Impacts of Pulp Chemistry on Gold Particle Surface Chemistry and Floatability*

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Abstract

Pulp chemical changes and surface chemistry play a crucial role in collector adsorption onto gold and copper minerals for an improved flotation. The expected recovery of gold is not always the same as copper minerals recovery due to the differences in mineralogy and surface chemistry. The current study investigates the surface behaviour of gold particles in a typical porphyry copper-gold ore flotation pulp. Due to the trace nature of gold in the ore, the surface behaviour was stimulated with a pure gold substrate. The surface chemistry changes before and after exposing the gold substrate to the pulp conditioned with air, XD5002, MIBC, and DETA were assessed using XPS and contact angle measurements. The substrate contained 92.3% Au and 7.7% O. Exposure to the pulp showed a drastic decrease in gold to 18% with an increase in oxygen to 42.3% and appearance of 3% S, 3.2% Fe, 2.1% Cu, 23.4% C, 6.6% Si and 1.2% Zn. The presence of these hydrophilic loadings decreased the contact angle of the pure gold substrate from 84° to 47°, and subsequently increased to 59° and 74° after re-exposing the contaminated gold surface to EDTA extraction and XD5002 collector solution, respectively. The study showed that the observed contamination for pure Au substrates exposed to the pulp may be more extensive on "in-ore" surface as they would be expected to contain more reactive sites and might be a contributing factor to Au losses encountered during copper-gold flotation, especially at the finer grind size.

Keywords: Pulp Chemistry, Contact Angle, DETA, Collector, XPS

1 Introduction

Floatability of a free gold particle is dependent on its exposed surface composition, whether coated with a hydrophilic iron species and slime coatings which are known to affect the floatability of free gold (Brook et al. 2003; Viljoen and Milhalik, 1968). Certain coatings on free gold particles inhibit collector interaction and therefore reduce particle hydrophobicity (Brook et al. 2003). For example, iron oxide or hydroxide forms as a result of ore formation or latter metamorphism, oxidation product of iron-containing minerals present in the ore (pyrite, pyrrhotite) or may be generated as a result of grinding media loss as often reported in the literature (Allan and Woodcock, 2001; De Kock 1964; Viljoen and Milhalik, 1968). All these coatings depress the flotation recovery of gold particles. Studies have shown that native gold with iron compound precipitates on its surface is more difficult to float due to its low hydrophobicity (Taggart, 1945; Aksoy and Yarar, 1989). A similar observation was made by Small et al. (2003) and Brook et al. (2003). They observed low recovery of gold in the fine size fraction (<38 µm) due to surface contamination as a result of excessive grinding and regrinding of already liberated gold particles. Addition of ethylenediaminetetraacetic acid, EDTA solution (Small et al., 2003) and nitric acid, HNO3 (Brook et al., 2003) improves gold recovery in the fine fraction as a result of surface cleaning. However, these chemicals can only be used in the laboratory for diagnostic purposes and

not in processing plants. In a typical gold processing plant, for example, the addition of HNO₃ to minimise gold surface contamination will impact negatively on the process by reducing the pulp pH and increase lime consumption (increase cost of operation). Notwithstanding this constraint, few physical methods have been used in the industry for cleaning surface contaminants. These are cycloning (Bushell, 1970; Broekman et al., 1987) and high-intensity attritioning (Duchen and Carter, 1986; Valderrama and Rubio, 1998; Allan and Woodcock, 2001). The former contention was further confirmed by Farokhpay et al. (2010) where gold particle surface obscured by iron oxide and hydroxide coatings during regrinding was cleaned after hydrocyclone separation as a result of silver reappearance on regrind cyclone underflow gold particles. The mechanism of the gold surface cleaning was attributed to attritioning during cyclone separation.

The current work assesses the impact of hydrophilic species loading from copper-gold ore flotation pulp on gold substrates to understand gold flotation behaviour in a porphyry copper-gold ore processing. Chemical, spectroscopic and contact measurements were used to understand and explain gold behaviour within the pulp.

2 Resources and Methods Used

2.1 Ore Sample, Gold Substrate and Reagents

The ore used was a porphyry copper-gold ore with 18.4% Fe, 12.6% S, 1.0% Cu and 1.7 g/t Au. Pure gold surfaces were prepared by sputter deposition (~600 nm) onto chromium (adhesion layer) plated Si wafer surface. This method provided reproducibly clean gold surfaces.

The collector used in this research work was thionocarbamate collector, N-butoxycarbonylnbutvl thionocarbamate (R'HN-(C=S)-OR", product name XD5002), supplied by Cytec Chemicals. The frother used in this study was methyl iso-butyl carbinol (MIBC) supplied by Cytec Chemicals. The pH during conditioning was kept constant at a value of 11.5, unless otherwise stated, with the addition of lime. Lime was supplied by AJAX Chemicals (Australia) with a purity of 97%. The main depressants investigated in this study were air and diethylenetriamine (NH2-CH₂-CH₂-NH-CH₂-CH₂-NH₂, abbreviated DETA, 99% pure). DETA was supplied by Sigma-Aldrich. Ethylene diaminetetraacetic acid di-sodium salt (abbreviated EDTA, 99% pure), supplied by AJAX CHEMICALS.

2.2.1 Sample preparation for gold surface analysis (probe method)

The pure gold surfaces were mounted in the flotation pulp ($P_{80} = 8 \ \mu m$ at 25% solids using deionized water) in perforated plastic bags to allow passage of the slurry through during conditioning and flotation period, in the presence of air (during the aeration period), DETA, XD5002 and MIBC at pH 11.5. After which, the gold samples were removed, rinsed in pH-matched solution (11.5), put into a sample container, then placed in liquid nitrogen and stored in the freezer prior to XPS analysis. Both the clean and contaminated surfaces were analysed by XPS and contact angle measurements were done on the surfaces using the sessile drop method. The contaminated surfaces were also subjected to EDTA solution to examine the effect of surface cleaning agents on gold floatability.

2.2.2 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is mostly used for analysing the chemical state of minerals. The analysis involves bombarding a sample with primary X-rays (photons) which cause a photoelectric process resulting in the emission of electrons of binding energy (BE) from the atomic orbitals of the solid (Fig. 1). The kinetic energy of the emitted electrons which is measured by the spectrometer is as given in eq.1:

$$KE = hv - BE - \phi_S \tag{1}$$

where hv is the energy of the photons (X-rays), *BE* is the binding energy of the atomic orbital from where the electron originates, and $\emptyset s$ is the spectrometer work function (Kibel, 1992; Attard and Barnes, 1998).

The photon bombardment results in emitting both photoelectrons and Auger electrons. The Auger electrons occur due to the relaxation of the energetic ions remaining after photoemission, e.g. from K levels. Based on the electrons produced after the photoemission, information regarding the type of elements and their relative atomic concentration can be extracted as well as their oxidation states. A survey spectrum (low resolution, XPS scan) serves as the basis for the determination of the elemental composition of the mineral sample, using elemental relative sensitivity factors (RSF's) and peak area (Fig.1).



Fig.1 X-Ray Photoelectron Spectroscopy (Xps) Measurement

XPS was used in the current study to investigate the surface species responsible for gold flotation and depression. The XPS measurements were performed using a Kratos Axis-Ultra X-ray photoelectron spectrometer equipped with a delayline detector. A monochromatised Al K α X-ray source was used, operating at ~300W and the spectrometer analysis area was ~0.3 x 0.7 mm dimensions. The broad scan survey and highresolution spectral data were processed using CasaXPS version 2.3.5. High resolution scans were also collected for the C 1s, O 1s, Fe 2p, Cu 2p and S 2p photoemission lines.

2.2.3 EDTA Extraction

Ethylene diaminetetraacetic acid (EDTA) was used to extract metal oxidation products (e.g. oxide/hydroxide, sulphate, carbonate, etc.) from the gold substrate surface (Kant *et al.*, 1994; Rumball and Richmond, 1996; He, 2003). A pulp volume of 0.1dm^3 was mixed with a 3% AR grade EDTA solution and conditioned for 5 min while purging with nitrogen to prevent further oxidation of the gold substrate surface. After which the cleaned gold substrates were removed and subjected to contact angle measurements.

2.2.4 Contact Angle Measurements

The static advancing contact angles of deionized water was taken on the gold surfaces which had undergone the various processes using a labdesigned sessile drop setup. The setup was made up of a rotatable stage (which moves in the x, y and z directions), a high-intensity Dolan-Jenner fibre optic illuminator (MI-150 by Edmund Optics) as a light source and an Arc Soft webcam with a 70 mm lens connected to a computer for image acquisition and analysis. Increasing volumes of droplets were deposited on surfaces and the contact angle of the liquid on the substrate was measured using Image-J and SCA20 software (Dataphysics). A fresh area on the surface was used each time and an average of four areas is reported. Contact angle hysteresis was below 1° in all conditions measured showing the smoothness of the gold substrate studied.

3 Results and Discussion

3.1 Gold Surface Chemistry

Table 1 shows the atomic concentrations of the major species on the surface of the pure gold substrate, before and after slurry exposure. The experiment was conducted in the presence of air, DETA and XD5002 as described in section 2.2.1. The XPS (of the contaminated gold surface) data are also presented as spectra (Fig. 2a-d).

The exposure of gold surfaces to the pulp, after regrinding and during the flotation conditioning stage after aeration, DETA and XD5002 addition resulted in the adsorption of Cu, S, Fe, Zn, Si, and O species. After 30 min of aeration and conditioning, the atomic concentration of Au decreased to 18%. Cu and S were present as Cu(I) and sulphide, respectively. A "shoulder" of near 935 eV binding energy is also observed in the Cu 2p spectrum, after DETA addition. As there is no evidence of the typical Cu(II) satellite structure normally seen in the 944-948 eV binding energy range, it is likely that this shoulder is due to a Cu(I)-DETA species adsorbed at the surface (Fig. 1a). Fe adsorbed mostly as oxide/hydroxide with little pyritic sulphide. The latter may result from adsorbed, colloidal pyrite particles but may also be due to a reductive reaction between Fe solution species and the sulphidised Au surface. Zn adsorbed as a mix of sulphide and hydroxide species. The presence of Zn-sulphide species supports the latter contention for Fe and needs further investigation. There was significant adsorption of O and Si (Table 1 and Fig. 1).

The significant loading of hydrophilic species on the gold surfaces may be due to the dissolution of metals from the associated minerals at low Eh (after grinding) and subsequent oxidation after discharge. Also, increase in pH (11.5) through lime addition may result in direct precipitation of metal hydrolysis products (e.g. hydroxides, sulphates, etc.) or non-sulphide gangue species (e.g. Si-, Al-, Mg- silicates).

Table 1 XPS Surface Composition (atomic %) of
a Pure Gold Exposed to Ore Slurry at
25% Solids Regrind Product after
Aeration (30 min), DETA and XD5002
Conditioning, pH 11.5.

Species/condition	Au	0	S	Fe	Cu	С	Si	Zn
Pure Au	92.3	7.7	-	-	-	-	-	1
Pure Au exposed to slurry	18.0	42.4	3.0	3.2	2.1	23.4	6.6	1.2





Fig. 2 XPS Spectra of (a) Cu 2p, (b) S 2p, (c) Fe 2p and (d) Zn 2p of Pure Gold Surface Exposed to Ore Slurry at 25% Solids Regrind Product after Aeration (30 min), DETA and XD5002 Conditioning, pH 11.5.

3.2 Contact Angle Changes

The adsorbed species on the gold surface decreased the contact angle of the pure gold from ~85 to 47° (Table 2). The introduction of the contaminated gold surface into EDTA solution for 10 min increased contact angle to 59°, which can be attributed to the removal of iron-rich coatings (e.g. Fe oxide/hydroxide species) (Brook *et al.*, 2003). When the clean gold surface was re-introduced into a 1% strength XD5002 collector solution, the contact angle increased significantly to 74° (Table 2). Table 2 Contact angle changes of the pure gold
surface exposed to ore slurry at 25%
solids regrind product after aeration
(30 min), DETA and XD5002
conditioning, pH 11.5

Condition	Contact Angle(CA, °)			
Pure Au (A)	85			
Au+Air+DETA+XD5002 (B)	47			
B+EDTA (C)	59			
C+XD5002	74			

The significant presence of hydrophilic loadings and reduction in the contact angle could affect gold floatability in copper-gold ores, especially after regrinding to finer grind size (~ 8 µm) as observed by Agorhom et al., 2014; where selectivity between pyrite and gold is paramount. The significant loading of hydrophilic species and decreased contact angle of the pure gold surface suggest that gold surface passivation may be one of the contributing factors for gold losses during coppergold ore flotation under the experimental conditions, particularly at the 8 µm grind size. Au surfaces in ores are rarely pure and already contain, typically, some Ag and other metals. It is likely that the observed contamination for pure Au substrates exposed to the slurry may be more extensive on "in-ore" surfaces as they would be expected to contain more reactive sites.

4 Conclusions

The effect of pulp chemistry on the floatability of gold particles in a typical porphyry copper-gold ore flotation has been discussed in this paper using a gold substrate. Exposure of the substrate to the flotation pulp shows the adsorption of hydrophilic species on the gold surface which is confirmed using XPS and contact angle measurement. This shows that the fine gold particles produced after regrinding in cleaner flotation circuits in most ores could suffer similar surface loadings and hence low floatability.

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