

Ammoniacal thiosulphate leaching of gold ore

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ABSTRACT

Ammoniacal thiosulphate leaching of gold finds a better substitute as it is non-toxic and environmentally safe as compared to the toxic cyanide system for gold extraction. In the present study, an attempt is made to assess the feasibility of ammoniacal thiosulphate leaching of gold ore samples from two different mines namely Akeshi and Hishikari of Japan. In this study, the effect of thiosulphate concentration, effect of ammonia, effect of cupric ions, and few other variables affecting the gold leaching have been studied. The ammoniacal thiosulphate leaching of gold is dependant on both ammonia and thiosulphate concentration. The leaching is improved significantly at a particular ratio of ammonia to thiosulphate concentration and that ratio varies from ore to ore. Copper ions act as an oxidant and the gold dissolution increases substantially in the presence of them. The gold leaching is minimum in the presence of an inert gas such as nitrogen and the leaching increases in presence of other gases like oxygen and air. © 2003 SDU. All rights reserved.

Keywords: Gold; Ammoniacal thiosulphate; Leaching

1. INTRODUCTION

In recent times, environment is one of the key factors while considering any leaching system in hydrometallurgy. Cyanide leaching has been in use since several decades for economic gold extraction although it is environmentally unfriendly. In last few years the growing environmental awareness factor made researchers to look for alternative leaching system for the extraction of gold. A good deal of research has been carried out by several workers in finding out a safe method for gold leaching (Woodcock, 1988; Ximing *et al.*, 1992; Davies *et al.*, 1993; Tremblay *et al.*, 1996). Among all the studies, ammoniacal thiosulphate leaching of gold finds a better substitute as it is non-toxic and environmentally safe. There are few reports available in the literature on ammoniacal thiosulphate leaching of gold (Yen *et al.*, 1996; Fujita *et al.*, 1997; Breuer and Jeffery, 2000; Navarro *et al.*, 2002). An excellent review article has been published by Alymore and Muir (2001) in which the chemistry and thermodynamics of ammoniacal thiosulphate leaching process of gold has been outlined.

In the present study, an attempt is made to assess the feasibility of ammoniacal thiosulphate leaching of gold ore samples from two different mines namely Akeshi and Hishikari of Japan. In this study, the effect of thiosulphate concentration, effect of ammonia, effect of cupric ions, and few other variables affecting the gold leaching have been studied.

2. EXPERIMENTAL

2.1. Materials

Two gold bearing ore samples were obtained from Akeshi and Hishikari mines of Kyushu region of Japan. The as received lump samples were crushed using a primary jaw crusher followed by a roll crusher to get a product passing through 1680 μ m sieve. The materials were homogenised thoroughly and a representative sample of 2kg were drawn and kept sealed in separate polyethylene bags for the ball mill

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grinding. The -1680 μ m representative ore sample was then subjected to ball mill and was ground for three hours to get a product 90% passing through 75 μ m. These materials were used for the leaching experiments.

2.2. Mineral characterisation

Both the mineral samples were characterized mineralogically. Polished thin sections of three different size ranges (-1680+600, -75+37 and -37 μ m) were prepared and observed under the optical microscope. It was possible to identify various species in the coarse samples only. Quartz and pyrite were the main gangue species that were present in both the samples. In addition to these impurities, oxides such as goethite and anatase (TiO₂) were present in Akeshi sample and traces of sphalerite and soft material like clays were present in Hishikari sample. It was very difficult to trace gold in both the samples, as the gold content was very less.

The gold content was analysed chemically using an Inductively Coupled Plasma (ICP) Spectrometer. The ore samples were first digested in an acid mixture using an Ethos Plus Microwave Labstation digester, supplied by Milestone Microwave Laboratory Systems, Japan. It was found out by ICP analysis that Akeshi and Hishikari ore samples contain 10.5 and 31 ppm of gold respectively.

2.3. Chemicals

All the chemicals used were of reagent grade and were supplied by Wako Chemicals Co Ltd. The chemicals used in this study are as follows: Sodium thiosulphate (Na₂S₂O₃·5H₂O), Ammonia water (28% NH₃) and Cupric sulphate (CuSO₄·5H₂O).

2.4. Method

Leaching experiments were carried out in a three-necked, 1L glass reaction vessel at room temperature. In a typical experiment, 300g of gold ore was mixed with 750ml of the ammoniacal thiosulphate leachant and was taken in a three necked glass reaction vessel. The solid particles were kept in suspension through a mechanical stirrer rotating at a speed of 400rpm. Between the other two necks, one was employed for a thermometer to measure the temperature of the leaching system and the other was for collecting suspensions at regular intervals of time to be chemically analysed. The solid concentration was maintained at 40% in all the experiments unless otherwise stated. In few experiments, gases such as nitrogen or oxygen or air were introduced into the leaching solution through an inlet tube replacing the thermometer. The excess gas was allowed to go through an outlet tube. The gas was allowed to pass through a jar containing water to make it saturated and was then connected to a gas flow meter to regulate the amount of gas flow before entering into the leaching system.

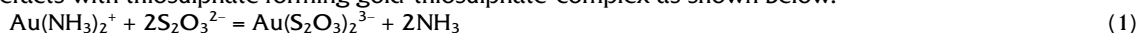
2.5. Titration methodology

Titration experiment was carried out by taking 75ml of buffer solution (1M NH₃+0.005M(NH₄)₂SO₄) containing a mineral sample (30g) and titrated against 0.1M cupric sulphate as oxidant using an Auto-Titration Instrument (Auto Titrator-AUT 501), TOA-DKK Corporation Japan. The suspension was agitated using a magnetic stirrer and the solution potential (E_n) was measured using a platinum electrode against an Ag/AgCl reference electrode.

3. RESULTS AND DISCUSSION

The results of various leaching tests are presented and discussed in this section. The following variables were tried such as the effect of thiosulphate concentration, effect of ammonia concentration, effect of cupric ions concentration, effect of temperature, effect of solid concentration, effect of various gases etc.

It is reported in the literature (Alymore and Muir, 2001) that ammonia is a prerequisite for thiosulphate leaching of gold as its absence makes gold passive by the build up of sulphur coating on the surface as a result of decomposition of thiosulphate. It is known that thiosulphate is a meta-stable species that readily undergoes decomposition in aqueous solutions. Ammonia adsorbs onto the gold surface preferentially over thiosulphate forming gold-ammine-complex thereby reducing the passivation. The gold-ammine-complex interacts with thiosulphate forming gold-thiosulphate-complex as shown below:



There is one more advantage on ammonia addition as it prevents the dissolution of iron oxides, silica, silicates and carbonates generally present in the ore body as gangue minerals.

3.1. Effect of time

The ammoniacal thiosulphate leaching of two gold ore samples namely Akeshi and Hishikari was carried out as a function of time and the results are given in Figure 1a. In this experiment, the thiosulphate and ammonia concentrations were kept at 0.5 and 1M respectively. The solid concentrations of the ores were kept at 40% and the stirrer was maintained at a speed of 400rpm. As can be seen from the figure, Au leaching increases with increase in time for both the samples. It is also noticed that the Au leaching is little higher with Akeshi sample for the first two hour of leaching and the trend reverses beyond 2h of leaching. The pH and E_h changes of these leaching systems are presented in Figure 1b. The pH changes are very minimum almost remains constant at around 11.2–11.4 for both the samples as a function of time. The E_h of the leaching systems were fluctuating 150–160 and 170–180mV vs. SHE respectively. The times of leaching were restricted for about 5h for the rest of the leaching experiments.

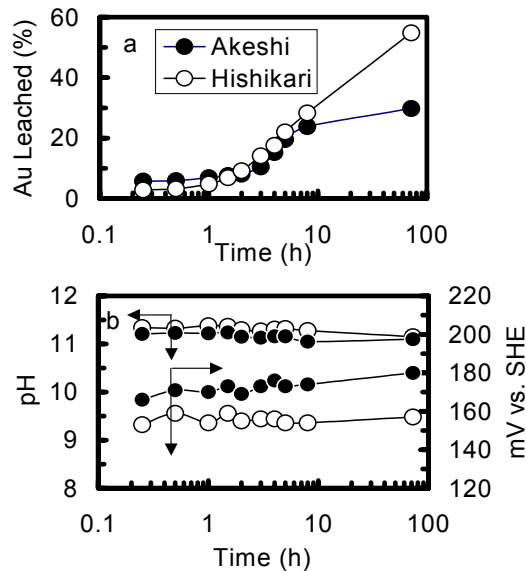
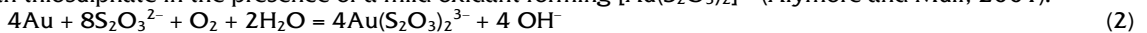


Figure 1. Ammoniacal thiosulphate leaching of Akeshi and Hishikari gold ores a) as a function of time and b) as a function of pH and E_h (Thiosulphate concentration, 0.5M; Ammonia concentration, 1M)

3.2. Effect of thiosulphate

The results of effect of thiosulphate concentration on leaching are portrayed in Figure 2. In these experiments, thiosulphate concentration was varied between 0.1–1M while the ammonia concentration was kept at 1M. It is seen from Figure 2a that the Au leaching decreases with increase in sample for Akeshi in the concentration range studied, whereas Au extraction increases from 0.1–0.5M thiosulphate concentration and decreases thereafter in the case of Hishikari sample (Figure 2b). It appears that there is a suitable concentration of ammonia and thiosulphate required for effective leaching for each ore sample and that concentration varies from ore to ore depending upon their composition. But it was observed that higher concentration of thiosulphate reduces Au dissolution and when the concentration was 2M, there was literally no extraction for both the samples (data not shown). This could possibly happen because of difficulty in preferential adsorption of ammonia onto gold at higher thiosulphate concentration. Ammonia is a precondition for Au leaching in comparison to thiosulphate alone. It is known that gold dissolves slowly with thiosulphate in the presence of a mild oxidant forming $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ (Alymore and Muir, 2001).



The pH change was almost negligible and found to fluctuate between 11.1–11.4 for both the samples. The pH was little lower for the Hishikari sample in comparison with Akeshi sample, which was in line with the percentage of Au leached. The E_h fluctuates in the range of 160–180 and 140–160mV vs. SHE for Hishikari and Akeshi samples respectively. It was noticed that the E_h for Hishikari sample was little higher than the Akeshi sample, which indicates a stronger oxidizing conditions for Hishikari sample.

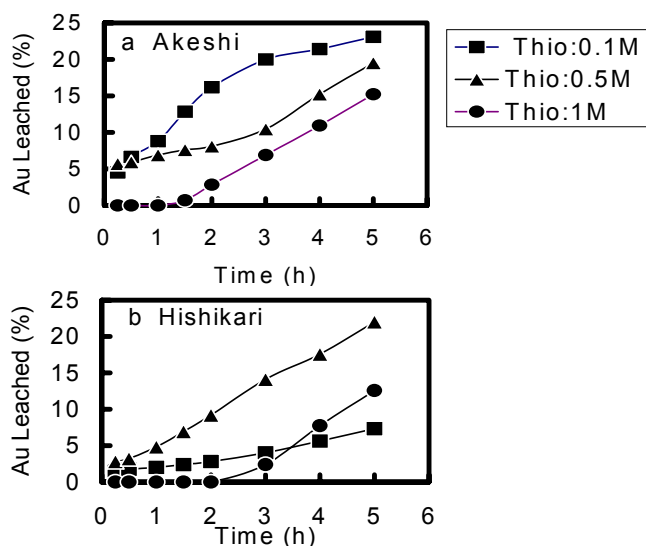


Figure 2. Effect of thiosulphate concentration on Au leaching as a function of time for a) Akeshi and b) Hishikari gold samples (Ammonia concentration, 1M)

3.3. Effect of copper

The effect of copper ions on Au leaching was investigated and the results are depicted in Figure 3. The results of Au dissolution in absence of copper ions were also incorporated in the same figure for comparison. The copper concentration was varied between 0.0001–0.01M while the thiosulphate and ammonia concentrations were kept constant at 0.5 and 1M respectively. It is evident from the figure that Au leaching increases with increase in copper ion concentrations from 0.0001–0.01M for both samples (Figures 3a and 3b). There was a fourfold increase in the amount of Au leached in the case of Hishikari gold sample from no copper to 0.01M copper ions. There was also an increase in the amount of Au leached for the Akeshi gold sample. Copper ions act as a catalyst for gold dissolution in ammoniacal thiosulphate system. There are few reports in the literature on copper ion activation of gold dissolution in ammoniacal thiosulphate system (Abbruzzese *et al.*, 1995; Aylmore and Muir, 2001). Copper ions readily form cupric-ammine complex $\text{Cu}(\text{NH}_3)_4^{2+}$ with ammonia which then interacts with Au forming gold-ammine complex.

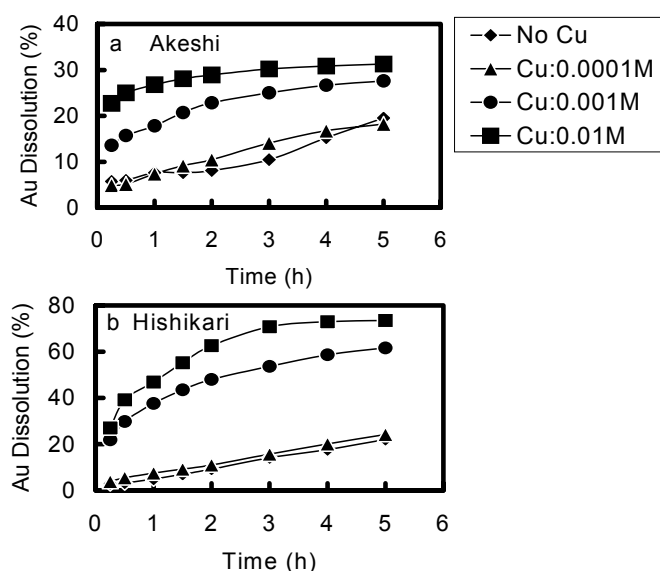


Figure 3. Effect of copper ion concentration on Au leaching as a function of time for a) Akeshi and b) Hishikari gold samples (Thiosulphate concentration, 0.5M; Ammonia concentration, 1M)



The pH change was negligible and found to fluctuate between 11.1–11.5 for both the samples. The E_h value was found to fluctuate between 180–160 and 160–140mV vs. SHE for Hishikari and Akeshi samples respectively. The copper concentration was kept constant at 0.001M for the remaining experiments as it is important to select a low concentration from economic and also from the analytical interference point of view.

3.4. Effect of ammonia

The results of the effect of ammonia concentration on leaching are portrayed in Figure 4. In these experiments, ammonia concentration was varied between 1–3M while the thiosulphate and copper concentration were kept at 0.5 and 0.001M respectively. It is seen from Figure 4a that gold dissolution decreases with increase in ammonia concentration upto 2M and thereafter remains more or less constant for Akeshi sample whereas the leaching decreases with increase in ammonia concentration for Hishikari sample (Figure 4b) for the entire concentration range studied. As expected, the pH of the solution increased to above 12 as a result of increase of ammonia concentration for both the samples. The E_h change was found to be fluctuating between 110-150 and 140-170mV vs. SHE for Akeshi and Hishikari samples respectively. The E_h values are also showing a gradual fall in their magnitude on increasing the ammonia concentration, which is also an indication that the system is not favouring for oxidation at higher ammonia concentration.

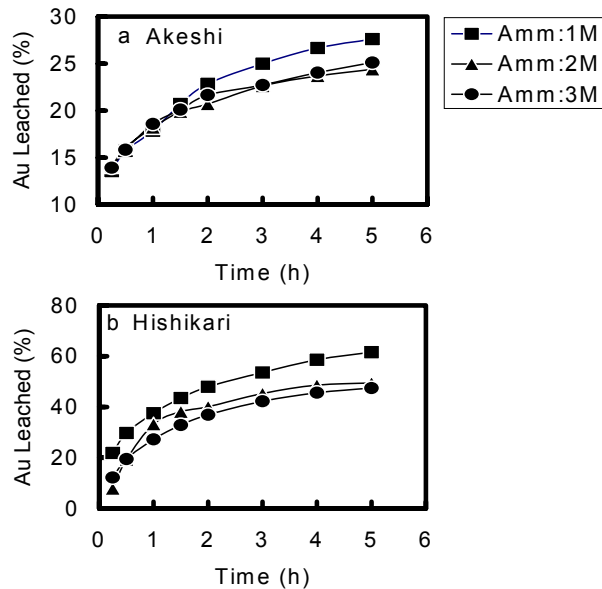


Figure 4. Effect of ammonia concentration on Au leaching as a function of time for a) Akeshi and b) Hishikari gold samples (Thiosulphate concentration, 0.5M; Cupric sulphate concentration, 0.001M)

3.5. Effect of temperature

The results of the effect of temperature on Au leaching in ammoniacal thiosulphate solution in presence of 0.001M copper ion concentrations are portrayed in Figure 5. The temperature was varied between 10–50°C while thiosulphate, ammonia and copper concentrations were kept constant at 0.5, 1 and 0.001M respectively. It is evident that there is a slight increase in Au leaching with increase in temperature. There are reports supporting the fact that leaching increases with rise in temperature (Zipperian, 1988; Hemmati *et al.*, 1989; Zhou *et al.*, 1999) and also reports contradicting this fact (Fujita *et al.*, 1997; Abbruzzese, 1995). The reactivity increases with the rise in temperature upto a certain temperature say 50°C and beyond that it decreases (data not shown) in our case. The Au leached was higher in case of Hishikari sample in comparison with Akeshi sample. The pH change fluctuates in the range of 11.2–11.6 for both the samples over the entire time range studied. The corresponding E_h values fluctuate between 160–175 and 130–160mV vs. SHE for Akeshi and Hishikari samples respectively.

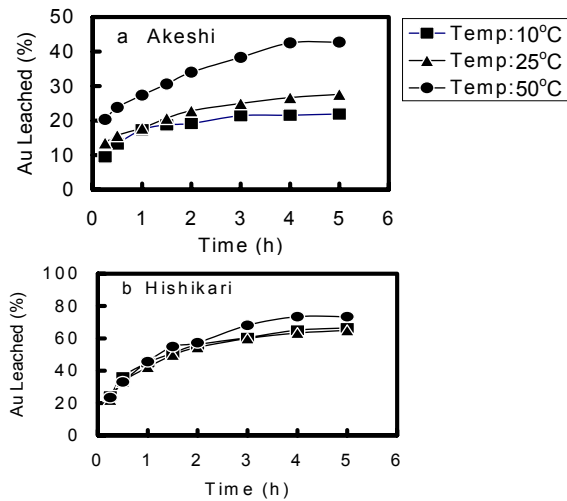


Figure 5. Effect of temperature on Au leaching as a function of time for a) Akeshi and b) Hishikari gold samples (Thiosulphate concentration, 0.5M; Ammonia concentration, 1M; Cupric sulphate concentration, 0.001M)

3.6. Effect of solid concentration

The results of the effect of solid concentrations on the Au leaching in the presence of 0.001M cupric sulphates are depicted in Figure 6. The solid concentration was varied between 20–60% while the thiosulphate, ammonia and copper concentrations were kept constant at 0.5, 1, and 0.001M respectively. The gold leaching decreases with increase in solid concentration from 20–60% in case of Akeshi sample (Figure 6a) whereas for Hishikari sample, there is an increase in Au leaching from 20–40% solids and beyond 40%, a decrease in Au leaching is observed (Figure 6b). The decrease may be attributed to the following two reasons. At the higher solid concentrations, the leach solution concentration may not be enough to leach the ore effectively in comparison to the low solid concentration where the leach solution concentration is sufficient enough for the purpose. Secondly, at high solid concentrations, there is crowding of the particles resulting lesser contact with the solution than particle–particle contact and thereby reducing the leaching. The pH change is marginal for the above leaching conditions and remains more or less constant in the pH range of 11.2–11.6 for both the gold samples. The E_h of the same leaching system fluctuates between 150–170 and 135–155mV vs. SHE for Hishikari and Akeshi sample respectively.

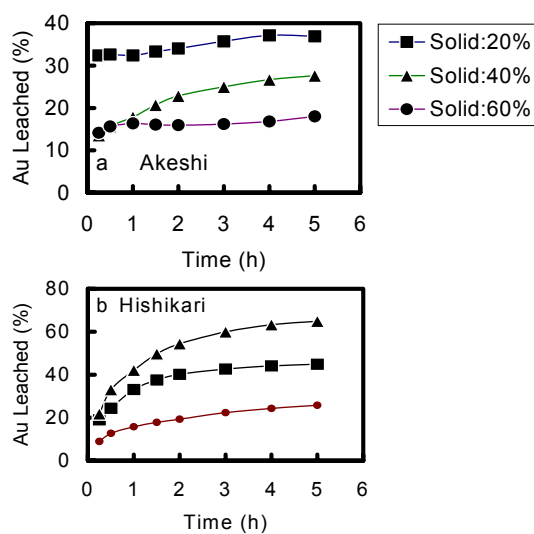


Figure 6. Effect of solid concentration on Au leaching as a function of time for a) Akeshi and b) Hishikari gold samples (Thiosulphate concentration, 0.5M; Ammonia concentration, 1M; Cupric sulphate concentration, 0.001M)

3.7. Effect of rotation speed

The results of the effect of the stirrer rotation speed are portrayed in Figure 7. The rotation speed of stirrer was varied from 200–600rpm while, thiosulphate, ammonia and copper concentrations were kept at 0.5, 1 and 0.001M respectively. It is evident from the figure that Au leaching increases with increase in rpm from 200–400 and beyond 400rpm, it was more or less constant in the case of Akeshi sample (Figure 7a). With Hishikari sample, Au leaching increases from about 200–400 and beyond 400rpm, a decrease in leaching was observed (Figure 7b). It appears that higher rotation create a turbulence, which may be affecting the leaching performance. The pH change is very minimum and fluctuates between 11.2–11.6 for the entire leaching time. The E_h of the same system fluctuates around 150–170 and 130–150mV vs. SHE for Hishikari and Akeshi samples, respectively.

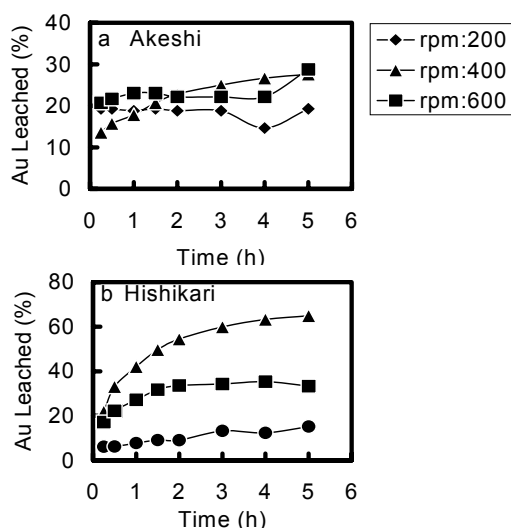


Figure 7. Effect of rotation speed on Au leaching as a function of time for a) Akeshi and b) Hishikari gold samples (Thiosulphate concentration, 0.5M; Ammonia concentration, 1M; Cupric sulphate concentration, 0.001M)

3.8. Effect of gases

The results of the effect of different gases such as oxygen, nitrogen and air are portrayed in Figure 8. Thiosulphate, ammonia and copper concentrations were maintained at 0.5, 1 and 0.001M respectively. The flow rates of oxygen, nitrogen and air were maintained at 0.2 and 1 and 2L/min respectively. In the nitrogen atmosphere, Au leaching was minimum for both samples, whereas, the Au leaching was higher in all the other cases for both the samples. Although the oxidant cupric ions were present in the system, the low recovery of leaching in presence of nitrogen atmosphere shows that oxygen is needed. The presence of small amount of oxygen inherently present in leachant solution helps in enhancing the leaching of gold as shown in the figure for the case without any gas purging. Oxygen enhances the Au leaching was also reported by other authors (Byerely *et al.*, 1973a,b, 1975). But increase in oxygen content does not increase the Au dissolution indefinitely which was observed in the case of Hishikari sample which means a suitable low concentration of oxygen is helpful for enhanced Au dissolution but not a very high concentration of oxygen.

The pH change fluctuates between 11.2–11.6 over the entire leaching time, for both samples. The E_h value fluctuates between 120-160 and 160-180mV vs. SHE for Akeshi and Hishikari samples respectively in the time range studied.

3.9. Comparison of leachability of Akeshi and Hishikari samples

It was observed from all the figures that the gold extraction was higher for Hishikari sample compared to that of Akeshi sample. There was not much of change in the pH value for both the samples in all the leaching experiments. However, there was a difference in the E_h values for both the samples. The E_h value was higher for Hishikari in comparison with the Akeshi sample in all the cases. The lower E_h value for Akeshi sample may be because of some reducing materials present in it. In order to evaluate the presence of reducing materials in both samples, we carried out a titration experiment on a buffer ($\text{NH}_3 + (\text{NH}_4)_2\text{SO}_4$)

containing a mineral sample against Cu^{2+} ions as oxidant. Sodium thiosulphate was not used in this experiment to avoid the consumption of cupric ions due to gold oxidation. The pH of the buffer solution was found to be around 12, which was very near to the leaching pH condition. The E_h values were measured as a function of the amount of oxidant (Cu^{2+} ions) and the results are shown in Figure 9. For comparison purpose, the result of a blank (buffer solution) without any mineral sample is also shown in the same figure.

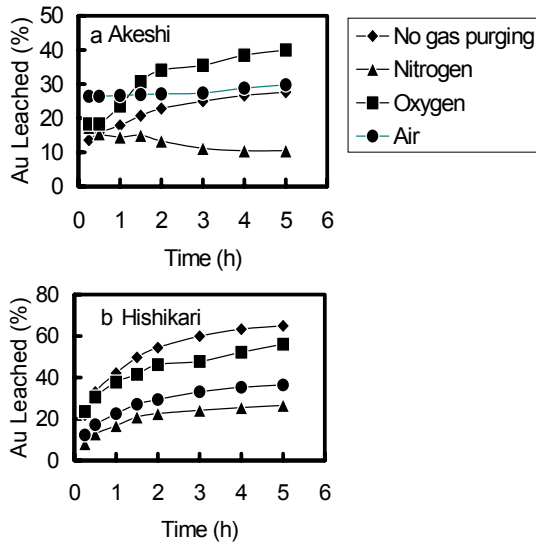


Figure 8. Effect of various gases on Au leaching as a function of time for a) Akeshi and b) Hishikari gold samples (Thiosulphate concentration, 0.5M; Ammonia concentration, 1M; Cupric sulphate concentration, 0.001M)

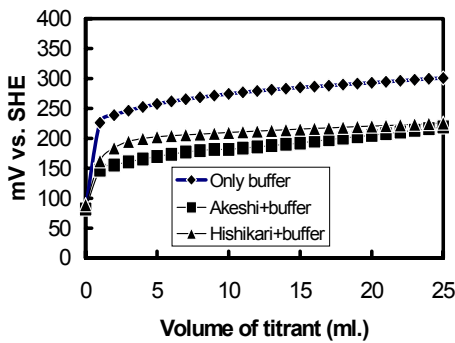


Figure 9. Variation of E_h as a function of the amount of cupric ions (oxidant) for both Akeshi and Hishikari gold samples in the presence of a (ammonia and ammonium sulphate) buffer

It is seen from the figure that E_h value increases with increase in Cu^{2+} ion amount in all the cases. As expected, there were lower E_h values for both Akeshi and Hishikari sample. The chemical analysis of the buffer solution-containing mineral after the titration showed almost no gold extraction. This could be because of the absence of thiosulphate in the buffer solution. Therefore the reduction of E_h values for both Akeshi and Hishikari samples in comparison to the values in absence of them indicates that both samples contain some reducing materials in their ore bodies. Upon careful look into the magnitude of the E_h values of the two samples confirms that buffer solution containing Akeshi sample has a lower E_h value compared to that of Hishikari sample. The presence of more reducing materials in the Akeshi sample cause a higher consumption of oxidant and brings the E_h values to lower during the ammoniacal thiosulphate leaching. This could be a reason for the low gold extraction behaviour of Akeshi sample in comparison with the Hishikari sample.

4. CONCLUSIONS

1. The ammoniacal thiosulphate leaching of gold is dependant on both ammonia and thiosulphate concentration. The leaching is improved significantly at a suitable concentration of ammonia and thiosulphate and that concentration varies from ore to ore.
2. Copper ions act as an oxidant and gold dissolution increases substantially in their presence.
3. The Au leaching increases with increase in temperature upto 50°C and beyond this temperature it starts decreasing.
4. The gold leaching is minimum in the presence of an inert gas such as nitrogen and the leaching increases in presence of other gases like oxygen and air.
5. The E_h of the leaching system was found to vary between 110-180mV vs. SHE.
6. A high gold extraction was observed for Hishikari sample compared to that of Akeshi sample.

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