Characterisation and Beneficiation of Complex Ores for Sustainable Use of Mineral Resources: Refractory Gold Ore Beneficiation as an Example

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There has been much attention paid to the utilization of complex ores due to decreasing the accessibility of high grade and easily extractable ores. In order to maintain the sustainable use of mineral resources, the effective beneficiation of complex ores is urgently required with the strong assist from mineralogical characterisation. In this paper, currently available characterisation and beneficiation methods of complex ores are reviewed and summarised to discuss the further development required for the sustainable utilisation of mineral resources for our society. Also, refractory gold ore beneficiation was discussed as an example.

Key Words: Complex ore, Sustainable utilisation, Mineral resources, Refractory gold ore

1 INTRODUCTION

Natural resources are limited and the availability of easily extractable ores is decreasing. The developing new capability of beneficiating complex ores is thus constantly demanded in order to selectively extract target minerals and maintain the sustainable use of mineral resources. This development can include new system and/or chemicals for less power/energy consumption. Complex ores are generally defined as the ores difficult to treat by using the conventional metallurgical unit operations. This difficulty is largely due to their complex mineralogy, which often associated with the low degree of liberation and fine discrimination of target minerals. Therefore, the full range of characterisation is required to properly beneficiate complex ores.

This paper provides a brief summary of characterisation and beneficiation of complex ores for sustainable use of mineral resources. First the currently available methods for quantitative and qualitative analysis to extract the useful information for the selective beneficiation of complex ores are summarized. Second part then discusses the process option for complex ore, especially refractory gold ores.

2 CHARACTERISATION OF COMPLEX ORES

2.1 Mineral analysis in dry state

Based on the mineralogy, the ore processing flowsheet can be properly designed. Ore mineralogy is always the essential and critical information giving the feedback to develop an efficient beneficiation process. Especially, complex ore requires the whole picture of mineralogy before designing the proper process. Typical information required for developing a process flowsheet are: mineral & chemical compositions, grain size, degree of liberation, and associated minerals of target minerals.

2.1.1 Destructive methods (quantitative)

Dissolve ore samples into acid, and measure the elemental composition by using chemical methods. They take time for sample preparation; but they have the high accuracy and low detection limit. The major methods are atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry/inductively coupled plasma optical emission spectrometry (ICP-AES/ICP-OES).

2.1.2 Non-destructive methods (quantitative)

Ore samples can be measured as powder without acid digestion. Compared with the destructive methods, they are quick and easy in manipulation; but they have the higher detection limit. The most common quantitative method for the elemental analysis is x-ray fluorescent analysis (XRF). X-ray diffraction (XRD) analysis can be performed to semi-quantify the mineral composition in the ores; but some limitation are always associated with this. For example, it can only quantify elements associated with the crystalline phases.

2.1.3 Imaging and image analysis (qualitative, semi-quantitative)

Ore particles are immobilised into resin and the resin surface is then polished to extract the useful mineralogical information of target minerals. For this purpose, scanning electron microscope (SEM) becomes a common and powerful method while optical microscope is the simplest and cheapest method but it requires skills for mineral identification.

Secondary ion mass spectrometry (SIMS) can perform a spot elemental analysis with low detection limit (< 1 ppm) [1] while quantitative evaluation of minerals by scanning electron microscopy (QEM-SCAN)/Mineral Liberation Analyser (MLA) is the SEM based image analysis method, which can automatically perform the liberation and mineral association analysis of individual mineral grains [2-5]. This automated SEM based...
image analysis utilizes the back scattered electron (BSE) image and energy dispersive (EDS) X-ray spectra. The MLA uses BSE for mineral identification while X-ray is applied only for results verification and resolution in order to speed up the analysis. BSE grey levels are based on the size of atom present in the mineral analysed [6]. Generally, with the large atom, the image becomes brighter. The indicator of grey level is often discussed by the mean atomic number in the chemical composition of the mineral. For example, the (mean) atomic number of native gold is 79 while the one of sulphide minerals is from 20-25. In the presence of gold within sulphide matrix, they can be easily distinguished by the differences in their brightness. On the other hand, the care needs to be taken if identification of minerals with small grey level difference (e.g. sulphide minerals, such as pentlandite and pyrite) is required. Use of BSE images only finds difficulty to distinguish them where the application of X-ray analysis with some knowledge of mineral composition is required to identify different minerals. QEM-SCAN uses X-ray as a main source of mineral identification with 4 element detectors followed by the differentiation of particles from background by BSE brightness [6]. They are a powerful methods to obtain a large number of important information for complex ore beneficiation in relatively short time frame; thus they are attracting a lot of attention from both academic institutions and mining industries [e.g. 2-6].

2.2 Mineral analysis in water
Since beneficiation often requires the separation of fine particles in a water medium, it is significantly important to fully understand the behaviour of particles in the system of unit operations (e.g. flotation, thickening). There are plenty of different methods available now in the market; but here two major methods relatively easily accessible and widely used for particle characterization will be introduced. They are zeta potential and suspension rheology measurement. Both of them are quite useful to understand the particle dispersion/coagulation and suspension flow behavior, which strongly affect the separation performance of target minerals from other gangue minerals.

2.2.1 Zeta potential
Particle zeta potential is the surface charge around the particle in a liquid and is experimentally measurable. It is one of the important physical properties of mineral fine particles to determine their separation performance. In the case of froth flotation, it can determine the mineral-collector [e.g. 7] and mineral-mineral interactions [e.g. 8], which significantly affect mineral flotation performance. For example, negatively charged mineral surface attracts cationic collector. Same logic applies to particle-particle interactions where oppositely charged particles attract each other while same charge particles repelle. Figure 1 shows an example of this interaction where heterocoagulation of nickel oxide-hematite and nickel oxide - quartz is formed, and the coagulation is proved by the fact that the zeta potential value of their mixture is in the middle of its single systems [8]. Recently the electroacoustic method for determining zeta potential, which utilizes the sound waves generated from the particle movement under an AC field, was developed [9]. This method allows us perform the above investigation in concentrated suspensions that commonly treated in process plants. On the other hand, the conventional zeta potential measurement machine requires the diluted suspension. This dilution potentially overlooks the particle coagulation happening in a concentrated suspension.

Origins of surface charge/zeta potential can be varied by many factors, such as broken bonds through comminution to electron imbalances; adsorption of ions (e.g. H+, OH- from pH adjustment) [10]; substitution of ions of different valency; ionisation of compounds; ion dissolution; and crystal structure mineral. Among them, pH is often a changeable parameter while many others are predetermined at the time of beneficiation process. Therefore, pH can be varied to investigate the separation behavior of target minerals although one may only need to carefully examine around the optimum pH reported in the past. For example, in froth flotation, often a collector has the reported optimum solution pH range (e.g. pH 10 for dodecylamine hydrochloride-quartz system; Ref. 11). Therefore, one can play around that range to investigate the effect of other contributions, such as associated gangue minerals, slime coating.

![Figure 1 Zeta potential of single and mixed mineral systems of nickel oxide, hematite and quartz [8].](image)

2.2.2 Suspension rheology
Rheology is a science of the transportation of the matter. It can be utilized to identify the degree of particle-particle interactions in concentrated suspensions that are processed to upgrade the target valuable minerals.

In mineral processing, a proper dispersion/liberation of fine particles in a concentrated suspension plays a key role in achieving selective enrichment of valuable minerals. Currently, many techniques are available for characterising fine particles by measuring size [12], turbidity [13], contact angle [14], zeta potential [15], force between particle and plate [16] as well as combination of these techniques [17,18]. However, these methods often require a diluted suspension [e.g. 19] and could overlook the coagulation potentially happening in highly concentrated suspensions which are commonly treated in plant operations. This coagulation is cause by an increase in particle-particle interactions as suspension concentration increases. Figure 2 illustrates the effect of higher solid concentrations on the shear yield stress [8], a good indicator of increased interactions and coagulation. Significantly higher particle interaction was observed in a highly concentrated mixed mineral system than single mineral system with less concentration.

Hence, precise characterisation and manipulation of particle dispersion and coagulation in a concentrated suspension are
necessary to beneficiate many industrial processes. Otuski et al. [8, 20, 21] showed the effectiveness of different particle characterisation methods still applicable to highly concentrated suspensions.

2.3 Mixture of complementary analysis

Even though the above mentioned analytical methods have been significantly improved and provided us useful insight of minerals, it is impossible to acquire all the necessary mineralogical information by using only one single method. By considering the strength of each method, the combination of the above different methods should apply to analyse the ore to obtain the whole aspect of mineralogy to develop the most suitable metallurgical flowsheet design for efficient extraction of target element.

3 BENEFICIATION OF COMPLEX ORES

3.1 Refractory gold ore beneficiation

3.1.1 Gold recovery difficulties

Gold is always considered as an exceptional precious metal because of its color and beauty. Besides its high demands in the jewelry, it is also used in high-tech industries and medical applications due to its unique physical and chemical properties. The increasing demand for gold inevitably leads to the development of gold recovery process [22]. A successful process for gold recovery will be applied in industries only if the cost of the process is much less than the value of the precious metal itself. In addition, environmental issues during the process have been valued nowadays. As a result, economically viable and eco-friendly technologies for gold recovery have been demanded. Selection of such technology is one of the major subjects in the gold industry and a major study topic for metallurgists. The selection mainly depends on the mineralogy of gold ores as discussed in the previous chapters.

According to Sen et al. [23], the factors that should be considered are: mineralogical mode of gold occurrence; properties of gold bearing minerals; properties of associated metallic and non-metallic minerals; distribution of gold in different host minerals; gold grain size distribution; grain size distributions of host and gangue minerals; mineral alterations; variations of the above factors within a deposit or with time; and textures of the gold ores.

Besides the mineralogical properties, project scale, location and life of the mine site, site-specific environmental condition and costs should also be considered to optimise a process of gold ores [24].

According to the depth of gold ore underneath the surface and their composition, it can be classified as free-milling gold ore and refractory gold ore (and sometimes also complex ore, i.e. ores containing cyanide consuming mineral(s), or oxygen consuming mineral(s), and preg-bobbing ore, is in the classification [25]). Processing free-milling ores is a much easier and cheaper way to recover gold, compared with the refractory gold ore processing. Usually the free-milling ore can be processed by direct cyanidation. Additionally, depending on the grain size of gold in the ore, the free-milling gold can also be recovered by gravity circuit. However as the deposits continue at depth, their mineralogy becomes more complex and refractory. Gold ore is generally classified into two categories, based on the amount of recoverable gold in the ore with the conventional cyanidation. They are free-milling (≥95% gold recovery [6]; or > 90% gold recovery [25]) and refractory (<95% gold recovery [6]; or < 90% gold recovery [25]) ores. There is also a more detailed classification, i.e. <50% recovery: highly refractory; 50-80% recovery: moderately refractory; 80-90% recovery: mildly refractory; 90-100% recovery: non-refractory (free-milling) [25]. As the accessible free-milling ore decreases, the extraction of refractory gold ore is now gaining much more attention. The major gold carrier in refractory ores is either pyrite (FeS2) and/or arsenopyrite (FeAsS) depending on the mineralogy [26]. The two major difficulties for processing refractory gold ore are to extract gold from: (1) "atomic gold" which is locked inside sulphide crystal lattices, and (2) "solid solution gold" in sulphide minerals which are poorly soluble or insoluble in cyanide.

3.1.2 Conventional gold recovery processes

Pyro- and hydrometallurgical technologies are two major conventional ways to recover gold, and have been extensively used. The pyro-metallurgical processing requires the smelting of gold ore in a furnace or blast furnace at high temperature for a certain time. Thus, this recovery process is inefficient in cost, energy and time, and also produces toxic gas, such as sulphur dioxide. Compared with the pyro-metallurgical process, the hydrometallurgical process is, however, more predictable and easily controlled [22]. Typical beneficiation process of refractory gold is the leaching with/without pretreatment that is conventional roasting or relatively new biological/chemical oxidation [25-27]. As leaching uses costly and toxic chemicals (e.g. cyanide), it raises environmental concerns. These chemicals would contaminate not only the plant but also animals near the site which could lead devastating effects to local residents. Froth flotation has thus been gradually employed to pre-concentrate gold ore before leaching. Flotation is the much more cost-effective and environment friendly method compared with
the subsequent unit operations (i.e. hydro- and prometallurgical operations). Thus, increasing the capability of flotation would significantly decrease the cost and environmental effect. In conclusion, the problems existed in gold industry are environment issues, time and cost efficiencies. Most of previous methods are associated with those problems. Therefore, a highly cost efficient and environment friendly gold recovery process with utilizing flotation more effectively is highly required to reduce the use of hydro- and pyro-metallurgical processes.

In this paper, two relatively new generation flotation technologies, called mixed collector flotation and coal-oil agglomeration assisted flotation, developed for achieving such targets, will be introduced in the sequent sections.

3.2 Mixed collector flotation

3.2.1 Role of collectors in flotation

Collectors are organic compounds and heteropolar molecules with a non-polar and a polar group [28]. In a froth flotation process, the function of collector is to improve the hydrophobicity of target minerals and selectively float them with the aid of gas bubbles. Because of the chemical or physical attraction between the polar group and the mineral surfaces sites, a collector adsorbs on the particle surface with the non-polar group assigned towards the bulk solution, thus the mineral particle surface becomes hydrophobic [29].

Thiol collectors are the largest group of collectors and they are widely used in sulphide mineral flotation. Xanthate (X), dithiocarbamate (DTC), dithiophosphate (DTP), mecaptonbenzothiazole (MBT) are some common thiol collectors. Previous studies reported that some mixed collectors systems enhance the flotation performance [e.g. 30-32].

Sulphide minerals are semi-conductors and can have electrochemical interactions with a thiol collector. Different types of collectors interacting with minerals can either be chemisorption or physisorption [31].

Thiol collector mixtures are commonly used in the flotation of sulphides ores [31] due to the synergistic benefits which include lowering the total collector dosage requirements, improving the sulphur recovery and the rate of flotation as well as the improving the froth characteristics.

The current paper mainly considered the mixture between two thiol collectors (e.g. PAX and DTC) to improve the flotation performance of refractory gold ore.

3.2.2 Adsorption of xanthate on sulphide mineral surface

There are a few mechanisms proposed in relation to the adsorption of xanthate on sulphide mineral surfaces, which include chemisorption at metal ion sites and physisorption. The details of proposed mechanisms will be discussed in the following section 3.2.3. The complexity of oxygen on adsorption in terms of forming the metal xanthate or metal dithiophosphates is still undergoing intensive researches. Several conclusions on thiol collector adsorption are as follow: In the absence of oxygen, the adsorption of short-chain xanthates forms monolayer on mineral surface due to chemisorption and only occurs at pH 8. It has been reported that in the absence of oxygen in the flotation system, the oxidized form of xanthate, dixanthogen in sufficient quantities, can play a role of initial adsorption at the mineral surface due to physisorption. This indicates that the xanthate adsorption involves both chemisorption and physisorption [33].

When the oxygen is present, the xanthate reacts with many metal ions and oxygen is required to form metal-xanthate which attributes to the hydrophobicity of the mineral surface. Metal ions are formed by reacting with oxygen in the presence of a suitable electron acceptor. The oxygen provides a charge transfer on the sulphide surface.

The electrochemical theory of adsorption includes the oxidation of thiol collectors to dimers. In a solution, a mineral develops a potential difference, called the rest potential. It also creates a reversible potential during the xanthate oxidation. The oxidation of metal xanthate will not occur if the rest potential is cathodic or lower than the reversible potential and then metal-xanthate is adsorbed on the sulphide surface [33].

A study using secondary ion mass spectrometry (SIM) concluded that one cannot confirm that dimers work as the predominant species on pyrite under practical flotation condition and determine the formation of iron-collector complexes for the adsorption on pyrite [34].

The surface product of xanthate and pyrite surface adsorption cannot be concluded due to the presence of only dixanthogen under different conditions. The product formed depends on oxygen occurrence, pH and collector chain length. However in the xanthate-pyrite adsorption studies, most of them regarded dixanthogen as the primary product. Nitrogen can be injected to avoid the appearance of oxygen to simplify the xanthate adsorption mechanisms since less species can be formed without oxygen [35].

3.2.3 Proposed mechanisms of mixed thiol collector system

Two collectors with different functional radicals could have "compensation" phenomenon. For example, xanthates have strong collecting ability while DTC has a strong selecting ability. The combination of these two usually improves the flotation performance proved by practical experience [31]. For another example, using only xanthate as a collector for oxide ores, the flotation performance is normally poor. However, when xanthate is combined with fatty acid collector, the performance improves. Some authors also stated that by using different collectors, the recovery in different size fractions and the recovery in total sulphide minerals improved because they have different emphases. However, this type of explanation only adds up two characteristics of different collectors.

From previous studies [e.g. 28, 31, 36, 37, 38], it is well known that there are synergistic effects in flotation when using mixed collectors. The word "synergism" means that the effect of the collector combinations on the flotation performance is better than the effect of simple summation of single collector performances [31]. A study reported when using mixed collector system of a weak collector and a strong collector, the flotation recovery increased 2-5% compared with that of the single strong collector system [39]. Glemotskii also stated that the larger the difference between the structures and compositions in two collectors, the stronger the synergistic effect. This effect is more noticeable at lower collector dosage [28]. The synergistic enhancement of mixed collector system was also observed in other flotation performances in addition to the recovery. The mixed collector system can improve the rate of flotation, the coarse particle recovery and reduce the collector dosage [28]. Experimental evidence indicated an improved flotation performance with mixed collectors, but there is no clear understanding about the synergistic mechanism. Some mechanisms were proposed in previous studies. Plaskin and Zaitseva [36] concluded that different sorption sites had different activities to the different collectors, and thus led a higher
adsorption kinetics and then a greater rate of flotation. They also suggested that mixed collectors form a more evenly distributed surface film because of a better orientation of different collectors. Figure 3 illustrates this proposed mechanism.

McFadzean et al. [40] proposed a mechanism that the adsorption of collectors onto particular mineral surface sites is selective or a better orientation of the molecules on the surface. Their study proposed that a stronger bond could be formed when mixed collectors were used. The stronger collector adsorbed onto the weaker, more oxidised sites while the weaker collector occupies the stronger and less oxidised sites. It results in a denser and more even collector-surface coverage.

Lotter and Bradshaw [28] reported that a lower dosage could be required with the mixed collectors because of a better adsorption distribution of collectors on the selected mineral surface to create the necessary hydrophobicity for bubble-particle attachment.

Woods [41] stated that a mixture of chemisorption type and physisorption type collectors can achieve a better distribution and more strongly adhered chemisorption species and less hydrophobic physisorbed dithiolates. These could result in a multilayer surface product and increase the mineral surface hydrophobicity and a stronger attachment between bubble and attachment [41]. Figure 4 illustrates this proposed mechanism.

Figure 3  Schematic illustration of different adsorption site mechanism (reproduced from [38]).

Figure 4  Schematic illustration of multi-layer adsorption mechanism (reproduced from [38]).

3.2.4 Factors affecting the mixed collector system

In a single collector flotation system, its performance depends on many factors, such as pH value [e.g. 42, 43], reagent type and dosage [43], adding sequence of the reagents. In a mixed collector system, the enhanced effect on flotation performance is also influenced by these factors. This section discusses previous studies that emphasis on the different effects of these factors on the mixed collector system. It gives an indication on how to design the batch flotation with various variables to achieve an optimal flotation enhancement. One of the factors may affect the mixed collector system is the adding sequence of the collectors. Woods [41] proposed a two-layer product formation in the mixed collector system. The first adsorbed layer is a chemisorption species and it provides the sites for the following physisorption species. Therefore, if the hypothesised mechanism is correct, the multi-layer product will not form if the physisorbed collector is added first. The experiment results from Bradshaw [30] indirectly supported this mechanism. In her study, when the physisorbed collector xanthate was added first, the sulphide grade was lower than when the chemisorbed DTC was added first.

The previous method to study adding sequence is reasonable; however, the test and logic to obtain the best dosage and ratio only consider the pure compensation effect of the mixed collector system, without considering the synergistic theory. This is a good example on how a mixed collector system is designed without the fundamental basis of the mixed collector adsorption mechanisms.

3.2.5 Gaps in the literature review of mixed collector system

First of all, most studies on sulphide flotation using mixed thiol collector regarded dixanthogen as the dominant species formed on the pyrite surface. A study using SIM [34] found out that one cannot say dixanthogen is the major product formed because on the spectrophotometric graph with many other products formed. They also mentioned that with different oxidised condition and other factors, the surface products became complex. The adsorption of other thiol collectors on pyrite are also not clear yet which makes the mixed thiol collector study more difficult.

Secondly, Bradshaw [30] reported that in some cases, an activator copper sulphate is not necessary and the dosage can be decreased when some mixed collector systems are used. Not many other studies mention this point but this is worth for further study due to its practical cost-saving effect. Although a limited number of studies on this area has been reported, there is some single collector flotation studies do not need the copper sulphate as the activator. Those studies might help explain this phenomenon.

Bradshaw [30] and Lotter and Bradshaw [28] also stated that the DTP had a better selectivity than DTC determined by electronegativity of atoms in the collector structure (i.e. O (3.5) > N (3.1) > P (2.1)). However, Nagaraj and Brinen [34] showed the opposite results from their SIMS measurements. This point needs further investigation.

Furthermore, the current analytical technologies hold a difficulty in studying mixed collector system. The mixed collector system has been intensively studied and also been applied to industry many years ago. However, for instance, in Valdiviezo's study [44], the result from surface tension was not consistent with the synergistic effect. In addition, most of the current tests were used to explain the result from batch flotation test work, but most of them were the indirect method, such as thermochemical method [31].

Many studies in mixed thiol collector system used less scientifically logic selection for the combination of thiol collectors. Although Bradshaw and Lotter [28] reported the idea of selecting the mixed collector system; but it doesn't cover much detailed selection procedure, instead it only raised the factors that need to be taken in to account when designing the combination. There was not much information on how to select the thiol collectors. The method Kai [45] used to improve the flotation performance seems more scientific but he only designed the collector combination and decided the condition based on adding up the effect of two collectors instead of considering the synergistic effect. In industry,
some plant simply combined two collectors that one has higher collecting power and the other has a higher selectivity without considering the synergistic principle. Thus, currently, there is no scientifically logic way to determine what combination of thiol collector should be used to a specific ore and most of the combination used now is based on experiences.

Within this context, one of the most important issues to be addressed is how to systematically analyse this synergism in order to select proper collector combinations for ore beneficiations.

3.3 Coal-oil gold agglomeration process

There are several gold recovery processes that are well capable of producing gold on an economical profitable, efficient and environment friendly way [46]. Coal-oil gold agglomeration (CGA) process is one of these processes, which was developed by British Petroleum (BP) research team in the early eighties [47]. CGA utilize the natural hydrophobicity of coal and gold compared to that of the most gangue materials [23]. The process is a selective recovery that hydrophobic gold particles attach and penetrate into the pre-formed coal-oil agglomerates from aqueous slurry. A schematic diagram of the agglomeration steps is shown in Figure 5. The coal-oil agglomerates are formed in a coal slurry and oil under intensive agitation which achieves the homogeneous distribution of oil in fine spherical droplets and the collisions of coal particles and fine oil droplets. The oil droplets further overspread on the coal surfaces to bridge the coal particles to form agglomerates (Figure 5 a). Next the pre-formed agglomerates are added into gold-bearing ore slurry under intensive agitation; the gold particles then contact, collide and attach with the coal-oil agglomerates, and eventually penetrate into the agglomerates (Figure 5 b) [46].

![Figure 5 Schematic diagram of coal-oil gold agglomeration steps](reproduced from [46]).

After the research by BP, CGA process has been investigated by many researchers in technical, economic and environmental aspects. Summary of comparison between conventional and CGA processes is shown in Table1. Generally this process has more advantage in environmental aspect compared to the conventional methods. In most metal processing operations, tailing disposal is one of the biggest concerns in terms of environmental impact. Unlike conventional gold processing plants where the tailings contain considerable amount of free cyanide and cyanide complexes, the tailings produced in CGA process only contain small amounts of harmless contaminants, such as coal fines, oil, collectors and possibly lime. The concentrations of these contaminants will be far below threshold levels in environmental regulations. Additionally the tank storage is much less than it would be required for a conventional cyanidation plant, since the contact residence time needed for CGA is low [46]. They stated that most investigations on this subject have shown that the process is viable both technically, economically and eco-friendly. As a result, the CGA process for the gold recovery, which can be applied in industry, will benefit all the gold processing companies for less or none hazard chemicals used, less time and money spent per ton of gold product. For the environment aspect, the development of CGA process would also benefit the communities and eco-system around gold processing plants.

<table>
<thead>
<tr>
<th>Item</th>
<th>Conventional</th>
<th>CGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost / energy consumption</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Time</td>
<td>Long</td>
<td>Short</td>
</tr>
<tr>
<td>Environmental impact</td>
<td>High</td>
<td>Low</td>
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</table>

3.3.1 Performance of the CGA process

The performance of CGA process with various types of gold bearing ores has been investigated in several countries since the early 1980s. All the investigations have proved the extensive suitability of the process to a variety of gold ores [46]. Some results are listed in Table 2 and their descriptions are followed in the text.

<table>
<thead>
<tr>
<th>Ore type</th>
<th>Gold recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Placer, alluvial ores/tailings and beach sand</td>
<td>80-99</td>
</tr>
<tr>
<td>Gravity tailing</td>
<td>75</td>
</tr>
<tr>
<td>Leaching residue</td>
<td>80-90</td>
</tr>
<tr>
<td>Hard rock ore</td>
<td>75</td>
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</tbody>
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Placer, alluvial ores and beach sands: The gold particles in these minerals are commonly free from gangue; therefore gold particles can be liberated by grinding or attrition scrubbing. The coarse gold particles can be primarily recovered by gravity circuit, while the fine gold particles are recovered by following flotation/leaching process. According to Akcil et al. [46], the optimal flow sheet for gold recovery includes attrition scrubbing, size fractioning and processing the undersize with CGA. Placer, alluvial ores and beach sands from Australia and New Zealand were treated with CGA process to recover gold in laboratory experiments and excellent recoveries were achieved ranging from 80% to 99%.

Gravity tailings: The gravity tailings in Australia consisted of placers and hard rock ores were tested in laboratory scale to check the performance of CGA process. A group of minerals such as quartz, kaolinite, muscovite, serpentine, goethite and limonite were detected in the tailing samples, whereas no sulphides were present. Since there are a few gold particles locked into gangue minerals, the highest recoveries were about 75% [46].

Leaching residues: A type of leaching residue with the gold grade of 4-6 g/t was treated with CGA process to recover the free gold particles. The remaining gold particles were associated with pyrite and arsenopyrite, along with some lime and cyanide from previous
leaching operation. The agglomerates collected from the process were analyzed and the gold content was 456 g/t [46].

**Hard rock ores:** A type of gold-in-quartz ore obtained from epithermal deposit was investigated. With an average gold grade of 10-11 g/t and the feed particle size ranging from 10 to 40 μm, the recovery was 75.2% under the optimum conditions with CGA process. Additionally it was discovered that the gold recoveries of hard-rock ores would be affected by grinding size [46].

From the previous study, it could be conclude that the CGA process is most suitable for treating alluvial or free milling ores, gravity concentrates and tailings. It is also noted that the efficiency would be affected if the gold ore involves sulphide minerals such as pyrite, arsenopyrite. It is believed that sulphide would be readily absorbed into the coal-oil agglomerates due to its lipophilicity [46]. However, there were contradictory results reported completely opposite trend. One reported satisfactory gold recovery while the other showed the poor recovery [46]. Therefore, this point has to be studied further.

### 3.3.2 Effect of various parameters on CGA process

The parameters that affect the performance of CGA process can be divided into two main groups: material parameters and operational parameters.

**Material parameters** are related to carbonaceous material and oil phases which are two main components of the agglomerates. The chemical, physical and physicochemical properties of these materials are key characteristics of agglomerates. More specifically, the performance of agglomerates is dependent on the type, amount and size of carbonaceous material and oil [46].

#### 3.3.2.1 Material parameters

**Type of coal for agglomerate formation**

The type of coal used in agglomerate formation is determined by its surface properties that strongly depend on three parameters listed below [46]:

- hydrocarbon structure depending on the coal rank;
- type and number of polar groups, especially oxygenated functional groups; and
- content of inorganic materials in coal.

**Coal quantity on the process**

Sen et al. [23] investigated the effect of coal quantity on the process at different coal/oil ratios with artificial ore samples with 4.58 g/t gold and natural ore samples (mostly composed of free gold) with 12 g/t gold from a gold ore deposit. Samples were treated with CGA process and the coal-oil-gold agglomerates were separated by flotation. The highest gold recovery was achieved at coal/oil ratio of 30/1. Higher coal/oil ratio, i.e. more coal particles, would increase the agglomerate surface; larger agglomerate surface for gold penetration increases the gold recovery accordingly. Larger agglomerate surface area also increases the chance that the fine gangue particles penetrate into the agglomerates. Hence, the grade of the concentrates decline with increasing coal/oil ratio above its optimum.

**Coal particle size**

Moses and Petersen [27] processed a synthetic gold ore with the grade of 7 g/t using CGA-flotation in a Wemco flotation cell. According to them, a remarkable flotation performance was observed using the coal particles with 500 to 650 μm. They stated that it was because larger coal particles have a larger surface area for each particle. Hence larger surface areas result in readily gold particle penetration as well as enhanced stability of agglomerates. Moreover, larger coal particles are more floatable because of their porous structure.

It is believed that the discussion is not that accurate. Because of the same mass of fine and coarse particles, the fine particles should have the larger surface area. The number of investigated size fractions was limited to identify the differences and trend of the results.

Sen et al. [48] performed the similar investigation on the effect of particle size on the gold recovery. They used finer bituminous coal particles (40, 70, 140 μm) than Moses and Peterson (45%-90 μm, 300-500 μm, 500-650 μm). Sen et al. used the gold ore including fine gold grains (< 50 μm) of electrum or native gold precipitated in the quartz crystals, and observed the increase of gold recovery from 68% (40 μm) to 74% (140 μm). Their gold recovery was similar to Moses and Peterson (75% with -90 μm coal) [27].

**Oil type**

Moses and Peterson [27] investigated the effect of viscosity of the oil by using different types of oil. The results illustrated a decrease in gold recovery with decreasing the oil's viscosity, which results in smaller agglomerate formation. They proposed a decrease in the viscosity of oil also would lead to the formation of weaker agglomerates under the high shear force applied in a flotation cell.

Sen et al. [49] compared the gold recovery from free-milling ore with 6 different oils. Among them, kerosene oil achieved the highest gold recovery of 82% with the grade of 109 g/t. They supported their results by the calculation of free energy changes that indicate the probability of coal-oil attachment (ΔG_attach). The ΔG_attach was determined by using the data from the contact angle and surface tension measurement. According to their calculation, ΔG_attach for kerosene was -53.78 while ΔG Attach for corn oil was -6.24 leading the lower gold recovery of 72%.

**Gold particle size on the process**

Moses and Peterson [27] stated that both fine (< 5 μm) and relatively coarse (ca. 500 μm) gold particles are able to be recovered by CGA process with equal ease. Otsuki and Chen [50] made additional comments on the effect of gold particle size on its recovery in case of CGA-flotation. They stated that by forming agglomeration fine gold particles are able to become appropriate size for bubble-particle attachment in flotation (i.e. 20-200 μm) while coarse particle can form agglomerates up to the coarse limit of flotation (i.e. 500 μm for coal [51]) due to their high hydrophobicity.

#### 3.3.2.2 Operational parameters

Several operational parameters affect the performance of agglomeration and gold recovery. The sub-processes, which are the dispersion, collision and adhesion of the phases in the pulp, are affected by these operational parameters. Because of the interfacial tension of the oil film and the capillary attraction of the oil bridge between particles, oil-coated coal particles collide with each other and form agglomerates [46]. Generally conditioned coal and emulsified oil are mixed to form coal-oil agglomerates followed by their addition to gold bearing mineral pulp to recover gold. The separation of agglomerates from the pulp could be achieved by flotation or screening. In relation to the use of flotation as a recovery process, the separate discussion will be provided in the section called, "Flotation as the agglomerate collection method".

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Agglomerate formation process

Sen et al. [23] compared two different paths of agglomeration formation (1) direct coal-oil-gold agglomerate formation, and (2) pre-agglomeration of coal-oil followed by agglomeration with gold ore. They found that with the path (1) less number of agglomerates has been formed because of slime coating on the coal particles and low oil concentrations in pulp. Therefore only about 25% of coal particles were converted to coal agglomerates. The performance of CGA process depends on the surface area of the coal-oil agglomerates for gold particle penetration and the amount of coal-oil agglomerates for particle collisions. Therefore the recovery decreased in the path (1) by increasing the amount of gold particles remained in pulp. In other words, more agglomerates generated in pulp and providing enough surface area for gold particles penetration by adopting the path (2). The pre-agglomeration stage resulted in the higher gold recovery. Sen et al. [23] stated that gold recovery by adopting CGA process was not affected by the initial number of gold particles in pulp. They, however, demonstrated that gold grade of the concentrate produced by coal-oil assisted gold flotation process increased linearly with increasing the feed grade.

3.3.2.3 Flotation as the agglomerate collection method

One of the significant achievements in relation to the CGA method was the application of froth flotation as an agglomerate collection method. Moses and Peterson [27] first implemented this combination and showed its scale-up capability over the other methods. After this investigation, the effectiveness of this CGA-flotation combination was reported; but their investigations were limited to free gold [27, 48, 49]. Also, there is a limited discussion on the effect of flotation collectors on the gold recovery. It will be discussed in the section called, "Carbon chain length in a collector".

Stirring rate

Moses and Peterson [27] investigated the effect of stirring rate, and found that there was an optimum stirring speed to maximize the gold recovery. This is because more coal-oil-gold agglomerates are formed in suspension at a higher contact speed. When the stirring speed was exceeded 1200 rpm, the recovery, on the other hand, decreased. It is because the high stirring speed would result in a breakage of the agglomerates and particle-bubble detachment in the recovery stage of flotation they employed. Moses and Petersen [27] also stated that the optimal stirring rate (cut-off contact speed) for any process is dependent on the equipment used for the operation.

Aeration rate

Moses and Peterson [27] reported that there is an optimum aeration rate to maximize the gold recovery in case of flotation is employed at the recovery stage. They reported the optimum aeration rate was 2.2 L/min with 85% gold recovery. The less air addition to the flotation cell reduces the number of agglomerates to float. On the other hand, the high aeration rate causes not only particle-bubble attachment but also detachment. It means that the bubbles would merely pass through slurry without enough time given to attach agglomerates. Therefore, both reducing and increasing the air rate have a negative effect on the gold recovery. Sen et al. [49] reported the similar trend, i.e. the existence of optimum aeration rate (3.5 L/min) and decrease in the gold grade with the further increase. The difference in the optimum aeration rate from Moses and Peterson (2.2 L/min) [27] could be explained by the difference in the flotation cell volume leading the generation of different numbers of air bubbles that change the probability of agglomerate-bubble collision.

Carbon chain length in a collector

Wu et al. [52] investigated the gold adhesion to agglomerates, by performing CGA-flotation with two different xanthate collectors of different chain lengths. After 5 min, 50% of the gold particles were recovered using decanethioxanthate (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 [52]. 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. Wu et al. [52] 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. In the case of beneficiation of complex ore composed of many different minerals (e.g. refractory gold ore), the use of longer chain collector may distract the selective collector attachment possibly leading the low gold recovery. Also, the price of the collector can be the strong decision indicator. As a matter of fact, PAX is one of the most common collectors being used in commercial refractory gold ore processing plant [43].

Gold particle size on the gold recovery by CGA-flotation

Sen et al. [23] investigated the effect of gold particle size on the CGA process efficiency by using artificial samples. Particle size is an important parameter in flotation if it is employed as a recovery process since the size affects the probability of particles-bubble collision, attachment, and detachment [53]. Fine particles usually have less probability of collisions with bubbles, which leads to low recovery. Coarse particles are typically less floatable because of the detachment from the bubble surface caused by turbulence and the particle weight. Likewise fine particles are readily affected by turbulence as well. Additionally coarse particles may need longer induction times which could lower the efficiency. In summary the recovery of both coarse and fine particles is relatively low in conventional flotation operations. Since flotation is now the main part of the recovery system, CGA process could still hold such disadvantages of flotation. The results, however, indicate that high gold recoveries of fine (< 53 μm; 75.2%) and poor recovery in coarse range (212-300 μm; 54%) with high grade in concentrate (1096 g/t in < 53 μm; 760 g/t in 212-300 μm) by applying CGA process compared with the conventional flotation (i.e. 65.36% recovery and 101.20 g/t grade for free-milling ore, and 47.19% recovery and 108.20 g/t grade for synthetic ore) [23].

3.3.3 Gaps in the review of CGA process

Even though CGA process was developed in the early eighties, it still has not been adopted into commercial production because the process is still being optimized. To optimize the CGA process, large amount tests have to be carried out and various parameters of the process, both material and operational, have to be investigated in batch tests. There were, however, not enough data representing the trend of results.

From the previous study, it was found that the performance of CGA process with various types of free-milling gold ores was promising. All the investigations have shown the extensive...
suitability of the process. Moreover all the results have proved the higher gold recovery and less impact on to the environment when using CGA process compared to those conventional gold recovery methods. Limited research, however, has been conducted on refractory ores with CGA process. Since refractory gold ores are becoming one of the most important gold ores to extract gold, the research and development of CGA process on refractory gold ore need further investigation. Only a few number of investigations performed on refractory ores; but they were contradictory [46].

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. Further investigation is required to verify the applicability of CGA to those complex gold ores.

3.3.4 Refractory gold ore processing

Otsuki and Chen [50] investigated the applicability of CGA process to refractory gold ore processing. Refractory gold ore was processed with the combination of CGA and froth flotation, which employed an amine collector and separated the agglomerates and the pulp. The batch tests were conducted in six different size fractions using different collectors and different collector dosages. For comparison, the conventional flotation method to recover gold was also performed under the same condition. The higher gold grade and recovery were achieved with the CGA-flotation tests than conventional flotation. CGA achieved higher than 20-60 times grade and recovery were achieved with the CGA-flotation tests. The higher gold 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. Further investigation is required to verify the applicability of CGA to those complex gold ores.

3.3.5 CGA options

Figure 6 summarises the possible options of CGA. The first selection is whether we perform the pre-agglomeration. As discussed in section called, "Agglomerate formation process", pre-agglomeration achieved the higher gold recovery due to more agglomerate formation providing enough surface area for gold particles penetration by pre-agglomeration; therefore, pre-agglomeration is recommended. The second selection is whether we use flotation as the agglomeration recovery/collector method. As discussed in the section 3.3.2.3, flotation is a definitely useful as the recovery process mainly due to its scale-up capability. In relation to flotation recovery, there are still limited numbers of investigation performed. More effort, therefore, needs to clarify the true value of CGA-flotation process, especially for the complex ore beneficitation.

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