SIMS Proceedings Papers

SURFACE and INTERFACE ANALYSIS

Received: 29 September 2009 Revised: 5 January 2010 Accepted: 14 March 2010 Published online in Wiley Online Library: 19 May 2010

(wileyonlinelibrary.com) DOI 10.1002/sia.3448

# Speciation and quantification of surface gold in carbonaceous matter by TOF-SIMS: a new approach in characterizing losses during the gold recovery process

**S. S. Dimov* and B. R. Hart**

**An increasing number of low-grade gold ore deposits are characterized by the presence of gold as solid solution into the mineral matrix of sulphide minerals which is not directly amenable to gold cyanidation. In order to liberate this submicroscopic gold the ore has to be oxidized before being subjected to gold cyanidation and exctraction. This is mainly done by autoclave pressure oxidation (AC POX) or roasting, two major technologies used by the mining industry. Very often, these ores contain an active carbonaceous compound which has the ability to adsorb, or preg-rob gold from the cyanide solution. Gold recovery can be adversely affected by preg-robbing on inherent carbonaceous material during autoclave pressure oxidation of sulphide ores.**

**The time of flight (TOF) SIMS (TOF-SIMS) technique has been applied for direct determination of gold species on individual carbonaceous particulates from AC POX stream samples. The speciation of the gold preg-robbed on carbonaceous matter from CIL tail sample showed presence of both metallic gold and $Au(CN)_2$ compound. Direct quantification of the metallic and compound gold provided an estimate for the fraction of gold losses due to preg-robbing in carbonaceous matter.** 

**Keywords:** TOF-SIMS; quantification; gold species; gold preg-robbing; carbonaceous matter; autoclave pressure oxidation; mining

## Introduction

The mining industry is facing increasing challenges in gold recovery of low-grade sulphide ore deposits in which the gold is finely disseminated in the sulphide mineral crystal structure or as a solid solution. Such ores, called refractory ores, are not amenable to gold recovery by direct cyanidation. Autoclave pressure oxidation (AC POX) of the sulphide ore and subsequent cyanidation is a common technology used to liberate the gold in these types of ores. A major obstacle for effective gold recovery during this process is the presence in the ores of an active carbonaceous matter (c-matter) which has the ability to adsorb, or preg-rob gold from the cyanide leach solution. Gold compounds are formed with thiosulfates, thiocyanide radicals or halogen ions on the surface of the carbonaceous particles and eventually reduced to metallic gold thus adversely affecting the gold recovery.[1]

The development of a reliable surface microbeam analytical technique for direct determination of gold species on individual carbonaceous particles would provide a new diagnostic tool in understanding the chemistry of gold sorption on carbonaceous matter from AC POX stream products and optimizing the process of gold recovery. Such a technique should be capable of analyzing small single particles (μm range size) and provide detection sensitivities for gold species at plant concentration levels in the low ppm range. S. Dimov *et al*.[2] reported the first application of two different microbeam techniques; TOF-SIMS and time of flight Laser Ionization Mass Spectrometry (TOF-LIMS) for characterization of sorbed gold species on c-matter from CIL tails samples which are the final waste product in the AC POX process. The TOF-SIMS instrument used in that study was PHI 7200 equipped with Ga liquid metal ion sources. The lower ionization efficiency of this ion source limited the detection sensitivities of the TOF-SIMS instrument and restricted the application of this technique for analyzing samples at plant concentration levels. At that stage the TOF-LIMS technique provided better sensitivity for gold compound (85 ppm detection limits for $Au(CN)_2$). However, recent development and introduction of a new generation of cluster liquid metal ion sources ($Bi^+$ and $Au^+$) into the TOF-SIMS instrumentation lead to a dramatic improvement of the detection sensitivities and ability to detect complex compounds with minimum fragmentation.

This study demonstrates the capacity of the state-of-the art TOF-SIMS technology to detect, speciate and quantify surface gold on individual carbonaceous particles at plant concentration levels.

## Experimental

Carbonaceous matter in CIL residue tails from AC POX operation was studied for presence of surface gold species using ION TOF IV TOF-SIMS instrument. It is equipped with $Bi^+$ cluster liquid metal ion source which was used in Bi3+ mode. Individual carbonaceous particles were selected under optical stereoscope and mounted on a Cu substrate. The composition of the particles was established by SEM EDX analysis. Raman Spectroscopy was used to determine the

* *Correspondence to: S. S. Dimov, Surface Science Western, University of Western Ontario, Room G-1, Western Science Centre, London, Canada N5A 5B7. E-mail: sdimov@uwo.ca*

*Surface Science Western, University of Western Ontario, Room G-1, Western Science Centre, London, Canada N5A 5B7*

SURFACE and INTERFACE ANALYSIS

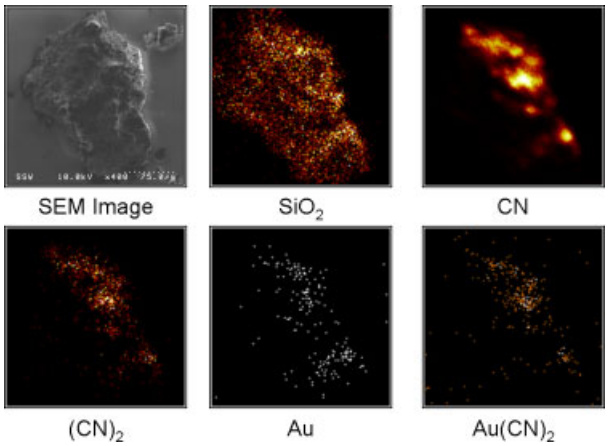


**Figure 1.** SEM image and TOF-SIMS elemental and compositional maps for carbonaceous particle from CIL tails sample. The quantified amount of metallic gold on this particle was 4.5 ppm while the amount of Au as Au(CN)2 compound gold was 38.1 ppm.

structure of the carbon present on these particles. The TOF-SIMS experimental study had two objectives: i) Detection and speciation of different forms of gold preg-robbed on carbonaceous matter: metallic gold $Au^o$ and gold compounds such as $Au(CN)_2^-$, $AuCl_2^-$ and $AuS(CN)_2^-$; and ii) Quantification of the established forms of preg-robbed gold based on compound specific Au standards in activated carbon.

## Results and Discussion

A compositional analysis of carbonaceous particles from the CIL tail samples identified two different groups of carbon-containing particles: carbonaceous particles containing almost 100% carbon (total carbonaceous matter, TCM) and quartz particles with variable amounts of finely disseminated carbonaceous matter (disseminated TCM particles). The surface content of both types of particles was analyzed using the TOF-SIMS instrument. Surface spectra and images of the surface Au distribution were established for each particle. The speciation of the gold preg-robbed on carbonaceous matter from CIL tail sample showed presence of both metallic gold and $Au(CN)_2$ compound (Fig. 1).

Raman spectroscopy was used to characterize the properties of the carbonaceous materials. The technique uses the shape and width of the detected Raman peaks to provide information on the nature of the carbon bonds. The degree of symmetry (or asymmetry) of characteristic Raman peaks combined with their shift in wavelength provides information on the structure (maturity) of the carbonaceous material.[3] A comparison between the Raman spectra of two different types of TCM material present in the CIL tail sample and two reference carbonaceous materials is shown in Fig. 2. The Raman spectra of these two TCM particles indicate that one of the TCM structure is similar to that of natural activated carbon while the other is more close to the highly organized graphitic carbon. The Raman study allows for some interpretation on the degree of organization of the carbonaceous material present in the ore sample. It is expected that the structure of the carbonaceous material will affect its preg-robbing properties. The Raman analysis can be used to fingerprint the structure of the carbonaceous materials present within or in different samples, and eventually to correlate this database with their preg-robbing properties for Au species established by TOF-SIMS analysis.

For quantification of the TOF-SIMS data on carbonaceous particles a set of elemental and matrix-specific standards were prepared in order to establish the calibration curves for gold species on carbonaceous matter at the same instrumental conditions. A series of external $Au(CN)_2$ in activated carbon standards were analyzed at the same experimental conditions and the corresponding calibration curve for quantitative analysis of $Au(CN)_2$ in carbonaceous matter was produced. The TOF-SIMS spectra recorded from the $Au(CN)_2$ standards are characterized by strong parent molecular peaks and exhibit very little fragmentation. The $Au(CN)_2$ standards were prepared by contacting 70–150 µm-sized activated carbon with aqueous solutions of gold cyanide at different nominal concentrations at a fixed activated carbon weight/solution volume ratio. Consequently all standards were assayed to determine the accurate gold content present as a surface compound $Au(CN)_2$. The metallic gold standards were produced using the following procedure. Initially, $AuCl_2$ standards on activated carbon were prepared by contacting activated carbon with aqueous solutions of hydrogen tetrachlorourate, $HAuCl_4.3H_2O$ in the same way the $Au(CN)_2$ were produced. These $AuCl_2$ were subjected to a thermal treatment in a furnace in order to reduce the $AuCl_2$ compound to metallic gold. Practically, 100% of the $AuCl_2$ compound was re-

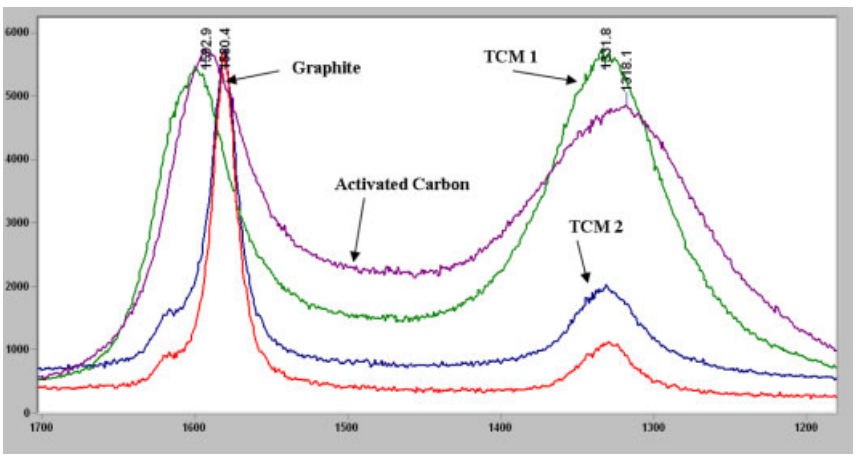


**Figure 2.** Comparative Raman spectra from two reference materials (graphitic carbon and activated carbon) and two TCM particles from CIL tail sample.



  

duced to metallic gold, Au$^o$ in the thermally treated standard. The established detection limits for surface metallic gold and Au(CN)2 compound gold on activated carbon were in the range of 2–5 and 15–20 ppm, correspondingly.

## Conclusion

This study demonstrates the capacity of the TOF-SIMS technology to detect, speciate and quantify surface gold on carbonaceous particles at plant concentration levels. The TOF-SIMS technique provides nondestructive elemental and molecular surface analysis and allows for simultaneous detection of metallic gold and gold compounds on individual carbonaceous particles. Owing to the very low molecular fragmentation during the TOF-SIMS analysis, it is possible to detect ('speciate') simultaneously the presence of Au in both elemental ($Au^0$) and compound forms such as $Au(CN)_2$, $AuCl_2$ or $Au(SCN)_2$.

Further efforts are under way to develop a routine, standardized procedure for a direct characterization of the preg-robbing properties of carbonaceous matter present in these types of ores which will use a combination of several microbeam analytical techniques, namely SEM/EDX, Raman spectroscopy and TOF-SIMS. Such an approach could become a valuable diagnostic tool during optimization of the treatment of preg-robbing carbonaceous ores. Possible applications range from characterization of the preg-robbing properties of different types of c-matter to evaluation and providing a feedback on the efficiency of different treatment options for minimizing the gold recovery losses due to preg-robbing in the AC POX process.

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