Coal-oil gold agglomeration assisted flotation to recover gold from refractory ore

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Abstract
This study aimed to investigate the applicability of coal-oil gold agglomeration (CGA) assisted flotation to recover gold from a refractory ore. The ore with the grade of 2-5 g/t was tested with the CGA-flotation process in six different size fractions from 38 to 300 μm using different collector types and dosages. In addition, the flotation without CGA was performed under the same condition for comparison. The results showed that the higher gold grade and recovery were achieved by applying the CGA-flotation, compared with the flotation without CGA. More than 20-60 times grade increase from the head grade was obtained with CGA-flotation. The elemental analysis of gold and sulphur explained their relationship with gold recovery. The results well indicated the applicability of CGA to upgrade the refractory gold ore.

1. Introduction
Gold is always highly demanded in jewelry as well as in high-tech industries and medical applications due to its unique physical and chemical properties. This high demand constantly leads to the development of a new gold recovery process [1] with economically viable and eco-friendly technologies. The process can be determined mainly by the ore mineralogy. In addition, the project scale, location and life of the mine site, site-specific environmental condition, and cost should be considered to optimize the process [2].

Hydro- and pyro-metallurgical processes are major approaches to recover gold, and have been extensively used. The pyro-metallurgical process is cost and energy intensive, and also produces toxic gas (e.g. sulphur dioxide). The hydrometallurgical process is, however, more predictable and easily controlled [1]. Its conventional method applied to refractory gold ores, on the other hand, is cyanidation which poses environmental concerns. Chemicals used in the process would contaminate not only the plants but also animals near the site which could lead devastating effects to local residents [3]. Thus, less cost intensive and more environmentally-friendly pre-concentration process is highly demanded to reduce the dependency on hydro- and pyro-metallurgical processes.

Several gold recovery processes were proven to efficiently beneficiate a gold ore on an economical profitable and environment friendly way [4]. Coal-oil gold agglomeration (CGA) process is one of these alternatives. CGA was developed by British Petroleum (BP) research team in the early eighties [5] and is based on the natural hydrophobicity of coal and gold compared with most gangue materials [6]. It allows a selective recovery of hydrophobic gold particles attaching and penetrating into the pre-formed coal-oil agglomerates from aqueous slurry. The coal-oil agglomerates form in a coal slurry and oil under intensive agitation which enhances the homogeneous distribution of oil in fine spherical droplets and
thus their collisions with coal particles. Further, the oil droplets spreading on the coal surfaces form the “oil bridges” which combine the coal particles to agglomerates (Fig. 1 a) due to the interfacial tension of the oil and capillary attraction of the oil bridges between particles. Once coal-oil agglomerates form, they are added into gold-bearing ore slurry under intensive agitation; the gold particles thus collide, contact and attach with the coal-oil agglomerates, and eventually penetrate into the agglomerates (Fig. 1 b) [4]. Then, the CGA agglomerates can be recovered by flotation or other methods (e.g. screening), dewatering to reject water and coal, and burning remained agglomerates to extract gold are suggested [6].

One of the significant progresses in relation to the CGA method was the application of froth flotation as the agglomerate recovery method. Moses and Peterson (2000) first implemented this combination and showed its scale-up capability over the other methods [3]. After this investigation, the effectiveness of this CGA-flotation combination was reported; but their investigations were limited to free gold [6-8]. In this investigation, on the other hand, we tested the CGA-flotation, in order to selectively upgrade refractory gold ore.

In most metal processing operations, tailings disposal is one of the biggest concerns in terms of economic and environmental impact. Gold processing plants generate the tailings containing cyanide and cyanide complexes. On the other hand, the tailings produced in CGA process contain only very small amounts of less harmful contaminants (e.g. coal fines, oil, collectors, lime). In addition, the tank storage should be much less than it is required for a conventional cyanidation plant, since the residence time needed for CGA is low [4].

The previous studies were, however, focused on the application of CGA to process artificial and natural ore samples having only free or native gold particles [3, 6-8]. Only available report on CGA application to refractory ore showed the contradictory results [4]. One reported the poor gold recovery (0-10 % for sulphide type flotation concentrate) while the other reported the successful recovery (93.3% for arsenopyrite-pyrite-quartz type ore with the head grade of 6.1 g/t; 95.5% for limonite-pyrite-quartz type ore with the head grade of 2.4 g/t; 79.7 % for pyrite-quartz type ore with the head grade of 1.5 g/t). Therefore, it is worth to make more effort to investigate the feasibility of CGA to upgrade refractory gold ore. Also, there have been only a limited numbers of researches performed to identify the effect of ore particle size and flotation collectors on gold recovery. Wu et al.[9, 10] investigated the effect of collector type on flotation kinetics; but they used a synthetic binary mixture composed of gold particle and quartz sand with collectors of large carbon chain length difference (i.e. C=6 vs. C=10). All the other CGA research investigated the agglomeration parameters (e.g. oil/ore ratio, agglomerate/ore ratio, coal/oil ratio) [e.g. 7, 11] and operational parameters (e.g. stirring rate, aeration rate, impeller speed) [e.g. 3, 8, 12].

Within these contexts, in this study, refractory gold ore was tested with the combination of CGA and froth flotation. Batch tests were performed in different flotation conditions (i.e. collector type and concentration) to evaluate the flotation behavior of the gold ore in different size fractions. This study revealed the relationship between the experimental parameters (e.g. particle size, flotation collector) and gold recovery in order to discuss the applicability of CGA to refractory gold ore processing. For comparison, the performance of two processes, the CGA-flotation and the flotation (without CGA), was also investigated.

2. Materials and methods
Reagents and CGA-flotation procedure stated in this work followed the procedure reported by Sen et al. [6] with necessary modifications.

2.1 Materials
The following reagents were used for flotation: 50 or 100 g/t of potassium amyl xanthate (PAX, C₉H₃₂O₅SₓK) (ORICA Ltd.), and 50 g/t of sodium isobutyl xanthate (SIBX, C₅H₁₀O₅S₂Na) (ORICA Ltd.) and copper sulphate (CuSO₄·5H₂O) (Chem-Supply Ltd.). The following reagents were used for agglomerate formation: 400 g/t olive oil (100% pure, MORO), 1200 g/t diesel oil (TITAN ULTRALUBE Ltd.), 200 g/t amyl alcohol (AJAX CHEMICALS SYDNEY AUSTRALIA Ltd.), and 200 g/t methyl isobutyl carbinol (MIBC, C₆H₁₂O) (ORICA Ltd.). The reagent used for gold analysis was aqua regia prepared with hydrochloric acid (32% by weight, Chem-Supply Ltd.) and nitric acid (92% by weight, Chem-Supply Ltd.) at the ratio of 2:1 by volume.

Refractory gold ore from a Western Australian mine was used as a sample. XRD analysis identified the following major minerals: quartz, sheet silicates (e.g. muscovite, kaolinite), dolomite, and pyrite. The ore was ground by a laboratory rod mill (ESSA, 520490) and sieved to obtain six different size groups (from 38 to 300 μm). Table 1 shows the gold and sulphur contents in each size fraction analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, VARIAN) and sulphur analyser (LECO), respectively. The products of CGA-flotation and flotation (without CGA) were also analyzed by the same methods. The results show the average values of 2 analyses of each size fraction/product. Mass of each size group tested in CGA-flotation and flotation was approximately 250 g for each flotation batch test after splitting for a representative sample. At least 2 flotation tests at each condition were performed separately and their average results were reported in this paper. Oxidized coal from Bowen Basin, Queensland, Australia was ground by laboratory rod mill and the -150 μm fraction was used for agglomerates. The results of duplicated ash analysis showed that the ash content of the coal used in this investigation was 16.7%.

2.2 Methods & Procedures

2.2.1 Coal-oil gold agglomeration (CGA)-flotation

Preparation of oil emulsions: olive oil, diesel oil, amyl alcohol and MIBC with the ratio of 2:6:1:1 by volume were added into a two-baffled emulsifying cell (Sunbeam) and agitated at 800 rpm for 5 min to produce an oil emulsion. The dosage of agglomeration reagents used for each batch test is mentioned in the section 2.1, following the values reported by Sen et al. [6].

Pre-agglomerate formation and coal-oil-gold agglomeration flotation: pre-agglomerate that coal particles agglomerated with oil emulsion was then formed before adding the agglomerate into the gold ore pulp. A mixture of 15 g of coal particles (coal/oil ratio was kept as 30:1) and oil-water emulsion were added to the emulsifying cell and agitated at 800 rpm for 5 min. In a 3.2 L flotation cell (Agitair model LA-500 R, Baker process technology), flotation collector (i.e. PAX or SIBX) was added to gold ore pulp, which contains 250 g of one size range sample produced in the manner stated in the section 2.1, and agitated at 850 rpm for 10 min. Pre-agglomerated coal particles-oil-water suspension was then added to the pulp and agitated at 1150-1250 rpm for another 5 min. Stirring speed was decreased to 850 rpm and pulp was conditioned for 5 min to form agglomerates with gold bearing minerals. Finally the produced coal-oil-gold agglomerates were recovered by flotation. The air valve was turned on and the froth was collected as a concentrate for 2 min. The CGA-flotation process was performed with six different size fractions of refractory ore to reveal the relationship between the particle size and gold recovery. To test the effect of collectors on the performance of CGA-flotation process, different types and dosages of collectors were used stated in the section 2. The natural pH of ore pulp was 8.5 and not modified during the flotation. Each series of tests were performed twice and their average values were reported in this paper.

2.2.2 Refractory gold ore flotation without CGA

To compare the CGA-flotation with the flotation (without CGA), a series of batch flotation tests with gold ore in six different size fractions was also conducted using the same flotation reagents to recover gold. Gold ore sample prepared by following the procedure in the section 2.1 Materials was added to
the laboratory flotation cell with tap water to produce a gold ore pulp. The pulp was agitated at 850 rpm with the air valve off. Then 50 g/t of copper sulphate was added into the pulp and conditioning for 5 min. 50 g/t of PAX and 200 g/t of MIBC frother were then added into the pulp for conditioning another 5 min. The pulp pH was maintained at natural pH 8.5. Finally the concentrate was collected for 2 min after the air valve was turned on.

3. Results and discussion

3.1 Comparison between CGA process and the conventional flotation process

The performance of two processes, CGA-flotation and the flotation without CGA, on refractory gold ore, was compared. These batch tests were conducted under comparable conditions except CGA process. The pre-formed coal-oil agglomerates were added into the gold bearing pulp before flotation and flotation was used to separate the coal-oil-gold agglomerates from the pulp. Figure 2-a shows that the gold recoveries in all six different size factions were higher with CGA-flotation, compared with the flotation (without CGA). The gold recovery increased in the range between 2 and 6 % by using CGA-flotation. The largest difference was observed in the coarsest fraction (i.e. 212-300 μm) while higher than 90% recovery was achieved in all the other fractions (i.e. 38-212 μm) with CGA-flotation. This good recovery in the wide size range agreed with the point Moses and Peterson made, i.e. gold grains in 1-500 μm can be recovered by CGA in equal ease [3]. In the case of CGA-flotation applied in this study, the wide size range of good recovery can be explained by the following two reasons: (1) for fine grain gold, it can form agglomerate to become suitable size (i.e. 20-200 μm) to be captured by air bubbles; (2) for coarse grain gold, it can form agglomerate until the upper limit of flotation with high hydrophobicity (i.e. 500 μm for coal particles [13]). Slight increment in recovery could be due to the less selectivity of coal-oil agglomerates to gold-bearing sulphide minerals that have less gold exposure in the ore than to free gold particles. The gold recovery can increase more significantly if CGA process is further optimized for processing refractory gold ore.

Figure 2-b indicates that the gold grades of concentrates in all six different size fractions are generally higher with CGA-flotation compared to the ones by using the flotation without CGA. As the recovery increased with finer size fractions, the gold grades in those fractions were relatively low compared to that of coarse size fractions. However, CGA-flotation obtained twice much grade compared with the flotation in the fine fraction of 38 to 53 μm. In the coarsest size fraction (212-300 μm), the gold grade was concentrated 60 times more than head grade of 1.5 g/t.

As a summary, the higher gold recovery and grade were achieved by applying CGA process prior to froth flotation compared to the flotation without agglomeration. The grade-recovery cures in Fig. 3 clearly captured the enhancement of gold recovery by CGA. The results proved that CGA process is applicable to upgrade a refractory gold ore. The further discussion on gold grade and recovery with two different methods will be provided with the results shown in Table 2 indicating the correlation between the recoveries of gold and sulphur that is the major element associated with gold in refractory gold ores.

Table 2 shows the correlation between the gold and sulphur recoveries in flotation concentrate in different size fractions by (a) flotation and (b) CGA-flotation. The general observed trend was that the
increase in sulphur recovery strongly correlates with gold recovery increase, and the recovery values of gold and sulphur is similar in fine size fractions (i.e. 38-106 μm). For example, in the 38-53 μm fraction with CGA-flotation, the gold recovery was 94.3% while the sulphur recovery was >92.2%. It means that in fine size fractions most of the gold particle was associated with sulphide minerals (e.g. pyrite). This agreed with the previous reports on gold associations [e.g. 14]. Also, generally higher sulphur recovery by CGA-flotation than flotation led that higher gold recovery by CGA-flotation. The similarity between sulphur and gold recoveries decreases with increasing the particle size, i.e. higher similarity in fine size fraction while less similarity in coarse size fraction. In the coarsest fraction (i.e. 212-300 μm) showed the largest difference between the sulphur and gold recoveries (e.g. 57.1% S vs. 82.5% Au in CGA-flotation). It indicates that more recovered gold was associated with sulphide minerals in fine size fractions while less recovered gold was associated with sulphide minerals and more recovered gold was associated with other host minerals (e.g. quartz) in coarse size fractions.

3.2 Effect of collector type on the CGA-flotation

The effect of collector type on the performance of the CGA-flotation was investigated. Two sets of batch flotation tests were carried out under same conditions except for the collector types, i.e. 50 g/t of PAX (C=6) or 50 g/t of SIBX (C=5). SIBX was selected as it is one of the most common collectors used in refractory gold ore flotation [15]. The comparison indicated that the gold recoveries between two series had little difference (Fig. 4-b) with different collectors which did not significantly enhance the physic-chemical properties of mineral particles by changing their wettability. In relatively coarse particle size fraction (+150-300 μm), the gold recoveries were slightly higher with SIBX. This can be due to the higher selectivity of a shorter chain length collector, SIBX in order to recover the gold bearing mineral particles with air bubbles. On the other hand, in general, the different collectors from PAX and SIBX had little effect on the CGA-flotation performance. This agreed with the froth flotation results of refractory gold ore reported by Bulatovic [16] that there was no significant change in the gold recovery with different collectors (i.e. 82% with 50 g/t of sodium ethyl xanthate (C₃H₅NaOS₂; C=3) while 88% with 50 g/t of PAX (C=6).

![Figure 3. Grade-recovery curves of two different gold recovery processes.](image)

Table 2 Gold and sulphur recoveries in flotation concentrate in different size fractions with (a) conventional flotation and (b) CGA-flotation. Note that the recoveries not having the exact value (e.g. >92.2%) are due to the small amount of sulphur content available in flotation tail below the detection limit of sulphur analysis for determination of sulphur recovery.

| Size (μm) | Flotation | CGA-flotation |
|----------|-----------|---------------|
|          | Gold recovery (%) | Sulphur recovery (%) | Gold recovery (%) | Sulphur recovery (%) |
| 38-53    | 92.4      | 89.1          | 94.3       | >92.2          |
| 53-75    | 88.5      | 86.8          | 91.6       | >90.6          |
| 75-106   | 90.0      | 87.0          | 92.5       | >89.1          |
| 106-150  | 87.7      | 80.0          | 91.9       | >83.3          |
| 150-212  | 90.0      | >80.0         | 92.4       | >80.0          |
| 212-300  | 76.2      | 66.7          | 82.5       | 57.1           |
Wu et al. [9] investigated the gold adhesion to agglomerates, by performing CGA-flotation with two different xanthate collectors of different chain lengths and synthetic ore (i.e. gold + quartz). After 5 min, 50% of the gold particles were recovered using decanthioxanthate (DX; C=10) collector. With shorter chain-length amyl xanthate collector (PAX; C=6), the gold flotation rate was slower and achieved only 30% gold recovery after 5 min [9]. In froth flotation general, difference in the length of the non-polar part of the molecule results in the different collecting ability of target minerals due to their difference in wettability. Wu et al. [9] proposed that, in CGA-flotation system, a collector with a longer chain-length was able to immerse into the oil film on the agglomerate surface more in depth and rigid. Additionally the gold particle with longer chain-length collector molecules would have a higher hydrophobicity, leading to a greater hydrophobic interaction force between the gold particles and the agglomerates.

Their study was performed with a synthetic binary ore composed of gold particles and quartz sand. It means that their gold particles were fully liberated from quartz and no other gangue minerals co-existed. In the case of refractory gold ore composed of many different minerals and limited degree of gold particle liberation due to their fine dissemination (e.g. solid solution), the use of longer chain collector may distract the selective collector attachment passively leading the low gold recovery. Also, the price of the collector can be the strong decision indicator. As a matter of fact, PAX is the most common collector being used in commercial refractory gold ore processing plant [15].

3.3 Effect of collector dosage on CGA-flotation

The effect of collector dosage on gold recovery with CGA-flotation process was investigated. Two sets of batch tests were conducted under similar conditions except for the collector dosage used in the flotation, i.e. 50 and 100 g/t of PAX. Figure 4-b shows that doubling the collector had almost no effect on the gold recovery in all six different size fractions. This may result from the high hydrophobicity of coal-oil-gold agglomerates even with 50 g/t. Since coal-oil-gold agglomerates were readily floatable after the agglomeration, higher collector addition in the flotation cell did not change the hydrophobicity of gold bearing particles; thus, no significant increase in the gold recovery was achieved. In flotation of refractory ore, adding more collectors would decrease the gold recovery because some sulphide minerals without gold particle were hydrophobized and floated as a concentrate. This reverse effect was not observed (Fig.4-b). The results suggest that changes in flotation conditions (i.e. collector type and concentration) did not significantly affect the flotation performance in this investigation.
4. Conclusions

The present study aimed to investigate the applicability of CGA to a refractory gold ore. Refractory gold ore was beneficiated with the combination of CGA and froth flotation in comparison with the flotation (without CGA) to improve the gold recovery under the same condition. The higher gold grade and recovery were achieved with the CGA-flotation tests than conventional flotation. Higher than 20-60 times grade increase from the head grade was obtained by CGA in coarse fractions. The differences in gold recovery by two methods were explained by examining the relationship between gold and sulphur recoveries in different size fractions. In addition, the effect of type and dose of collectors were investigated. It was found that there was no difference under different (a) collector type (i.e. PAX vs. SIBX) and (b) dosage (50 g/t vs. 100 g/t), explained by (a) fine dissemination of gold particle and (b) high enough hydrophobicity given by even small collector dosage. The results indicated the applicability of CGA to upgrade a refractory gold ore. Application of CGA to the cleaning stage of flotation circuit would be recommended due to its high grade product after CGA.

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