An investigation of the carbonaceous component of preg-robbing gold ores

M. HELM*, J. VAUGHAN†, W.P. STAUNTON†, and J. AVRAAMIDES*

*Parker Centre/Faculty of Minerals and Energy, Murdoch University, Murdoch Western Australia
†Parker Centre/Western Australian School of Mines, Curtin University of Technology, Bentley Western Australia

Over the last 40 years, numerous investigations have focussed on the preg-robbing capacity of carbonaceous material during gold ore processing. Various techniques have been applied to characterize the physical and chemical properties of the carbonaceous material in efforts to predict its preg-robbing capacity. The present study, which forms part of an ongoing investigation, is specifically designed to increase the understanding of preg-robbing in ores containing carbonaceous material.

In excess of 100 samples from 13 gold mines located in major gold provinces of the world have been incorporated into the present study. These samples were characterized using industry standard metallurgical techniques and were shown to have gold adsorption capacities ranging from a few grams to many hundreds of grams of gold per ton of ore. Further analysis showed that the crystalline nature of the carbonaceous material, which is related to its geological history, is important in determining the preg-robbing capacity of an ore. This finding builds on the common understanding that the preg-robbing behaviour of an ore is related to the amount (or abundance) of carbonaceous material present in that ore.

In this study, Raman spectroscopy was used to evaluate the physical nature of carbonaceous material. This is a tool which has been successfully applied by researchers for the characterisation of carbon materials, with respect to crystallite size and lattice defects. Raman analysis of the samples included in this study showed varying degrees of disorder in the carbonaceous materials from the different deposits. Comparison of the Raman spectra with the gold loading capacities of the samples indicated a direct relationship between the structure of the carbonaceous material and its capacity to preg-rob gold. From this, a simple and robust method has been developed based on the Raman spectra of the sample and carbonaceous material content to predict the preg-robbing capacity of an ore.

The potential exists to develop a predictive tool using Raman spectroscopy for characterising the preg-robbing capacity of an ore. Such a tool would have potential application in projects ranging from the early stage of exploration through to more detailed feasibility studies and mining operations. The result of applying the predictive method outlined in this paper would be the effective and proactive management of the deleterious influence of carbonaceous material on gold recovery in mining operations.

Introduction

For many years carbonaceous gold ores have been identified as having the ability to adsorb gold (I) cyanide from leach solutions1-14. This phenomenon, known as preg-robbing, is responsible for poor recoveries as the carbonaceous component of the ore competes with activated carbon used during the leaching and adsorption phase of processing. The ability of carbonaceous material to adsorb gold (I) cyanide from solution is widely acknowledged and documented2,7,8,12-14.

Early characterization studies by Radtke and Scheiner15 into the physical and chemical nature of carbonaceous gold ores identified two distinct organic components in addition to an activated carbon type material. High molecular weight hydrocarbons were thought to coat the surfaces of the activated carbon type component, while the other organic component was considered to comprise an organic acid with functional groups capable of reacting with gold complexes. Subsequent to the findings in this investigation, numerous attempts have been made to characterize carbonaceous gold ores in terms of hydrocarbon, organic acid and activated carbon type content and assess the influence these components have on preg-robbing. Although many analytical methods such as elemental analysis2,8, microscopy2,6,10,16,17, surface area measurements9,14, x-ray diffraction2,5,9,16-18, gas chromatography, mass spectroscopy7,8, various spectroscopic methods5,7,8,13,14,16-19 and stable carbon isotopic analysis2 have been applied, the exact nature of the carbonaceous component and its role in preg-robbing remains poorly understood. As a result of these investigations, a wide range of descriptions have been used to characterize the physical nature of the carbonaceous material. The structure has been described as ranging from fine grained amorphous...
carbon to hydrogen poor crystalline graphite with maturity equal to, or greater than anthracite coal. The process of transformation into amorphous carbon, hydrogen poor graphite or anthracite coal occurs as the original organic material present in the host sedimentary rock undergoes metamorphism. During this process, the organic material progressively evolves into well crystallized graphite, with the final degree of graphitization dependent upon temperature, pressure and the type of organic precursor. The unit structure formed as the organic material graphitises is called a crystallite (stacked planes of aromatic rings). As the organic material matures towards graphite, the distance between the layer sheets (Lc) and the layer sheet direction (La) increases, i.e. (the carbonaceous material becomes more ordered). Graphite and commercially activated carbon are examples of carbonaceous material comprising crystallites.

The degree of disorder (disorder refers to structural deviations from the well defined three dimensional structure of crystalline graphite) of the carbonaceous material in gold ores has previously been linked to its structure and nature of the carbonaceous material under consideration. The work presented in this study, includes descriptions of the characteristics and behaviour of a wide range of carbonaceous gold ores collected from major gold provinces. This project aims to improve the understanding of preg-robbing carbonaceous ores by combining metallurgical assessments used as standard practice by industry together with Raman spectroscopy as a tool for characterizing the nature of the carbonaceous material.

### Ore characterization

The findings presented in this paper are based on assessment of carbonaceous gold ore samples collected from 13 gold mines. This sample distribution ensured a full spectrum of ore variability and preg-robbing behaviour was incorporated into the study. In total, over 100 samples have been collected and analysed to establish the characteristics and behaviour of the carbonaceous material. For the purpose of this paper, and to provide a high level summary of the results, only one representative sample from each deposit is reported.

The samples were generally collected as broken coarse ore taken from underground, open pit or stockpile. From these polished section samples were handpicked for mineralogical and Raman spectroscopy analysis.

The 13 samples, which form the basis of this paper, were crushed to -2 mm and rotary split to obtain representative sub samples for each given sample for further testwork. The sub samples were then analysed for gold, total carbon, non-carbonate carbon (sometimes referred to as organic carbon by commercial laboratories) and total sulphur (Table I). Gold content was determined using fire assay and Inductively Coupled Plasma Optical Emission spectrometry (ICP-OES). Total sulphur and carbon concentrations were determined using thermal decomposition at 1390°C in a Leco combustion unit. Non-carbonate carbon was determined by adding acid to the fresh sample which evolves carbon dioxide associated with carbonates and the residue was then tested by Leco to determine the percentage of non-carbonate carbon in the sample. It has been assumed that the non carbonate carbon assay is representative of all the preg robbing graphitic carbon in the ore.

The graphic carbon content of the samples ranged from 0.53 to 3.62%. It is noteworthy that these grades do not necessarily reflect the average grade of the deposit. The sulphur levels were measured to provide an indication of the presence of sulphide minerals which may contribute to any refractoriness in the ore.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Location</th>
<th>Au head assay (ppm)</th>
<th>Total carbon (%)</th>
<th>Non-carbonate (Graphitic Carbon) (%)</th>
<th>Total Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO 1</td>
<td>Australasia</td>
<td>2.68</td>
<td>1.03</td>
<td>0.53</td>
<td>0.71</td>
</tr>
<tr>
<td>CGO 2</td>
<td>Australasia</td>
<td>1.74</td>
<td>4.38</td>
<td>1.55</td>
<td>5.22</td>
</tr>
<tr>
<td>CGO 3</td>
<td>Australasia</td>
<td>0.04</td>
<td>3.08</td>
<td>1.72</td>
<td>3.20</td>
</tr>
<tr>
<td>CGO 4</td>
<td>Australasia</td>
<td>2.23</td>
<td>1.97</td>
<td>0.53</td>
<td>2.13</td>
</tr>
<tr>
<td>CGO 5</td>
<td>Australasia</td>
<td>1.85</td>
<td>1.94</td>
<td>1.76</td>
<td>1.98</td>
</tr>
<tr>
<td>CGO 6</td>
<td>Australasia</td>
<td>1.70</td>
<td>1.44</td>
<td>1.35</td>
<td>2.42</td>
</tr>
<tr>
<td>CGO 7</td>
<td>Australasia</td>
<td>3.40</td>
<td>4.31</td>
<td>1.69</td>
<td>0.92</td>
</tr>
<tr>
<td>CGO 8</td>
<td>Africa</td>
<td>0.11</td>
<td>5.01</td>
<td>3.43</td>
<td>0.52</td>
</tr>
<tr>
<td>CGO 9</td>
<td>North America</td>
<td>3.01</td>
<td>0.58</td>
<td>0.57</td>
<td>3.99</td>
</tr>
<tr>
<td>CGO 10</td>
<td>North America</td>
<td>5.41</td>
<td>3.62</td>
<td>3.62</td>
<td>2.21</td>
</tr>
<tr>
<td>CGO 11</td>
<td>North America</td>
<td>11.33</td>
<td>7.42</td>
<td>2.42</td>
<td>1.74</td>
</tr>
<tr>
<td>CGO 12</td>
<td>South America</td>
<td>0.06</td>
<td>1.52</td>
<td>0.97</td>
<td>1.37</td>
</tr>
<tr>
<td>CGO 13</td>
<td>Europe</td>
<td>1.88</td>
<td>2.60</td>
<td>1.97</td>
<td>2.01</td>
</tr>
</tbody>
</table>
Metallurgical assessment

Preg-robbing index test
The industry standard approach for detection and quantification of preg-robbing is to run, in parallel, a cyanide leach test with a gold spiked cyanide leach. The cyanide leach effectively determines the amount of cyanide soluble gold in the ore, while the gold spiked leach indicates the capacity of an ore to absorb gold (I) cyanide from solution. From these results, an index or value is calculated based on the gold concentration remaining in each solution at the end of each test. There is no industry standard in place for analysing the results resulting in many variations to the way the tests are performed and the methods for calculating the preg-robbing index (PRI) or value. The most commonly used tests are implemented at Barrick Gold (Barrick) and Newmont Mining (Newmont) operations. The Newmont tests report a preg-rob index based on the concentration of gold adsorbed by the ore while the Barrick preg-rob value is based on a percentage change in gold concentration. This study utilised the PRI test described by Dunne et al.. In these tests, a PRI value of zero indicates the ore is not preg-robbing, a value between zero and 1.0 indicates minimal preg-robbing activity, between 1.0 and 2.5 moderate activity, and a PRI > 2.5 indicates the ore is highly preg-robbing. These tests are designed to provide meaningful information in an operating plant situation, but not to determine an absolute value of preg-robbing.

Gold loading test
The PRI test outlined only identifies preg-robbing gold adsorption to a maximum of 3.4 g Au per ton of ore. In order to expand the range of preg-robbing beyond this, the samples used in this study were loaded to achieve maximum gold adsorption. Therefore, the absolute preg-robbing capacities or preg-robbing strength (PRS) of these samples was determined by ascertaining the gold loading to a maximum of 3.4 g Au per ton of ore. The gold loading test was used as a more definitive method for assessing their absolute preg-robbing capacity. The results of the gold loading test (PRS), effectively highlight the extreme nature and variability in the preg-robbing capacity of these ores. The samples with a PRI below 3.4 had PRS values of approximately 3.0 g Au/t ore or less. By contrast, ores with the maximum PRI value exhibited a wide range in preg-robbing capacity ranging from 5.0 g Au/t ore to as high as 544 g Au/t ore. Over half of these samples had a PRS greater than 50 g Au/t ore. These results imply that even minor contamination of a free milling ore by preg-robbing ores containing highly adsorbing carbonaceous material must be avoided.

One of the difficulties faced when comparing the preg-robbing behaviour of these ores is variability in their graphitic carbon concentrations. Given this, application of the PRV method enables direct comparison between the samples with respect to preg-robbing capacity. The PRV of these samples range from 2.1 to 225 g Au/t ore. This highlights that preg-robbing capacity is not solely a function of the concentration of graphitic carbon. Furthermore, it suggests that other properties of the carbonaceous material, such as crystallinity, surface area and physico-chemical surface properties, which vary with metamorphic grade (i.e. temperature and pressure), may contribute to the preg-robbing nature of these samples.

Results and discussion

Preg-robbing assessment
The metallurgical assessments of the samples are summarized in Table II. The results from the PRI tests indicate the samples are moderately to highly preg-robbing, with 8 of the 13 samples tested having a maximum PRI value of 3.4. As it is not possible to differentiate between preg-robbing behaviour for samples with PRI values below this value, the gold loading test was used as a more definitive method for assessing their absolute preg-robbing capacity. The results of the gold loading test (PRS), effectively highlight the extreme nature and variability in the preg-robbing capacity of these ores. The samples with a PRI below 3.4 had PRS values of approximately 3.0 g Au/t ore or less. By contrast, ores with the maximum PRI value exhibited a wide range in preg-robbing capacity ranging from 5.0 g Au/t ore to as high as 544 g Au/t ore. Over half of these samples had a PRS greater than 50 g Au/t ore. These results imply that even minor contamination of a free milling ore by preg-robbing ores containing highly adsorbing carbonaceous material must be avoided.

All the samples tested as part of this study have variable graphitic carbon concentrations. Given this, application of the PRV method enables direct comparison between the samples with respect to preg-robbing capacity. The PRV of these samples range from 2.1 to 225 g Au/t ore. This highlights that preg-robbing capacity is not solely a function of the concentration of graphitic carbon. Furthermore, it suggests that other properties of the carbonaceous material, such as crystallinity, surface area and physico-chemical surface properties, which vary with metamorphic grade (i.e. temperature and pressure), may contribute to the preg-robbing nature of these samples.

Raman spectroscopy
Raman spectroscopy was used to characterise the graphitic carbon in situ using polished sections. An Olympus microscope attached to a Dilor Labram 1B Raman microspectrometer was used to select the region for recording as well as focus the laser through a 50 x objective onto the grains of graphitic carbon. During the measurement, the red-line of a helium neon laser (λ = 632.8 nm) was used as an excitation source to record spectra in the region 900 to 1800 cm⁻¹ at room temperature. Spectra were collected from 10 to 20 separate grains within each section to establish any variation in the degree of crystallinity of the graphitic carbon within an individual sample.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Graphitic carbon (%)</th>
<th>PRI</th>
<th>PRS</th>
<th>PRV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO 0</td>
<td>0.53</td>
<td>2.0</td>
<td>1.3</td>
<td>2.5</td>
</tr>
<tr>
<td>CGO 2</td>
<td>1.55</td>
<td>2.5</td>
<td>3.2</td>
<td>2.1</td>
</tr>
<tr>
<td>CGO 3</td>
<td>1.72</td>
<td>3.4</td>
<td>5.8</td>
<td>34</td>
</tr>
<tr>
<td>CGO 4</td>
<td>0.53</td>
<td>2.7</td>
<td>2.0</td>
<td>3.8</td>
</tr>
<tr>
<td>CGO 5</td>
<td>1.76</td>
<td>3.4</td>
<td>100</td>
<td>57</td>
</tr>
<tr>
<td>CGO 6</td>
<td>1.35</td>
<td>3.4</td>
<td>152</td>
<td>113</td>
</tr>
<tr>
<td>CGO 7</td>
<td>1.69</td>
<td>3.4</td>
<td>142</td>
<td>84</td>
</tr>
<tr>
<td>CGO 8</td>
<td>3.43</td>
<td>3.4</td>
<td>9.0</td>
<td>2.6</td>
</tr>
<tr>
<td>CGO 9</td>
<td>0.27</td>
<td>1.7</td>
<td>2.2</td>
<td>6.5</td>
</tr>
<tr>
<td>CGO 10</td>
<td>3.62</td>
<td>3.4</td>
<td>54</td>
<td>15</td>
</tr>
<tr>
<td>CGO 11</td>
<td>2.42</td>
<td>3.4</td>
<td>544</td>
<td>225</td>
</tr>
<tr>
<td>CGO 12</td>
<td>0.97</td>
<td>3.4</td>
<td>7.5</td>
<td>7.7</td>
</tr>
<tr>
<td>CGO 13</td>
<td>1.97</td>
<td>3.4</td>
<td>98</td>
<td>30</td>
</tr>
</tbody>
</table>
Raman spectroscopy

Raman spectroscopy analysis was undertaken on the graphitic carbon component of the samples in addition to an activated carbon and natural graphite sample. A commercially activated carbon (Haycarb) was used for comparative purposes, as the degree of graphitization in activated carbon is one of the main factors influencing its adsorption of gold (I) cyanide\textsuperscript{23,32}. A natural graphite sample was used, as it represents well ordered graphic material of high thermal maturity to simulate the potential influence of metamorphism on the rocks sampled.

A selection of first order Raman spectra corresponding to the different carbonaceous samples studied is presented in Figure 1. Common features visible in the spectra are dominant bands located at approximately 1 330 and 1600 cm\textsuperscript{-1}, characteristic of disordered graphite. In Figure 1, the evolution of the spectral profile is illustrated according to the degree of disorder in the graphitic carbon. From this, it is evident that recognizable changes occurring in the spectra, between samples, correspond with changes in PRVs. It can be seen that the mild preg-robbing carbonaceous ores, such as CGO 1 and CGO 2 have different spectra from highly gold adsorbing activated carbon or high preg-robbing carbonaceous material present in some of the ores. Samples with the highest PRV have spectra similar to that of activated carbon and samples that have the lowest PRV have spectra similar to that of natural graphite, which is known to adsorb only small quantities of gold (I) cyanide\textsuperscript{33}.

These spectral changes can be explained in terms of the dominant D and G bands. As the degree of disorder in the material increases, there is a corresponding decrease in intensity and broadening of the G band along with the broadening and increased intensity of the D band. Changes in the shape and intensity of these bands reflect changes in disorder and crystallite size\textsuperscript{20,21,29} with the broadening of the D and G bands corresponding to an increase in disorder within the graphite structure\textsuperscript{25,29,30,31}. The Raman spectra of the graphitic carbon found in these samples indicate that varying degrees of disorder exist which appear to be influencing the preg-robbing capacity noted in the samples.

Correlation between preg-robbing and Raman spectroscopy

The differences in the preg-robbing behaviour of the graphitic carbons in Figure 1 can be visually correlated with changes in peak heights and shape. However, in order to provide a more definitive correlation of preg-robbing with the degree of disorder the evolution of the Raman spectra was quantified using the height and widths (FWHM) of the D and G bands. The height and width of the D and G bands, obtained through the deconvolution of the spectra, were used to calculate a Raman Ratio for each sample. This Raman Ratio was then correlated against the preg-robbing nature of the samples as defined by the PRV.

A plot of the Raman Ratio against the PRV (Figure 2) clearly indicates that the structural characteristics of the graphitic carbon are influencing preg-robbing behaviour. The line of best fit indicates a strong log linear correlation exists between preg-robbing and the graphitic structure of the carbonaceous material. This line of best fit or Raman Calibration Line can be used to explain the observed variation in preg-robbing between the samples from the 13 different deposits. It is considered that similar analysis could be used to measure variation within a deposit.

Figure II also highlights the potential benefit of Raman spectroscopy as a tool for predicting and quantifying the absolute preg-robbing capacity of an ore using the Raman Calibration Line.

Conclusions

Investigation into the nature and behaviour of carbonaceous preg-robbing gold ores has shown that a wide range in preg-robbing capacity exists between ores from different deposits. Using an industry standard preg-robbing test, in conjunction with a gold loading test, it was found that high preg-robbing samples could potentially preg-robb 10 to 100 times more gold than the maximum gold spike concentration typically used in industry tests. As these samples had varying concentrations of graphitic carbon it was necessary to normalize the gold loadings to a concentration of 1% graphitic carbon in order to effectively compare preg-robbing capacities. The corresponding PRV of the samples established that a wide range in preg-robbing behaviour exists between samples from different locations. As this variation could not be solely attributed to the concentration of graphitic carbon in the ore, it demonstrates that other properties are potentially influencing preg-robbing.

---

Figure 1. Spectral evolution of preg-robbing graphitic carbon found in carbonaceous gold ores and other carbonaceous samples

Figure 2. Correlation between degree of disorder of graphitic carbon and preg-robbing
Raman spectroscopy was effectively used to explain this variation and show the physical structure of the graphitic carbon plays an important role in influencing preg-robbing behaviour. Highly preg-robbing graphitic carbon has similar Raman spectra to that of activated carbon, while the graphitic carbon present in low preg-robbing ores has spectra more aligned to natural graphite. The degree of disorder can be quantified using the parameters of the spectra and this can then be correlated with the preg-robbing capacity of the samples. From this, a simple and robust method has been developed with which to predict the preg-robbing capacity of carbonaceous gold ores based on Raman spectra and graphitic carbon concentration.

Acknowledgements

The authors gratefully acknowledge the support of Module 4 sponsors of AMIRA Project P420C Gold Processing Technology (AngloGold Ashanti, Barrick Gold, Intec Ltd, OceanaGold and Rio Tinto)

The support of the Parker CRC for Integrated Hydrometallurgy Solutions (established and supported under the Australian Government’s Cooperative Research Centres Program) is gratefully acknowledged.

M. Helm acknowledges the support of Murdoch University through a Murdoch University Research Scholarship.

References


17. TAN, H., FENG, D., LUKEY, G.C., and VAN...


Michelle Helm

*PhD Candidate, Parker Centre/Faculty of Minerals and Energy, Murdoch University*

Michelle graduated with Bachelor of Science in Extractive Metallurgy from Curtin University (WA School of Mines). Thereafter, she completed her honours year at Murdoch University, investigating carbonaceous preg-robbing gold ores. Michelle then joined the Gold Technology Group (WA School of Mines, Curtin University) as a project metallurgist where she was involved in various research projects including the AMIRA P420 project. Continuing her involvement with the Gold Technology Group, Michelle is currently enrolled as a PhD student, studying the behaviour of carbonaceous preg-robbing gold ores during CIL processing.