A NEW ROUTE TO PRECIOUS METAL RECOVERY AND SUBSEQUENT ELECTRODEPOSITION USING IONIC LIQUIDS

Jacqueline A. Whitehead, Geoffrey A. Lawrance, Michael P. Owen and Adam McCluskey
Discipline of Chemistry, School of Environmental and Life Sciences, The University of Newcastle, Callaghan, NSW, 2308, Australia

ABSTRACT

Gold extraction from complex sulfidic ore occurs in 1-butyl-3-methylimidazolium hydrogen sulfate (bmim+HSC>4') ionic liquid in the presence of thiourea in a facile, high yielding (86%), recyclable process. Silver recovery from the ore is also enhanced. Gold recovery from ionic liquid / water environments directly by electrodeposition is described. Changing from aqueous acid to ionic liquid solvent causes a growth mode transition to dendritic growth patterns for deposited gold.

INTRODUCTION

Ionic liquids have been shown to enhance the yield and selectivity of organic reactions and have also been employed in electrochemistry (1). Early work in the application of ionic liquids to metallurgical processing has focused primarily on the electrodeposition of metals from air and water sensitive chloroaluminate ionic liquids (2) and not on the preliminary extraction of metals from ores. Recently, we have established a role for ionic liquids in the cyanide-free extraction of precious metals from ores using thiourea (3), and have now extended this to consider the recovery of the metal from the ionic liquid leach liquor. While gold can be recovered through adsorption onto carbon, electrodeposition offers a direct route for the removal of metals from a leach liquor yielding a potential ore-to-metal process in ionic liquid. The electrodeposition of gold from solutions containing thiourea has been investigated previously in aqueous and alcohol solutions (4-6) but has not been examined from ionic liquids or directly from ore leach solutions. Traditionally, the recovery of gold from cyanide leach solutions involves the adsorption of the gold complex from the leach solution onto activated carbon and then subsequent stripping of the carbon to give a solution suitable for electrodeposition (7). Ionic liquids offer potential for the electrodeposition of gold with omission of the adsorption and stripping steps present in the hydrometallurgical process. Another advantage of electrodeposition is the ability to reuse the non-volatile stripped ionic liquid solution for further leaching cycles, increasing the cost effectiveness of the process. Figure 1 outlines the complete ore to metal process and includes the option of reloading the leach liquor to increase precious metal concentration in the leachate.
EXPERIMENTAL

Materials

The 1-butyl-3-methylimidazolium hydrogen sulfate (bmimHSO4) ionic liquid was prepared as described (8) with samples being spectroscopically pure as gauged by 1H NMR spectroscopy. Thiourea (reagent grade) was used without further purification. A gold standard solution containing 1000 mg/l Au was used to prepare model solutions for the electrochemical studies.

A synthetic ore was used in preliminary experiments with a matrix composed of SiO2 (81%w/w), CaSO4 (10%w/w), Fe2O3 (6%w/w), Al2O3 (2.5%w/w), MnO2 (0.3% w/w) and TiO2 (0.2%w/w). Colloidal gold was added to the matrix to give a gold content of 42 g/tonne. A complex natural ore sample was obtained from Peak Gold Mine Pty Ltd from the Perseverance mine, NSW, Australia. The predominant minerals in the ore were chalcopyrite, pyrite, pyrrhotite and sphalerite with a gold content of 5 g/tonne and a silver content of 18 g/tonne. The ore was ground, sieved and the 45-106 μm fraction used.

Leaching

A leach solution was prepared by dissolving thiourea in either water (adjusted to pH 1 with H2SO4) or 1-butyl-3-methylimidazolium hydrogen sulfate or a combination of both (100 cm3). This leach solution was stirred to dissolve the thiourea. The leach solution was added to the ore sample (25 g) and Fe2(SO4)3 (0.5 g / kg ore) with a solid to liquid ratio of 1:4, capped and tumbled end-over-end for 48 hrs. After leaching, the samples were diluted 1:1 with milli-Q water and immediately centrifuged at 3000 rpm for several minutes. The leach liquor was then decanted and filtered using a 0.45 μm cellulose ester filter paper. Analysis of the leach liquor was performed using ICP-AES (8).

Figure 1. Proposed process for metal recovery from ore in an ionic liquid.
The ability of the bmimHSO$_4$ leaching sample to be reloaded was examined using the leaching process described above with the solution cycled four times with volumes and masses reduced proportionally to allow for progressive diminution due to sampling for analyses. Transfer losses due to processing were very small, from monitoring mass in a cycle, and were not adjusted for. The leach liquor was rotary evaporated after filtration in every cycle to remove the water prior to re-use for leaching.

Electrochemistry

Electrodeposition employed a cell (Figure 2) with concentric platinum basket electrodes and an EG&G Princeton Applied Research Model 362 scanning potentiostat as the power supply. A lid fitted to the cell permitted controlled deoxygenation with N$_2$ gas. The surface area of the working electrode was determined electrochemically to be 0.6 dm$^2$. Deposition progress was monitored by collecting small aliquots at intervals and determining the concentration of metals by ICP-AES (8). Deposition quality was examined by replacing the working electrode with a platinum foil electrode with a surface area of 0.0025 dm$^2$. SEM images were obtained using a Phillips XL30 scanning electron microscope.

![Electrodeposition cell](image)

Figure 2. Electrodeposition cell.

Cyclic voltammetry employed a conventional three-electrode system with a platinum working electrode, a platinum counter electrode and a saturated calomel reference electrode, operated under a nitrogen atmosphere. A Perkin multichannel potentiostat was employed. Data was collected via EC-Lab v.6.80 and treated using Microsoft Excel.

RESULTS AND DISCUSSION

The bmimHSO$_4$ ionic liquid is stable to high temperatures and undergoes no decomposition, even in the presence of a range of metal ions and organic molecules as determined by spectroscopy. With negligible volatility but complete water miscibility, it is particularly suitable for recycling and repeated water addition / removal steps, such as employed here.
Leaching

A series of preliminary experiments were undertaken using a synthetic ore sample to allow greater control of the experimental conditions. These studies examined the effect of thiourea concentration on the extraction of gold from the ore sample and the effect of bmimHSO$_4$:\textsubscript{2}H$_2$O ratio.

An increase in thiourea concentration (1 to 50 g/kg ore) in the aqueous leach solution caused no significant change in the extraction of gold from the synthetic ore. The extraction of gold varied slightly between 82\% and 86\% at 24 hrs with the maximum extraction of 86\% at 20 g/kg ore.

As the concentration of bmimHSO$_4$ in mixed aqueous leach solution was increased there was no significant change in the extraction of gold. Minor variations observed for the differing concentrations of bmimHSO$_4$ were attributed to the minor variations in the gold content of the samples. For the 100\% bmimHSO$_4$ sample, the rate of extraction was slower than in the aqueous samples, attributed to the high viscosity of the bmimHSO$_4$ reducing the mixing of the sample and subsequently decreasing the extraction rate observed. This effect is not observed with the leach solutions containing bmimHSO$_4$/water mixtures because the viscosity of ionic liquids decreases exponentially as the mole fraction of water or other co-solvent increases (9).

Studies were carried out using a complex sulfidic ore sample from the Perseverance Gold Mine. The rate of extraction for this ore sample was slower than for the synthetic ore samples used in the preliminary experiments. The difference in extraction rates is attributed to the close association of gold with other minerals in the natural Perseverance ore. The extraction of gold from the Perseverance ore with an aqueous pH 1 thiourea leach solution was 85\% after 50 hrs. No significant increase was observed in the extraction of gold from the Perseverance ore for the 100\% bmimHSO$_4$ leach solution (86\% after 50 hrs). However, as previously reported (3), there was a significant increase in the extraction of silver using the bmimHSO$_4$ leaching solution and limited uptake of other metal species (Figure 3).

Increasing the leaching temperature to 50°C to decrease the viscosity of the bmimHSO$_4$ and subsequently allow more thorough mixing of the sample was found to increase the rate of extraction of the precious metals. However, when the temperature was increased to 100°C, the extraction of the precious metals was decreased significantly (Figure 4) due to the decomposition of the thiourea at the higher temperature. This decomposition had been observed in the aqueous leaching system by Ubaldini and coworkers (5) and was not altered by the different solvent environment used here.

The ability of the bmimHSO$_4$ sample to be cycled and reloaded in the leaching of the Perseverance ore to increase the precious metal loading in the leach liquor was examined. The effect on the uptake of the other metals into the leach solution was also investigated. The elements gold, silver and copper displayed similar behavior, with the uptake of each metal into the leach liquor at each cycle remaining constant over the four cycles, without any further addition of thiourea to the sample after the initial dose. The uptake of the other metals (Fe, Zn, and Pb) was limited by their solubility in the bmimHSO$_4$ sample.
Electrodeposition

Recovery of a metal from solution by reduction of the ion and deposition onto a surface represents a usually facile route to a relatively pure material, with both electrodeposition and electroless deposition well known. Although gold recovery by electrochemical routes is well known, gold electrodeposition from ionic liquids has not been previously examined. Consequently, preliminary studies into the behaviour of the electrodeposition of gold were carried out using model solutions containing gold at a concentration of 50 mg/L depositing at a platinum cathode.
The rate of deposition was studied by monitoring the concentration of gold remaining in the solution over time. An increase in the bmimHSO₄ concentration (0 to 95%) in the deposition solution decreased the rate at which the gold was deposited onto the platinum electrode (Figure 5). This is presumed to arise due to the increasing viscosity of the solutions, which subsequently reduced the rate of transport of gold to the electrode surface. The current density was varied over the range 5mA/dm² to 200mA/dm² but did not alter the rate of deposition of gold onto the large basket electrode.

![Figure 5. Effect of ionic liquid concentration on the rate of deposition of gold; 0.1M H₂SO₄(+), 10% bmimHSO₄ (•), 20% bmimHSO₄ (□) and 50% bmimHSO₄(Δ).](image)

The current efficiency was calculated to be 30% for the 20% bmimHSO₄ solution at a current density of 5mA/dm². The rate of deposition was also monitored for the 50% bmimHSO₄ solution in the presence of other species at concentrations approximating those found in the leach solution after 4 cycles. When copper sulfate was added to the 50% bmimHSO₄/Au solution there was no change in the rate of deposition of gold onto the electrode; however, copper was also deposited. Silver displayed similar behavior. When iron sulfate was added to the solution, the rate of gold deposition increased 5-fold. Fast gold precipitation in Fe³⁺ solution occurs because reduction may be mediated in solution in the double layer by ferrous ion. The iron in solution is reduced from Fe³⁺ to Fe²⁺ but metallic iron is not deposited at the current densities used. However, when all three metals were present in the same solution, there was no copper or silver deposition and the rate of gold deposition was equivalent to that in the solution containing iron alone (Figure 6). This behavior has been previously reported in the deposition of copper from aqueous solution in the presence of Fe³⁺ (10), where the copper is initially deposited on the electrode but is then re-oxidized by Fe³⁺. Consequently, gold is deposited cleanly in the combined presence of Cu²⁺, Ag⁺ and Fe³⁺, which are the major other components of the ore leachate.

The addition of thiourea to the bmimHSO₄/Au solution slowed the rate of deposition onto the electrode, but not the percentage recovery. This is indicative of a different species being present; here a gold thiourea complex, [Au(thiourea)₂]⁺ with different electron transfer and mass transport behavior, is anticipated, and supported by cyclic voltammetry experiments.
Cyclic voltammograms were recorded for the model solutions. Behavior in aqueous acidic and 20% w/v ionic liquid are compared in Figure 7. The oxidation and reduction waves shifted position and pattern as the ionic liquid concentration in the solution was increased (Figure 8). The oxidation peak moved to more negative potentials and was split into two peaks as ionic liquid concentration increased. The different waves are presumably associated with separate gold species, with changes reflecting change in speciation in solution as ionic liquid level is raised. This implies that some species may be especially stabilized by the ionic liquid environment, most likely tightly ion paired adducts such as Au⁺·HSO₄⁻. The reduction wave also moved in concert with the oxidation wave. Some evidence of at least two species is observed for the reductive wave also. The peak current also decreased as the ionic liquid concentration increased, which may reflect diminishing diffusion rates in the highly viscous medium. An analysis of the 50% bmimHSO₄ solution at 60°C led to an increase in the peak current compared to the room temperature sample; since the viscosity of the ionic liquid falls with increasing temperature, a link may be made.

Cyclic voltammograms measured following thiourea additions to the 50% bmimHSO₄ / gold solution exhibited the effect that thiourea complexation has on the oxidation / reduction waves in the cyclic voltammogram (Figure 9). The oxidation wave is shifted 0.3V cathodically with substantial parallel shifts in the reduction wave. The initial reduction wave is essentially absent even after a 1:2 Au⁺:thiourea ratio is established, indicative of the stability of the presumed [Au(thiourea)₂]⁺ complex formed.

Electrodeposition of metal films from room temperature ionic liquids has been reported, (11, 12) but gold deposition has not been examined. Since we observed visually that deposition character of the gold appears to vary with current density and ionic liquid concentration, it was appropriate to probe electrodeposition more closely using scanning electron microscopy (SEM).
Figure 7. Cyclic voltammograms of the gold solution in 0.1M aqueous H$_2$SO$_4$ and 20% w/v bmimHSO$_4$ ionic liquid.

Figure 8. Cyclic voltammograms of Au/bmimHSO$_4$ solution at varying ionic liquid concentrations. The numbers correspond to the concentration % (w/v) of ionic liquid; 0% ionic liquid is 0.1M H$_2$SO$_4$. 

908 Electrochemical Society Proceedings Volume 2004-24
In preliminary studies, we observe a growth mode transition with current density from aqueous to 20:80 ionic liquid:water medium (Figure 10) at a platinum electrode. In aqueous acid at 80mA/dm² dense rounded and or elongated particles are formed, whereas in the ionic liquid / water medium at 80mA/dm², a transition to dendritic growth is observed. Such transitions have been observed in aqueous systems under different conditions, such as gold electrodeposition on highly oriented pyrolithic graphite or silver on platinum (13, 14). Explanations for these transitions are not finitely resolved, but mechanisms have been proposed (13). Change from equilibrium to non-equilibrium conditions for growth may be involved and the change in diffusion rate constant as the ionic liquid concentration rises may play a role in this. However, the significant change in ionic strength in the aqueous / ionic liquid environment may also play a role. At this stage, the remarkable change in growth mode observed is noted and the subject of further study. The differing surface textures achievable by ‘tuning’ ionic liquid concentration may be of structural and practical interest.

Figure 10. SEM images of the gold deposition surface from 0.1M H₂SO₄ (left) and 20% bmimHSO₄ (right).

Electrochemical Society Proceedings Volume 2004-24
CONCLUSIONS

Gold extraction from ore with thiourea in ionic liquid is a facile, high yielding and recyclable process that is supported by the non-volatility and stability of the ionic liquid component. Subsequently, gold may be recovered directly from leach solutions by electrodeposition, since model experiments have established that gold is deposited effectively exclusively when other metals are collectively present in the leach liquor (Fe, Cu and Ag). Electrodeposition of gold in the presence of an ionic liquid even at relatively low percentages sees a growth mode transition towards dendritic growth patterns on the electrode surface, a phenomenon possibly associated with changes in the diffusion rate or ionic strength.

ACKNOWLEDGMENT

Support of the Australian Research Council is gratefully acknowledged. We would also like to thank Bob Colquhoun, Production Metallurgist, of Peak Gold Mine Pty Ltd for a sample of ore.

REFERENCES

1. R. D. Rogers and K. R. Seddon, eds., Ionic Liquids: Industrial Applications to Green Chemistry, American Chemical Society, Washington DC, (2002).
2. F. Endres, ChemPhysChem, 144 (2002).
3. J. A. Whitehead, G. A. Lawrance, and A. McCluskey, Green Chemistry, 6, 313 (2004).
4. C. M. Juarez and A. J. B. Dutra, Minerals Engineering, 13, 1083 (2000).
5. S. Ubaldini, P. Fornari, R. Massidda, and C. Abbuzzese, Hydrometallurgy, 48, 113 (1998).
6. T. S. Urbanski, P. Fornari, and C. Abbussese, Hydrometallurgy, 55, 137 (2000).
7. E. Jackson, Hydrometallurgical Extraction and Reclamation, John Wiley & Sons, New York, 1986.
8. J. A. Whitehead, G. A. Lawrance, and A. McCluskey, Aust. J. Chem., 57, 151 (2004).
9. K. R. Seddon, A. Stark, and M.-J. Torres, Pure Appl. Chem., 72, 2275 (2000).
10. E. L. Larison, Engineering and Mining Journal, 84, 422 (1908).
11. W. Freyland, C. A. Zell, S. Z. E. Abedin, and F. Endres, Electrochimica Acta, 48, 3053 (2003).
12. F. Endres, Phys. Chem. Chem. Phys., 3, 3165 (2001).
13. H. Martin, P. Carro, A. Hernandez Creus, S. Gonzalez, R. C. Salvarezza, and A. J. Arvia, Langmuir, 13, 100 (1997).
14. A. Hernandez Creus, P. Carro, S. Gonzalez, R. C. Salvarezza, and A. J. Arvia, Journal of the Electrochemical Society, 139, 1064 (1992).