal thiosulfate leaching (open vessel, room temperature, 33% solids. Cyanidation parameters: 1% NaCN and 5% NaOH. Thiosulfate leaching parameters:  $[S_2O_3^{2-}] = 2.3 \text{ mol/L}$ ,  $[NH_3] = 4.8 \text{ mol/L}$ ,  $[SO_3^{2-}] = 0.05 \text{ mol/L}$ )

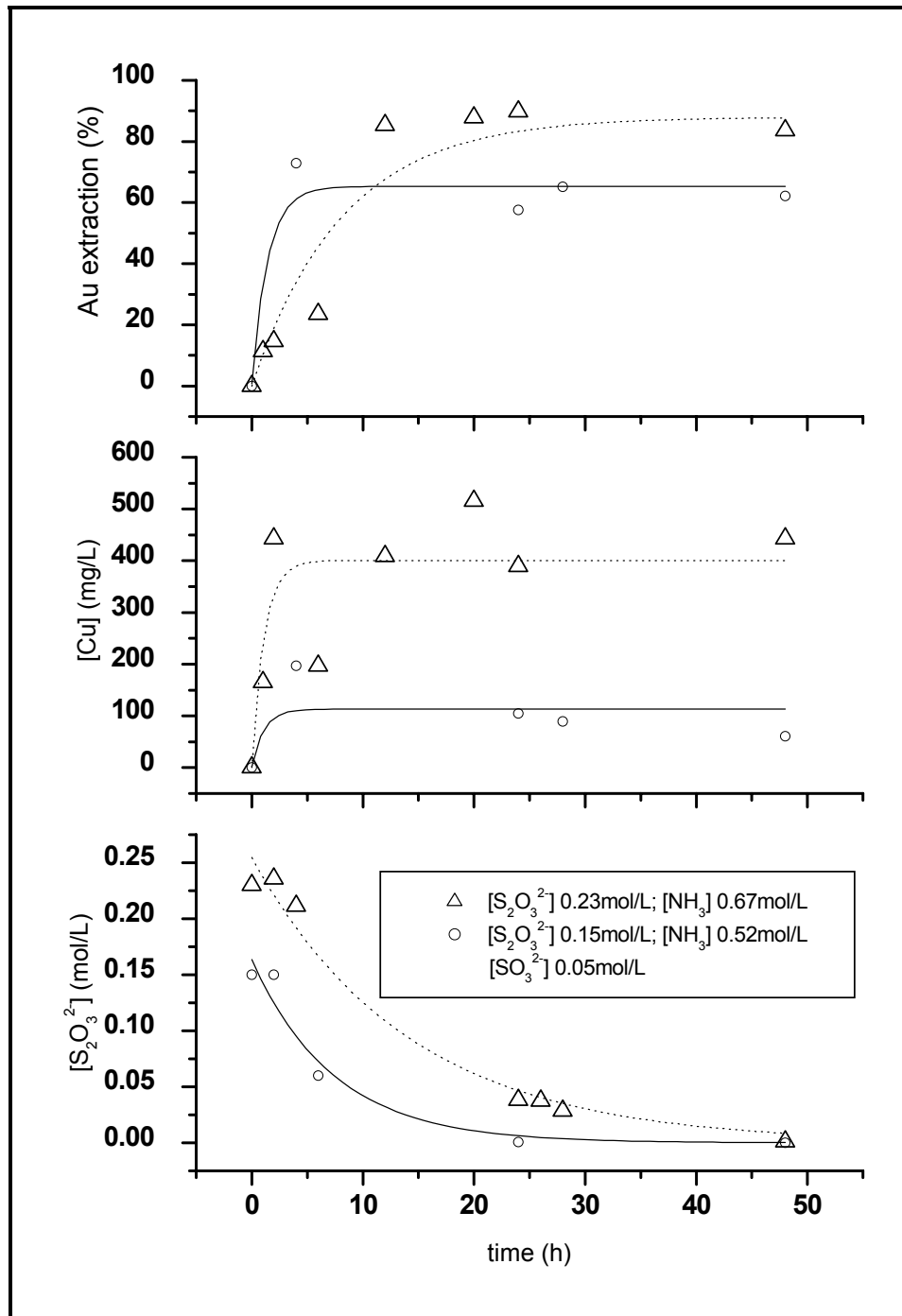


Figure 4.2 Thiosulfate leaching, effect of thiosulfate concentration in slurry (open vessel, 25°C, 33% solids, [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] = 0.23mol/L and 0.15mol/L, [NH<sub>3</sub>] = 0.67mol/L and 0.52mol/L, [SO<sub>3</sub><sup>2-</sup>] = 0.05mol/L)



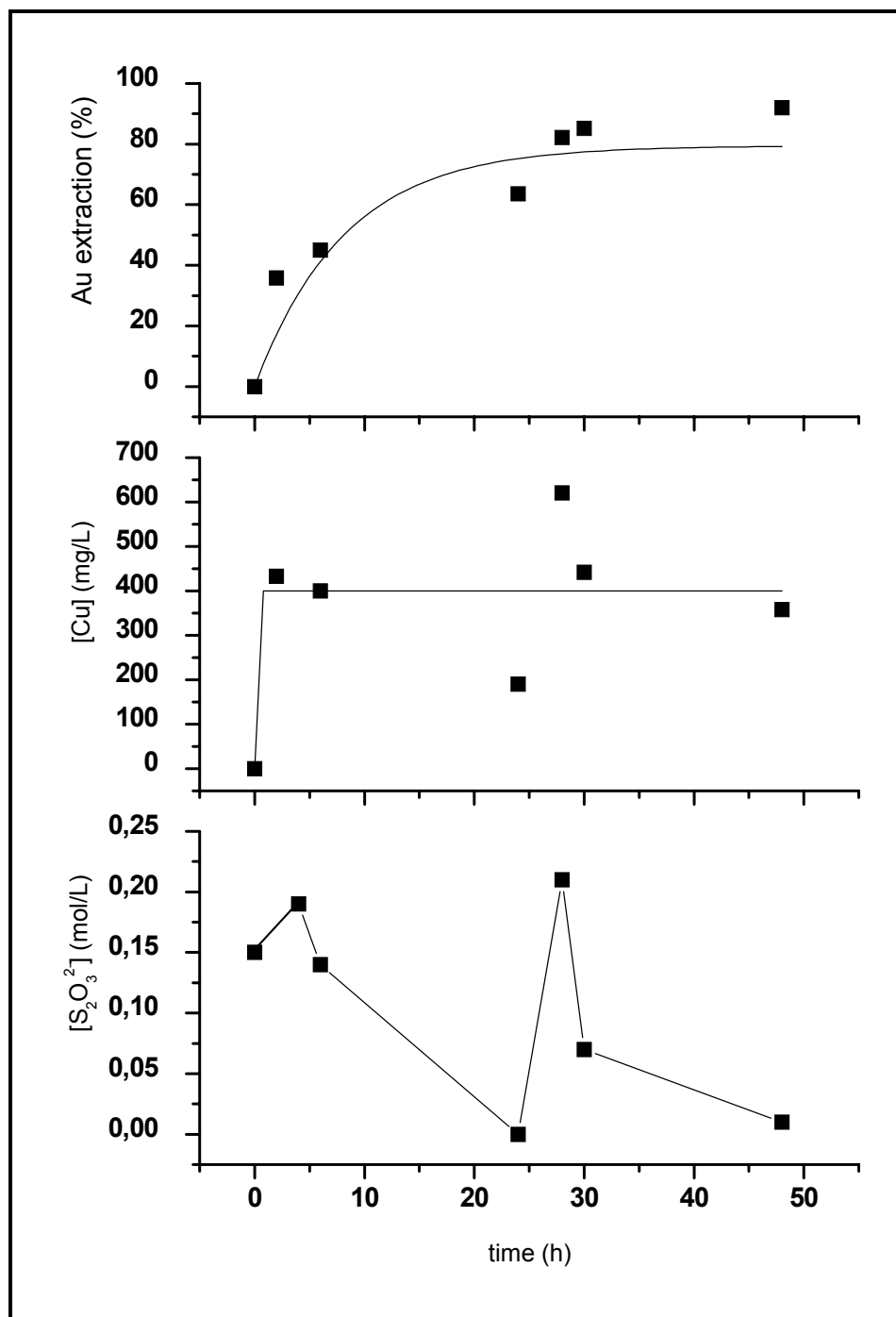
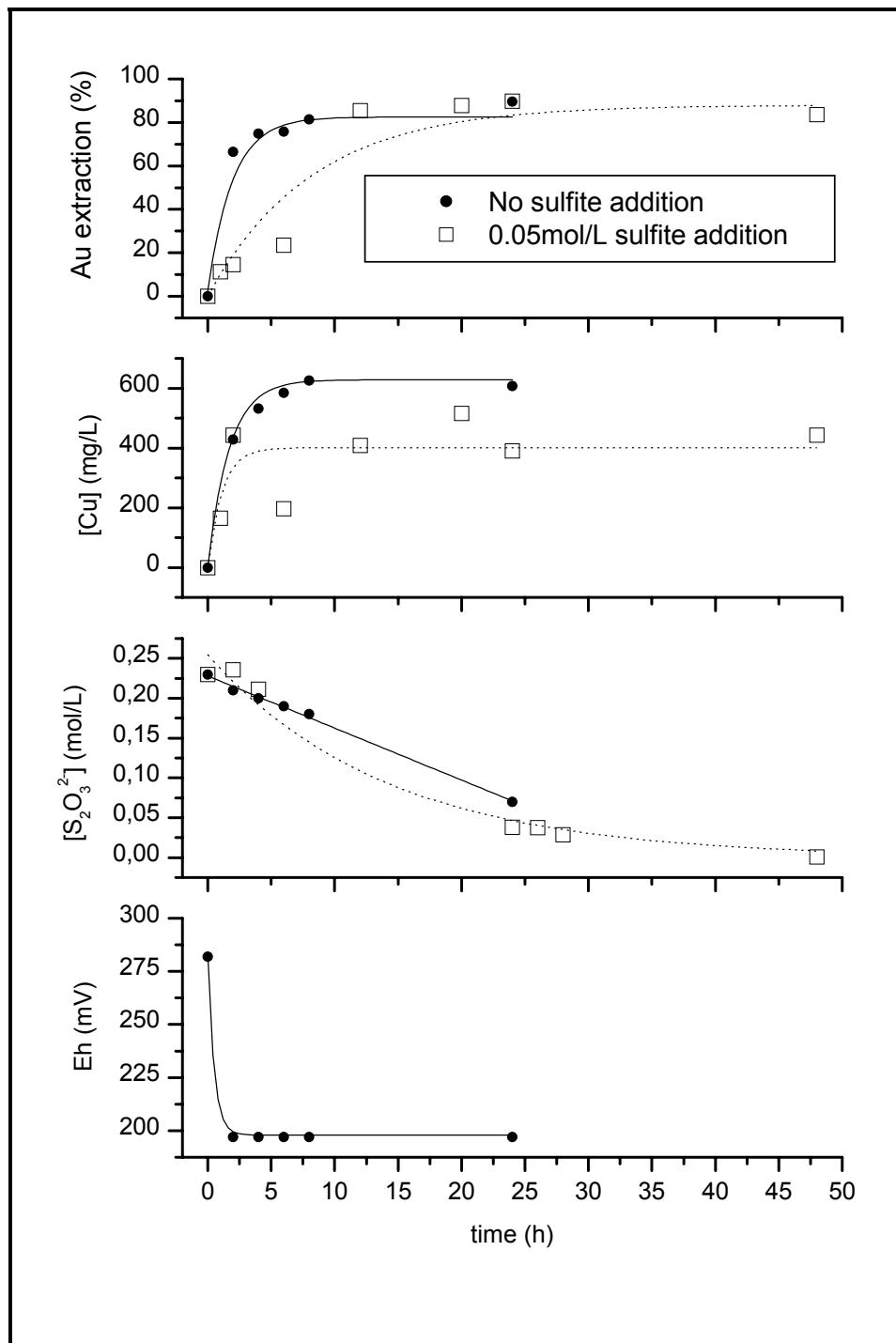


Figure 4.3 Effect of thiosulfate concentration adjustment by addition of ATS during leaching (open vessel, room temperature, 33% solids,  $[S_2O_3^{2-}]_{\text{initial}} = 0.15\text{mol/L}$ ,  $[NH_3]_{\text{initial}} = 0.52\text{mol/L}$ ,  $[SO_3^{2-}] = 0.05\text{mol/L}$ )



**Figure 4.4** Thiosulfate leaching – effect of sodium sulfite addition (open vessel, room temperature, 33% solids,  $[S_2O_3^{2-}] = 0.23\text{mol/L}$ ,  $[NH_3] = 0.67\text{mol/L}$ )

#### **4.2. The effect of varying the $\text{NH}_3/\text{S}_2\text{O}_3$ ratio**

Cupric ion is regarded as a catalyst for both gold and thiosulfate oxidation. In the ammoniacal thiosulfate system, ammonia complexes and stabilizes cupric ions, this reaction resulting in a solution with a deep blue color. Thus, by reducing cupric ions concentration, the increase of  $\text{NH}_3/\text{S}_2\text{O}_3$  ratio (R) could help reduce thiosulfate oxidation rate.

Despite leaching of gold was not the focus of his project, O'Malley (2002) investigated the influence of  $\text{NH}_3/\text{S}_2\text{O}_3$  ratio on gold leaching with ammoniacal thiosulfate. O'Malley found that, for his ore sample, increasing this ratio gold leaching is favored and thiosulfate consumption decreases. It is important to mention that copper concentrations of his experiments were much smaller ( $3 \times 10^{-4} \text{ mol/L}$ ) than those obtained in the leaching of oxidized gold-copper ores (around  $0.01 \text{ mol/L}$ ).

In order to verify the effects of varying this ratio on the leaching of this particular ore sample, a set of experiments was planned and executed, as described in this chapter. The assumption was that by keeping thiosulfate concentration constant and adding enough ammonia to raise the  $\text{NH}_3/\text{S}_2\text{O}_3^{2-}$  ratio from 2.9 (control experiment) up to 6, one would be able to stabilize  $\text{Cu}^{2+}$  ions and thus avoid excessive thiosulfate oxidation. The results of the present study (Figure 4.5) show that increasing the  $[\text{NH}_3]/[\text{S}_2\text{O}_3^{2-}]$  ratio a higher  $\text{Cu}^{2+}/\text{Cu}^+$  ratio in solution is obtained, as indicated by Eh values, which are higher for higher  $[\text{NH}_3]/[\text{S}_2\text{O}_3^{2-}]$  ratio (Dai *et al.*, 2003). These conditions were not able to affect thiosulfate consumption of in comparison to the control experiment. Although, in the first 2h of leaching, gold extraction achieved was nearly 80% for  $R = 6$ , against 60% for  $R = 2.9$ , final extraction of gold was not improved by increasing ammonia concentration with respect to thiosulfate, remaining around 90% gold extraction.

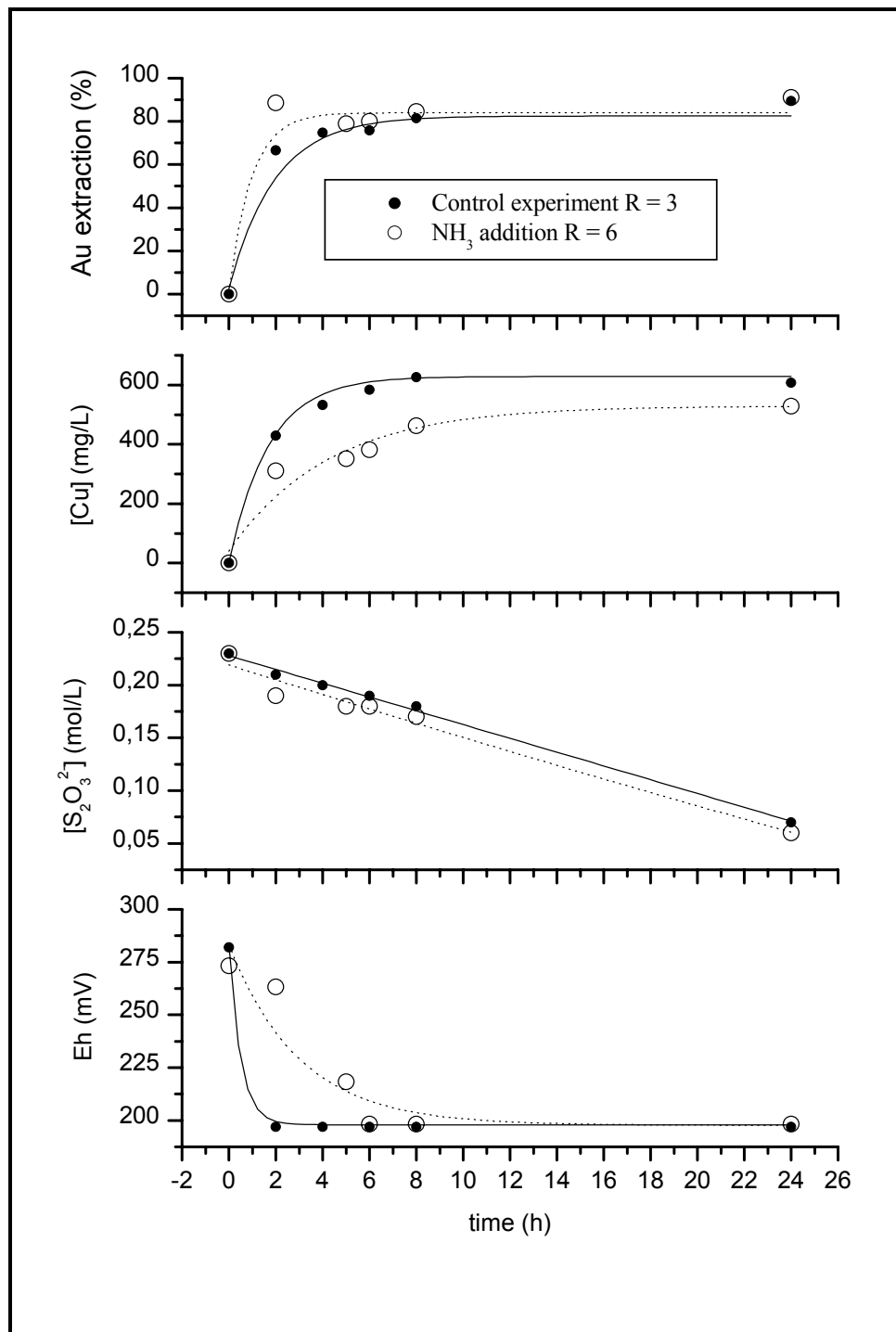


Figure 4.5 Effect of increasing ammonia/thiosulfate ratio on metals extraction and thiosulfate concentration (open vessel, room temperature, 33% solids, and  $[S_2O_3^{2-}] = 0.23\text{mol/L}$ )

### 4.3. Sulfuric acid leaching pretreatment

Sulfuric acid is a common and relatively inexpensive reagent (~US\$ 50/t) employed to leach copper ores. Recent work with a similar ore sample (Cunha, 2002) indicated that nearly 25% of the copper could be extracted in 15 minutes leaching time. Thus, sulfuric acid leaching pretreatment was considered as an alternative to reduce the concentration of cupric ions in thiosulfate leaching (pretreatment parameters are summarized in Table III.3).

The pretreatment was able to extract up to 28% of copper from the ore in 15 minutes leaching. Leaching at 60°C resulted in higher copper extraction and weight loss than at room temperature, (Table IV.1). Obviously more gangue minerals are dissolved at 60°C, since there was not copper enough in the ore to cause a weight loss higher than 0.61%.

**TableIV.1 Sulfuric acid leaching**

Temperature	Initial Cu grade	Final Cu grade	Weight loss	Copper extraction*
25°C	0.62%	0.45%	0.36%	28%
60°C	0.61%	0.42%	2.08%	33%

\*With respect to total copper in the ore.

Final gold extractions near 80% were obtained when leaching the pretreated ore samples (Figures 4.8 and 4.9). Copper concentrations above 100mg/L were obtained only after 6h leaching, and gold dissolution was slower than in the control experiment, especially after leaching at 60°C.

Despite the significant decrease in copper concentration (that fell from near to 600mg/L in the control experiment to less than 200mg/L after the pretreatment) there was no appreciable gain in thiosulfate consumption by using sulfuric acid pretreatment. As can be observed in Figures 4.6 and 4.7, the decline of thiosulfate concentration in solution for any condition follows the same trend, regardless of the condition employed.

Figures 4.6 and 4.7 also show higher Eh values for the pretreated samples, which may indicate a higher  $\text{Cu}^{2+}/\text{Cu}^{+}$  ratio for these samples, since Eh is a function of this ratio and is a measure of the equilibrium potential of reaction (4.1) (Dai et al., 2003).



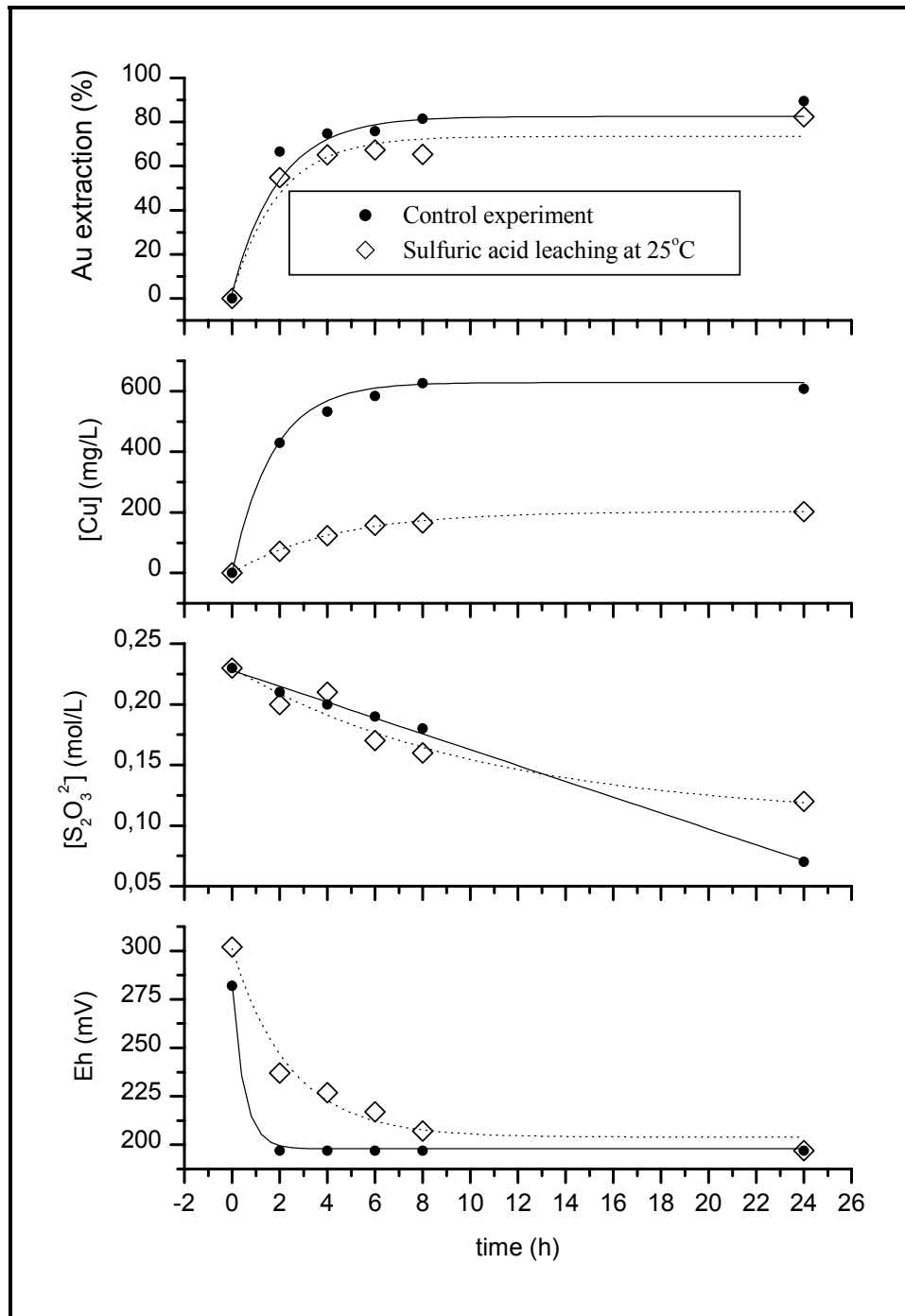


Figure 4.6 Effect of sulfuric acid pretreatment at room temperature (open vessel, 33% solids, [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] = 0.23mol/L, [NH<sub>3</sub>] = 0.67mol/L)

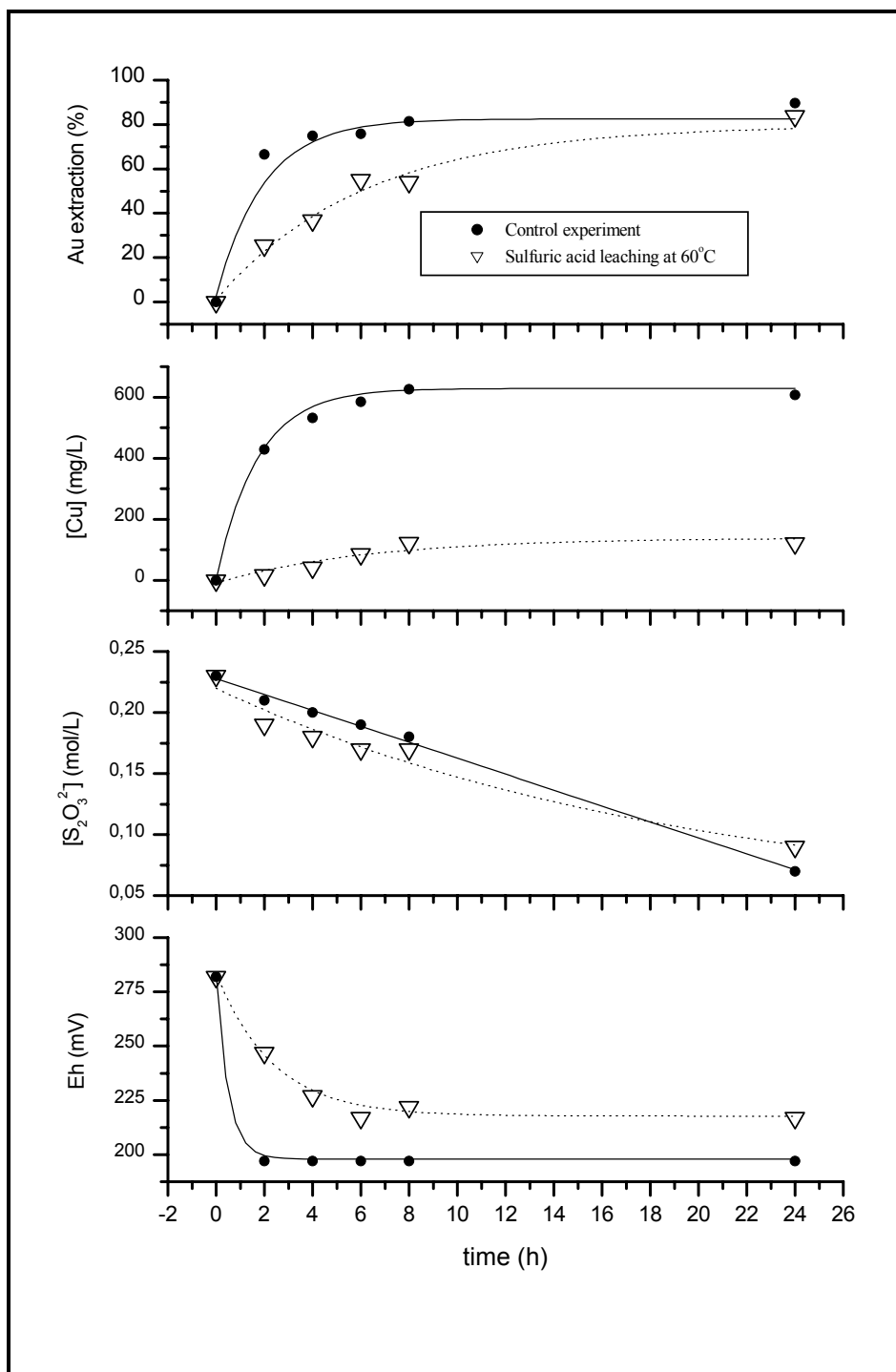
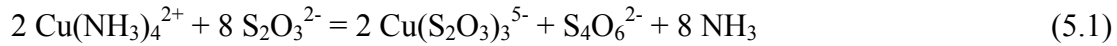


Figure 4.7 Effect of sulfuric acid pretreatment at 60°C (open vessel, 25°C, 33% solids, [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] = 0.23mol/L, [NH<sub>3</sub>] = 0.67mol/L)

#### **4.4. Leaching at inert atmosphere provided by nitrogen injection**

Cupric ions or oxygen alone can slowly oxidize thiosulfate (Chu *et al.*, 2003). In addition, when reacting with thiosulfate or gold, cupric ions are reduced to the cuprous state. However, oxygen can also oxidize  $\text{Cu}^+$  to  $\text{Cu}^{2+}$ , according to the following reactions:



Thus, the presence of oxygen in solution could have the end effect of increasing thiosulfate consumption that being the main reason behind the use of an inert gas during leaching. Moreover, leaching in an inert atmosphere can also provide other benefits, according to Chu and co-workers (2003), as thiosulfate reaction with oxygen produces compounds that may hinder gold dissolution.

The results of experiments in which nitrogen was used are illustrated in Figure 4.10. It can be seen that the use of an inert gas resulted in faster kinetics of gold extraction – nearly 80% of gold was leached in the first 2 hours of leaching, against approximately 60% in the case of the control experiment. Final gold extractions were similar, 89.5% for control experiment and 90.9% for the experiment with nitrogen injection.

Reagent consumption was also higher in the first 6 to 8 hours of reaction, although final thiosulfate consumption was comparable to the one obtained in the control experiment. This result can probably be attributed to the fact that in the case of oxide ores, such as Igarapé Bahia ore, in which copper concentration in solution is far above the critical range of 50 to 100 mg/L Cu – suggested by Molleman and Dreisinger (2002) – the issue of increased thiosulfate consumption due to oxidation of cupric ions by oxygen is of less importance. Therefore, the use of an inert gas during leaching appears to be more relevant for cupric assisted ammoniacal thiosulfate leaching, as in the case of sulfidic ores.



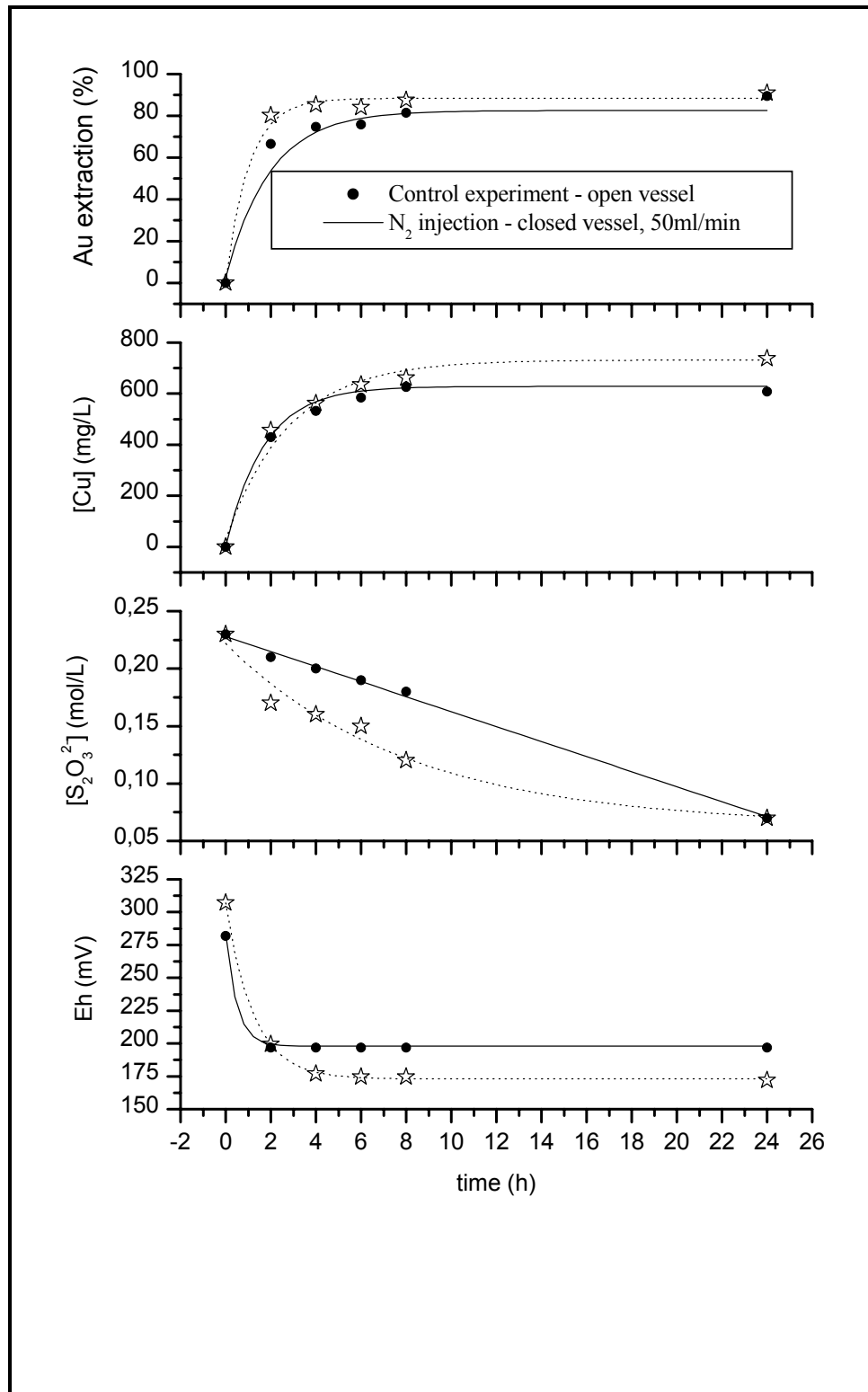


Figure 4.8 Effect of N<sub>2</sub> injection (open vessel, 25°C, 33% solids, [S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] = 0.23mol/L, [NH<sub>3</sub>] = 0.67mol/L)

#### **4.5. General remarks**

This particular ore sample was found to be amenable to ammoniacal thiosulfate leaching; maximum gold extraction obtained through this process was equivalent to that achieved when submitting the ore to cyanidation (92.7% and 93.6%, respectively).

For each condition tested, ammonium thiosulfate consumption and final gold extraction are summarized in Table IV.2. Lower copper concentrations were obtained by sulfuric acid leaching pretreatment, but this alternative also resulted in lower final gold extractions. Gold dissolution kinetics was also poorer by working under lower copper concentrations, although Eh values indicate a higher cupric/cuprous ratio. But even after sulfuric acid leaching pretreatment this ore is able to provide enough copper enough to leach gold without the need of addition of cupric ions from other sources. Gold dissolution kinetics was found to be slower when copper concentration in solution fell below 100mg/L. Thiosulfate consumption is not affected when copper concentration in solution varies between 100mg/L and 600mg/L.

Nitrogen injection did reduce slurry redox potential (Eh), but did not result in lower thiosulfate consumption. By leaching this ore under inert atmosphere conditions faster gold extraction was achieved and higher copper extraction as well. Thiosulfate stability was not improved; actually thiosulfate consumption was faster with nitrogen injection. As cupric concentration was not measured, it is not possible to state if in this case Eh lower values are related to a lower  $\text{Cu}^{2+}/\text{Cu}^{+}$  ratio or this is only the effect of displacing oxygen from slurry. Without oxygen to regenerate cupric ions it is possible that their concentration dropped after 4h leaching. At this moment it was possible to observe that slurry potential dropped 30mV.

Trying to keep thiosulfate concentration above 0.1mol/L starting from 0.15mol/L resulted in high gold extraction, but also elevated reagent consumption. Maybe reducing further both initial and target concentration of thiosulfate, a fair ATS consumption could be achieved. As shown in Table IV.2, both the use of an inert gas during leaching or raising the  $\text{NH}_3/\text{S}_2\text{O}_3$  ratio did not provide any significant reduction in thiosulfate consumption. Sulfuric acid pretreatment was effective in reducing thiosulfate consumption, but resulted in lower gold extraction.

TableIV.2 Summary of the tested leaching conditions

Conditions	Initial [S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ] (mol/L)	Initial [NH <sub>3</sub> ] (mol/L)	Initial [SO <sub>3</sub> <sup>2-</sup> ] (mol/L)	Final [Cu] (mg/L)	ATS consumption (kg/t)	Gold extraction (%)
Standard	0.23	0.67	-	607.8	47.4	89.5
Standard with sulfite ( <i>48h leaching</i> )	0.23	0.67	0.05	442.73 (24h leaching: 312.85)	69.2 (24h leaching: 57.7)	89.0 (24h leaching: 89.9)
Lower thiosulfate concentration ( <i>48h leaching</i> )	0.15	0.52	0.05	60.3 (24h leaching: 105.1)	45.1 (24h leaching: 45.1)	61.5 (24h leaching: 58.2)
Thiosulfate addition in stages ( <i>48h leaching</i> )	0.15	0.52	0.05	358.02 (24h leaching: 105.6)	101.4 (24h leaching: 55.2)	92.0 (24h leaching: 63.5)
Ammonia/thiosulfate ratio = 6	0.23	0.67	-	527.9	50.4	91.1
Sulfuric acid pretreatment 25°C	0.23	0.67	-	201.7	32.6	82.5
Sulfuric acid pretreatment 60°C	0.23	0.67	-	121.1	41.5	83.9
Nitrogen injection* ( <i>l N<sub>2</sub> flow rate = 50mL/min</i> )	0.23	0.67	-	737.9	47.4	90.9

Open vessel except for \*.

All these consumptions are still high, not only in terms of reagent cost, but also in terms of operational problems, which may be expected to occur if thiosulfate comes to replace cyanide in an actual gold mine. For example, considering that a hypothetical plant can process 6000t ROM/d, nearly 284t ATS/d would be consumed, requiring large storage facilities and a complex supply logistic, depending on factors as mine location, distance from supplier, transport limitations, among other factors.

De Voto and McNulty (2000) discussed this issue. Their work focused on problems faced by a gold mine located in Montana State, where cyanide was banned from open pit projects, and highlights that if in this mine cyanide were replaced by thiosulfate the big number of daily truck shipments (49 shipments/day) would become a safety and environmental problem even worse than the use of cyanide itself.

## 5. Conclusions

The ore sample tested is amenable to ammoniacal thiosulfate leaching which may extract as much gold as cyanidation (93%). Adding thiosulfate in stages in order to keep its concentration above 0.1mol/L starting from 0.15mol/L did increase gold extraction, but at the expense of higher reagent consumption. Future works may employ lower levels for both initial and target concentrations. For the sample under study sulfite addition did not work as expected, since no significant improvement in thiosulfate stability was observed. Regarding metal extraction, its addition was deleterious to gold dissolution kinetics, thus it was abandoned for subsequent experiments.

Increasing ammonia/thiosulfate ratio seems to increase  $\text{Cu}^{2+}/\text{Cu}^+$  ratio (as Eh is increased) and improves gold leaching kinetics. However, thiosulfate consumption also increased. Considering that thiosulfate consumption and gold oxidation are functions of  $\text{Cu}^{2+}$  concentration, the results are justified. Whether or not this conclusion is valid for all types of ore is a matter opened for discussion. At all events, the results of the present work, in which an oxide gold-copper ore was employed, clearly indicate that there is no advantage in increasing ammonia concentration in solution.

Although leaching with  $\text{H}_2\text{SO}_4$  did reduce copper content of the ore, there remained enough cupric ions in the ore to allow gold extraction up to 80% in thiosulfate leaching. The resulting lower copper content affected only the kinetics of gold dissolution, but there was little change in thiosulfate concentration during leaching.

It was found that nitrogen injection and the increase of ammonia/thiosulfate ratio can improve gold dissolution kinetics. These two conditions improved gold extraction in nearly 20% in the two first hours of leaching, but final extractions were approximately the same observed in the control experiment, around 90% gold extraction.

As research on gold thiosulfate leaching chemistry advances and environmental constraints are created, in the future this process may become an option to cyanidation for various types of ore. By now, cyanide is still the best choice for gold extraction, in spite of all thiosulfate advantages as low unitary cost and low toxicity. Gold-copper ores, carbonaceous preg-robbing ores, and other types of refractory ores may experience the first industrial applications of copper catalyzed gold ammoniacal thiosulfate leaching.

## 6. References

- C. Abbruzzese, P. Fornari, R. Massidda, F. Vegliò, S. Ubaldini (1995), **Thiosulphate leaching for gold hydrometallurgy**, *Hydrometallurgy* 39, pp. 265-276.
- M.G. Aylmore (2001), **Treatment of a refractory gold-copper sulfide concentrate by copper ammoniacal thiosulfate leaching**, *Minerals Engineering*, Vol. 14, No. 6, pp. 615-637.
- M.G. Aylmore and D.M. Muir (2001a), **Thermodynamic analysis of gold leaching by ammoniacal thiosulfate using Eh/pH and speciation diagrams**, SME Annual Meeting, Denver, Colorado.
- M.G. Aylmore and D.M. Muir (2001b), **Thiosulfate leaching of gold – A review**, *Minerals Engineering*, Vol. 14, No. 2, pp.135-174.
- P.L. Breuer and M.I. Jeffrey (2000), **Thiosulfate leaching kinetics of gold in the presence of copper and ammonia**, *Minerals Engineering*, Vol. 13, No. 10-11, pp. 1071-1081.
- P.L. Breuer and M.I. Jeffrey (2002), **An electrochemical study of gold leaching in thiosulfate solutions containing copper and ammonia**, *Hydrometallurgy* 65, pp. 145-157.
- C. Changlin, H. Jiexue, G. Qian (1992), **Leaching gold by low concentration thiosulfate solution**, Randol, Vancouver.
- C.K. Chu, P.L. Breuer, M.I. Jeffrey (2003), **The impact of thiosulfate oxidation products on the oxidation of gold in ammonia thiosulfate solutions**, *Minerals Engineering* 16, pp. 265-271.
- F.A. Cunha (2002), **Remoção de cobre contido no minério de ouro de Igarapé Bahia**, relatório de iniciação científica, Departamento de Engenharia Metalúrgica e de Materiais, Escola de Engenharia, Universidade Federal de Minas Gerais, Brasil.
- X. Dai, C.K. Chu, M. Jeffrey, P. Breuer (2003), **A comparison of cyanide and thiosulfate leaching for the recovery of gold from a copper containing ore**, *Hydrometallurgy 2003 – 5<sup>th</sup> International Conference in Honor of Professor Ian Ritchie*, Vol. 1, Vancouver.

- R.H. De Voto and T.P. McNulty (2000), **Banning cyanide at McDonald – An attack on open-pit mining**, Mining Engineering 12, pp. 19-27.
- D. Feng, J.S.J. Van Deventer (2001), **Preg-robbing phenomena in the thiosulphate leaching of gold ores**, Minerals Engineering, vol. 14, No. 11, pp. 1387-1404.
- C. Fleming, J. Wells, K.G. Thomas (2000), **Process for recovering gold from thiosulfate leach solutions and slurries with ion exchange resin**, United States Patent 542736.
- E. Fonseca, D. Santos, J. Aguiar, N. Ferreira (2000), **Geometalurgia: O caso de Igarapé Bahia**, trabalho técnico, CVRD, Carajás.
- L.R. Freitas, R.B.E. Trindade, T. Carageorgos (2001), **Thiosulphate leaching of gold-copper ores from Igarapé Bahia mine**, VI SHMMT / XVIII ENTMH, Rio de Janeiro.
- L.H. Fujikawa (2001), **Análise mineralógica de amostras de Igarapé Bahia – desenvolvimento de processo para minério de alto cobre**, relatório técnico, CVRD, Santa Luzia.
- N.P. Gallagher, J.L. Hendrix, E.B. Milosavljevic, J.H. Nelson, L. Solujic (1990), **Affinity of activated carbon towards some gold (I) complexes**, Hydrometallurgy 25, pp. 305-316.
- R.M. Genik-Sas-Berezowski, V.B. Sefton, L.S. Gormely (1978), **Recovery of precious metals from metal sulphides**, United States Patent 4070182.
- M. Goyal, V.K. Rattan, D. Aggarwal, R.C. Bansal (2001), **Removal of copper from aqueous solutions by adsorption on activated carbons**, Colloids and Surfaces A: Physicochemical and Engineering Aspects 190, pp 229-238.
- M.I. Jeffrey (2001), **Kinetic aspects of gold and silver leaching in ammonia-thiosulfate solutions**, Hydrometallurgy 60, pp. 7-16.
- M.I. Jeffrey, P. Breuer e W.L. Choo (2001), **How rapidly do alternative lixiviants leach gold?**, Cyanide: Social, Industrial and Economic Aspects, TMS.
- B.J. Kerley, Jr. (1981), **Recovery of precious metals from difficult ores**, United States Patent 4269622.

B.J. Kerley, Jr. (1983), **Recovery of precious metals from difficult ores**, United States Patent 4369061.

O.N. Kononova, A.G. Kholmogorov, Y.S. Kononov, G.L. Pashkov, S.V. Kachin e S.V. Zotova (2001), **Sorption recovery of gold from thiosulphate solutions after leaching of products of chemical preparation of hard concentrates**, *Hydrometallurgy* 59, pp. 115-123.

A.C.Q. Ladeira, M.E.M. Figueira, V.S.T. Ciminelli (1992), **Caracterização de carvões ativados utilizados na indústria do ouro: propriedades físicas, químicas e estudo cinético**, *Extração de Ouro: Fundamentos, Prática e Meio Ambiente*, Anais do III Encontro do Hemisfério Sul sobre Tecnologia Mineral/XV Encontro Nacional de tratamento de Minérios e Hidrometalurgia, São Lourenço, Minas Gerais, Brasil, pp 132-151.

J.W. Langhans Jr., K.P.V. Lei, T.G. Carnahan (1992), **Copper catalyzed thiosulfate leaching of low-grade gold ores**, *Hydrometallurgy* 29, pp. 191-203.

W.C. Lenahan and R.L. Murray-Smith (1986), **Assay and analytical practice in South African mining industry**, pp. 577-581, The South African Institute of Mining and Metallurgy, Johannesburg.

F.D. Mendes (1999), **Tratamento do minério de ouro-cobre de Igarapé Bahia através de lixiviação sulfúrica seguida de cianetação**, tese de mestrado, Departamento de Engenharia Metalúrgica e de Materiais, Escola de Engenharia, Universidade Federal de Minas Gerais, Brasil.

E. Molleman and D.B. Dreisinger (2002), **The treatment of copper-gold ores by ammonium thiosulfate leaching**, *Hydrometallurgy* 66, pp. 1-21.

P. Navarro, C. Vargas, A. Villarroel, F.J. Alguacil (2002), **On the use of ammoniacal/ammonium thiosulphate for gold extraction from a concentrate**, *Hydrometallurgy* 65, pp. 37-42.

M.J. Nicol e G.P. O'Malley (2001), **Recovery of gold from thiosulfate solutions and pulps with ion-exchange resins**, *Cyanide: Social, Industrial and Economic Aspects*, TMS.

M. Niinae, N. Komatsu, Y. Nakahiro, T. Wakamatsu, J. Shibata (1996), **Preferential leaching of cobalt, nickel and copper from cobalt-rich ferromanganese crusts with**



**ammoniacal solutions using ammonium thiosulfate and ammonium sulfite as reducing agents**, Hydrometallurgy 40, pp. 111-121.

G.P. O'Malley (2002), **Recovery of gold from thiosulfate solutions and pulps with anion-exchange resins**, PhD thesis, Murdoch University, Perth, Western Australia.

A.E. Perez and H.D. Galaviz (1987), **Method for recovery of precious metals from difficult ores with copper-ammonium thiosulfate**, United States Patent 4654078.

I.M. Ritchie, M.J. Nicol, e W.P. Staunton (2001), **Are there realistic alternatives to cyanide as a lixiviant for gold at the present time?**, Cyanide: Social, Industrial and Economic Aspects, TMS.

J.A.M. Romayna (2000), **Cianetação amoniaca de minérios de ouro-cobre de Igarapé Bahia**, dissertação de mestrado, Departamento de Engenharia Metalúrgica e de Materiais, Universidade Federal de Minas Gerais.

R.B.E. Trindade, T. Carageorgos, O.B. Filho, J.P. Barbosa (1998), **Lixiviação de ouro em solução amoniaca de tiosulfato de sódio**, XVII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa, Águas de São Pedro.

C. Xia, W.T. Yen, G. Deschenes (2002), **An investigation on minimizing reagent consumption in ammonium thiosulphate gold leaching**, 34<sup>th</sup> Annual Meeting of the Canadian Mineral Processors, Ottawa.

W.T. Yen, G. Deschenes, M. Aylmore (2001), **Thiosulfate leaching as an alternative to cyanidation: A review of the latest developments**, CIM, Paper 24.

R.Y. Wan and J.A. Brierley (1997), **Thiosulfate leaching following biooxidation pretreatment for gold recovery from refractory carbonaceous-sulfides ore**, Mining Engineering, august 1997, pp. 76-80.

H. Zhang and D.B. Dreisinger (2002a), **The adsorption of gold and copper onto ion-exchange resins from ammoniacal thiosulfate solutions**, Hydrometallurgy 66, pp. 67-76.

H. Zhang and D.B. Dreisinger (2002b), **The kinetics for decomposition of tetrathionate in alkaline solutions**, Hydrometallurgy 66, pp. 59-65.

D. Zipperian e S. Raghavan (1988), **Gold and silver extraction by ammoniacal thiosulfate leaching from a rhyolite ore**, *Hydrometallurgy*, 19, pp. 361-375.

**Appendix 1 – Thermodynamic data**

Formula	$\Delta G_{298}$ (kJ/mol)	Source	Formula	$\Delta G_{298}$ (kJ/mol)	Source
Au	0,00	HSC	Cu(S2O3)(-a)	-540,99	Aylmore and Muir, 2001b
Au(+a)	127,38	HSC	NH3(a)	-26,49	HSC
AuO2	200,80	Aylmore and Muir, 2001b	NH4(+a)	-79,37	HSC
Au2O3	77,92	HSC	S	0,00	HSC
Au(OH)3	-290,42	HSC	HS(-a)	12,19	HSC
Au(S2O3)2(-3a)	-1050,20	Aylmore and Muir, 2001b	H2SO3(a)	-538,23	HSC
Au(NH3)4(3a)	64,40	Aylmore and Muir, 2001b	HSO3(-a)	-528,04	HSC
Au(NH3)2(a)	-41,40	Aylmore and Muir, 2001b	S(-2a)	86,03	HSC
Cu	0,00	HSC	S2(-2a)	79,72	HSC
Cu(+a)	50,01	HSC	S3(-2a)	73,88	HSC
Cu(+2a)	65,44	HSC	S4(-2a)	69,45	HSC
CuO	-128,38	HSC	S5(-2a)	66,16	HSC
Cu2O	-147,98	HSC	SO3(-2a)	-486,91	HSC
Cu(OH)2	-359,26	HSC	S2O3(-2a)	-519,07	HSC
CuS	-53,51	HSC	S2O4(-2a)	-601,01	HSC
Cu2S	-86,52	HSC	S2O5(-2a)	-787,23	HSC
Cu(NH3)(+2a)	15,43	HSC	S2O6(-2a)	-969,70	HSC
Cu(NH3)2(+2a)	-30,56	HSC	S2O8(-2a)	-1115,73	HSC
Cu(NH3)3(+2a)	-73,26	HSC	S3O6(-2a)	-1025,00	HSC
Cu(NH3)4(+2a)	-111,23	HSC	S4O6(-2a)	-1040,93	HSC
Cu(S2O3)3(-5a)	-1624,65	Aylmore and Muir, 2001b	S5O6(-2a)	-956,00	HSC
Cu(S2O3)2(-3a)	-1084,07	Aylmore and Muir, 2001b		0,00	

### **Appendix 2 – Iodometric determination of thiosulfate, sulfite and sulfide in ammoniacal thiosulfate media**

Leaching liquors contain many interfering ions, such as sulfite and sulfide, which also react with iodine. The methodology utilized was based in a determination method of sulfide, sulfite, and thiosulfate in cyanide media (Lenahan and Murray-Smith, 1986). The principle is the oxidation of sulfite, sulfide and thiosulfate to sulfate, sulfur and tetrathionate by iodine in acid solution, indicated below:



Each species may be determined by titration if a separation method is performed prior to titration. Three titrations are enough to determine the concentrations. In the first one the result is the sum of all three species. In the second titration the sample is treated with formaldehyde that reacts with sulfite, as follows:



The product formed, hydrosulfonate, does not react with iodine, and thus only sulfide and thiosulfate are determined. In the third titration the sample is treated with zinc acetate, to precipitate zinc sulfide:



By titration, the combined concentrations of sulfite and thiosulfate are determined. Sulfite and sulfide individual concentrations are obtained subtracting the values of the last two titrations from the first one. Thiosulfate concentration is obtained by deducting the combined sulfite and sulfide concentrations from the total concentration.

As the concentrations of the considered sulfur species are supposed to be high in liquors, a 0.1N iodine solution and a 5mL liquor sample are used in all titrations. Iodine reacts with sulfur species in slightly acidic media, so glacial acetic acid is added to samples just before titration to adjust sample pH to a value below 6. Nearly 2mL of starch are used as indicator.

**Sulfite, sulfide and thiosulfate determination (A sample).** The determination of the sum of these three species is the simplest one. A deep blue color indicates the end point of titration.

**Sulfide and thiosulfate determination (B sample).** After adding a 5mL sample to the flask, pour 40mL of 370g/L formaldehyde and adjust pH to 8.2 with a 6mol/L NaOH solution. Add distilled water, adjust pH with acetic acid, and add starch. The solution becomes yellow, starch must be dripped during all titration, and the end point is indicated by a gray or black coloration.

**Sulfite and thiosulfate determination (C sample).** To the liquor sample, add 5mL of zinc acetate, and adjust pH to 12 with a 6mol/L NaOH solution. A white precipitate is formed and filtered with Milipore. The titration is carried out and a deep blue color indicates the end point.

To assure the accuracy of results obtained through this methodology it is necessary to compare the iodometric titration results with high performance liquid chromatography (HPLC).

Once the volumes A, B, and C are obtained from the titrations the individual concentrations are calculated, as indicated in Table A.1.

**Table A.1 Individual concentrations calculation**

Species	Calculations (g/L)	Legend
Sulfite	$(A-B) \times [I] \times 80 / v$	[I] = iodine concentration (mol/L) v = sample volume (mL)
Sulfide	$(A-C) \times [I] \times 32 / v$	
Thiosulfate	$(B+C-A) \times [I] \times 224 / v$	

*Appendix*

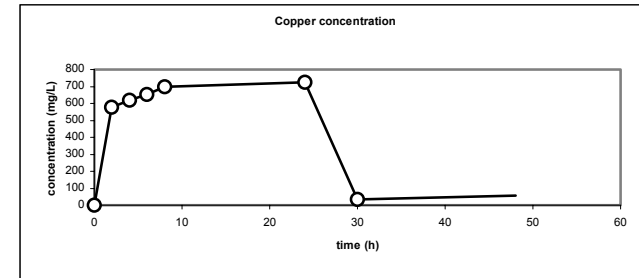
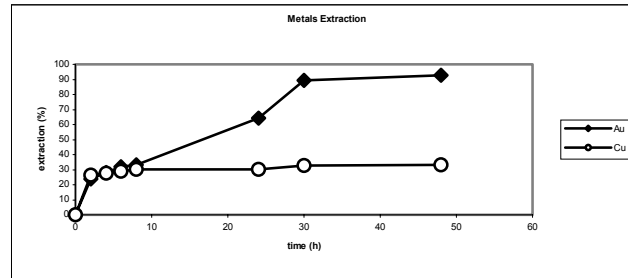
***Appendix 3 – Leaching experiments data***

Appendix

**Project:** Maximum extraction using ATS  
**Date:** 04/26/2002 to 04/28/2002

**Experimental Settings**

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 2700  
**% solids:** 33  
**ATS (g):** 345  
**NH<sub>4</sub>OH (mL):** 100  
<sup>1</sup>**Liq. sample (mL):** 25  
<sup>2</sup>**Cyanide (mL):** 20



**Residue chemical analysis**

Metal	a	b	Average	Head grade
Au (g/t)	0,3	0,27	0,285	7,8
Cu (%)	0,3	0,3	0,3	0,45

Time (h)	Liquor (mL)	Au				Cu			
		<sup>3</sup> (mg/L)	(mg/L)	extr. (mg)	extr. (%)	<sup>3</sup> (mg/L)	(mg/L)	extr. (mg)	extr. (%)
0	1015	0	0	0	0	0	0	0	0
2	1015	0,506	0,91	0,92	23,78	321,60	578,88	587,65	26,25
4	990	0,606	1,09	1,09	28,11	344,50	620,10	622,03	27,78
6	965	0,7	1,26	1,24	32,00	363,40	654,12	647,98	28,94
8	940	0,736	1,32	1,29	33,21	387,10	696,78	672,78	30,05
24	915	1,48	2,66	2,50	64,35	401,90	723,42	680,80	30,41
30	940	0,511	3,58	3,47	89,26	18,18	756,14	730,61	32,63
48	915	0,638	3,81	3,60	92,67	30,77	778,81	738,92	33,00

<sup>1</sup> Sum of the volumes of an ATS and a metals sample.

<sup>2</sup> Volume of 5% cyanide solution added to metals sample as preservative.

<sup>3</sup> Uncorrected concentration as received from DEMet/UFMG chemical analysis laboratory.

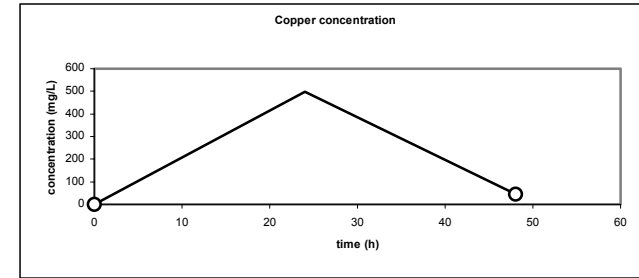
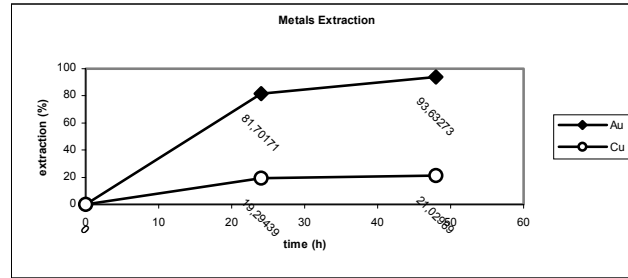
\*Second leaching stage of 24 hours

Appendix

**Project:** Cyanidation  
**Date:** 01/04/2002 to 01/06/2002

**Experimental Settings**

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 2700  
**% solids:** 33  
**NaCN initial (%):** 1  
**NaOH initial (%):** 5



**Residue chemical analysis**

Metal	a	b	Average	Head grade
Au (g/t)	0,26	0,24	0,25	3,9
Cu (%)	0,413	0,413	0,413	0,52

Time (h)	Liquor (mL)	Au			Cu		
		(mg/L)	extr. (mg)	extr. (%)	(mg/L)	extr. (mg)	extr. (%)
0	1015	0	0	0	0	0	
24	1015	1,58	1,60	81,70	497,00	504,53	19,29
48	1015	0,23	1,84	93,63	44,78	549,91	21,03

\*Second leaching step of 24h

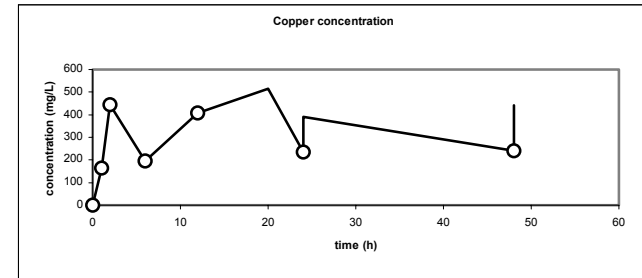
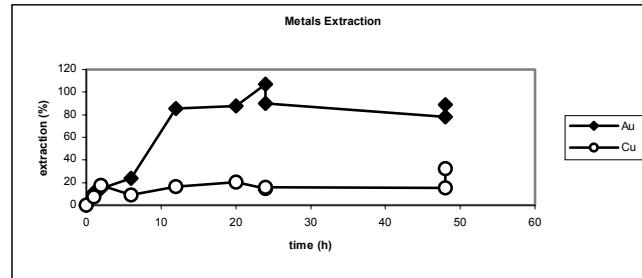


Appendix

**Project:** Preliminary tests  
**Date:** 11/21/2001 to 04/03/2002

**Experimental Settings**

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 2700  
**% solids:** 33  
**ATS initial (mol/L):** 0,23  
**NH3 initial (mol/L):** 0,67  
<sup>1</sup>**Liq. sample (mL):** 25  
<sup>2</sup>**Cyanide (mL):** 20



Each time represents an individual leaching test

Time (h)	Liquor (mL)	Au				Cu				Eh (mV)
		(mg/L)	Grade (g/t) <sup>1</sup>	extr. (mg)	extr. (%)	(mg/L)	Grade (%) <sup>1</sup>	extr. (mg)	extr. (%)	
0	1015	0	0,00	0	0,0	0	0	0	0,0	
1	1015	0,20	3,58	0,20	11,3	165,00	0,46	167,48	7,3	165
2	1015	0,28	3,86	0,28	14,6	443,20	0,51	449,85	17,7	200
6	1015	0,39	3,36	0,39	23,5	196,60	0,45	199,55	9,0	170
12	1015	1,28	3,04	1,30	85,4	408,70	0,51	414,83	16,2	
20	1015	1,32	3,05	1,34	87,9	516,00	0,51	523,74	20,3	
24	1100	1,28	2,63	1,41	107,2	235,80	0,35	259,38	14,7	*
24	1015	1,57	3,55	1,59	89,9	389,90	0,50	395,75	15,9	
48	1100	0,94	2,63	1,03	78,4	241,10	0,35	265,21	15,0	*
48	1100	1,65	4,08	1,82	89,0	442,73	0,30	487,00	32,5	

<sup>1</sup> Recalculated head grade

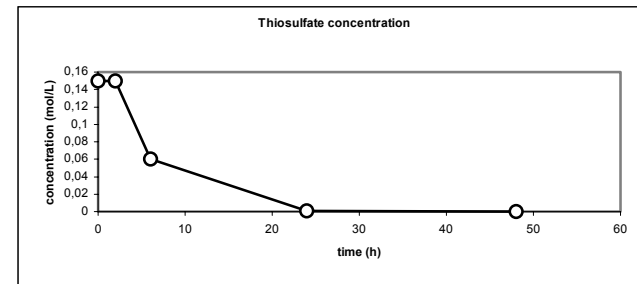
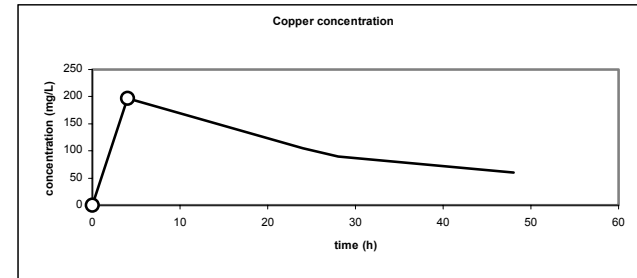
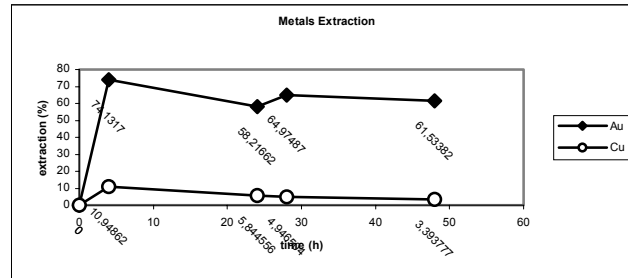
\* Duplicate

Appendix

**Project:** Preliminary tests - lower thiosulfate concentration  
**Date:** 04/03/2002 to 04/05/2002

**Experimental Settings**

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 2700  
**% solids:** 33  
**ATS initial (mol/L):** 0,15  
**NH3 initial (mol/L):** 0,52  
<sup>1</sup>**Liq. sample (mL):** 25  
<sup>2</sup>**Cyanide (mL):** 20



**Residue chemical analysis**

Metal	a	b	Avarage	Head grade
Au (g/t)	1,47	1,4	1,435	3,7
Cu (%)	0,4	0,4	0,4	0,41

Time (h)	Liquor (mL)	Au				Cu			
		<sup>2</sup> (mg/L)	(mg/L)	extr. (mg)	extr. (%)	<sup>2</sup> (mg/L)	(mg/L)	extr. (mg)	extr. (%)
0	1150	0	0,0	0,0	0,0	0	0,0	0,0	0,0
4	1150	0,668	1,2	1,4	74,1	109,50	197,1	226,7	10,9
24	1125	0,528	1,0	1,1	58,2	58,40	105,1	121,0	5,8
28	1100	0,597	1,1	1,2	65,0	49,60	89,3	102,4	4,9
48	1075	0,57	1,0	1,1	61,5	33,50	60,3	70,3	3,4

Time (h)	ATS (mol/L)
0	0,15
2	0,15
6	0,06
24	6,00E-04
48	6,00E-05

<sup>1</sup> Sum of the volumes of an ATS and a metals sample.

<sup>2</sup> Volume of 5% cyanide solution added to metals sample as preservative.

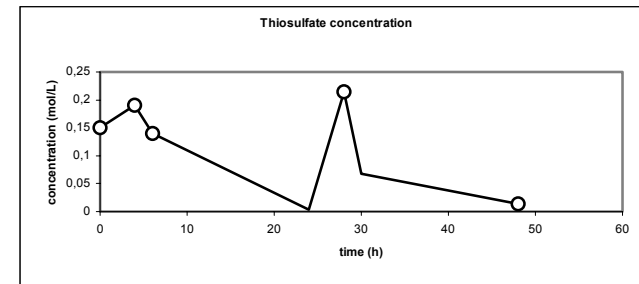
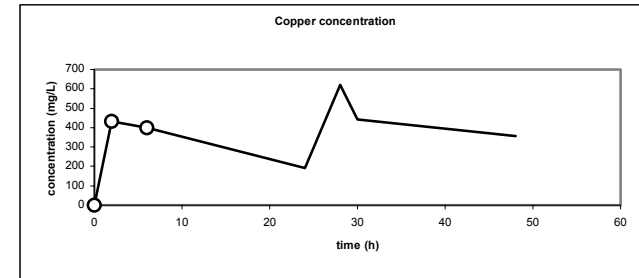
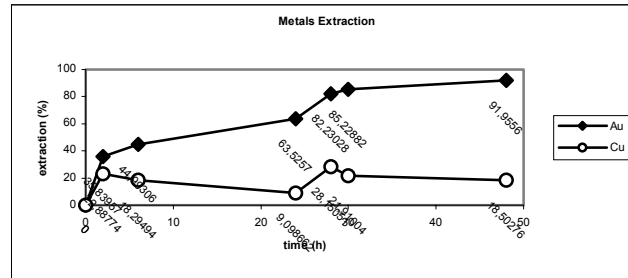
<sup>3</sup> Uncorrected concentration as received from DEMet/UFMG chemical analysis laboratory.

Appendix

**Project:** Constant thiosulfate concentration  
**Date:** 04/11/2002 to 04/13/2002

**Experimental Settings**

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 2700  
**% solids:** 33  
**ATS initial (mol/L):** 0,15  
**NH3 initial (mol/L):** 0,52  
<sup>1</sup>**Liq. sample (mL):** 25  
<sup>2</sup>**Cyanide (mL):** 20



**Residue chemical analysis**

Metal	a	b	Average	Head grade
Au (g/t)	0,49	0,48	0,485	3,3
Cu (%)	0,3	0,3	0,3	0,38

Time (h)	Liquor (mL)	Au				Cu			
		<sup>2</sup> (mg/L)	(mg/L)	extr. (mg)	extr. (%)	<sup>2</sup> (mg/L)	(mg/L)	extr. (mg)	extr. (%)
0	1015	0	0	0	0	0	0	0	0
2	1015	0,322	0,58	0,59	35,84	240,60	433,08	439,64	22,89
6	864	0,47	0,85	0,74	44,99	222,20	399,96	351,42	18,29
24	859	0,662	1,19	1,04	63,53	105,60	190,08	174,77	9,10
28	849	0,86	1,55	1,35	82,23	344,70	620,46	540,73	28,15
30	900	0,828	1,49	1,40	85,23	245,70	442,26	420,86	21,91
48	929	0,861	1,55	1,51	91,96	198,90	358,02	355,41	18,50

Time (h)	ATS (mol/L)
0	0,15
4	0,19
6	0,14
24	0,004
28	0,214
30	0,068
48	0,014

<sup>1</sup> Sum of the volumes of an ATS and a metals sample.

<sup>2</sup> Volume of 5% cyanide solution added to metals sample as preservative.

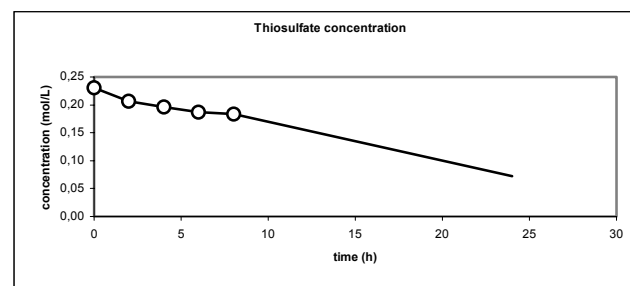
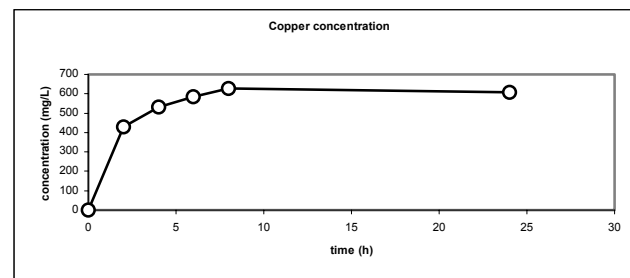
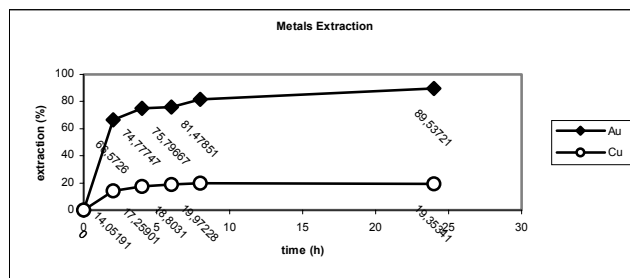
<sup>3</sup> Uncorrected concentration as received from DEMet/UFMG chemical analysis laboratory.

Appendix

**Project:** Base Experiment  
**Date:** 07/14/03 to 07/15/03

**Experimental Settings**

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 2700  
**% solids:** 33  
**ATS initial (mol/L):** 0,23  
**NH3 initial (mol/L):** 0,67  
<sup>1</sup>**Liq. sample (mL):** 30  
<sup>2</sup>**Cyanide (mL):** 5



**Residue chemical analysis**

Metal	a	b	Average	Head grade
Au (g/t)	0,34	0,35	0,345	3,3
Cu (%)	0,51	0,49	0,5	0,62

Time (h)	Liquor (mL)	Au				Cu				ATS (g/L)	Eh (mV)		
		̄(mg/L)	(mg/L)	extr. (mg)	extr. (%)	̄(mg/L)	(mg/L)	extr. (mg)	extr. (%)				
0	1015	0	0	0	0	0	0	0	1,29	25,79	0,23	282	
2	1015	0,901	1,08	1,10	66,57	367,80	429,10	435,60	14,05	1,16	23,20	0,21	197
4	985	1,02	1,22	1,23	74,78	455,90	531,88	535,02	17,26	1,10	22,00	0,20	197
6	955	1,04	1,25	1,25	75,80	500,90	584,38	582,89	18,80	1,05	21,00	0,19	197
8	925	1,13	1,36	1,34	81,48	536,80	626,27	619,13	19,97	1,03	20,60	0,18	197
24	895	1,26	1,51	1,48	89,54	521,00	607,83	599,94	19,35	0,41	8,15	0,07	197

<sup>1</sup> Sum of the volumes of an ATS and a metals sample.

<sup>2</sup> Volume of 5% cyanide solution added to metals sample as preservative.

<sup>3</sup> Uncorrected concentration as received from DEMet/UFMG chemical analysis laboratory.

## Appendix

**Project:** Acid leaching for ATS leaching at 25°C and lower NH<sub>3</sub>/ATS ratio  
**Date:** 02/10/03 to 02/13/03

### Experimental Settings

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 700  
**Particle size:** 74% < 0.074mm  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 3780  
**% solids:** 40  
**H<sub>2</sub>SO<sub>4</sub> initial (g/kg):** 98,5  
**Leaching time:** 15'  
**Cu in liquor (mg/L):** 883,2  
**Cu extraction (mg):** 927,36  
**Cu extraction (%):** 23

### Residue chemical analysis

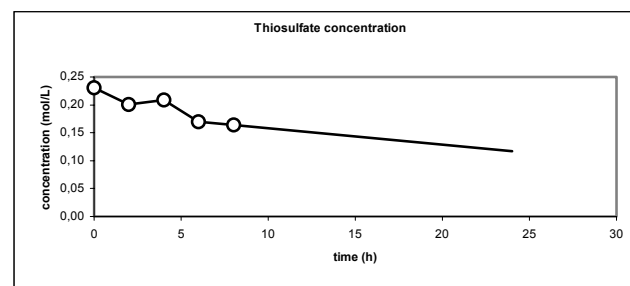
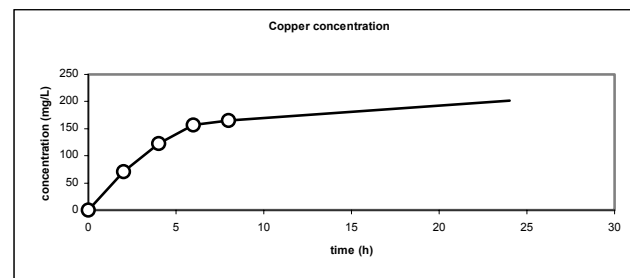
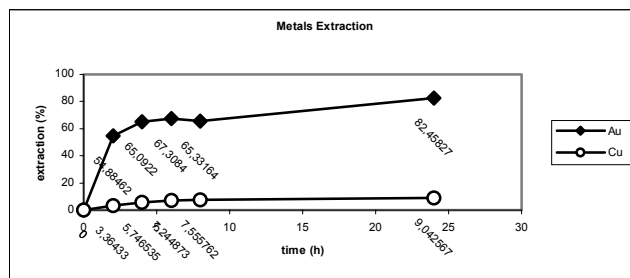
Metal	a	b	Avarage	Head grade
Cu (%)	0,44	0,44	0,44	0,57

Appendix

**Project:** Leaching a pretreated ore at 25°C  
**Date:** 07/12/03 to 07/13/03

**Experimental Settings**

**Material:** pretreated gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,42%  
**Total Cu (mg):** 2100  
**% solids:** 33  
**ATS initial (mol/L):** 0,23  
**NH3 initial (mol/L):** 0,67  
<sup>1</sup>**Liq. sample (mL):** 30  
<sup>2</sup>**Cyanide (mL):** 5



**Residue chemical analysis**

Metal	a	b	Average	Head grade
Au (g/t)	0,45	0,5	0,475	2,7
Cu (%)	0,39	0,39	0,39	0,43

Time (h)	Liquor (mL)	Au				Cu				ATS (g/L)	Eh (mV)		
		~(mg/L)	(mg/L)	extr. (mg)	extr. (%)	~(mg/L)	(mg/L)	extr. (mg)	extr. (%)				
0	1015	0	0	0	0	0	0	0	1,70	34,09	0,23	302	
2	1015	0,61	0,73	0,74	54,88	60,90	71,05	72,13	3,36	1,13	22,50	0,20	237
4	985	0,73	0,88	0,88	65,09	105,60	123,20	123,20	5,75	1,17	23,40	0,21	227
6	955	0,76	0,91	0,91	67,31	134,90	157,38	155,32	7,24	0,95	19,05	0,17	217
8	925	0,74	0,89	0,88	65,33	141,70	165,32	161,98	7,56	0,92	18,45	0,16	207
24	895	0,96	1,15	1,12	82,46	172,90	201,72	193,86	9,04	0,66	13,14	0,12	197

<sup>1</sup> Sum of the volumes of an ATS and a metals sample.

<sup>2</sup> Volume of 5% cyanide solution added to metals sample as preservative.

<sup>3</sup> Uncorrected concentration as received from DEMet/UFMG chemical analysis laboratory.

## Appendix

**Project:** Acid leaching for ATS leaching at 60°C  
**Date:** 07/21/03 to 07/22/03

### Experimental Settings

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Initial mass (g):** 1149,9  
**Final mass (g):** 1126  
**Particle size** 74% < 0.074mm  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 6209,46  
**% solids:** 40  
**H<sub>2</sub>SO<sub>4</sub> initial (g/kg):** 98,5  
**Leaching time:** 15'  
**Cu in liquor (mg/L):** 1330  
**Cu extraction (mg):** 2294,1  
**Cu extraction (%):** 33

### Residue chemical analysis

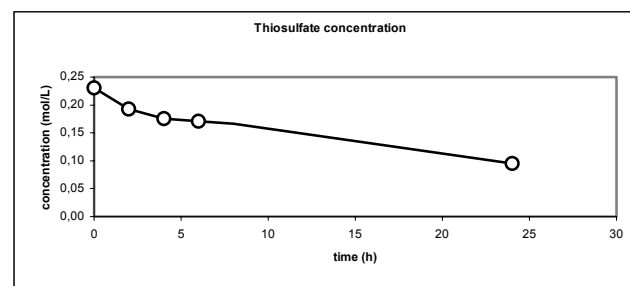
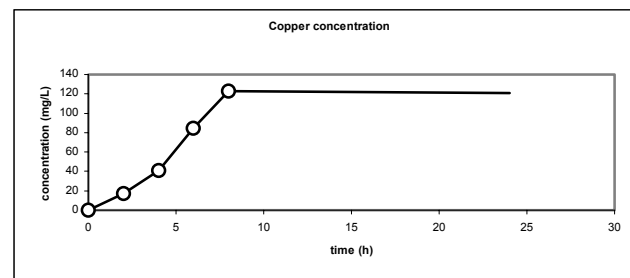
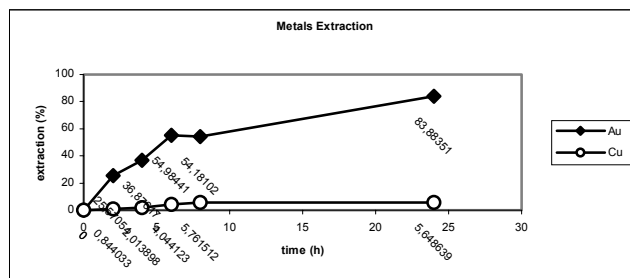
Metal	a	b	Avarage	Head grade
Cu (%)	0,4	0,44	0,42	0,61

Appendix

**Project:** Leaching a pretreated ore at 60°C  
**Date:** 07/21/03 to 07/24/03

**Experimental Settings**

**Material:** pretreated gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,42%  
**Total Cu (mg):** 2100  
**% solids:** 33  
**ATS initial (mol/L):** 0,23  
**NH3 initial (mol/L):** 0,67  
<sup>1</sup>**Liq. sample (mL):** 30  
<sup>2</sup>**Cyanide (mL):** 5



**Residue chemical analysis**

Metal	a	b	Average	Head grade
Au (g/t)	0,4	0,42	0,41	2,5
Cu (%)	0,38	0,39	0,385	0,41

Time (h)	Liquor (mL)	Au				Cu				ATS (g/L)	Eh (mV)	
		²(mg/L)	(mg/L)	extr. (mg)	extr. (%)	²(mg/L)	(mg/L)	extr. (mg)	extr. (%)			
0	1015	0	0	0	0	0	0	0	1,70	34,09	0,23	282
2	1015	0,267	0,32	0,33	25,57	14,54	16,96	17,22	0,84	21,60	0,19	247
4	985	0,39	0,47	0,47	36,88	35,37	41,27	41,09	2,01	19,72	0,18	227
6	955	0,593	0,71	0,70	54,98	72,70	84,82	82,51	4,04	19,10	0,17	217
8	925	0,587	0,70	0,69	54,18	105,50	123,08	117,55	5,76	18,63	0,17	222
24	895	0,942	1,13	1,07	83,88	103,80	121,10	115,25	5,65	10,65	0,09	217

<sup>1</sup> Sum of the volumes of an ATS and a metals sample.

<sup>2</sup> Volume of 5% cyanide solution added to metals sample as preservative.

<sup>3</sup> Uncorrected concentration as received from DEMet/UFMG chemical analysis laboratory.

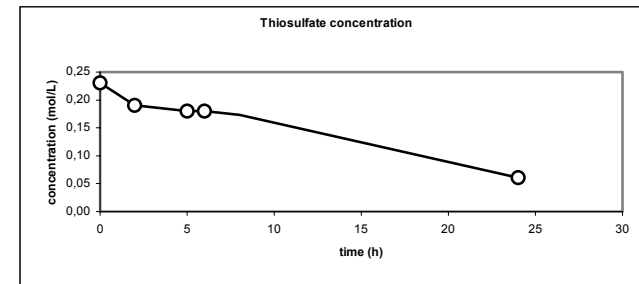
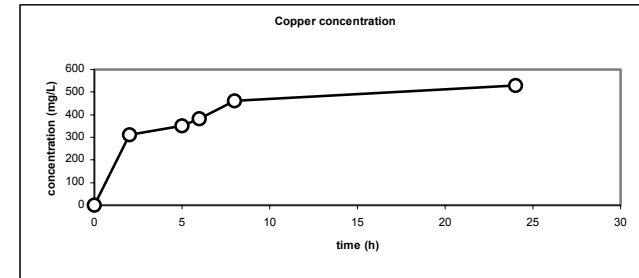
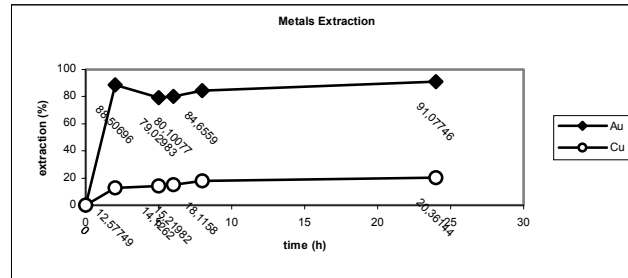


Appendix

**Project:** NH<sub>3</sub>/S<sub>2</sub>O<sub>3</sub> ratio  
**Date:** 07/16/03 to 07/17/03

**Experimental Settings**

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 2700  
**% solids:** 33  
**ATS initial (mol/L):** 0,23  
**NH<sub>3</sub> initial (mol/L):** 1,38  
<sup>1</sup>**Liq. sample (mL):** 30  
<sup>2</sup>**Cyanide (mL):** 5



**Residue chemical analysis**

Metal	a	b	Average	Head grade
Au (g/t)	0,28	0,28	0,28	3,1
Cu (%)	0,4	0,4	0,4	0,50

Time (h)	Liquor (mL)	Au				Cu				ATS (g/L)	Eh (mV)		
		°(mg/L)	(mg/L)	extr. (mg)	extr. (%)	°(mg/L)	(mg/L)	extr. (mg)	extr. (%)				
0	1015	0	0	0	0	0	0	0	0,00	34,09	0,23	272	
2	1015	1,14	1,37	1,39	88,51	266,70	311,15	315,86	12,58	1,07	21,40	0,19	262
5	985	1,02	1,22	1,24	79,03	301,70	351,98	354,76	14,13	1,01	20,20	0,18	217
6	955	1,04	1,25	1,26	80,10	327,70	382,32	382,22	15,22	1,01	20,20	0,18	197
8	925	1,11	1,33	1,33	84,66	396,60	462,70	454,95	18,12	0,97	19,43	0,17	197
24	895	1,21	1,45	1,43	91,08	452,50	527,92	511,35	20,36	0,34	6,80	0,06	197

<sup>1</sup> Sum of the volumes of an ATS and a metals sample.

<sup>2</sup> Volume of 5% cyanide solution added to metals sample as preservative.

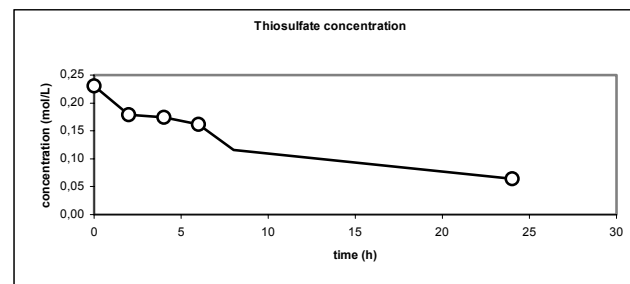
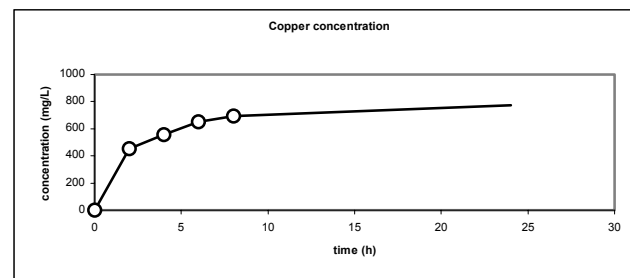
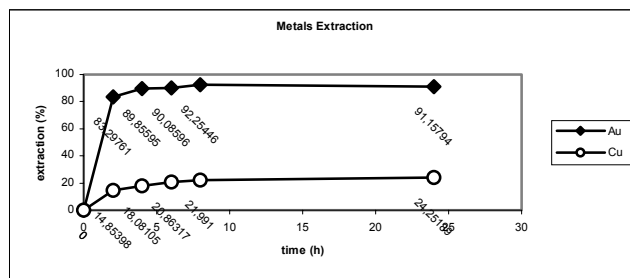
<sup>3</sup> Uncorrected concentration as received from DEMet/UFMG chemical analysis laboratory.

Appendix

**Project:** Nitrogen injection 1  
**Date:** 08/13/03 to 08/14/03

**Experimental Settings**

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 2700  
**% solids:** 33  
**ATS initial (mol/L):** 0,23  
**NH3 initial (mol/L):** 0,67  
<sup>1</sup>**Liq. sample (mL):** 30  
<sup>2</sup>**Cyanide (mL):** 5



**Residue chemical analysis**

Metal	a	b	Average	Head grade
Au (g/t)	0,32	0,28	0,3	3,4
Cu (%)	0,47	0,47	0,47	0,62

Time (h)	Liquor (mL)	Au				Cu				ATS (g/L)	Eh (mV)	
		<sup>3</sup> (mg/L)	(mg/L)	extr. (mg)	extr. (%)	<sup>3</sup> (mg/L)	(mg/L)	extr. (mg)	extr. (%)			
0	1015	0	0	0	0	0	0	0	1,70	34,09	0,23	307
2	1015	1,16	1,39	1,41	83,30	389,10	453,95	460,83	14,85	20,00	0,18	207
4	985	1,26	1,51	1,52	89,86	477,90	557,55	560,94	18,08	19,48	0,17	177
6	955	1,27	1,52	1,53	90,09	557,50	650,42	647,26	20,86	18,09	0,16	172
8	925	1,31	1,57	1,57	92,25	592,50	691,25	682,25	21,99	12,93	0,12	172
24	895	1,3	1,56	1,55	91,16	662,50	772,92	752,39	24,25	7,16	0,06	172

<sup>1</sup> Sum of the volumes of an ATS and a metals sample.

<sup>2</sup> Volume of 5% cyanide solution added to metals sample as preservative.

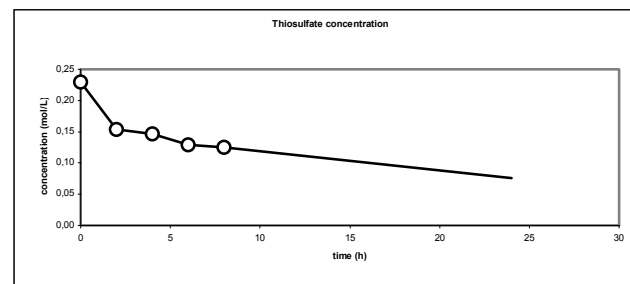
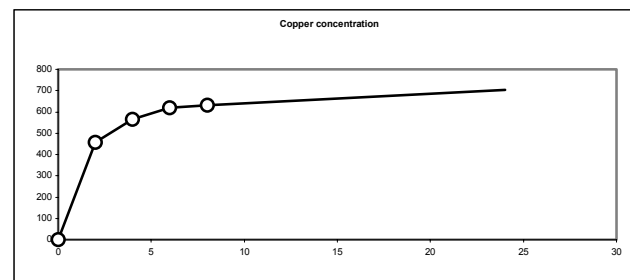
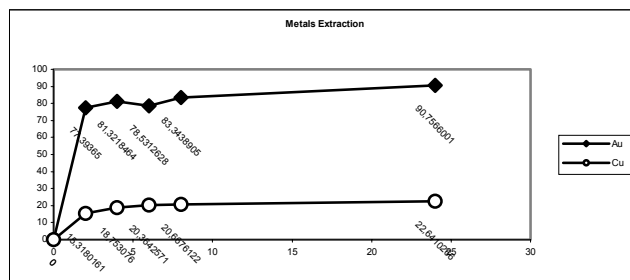
<sup>3</sup> Uncorrected concentration as received from DEMet/UFMG chemical analysis laboratory.

Appendix

**Project:** Nitrogen injection 2  
**Date:** 08/21/03 to 08/24/03

**Experimental Settings**

**Material:** oxidized gold-copper ore  
**Sample:** trench  
**Mass (g):** 500  
**Particle size:** 74% < 0.074mm  
**Au head grade:** 3,88g/t  
**Total Au (mg):** 1,94  
**Cu head grade:** 0,54%  
**Total Cu (mg):** 2700  
**% solids:** 33  
**ATS initial (mol/L):** 0,23  
**NH3 initial (mol/L):** 0,67  
<sup>1</sup>**Liq. sample (mL):** 30  
<sup>2</sup>**Cyanide (mL):** 5



**Residue chemical analysis**

Metal	a	b	Average	Head grade
Au (g/t)	0,43	0,28	0,355	3,8
Cu (%)	0,47	0,47	0,47	0,61

Time (h)	Liquor (mL)	Au				Cu				ATS (g/L)	Eh (mV)		
		̂(mg/L)	(mg/L)	extr. (mg)	extr. (%)	̂(mg/L)	(mg/L)	extr. (mg)	extr. (%)				
0	1015	0	0	0	0	0	0	0	1,70	34,09	0,23	307	
2	1015	1,22	1,46	1,49	77,39	392,90	458,38	465,33	15,32	0,86	17,22	0,15	192
4	985	1,29	1,55	1,56	81,32	485,40	566,30	569,68	18,75	0,82	16,41	0,15	177
6	955	1,25	1,50	1,51	78,53	531,50	620,08	618,62	20,36	0,73	14,53	0,13	177
8	925	1,34	1,61	1,60	83,34	542,50	632,92	627,84	20,67	0,70	14,07	0,13	177
24	895	1,48	1,78	1,74	90,76	602,50	702,92	687,79	22,64	0,42	8,49	0,08	172

<sup>1</sup> Sum of the volumes of an ATS and a metals sample.

<sup>2</sup> Volume of 5% cyanide solution added to metals sample as preservative.

<sup>3</sup> Uncorrected concentration as received from DEMet/UFMG chemical analysis laboratory (Olivia's lab).