Ammoniacal thiosulfate and sodium cyanide leaching of preg-robbing Goldstrike ore carbonaceous matter

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Abstract

The aim of this work was to establish a relationship between the preg-robbing behavior of Goldstrike ore and the leaching behavior of carbonaceous matter within the ore. Carbonaceous matter obtained by acid demineralization of Goldstrike ore was leached using either an ammoniacal thiosulfate system or a sodium cyanide system. Leaching of the carbonaceous matter was conducted in batch experiments, as well as in columns at various flow rates to compare the mass of gold leached from the carbonaceous matter to its initial gold content. Ammoniacal thiosulfate leaching of carbonaceous matter from autoclaved Goldstrike ore resulted in 90–100% solubilization of the gold initially present regardless of the preg-robbing behavior of the parent ore. For carbonaceous matters from non-autoclaved ores, ammoniacal thiosulfate leaching only solubilized about 40% of the gold initially present in the carbonaceous matter, indicating that approximately 60% of the gold was encapsulated in sulfides. The percentage of gold leached by ammoniacal thiosulfate was found to depend on the initial gold content of the carbonaceous matter since an equivalent, small amount of gold was taken up by all carbonaceous matters examined. Gold leaching was primarily limited by the volume of lixiviant contacting the carbonaceous matter; however, a slight kinetic limitation was observed in ammoniacal thiosulfate leaching at higher flow rates. The percentage of gold leached by sodium cyanide from carbonaceous matter demineralized from autoclaved Goldstrike ore was inversely related to the preg-robbing behavior of the parent ore, suggesting that preg-robbing is controlled by the retention of gold by carbonaceous matter during leaching. Similarities between the naturally occurring carbon and commercial activated carbon suggest that the mechanism of gold retention by the naturally occurring carbon during leaching is the same as gold cyanide complex adsorption by commercial activated carbon. Similar to leaching with ammoniacal thiosulfate, kinetics of sodium cyanide leaching also depended primarily on the volume of lixiviant contacting the carbonaceous matter; however, the kinetics of sodium cyanide leaching were also influenced by the preg-robbing behavior of the ore. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Goldstrike ore; Carbonaceous matter; Preg-robbing behavior

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1. Introduction

Gold ore from Barrick Goldstrike Mines (BGMI) and other ores from the Carlin trend in N.E. Nevada, suffer from two forms of refractorness. More than 50% of the gold in Goldstrike ore is estimated to be encapsulated within sulfides [1] and is, therefore, not amenable to leaching. Also, naturally occurring organic carbon found within Carlin trend ore deposits has been implicated in a phenomenon known as "preg-robbing" [2]. Preg-robbing occurs during ore processing when the ore sequesters gold from the pregnant cyanide solution during leaching.

Carlin trend ores contain natural organic carbon that varies in preg-robbing behavior [3]. Since the preg-robbing nature of Carlin trend ore may prevent recovery of a significant fraction of gold present in the ore, it is imperative to have techniques in place to predict the effects of preg-robbing by the ore during processing. However, the current methods of assessing the preg-robbing behavior of the ore do not always give results that are consistent with one another; therefore, better methods are needed to assess how preg-robbing ores will act during ore processing.

The natural organic carbon in Carlin ore has been shown to be of high maturity, equal to or greater than anthracite coal [4–6]. The carbon is composed of featureless aromatic (graphitic) rings with a structure similar to commercial activated carbon [5,6]. The physical properties of commercial activated carbon (e.g. size of the microcrystallites) have been shown to influence aurocyanide complex adsorption [7]. Similarly, physical properties of Goldstrike carbonaceous matter have been shown to correlate with the preg-robbing behavior of the whole ore [8]. The similarities between commercial activated carbon and Goldstrike carbonaceous matter suggest that preg-robbing by the natural organic carbon occurs by a mechanism similar to gold uptake by commercial activated carbon.

The objective of this study was to confirm a correlation between the preg-robbing behavior of the whole ore and the gold uptake behavior of the carbonaceous matter by examining gold-cyanide complex recovery during leaching of the carbonaceous matter with sodium cyanide and ammoniacal thiosulfate. Although autoclaving is used during ore processing, Stenebråten et al. [8] only examined carbonaceous matter from non-autoclaved ore; thus, carbonaceous matters from autoclaved and non-autoclaved ores were examined in this study to determine the effect of autoclaving on the carbon.

2. Background

The extraction procedure at BGMI is currently designed to address sulfide refractoriness. After ball mill grinding (80% of 200 mesh), a slurry (51% solids) is acidulated with H_2SO_4 (up to 75 kg/ton ore) to remove carbonates. The acidified slurry is passed through a continuous autoclave for 52 min. During autoclaving, high temperatures (225°C) and pressures (2893 kPa with oxygen overpressure 420 kPa) oxidize over 95% of the sulfides in the ore and release submicron elemental gold particles. After the ore is neutralized with lime, a carbon-in-leach (CIL) process is used to solubilize and capture the gold. In the CIL process, ore slurry (30–38% solids) and sodium cyanide (0.55–0.75 kg/ton) cascade (10–13 h) through 16 tanks in countercurrent fashion with respect to commercial activated carbon (15 g/l). Commercial activated carbon is screened (16 mesh) and recovered upstream. Gold is then stripped from the commercial activated carbon using the Zadra method [9]. Preg-robbing by the ore is thought to occur during the CIL process when the aurocyanide complex adsorbs to the fine-grained natural organic carbon in the ore, which is not collected during screening [4].

Smith [3] recognized that the carbonaceous ores from the Carlin trend had varying degrees of preg-robbing behavior. Since the presence of carbonaceous matter in some ores results in the loss of significant gold, it is crucial to be able to accurately assess the potential gold loss due to preg-robbing. Two tests are used by BGMI to assess the preg-robbing behavior of the ore. The preg-robbing test (%PR) is a simple test in which slurry is created by adding 10 ml of a 2.0 g/l NaCN solution with 3 ppm gold to 5.0 g of ore. After equilibrating for 15 min, the slurry is centrifuged, and the supernatant is analyzed to determine the gold concentration in the solution in ppm ([Au]). The %PR value is determined by assessing the concentration of gold lost

from the original solution gold concentration and converting to a percent (Eq. (1)):

$$\%PR = \left(1 - \frac{3 - [Au]}{3}\right) \times 100. \qquad (1)$$

The second test (%REC) involves bench-top autoclaving followed by a carbon-in-leach system (BTAC–CIL), which measures the gold recovered by commercial activated carbon. Slurry composed of a 1:1 mass ratio of solids to solution is acidified with sulfuric acid to dissolve any carbonates. The acidified slurry is then autoclaved for 1 h at 240°C with an oxygen overpressure of 880 kPa. Sodium cyanide (2.3 kg/ton of slurry) and commercial activated carbon (12 g/l of slurry) are added to the slurry and allowed to equilibrate for 16 h while rolling. The commercial activated carbon is separated by screening and analyzed for gold by fire assay. The %REC is determined by dividing the gold content of the commercial activated carbon by the gold content of the untreated ore and multiplying by 100 [8].

While the %PR test simply measures aurocyanide complex adsorption by the ore, measurements of

%REC involves additional ore treatment, such as acidification, autoclaving, and competition between the natural carbon and commercial activated carbon, all of which may have an effect on the recovery of the aurocyanide complex. Despite these differences, most ores show an inverse relationship between the %PR and %REC. However, some ores are problematic in that they may show "contradicting" %PR and %REC values. The ores examined in this study varied with respect to their %PR and %REC values, but did not include ores with poor correlation between %PR and %REC.

Several similarities between Carlin trend natural organic carbon and commercial activated carbon have been noted. Radtke and Scheiner [10] first reported that the organic carbon in Carlin ore was similar in nature to activated carbon. Subsequent studies have also shown that Carlin trend natural organic carbon is composed of aromatic carbon with probable ether linkages, imparting polarity to the structure. The carbon largely lacks significant carboxylic or phenolic functionality and is of high maturity with a coal rank equal to or greater than that of anthracite coal
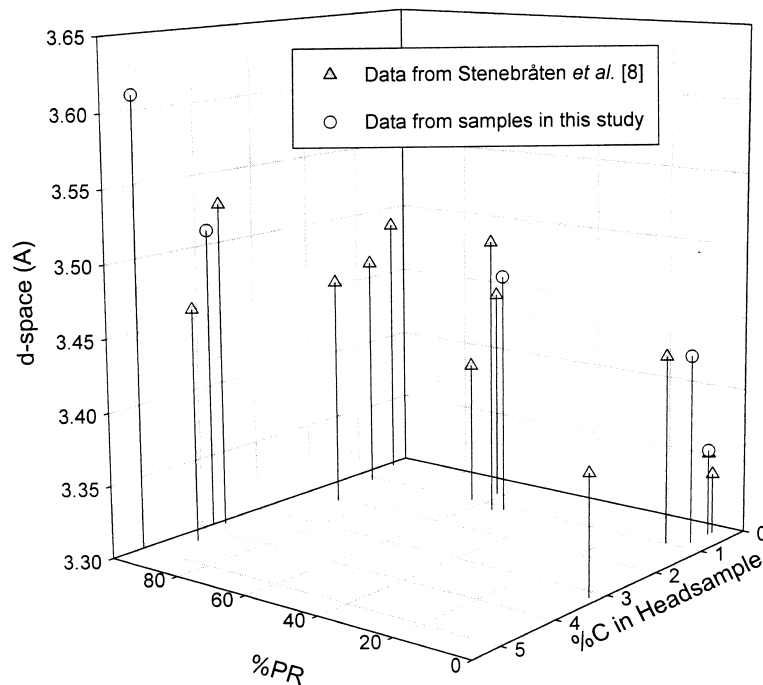

Fig. 1. Relationship between microcrystallite *d*-spacing, ore carbon content, and %PR for the Goldstrike ores studied in Stenebråten et al. [8] and in this study.

[4–6,11,12]. These descriptions of Carlin trend naturally occurring organic carbons are very similar to descriptions of commercial activated carbon activated at temperatures greater than 750°C [7].

Commercial activated carbon, graphite, and naturally occurring carbon in Goldstrike ore are composed of microcrystallites, which are stacked planes of aromatic carbon rings [8,13,14]. The size of the microcrystallite can be described using three parameters: the length of the microcrystallite in the plane of the stacked aromatic sheets (L_a dimension), the height of the microcrystallite through the stacked aromatic sheets (L_c dimension), and the distance between the aromatic sheets (d-spacing). As carbon matures, the microcrystallite grows in the L_a and L_c dimensions with a corresponding decrease in d-spacing [13]. Using X-ray diffraction, Adams [7] determined that commercial activated carbons with high aurocyanide complex affinity had an average d-spacing of about 3.7 Å, a value that is similar to the average d-spacing (3.50 ± 0.03 Å) in carbonaceous matter from high preg-robbing Goldstrike ores [8].

These values are larger than the average value (3.36 ± 0.03 Å) for carbon from low preg-robbing Goldstrike ores [8], which are closer to the d-spacing value for graphite (3.349 Å) [13]. Furthermore, Adams [7] reported a higher L_c length for graphite (150 Å) than for commercial activated carbon (6.9–12.3 Å). Likewise, Stenebråten et al. [8] reported higher L_c values (117–372 Å) for carbonaceous matter from low preg-robbing ores relative to carbonaceous matter from high preg-robbing ores (30–88 Å).

An inverse correlation exists between crystallite size in the L_c dimension of commercial activated carbon and gold adsorption [7]. A correlation also exists between crystallite size in the L_c dimension of Goldstrike ore carbonaceous matter and the preg-robbing behavior of the parent ore [8]. Since microcrystallite d-spacing is related to the L_c dimension [8,13], a correlation also exists between the preg-robbing behavior of Goldstrike ore and microcrystallite d-spacing. Figs. 1 and 2 show the correlation between d-spacing and preg-robbing behavior for the
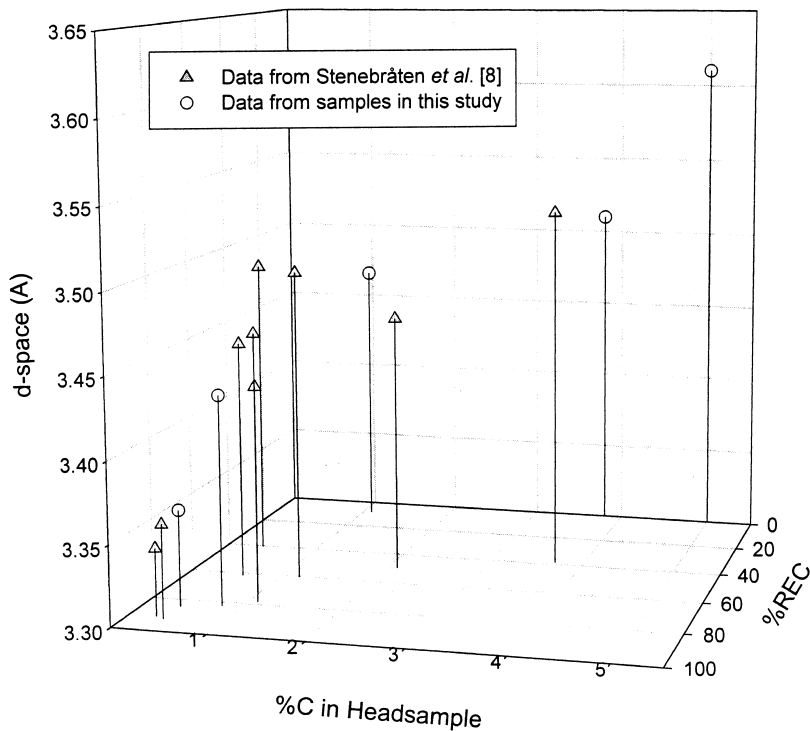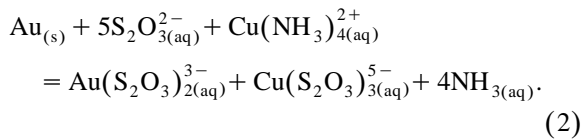

Fig. 2. Relationship between microcrystallite d-spacing, ore carbon content, and %REC for the Goldstrike ores studied in Stenebråten et al. [8] and in this study.

Goldstrike ores studied in Stenebråten et al. [8], as well as the Goldstrike ores used in this study. Although the correlation between L_c and %PR is nonlinear [8], Fig. 1 shows a nearly linear, direct relationship between the microcrystallite d-spacing, percent carbon, and the %PR of the parent ore. Similarly, the correlation between L_c and %REC is also nonlinear [8], whereas Fig. 2 shows a nearly linear, inverse correlation between increased the microcrystallite d-spacing, percent carbon, and decreased %REC of the parent ore. Figs. 1 and 2 indicate that for a given carbon content, ores with larger d-spacing in the microcrystallite have higher %PR and lower %REC.

Since 1980, alternatives to cyanide leaching have been pursued because of environmental concerns and the high toxicity of cyanide [15]. Thiosulfate has a low toxicity and has been shown to be technically viable in recovering gold from low-grade ore [15,16]. Gold dissolution by ammoniacal thiosulfate utilizing cupric ion as a catalyst is described by the net reaction:

$$Au_{(s)} + 5S_2O_{3(aq)}^{2-} + Cu(NH_3)_{4(aq)}^{2+}$$
$$= Au(S_2O_3)_{2(aq)}^{3-} + Cu(S_2O_3)_{3(aq)}^{5-} + 4NH_{3(aq)}.$$
$$(2)$$

The reaction involves the surface complexation of the oxidized gold by the ammonia, followed by the formation of more stable, soluble gold thiosulfate complexes. Simultaneously, cupric ammonia complexes are reduced to cuprous ammonia complexes. This is followed by the formation of more stable cuprous thiosulfate complexes, which are subsequently oxidized by oxygen or another oxidizing agent. Thus, the ammonia catalyzes the anodic dissolution of gold, while the copper ions catalyze the cathodic reaction [17]. Since Gallagher et al. [18] noted less than 1% adsorption of thiosulfateaurate(I) during bed saturation of commercial activated carbon, ammoniacal thiosulfate has been tested as a lixiviant for carbonaceous gold ores [15,19,20]. Pilot plant tests on carbonaceous Carlin gold ore achieved a total gold recovery of about 66% after leaching with ammoniacal thiosulfate, while traditional cyanide leaching of the same ore followed by carbon adsorption resulted in only 17% recovery [20].

3. Methods

BGMI Metallurgical Services dry-ground five ore samples to 80% of 200 mesh. After performing fire assays of these head samples, carbon and sulfide content were determined by LECO analysis, and %PR and %REC tests were performed (Table 1). A portion of each ore sample was then autoclaved utilizing the same autoclaving conditions as described in the BTAC-CIL recovery test.

3.1. Demineralization of ore

The ore was demineralized to concentrate the carbon, as well as to remove quartz and other minerals that interfere with analysis [6]. Demineralization involved a two-step acid digestion, utilizing HCl to remove carbonates and HF to remove quartz as described in detail by Stenebråten et al. [6]. After

Table 1
Chemical composition of the Goldstrike ores used in this study

Sample source	Sample ID	%PR	%REC	Au (opt)	%C$_{(organic)}$	%S$_{(sulfide)}$
Betze COF composite 8/26/97–9/25/97	BTZ #3	< 5.0	92.5	0.326	0.5	1.67
Betze COF composite 12/25/97–1/25/98	BTZ #4	< 5.0	84.6	0.192	0.4	1.71
PR-1G	PR-1G	32.0	53.6	0.321	1.1	1.77
6th West	6th West	53.0	8.3	0.084	0.8	2.4
BR-22	BR-22	100.0	0.0	0.088	3.8	1.45

Organic carbon and sulfide contents determined by LECO analysis and gold content determined by fire assay. The term opt refers to ounces per ton.

Table 2
Chemical composition of carbonaceous matter demineralized from non-autoclaved Goldstrike ores

Sample ID	Au (opt)	%C$_{(organic)}$	%S$_{(sulfide)}$	L_c (Å)	d-spacing (Å)
BTZ #3	6.54	10.0	42.0	620 ± 60	3.36 ± 0.01
BTZ #4	6.36	6.8	32.8	523 ± 90	3.36 ± 0.01
PR-1G	5.50	18.8	21	NA	NA
6th West	2.12	16.6	28.2	40.5 ± 3.8	3.47 ± 0.01
BR-22	0.82	36.8	4.6	35.5 ± 3.2	3.51 ± 0.01

Organic carbon and sulfide sulfur composition determined by LECO analysis, gold content determined by fire assay, and microcrystallite L_c and d-spacing determined for the CM from non-autoclaved ore by X-ray diffraction analysis of the 002 carbon peak. The term opt refers to ounces per ton.

filtering, the acid leachates were analyzed for gold using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Perkin Elmer Plasma 400). X-ray diffraction was used to confirm the removal of quartz, as well as to measure carbon crystallite size as described in Stenebråten et al. [8]. A portion of each carbonaceous matter (CM) was returned to BGMI for LECO analysis and fire assay. Table 2 shows the chemical and physical analysis of CM demineralized from non-autoclaved Goldstrike ore while Table 3 shows the chemical analysis of the CM demineralized from Goldstrike ore after autoclaving.

3.2. Analytical analysis of CM

After demineralization, the resulting CMs were analyzed for chemical changes by X-ray photoelectron spectroscopy (XPS). CMs were examined in a Fisions 220I-XL spectrometer using AlK$_\alpha$ radiation at a background pressure of less than 1×10^{-5} Pa. In samples where the buildup of static charge was problematic, a 4-eV electron flood gun was used. Samples were initially scanned with a 320-W X-ray from 0 to 1200 eV (1 eV step) to determine

Table 3
Chemical composition of carbonaceous matter demineralized from autoclaved Goldstrike ores

Sample ID	Au (opt)	%C$_{(organic)}$	%S$_{(sulfide)}$
BTZ #3	14.78	23.8	8.6
BTZ #4	7.94	8.2	2.0
PR-1G	8.64	23.6	4.6
6th West	5.72	43.0	9.0
BR-22	3.12	33.4	0.2

The term opt refers to ounces per ton.

major elemental components. Subsequent scans (0.1 eV step) in the bond energy regions for carbon (275–295 eV) and oxygen (522–542 eV) determined binding energy shifts due to the presence of carbon–oxygen functional groups [21]. Relative elemental and functional group concentrations were determined by integrating peak areas.

Although analysis of the CMs by XPS revealed significant amounts of fluorine, there was no evidence of carbon–fluorine bonding. XPS analysis revealed a significant calcium component approximately one-half the magnitude of the fluorine component indicating fluorite (CaF_2), a highly insoluble mineral, was present after HF digestion.

CMs were also investigated by Fourier Transform infrared spectroscopy (FT-IR) according to the procedure outlined in Stenebråten et al. [6]. Changes in spectra obtained by FT-IR spectroscopy at each stage of the demineralization process were consistent with expected mineral losses due to acid digestion, as observed by Stenebråten et al. [6].

Gold was not detected in the acid leachates produced during demineralization, indicating that gold remained with the solid phase during demineralization. A gold mass balance, based on fire assays of the non-demineralized ore and the demineralized CMs, indicated that all of the gold initially present in the ores was concentrated in the CMs during demineralization. In addition to carbon, gold, and fluorite, the CMs also contained sulfides, as well as other unidentified minerals.

3.3. Leaching procedure

Three different lixiviant systems were used to determine the leachability of the gold in the CMs at

room temperature. Two sodium cyanide concentrations (0.5 g/l NaCN and 2.0 g/l NaCN, adjusted to pH 10.8 with NaOH) were used to approximate the range of cyanide conditions that Goldstrike ore might encounter during processing. Because of its success in leaching preg-robbing ores [19,20], and ammoniacal thiosulfate leaching system (100 g/l $NaS_2O_3 \cdot 5H_2O$, 120 ml/l NH_4OH (29.5% NH_3), 4 g/l $CuSO_4 \cdot 5H_2O$, and 5 g/l $NaSO_3$) was also used. Carbonaceous matter was placed inside syringe filter housings (Swinnex 11 mm) along with filters (22 μm) and attached to syringes (10 ml) used as lixiviant reservoirs (Fig. 3). A syringe pump was used to elute 50 ml of leachate, which were collected in aliquots (5–10 ml), at three different flow rates (0.5, 0.07, and 0.008 ml/min). The procedure monitors the combination of gold leaching by cyanide and gold cyanide complex adsorption by the CM.

In initial studies, 50 mg of carbon was used; however, in subsequent columns, the mass of CM in the syringe housing was varied to achieve equal masses of carbon in each column (10 mg). CM from BTZ #4 ore was omitted from analysis after initial studies due to its low carbon content, which required the mass of CM (100 mg) to exceed the maximum capacity of the filter housing (80 mg). Additionally, since the tests used by BGMI to assess the preg-robbing behavior of the ore are performed in batch, CMs from autoclaved ores were also studied in a batch system. Sufficient CM to achieve 7 mg of carbon was equilibrated in a bottle roll for 72 h wit 20 ml of lixiviant. The leachate was then collected by filtering to analyze the gold in solution.

All solutions were analyzed for gold in solution using ICP-AES at a wavelength of 242.795 nm. The percent of gold leached (%Au leached) from the CM was determined relative to the mass of gold initially present on the CM as determined by fire assay. Since some of the CMs adsorbed gold complexes, the %Au leached represents solubilized gold that was not adsorbed during the contact time. The total %Au leached was the sum of gold present in all of the aliquots collected for a given CM.

4. Results and discussion

4.1. Effects of autoclaving in the CM

Autoclaving of low preg-robbing ore did not alter the XPS and FT-IR spectra of the associated carbonaceous matter. For CMs from high preg-robbing ores, autoclaving the ore produced shifts in the regions of the XPS spectra associated with carbon and oxygen bonding indicating increased oxidation of the carbon. Additionally, an additional peak in the 1720 cm^{-1} region of the FT-IR spectra was present in CMs from high preg-robbing ores after autoclaving. Similarly, Sibrell et al. [5] observed formation of 1720 cm^{-1} peaks in the FT-IR spectra of commercial activated carbons after autoclaving and attributed these peaks to the formation of carboxylate groups. Since adsorption of aurocyanide complex by commercial activated carbon decreased in the presence of carboxylate functionalities [5], studies are currently being performed to examine the effect of
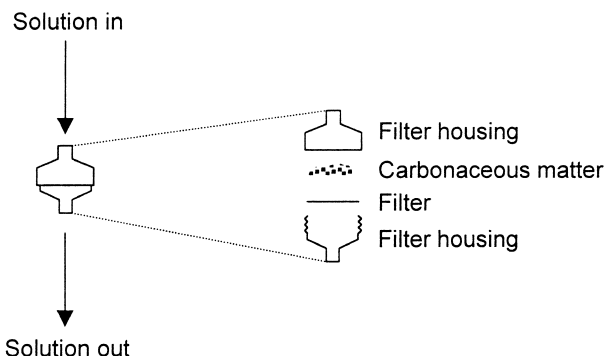

Fig. 3. Diagram of CM packed into reusable syringe filter used for the column setup.

autoclaving on adsorption of aurocyanide complexes by Goldstrike CM.

4.2. Leaching results

4.2.1. Ammoniacal thiosulfate

Fig. 4 shows the total %Au leached from 50 mg of CM during a 7-h period at a flow rate of 0.06 ml/min. Leaching was performed on CM from autoclaved (open symbols) and non-autoclaved (closed symbols) ores representing a variety of preg-robbing behaviors. Ammoniacal thiosulfate removed between 90% and 100% of the gold initially associated with CMs from autoclaved ores, indicating that naturally occurring organic carbon in these ores had a low affinity for the thiosulfateaurate(I) complex as has been observed for commercial activated carbon [18]. Only 40% of the gold associated with CMs from

non-autoclaved ores was leached using ammoniacal thiosulfate. It can be presumed that the remaining 60% of the gold was not amenable to a leaching due to encapsulation within the sulfides, corroborating the work of Chryssoulis et al. [1], who estimated a similar percentage of gold encapsulation based on secondary ion mass spectroscopy.

Fig. 5 shows the total %Au leached from four CMs by ammoniacal thiosulfate in both the batch system and column systems at flow rates of 0.5, 0.06, and 0.008 ml/min. The total %Au leached in the batch system decreased from over 90% leached from the lowest preg-robbing CM (BTZ #3) to only 75% leached from the most preg-robbing CM (BR-22). In the column system, the decrease in total %Au leached from BTZ #3 (95%) to BR-22 (90%) was smaller than in the batch system (Fig. 5). The smaller change in %Au leached (5%) would be expected in a
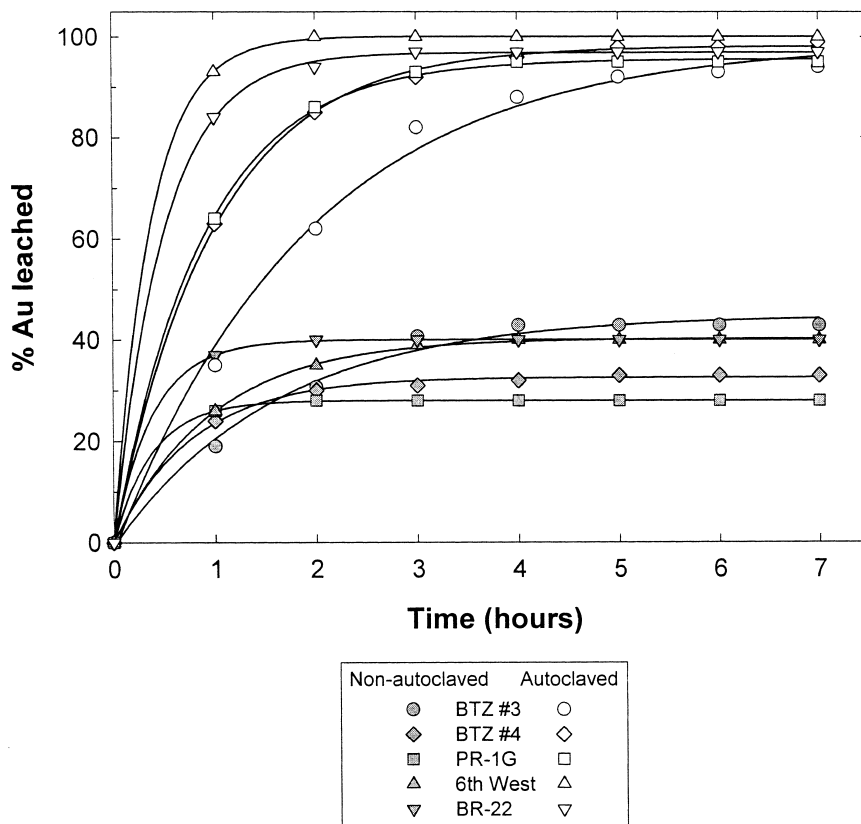

Fig. 4. The percentage of gold leached by ammoniacal thiosulfate from CMs over time. Open symbols denote that the CM came from autoclaved ore, whereas closed symbols denote ores, which have not been autoclaved.
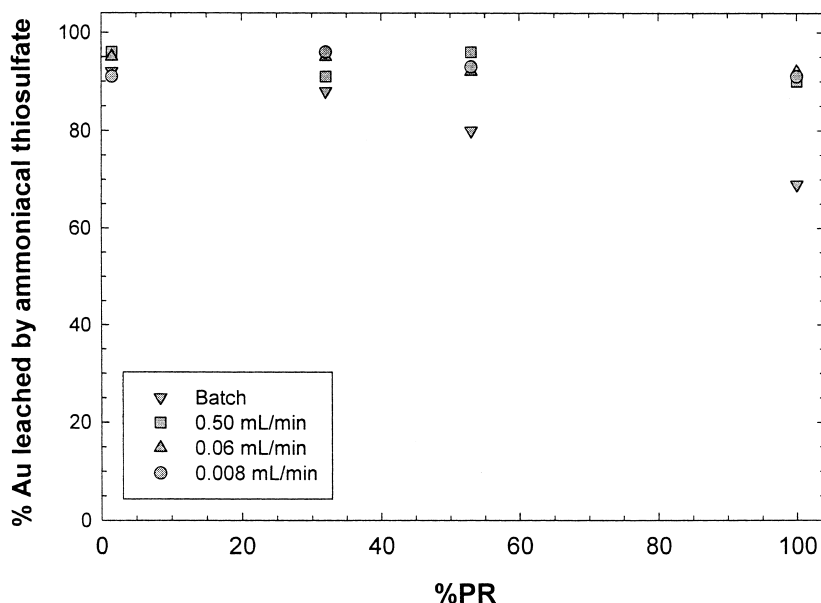
Fig. 5. Total percentage of gold leached by ammoniacal thiosulfate from CMs obtained from four autoclaved Goldstrike ores with varying values of %PR. Leaching was done in batch as well as in a column system at flow rates of 0.5, 0.06, and 0.008 ml/min.

column system, since continual reintroduction of gold-free lixiviant would enhance the dissolution of gold.

Although the results indicate a possible relationship between decreased gold leaching of the CM with increased %PR of the ore, initial gold content also decreased with increasing %PR of the ore. In fact, the actual concentration of gold remaining on the CM after leaching was relatively constant despite variations in the %PR of the parent ore $(12 \pm 4$ mg Au/kg carbon in batch, and 36 ± 4 mg Au/kg carbon in column); thus, the apparent inverse relationship between %Au leached from CM and %PR of the parent ore resulted from the inverse relationship between initial gold content of the CM and %PR of the parent ore. Since a constant mass of gold was retained by the carbon for all CMs, CMs with lower initial gold content showed a lower %Au leached. The fact that constant gold concentration remained on the carbon despite variation in %PR of the ore indicates that gold retention by the CM during ammoniacal thiosulfate leaching is not controlled by the same mechanism that controls gold retention by the ore during processing (preg-robbing). Regardless of the mechanism of gold retention dur-

ing ammoniacal thiosulfate leaching, it is clear that thiosulfateaurate(I) uptake by the natural carbon is highly limited, further indicating similarity between the natural organic carbon and commercial activated carbon.

4.2.2. Sodium cyanide

Fig. 6 shows a decrease in the total %Au leached from four CMs with increasing %PR. Leaching was done using two concentrations of sodium cyanide in both batch and column systems at flow rates of 0.5, 0.06, and 0.008 ml/min. As we seen in the ammoniacal thiosulfate system, overall gold recovery in the batch system was generally smaller than that in the column system, again presumably due to constant introduction of gold-free lixiviant in the column system.

While the gold remaining on the carbonaceous matter after ammoniacal thiosulfate leaching was constant despite variations in %PR of the ore, the fraction of gold remaining with the CM after sodium cyanide leaching was directly related to the %PR of the ore. Since the concentration of gold remaining with the carbon after sodium cyanide leaching directly correlated to the %PR of the ore, it is likely
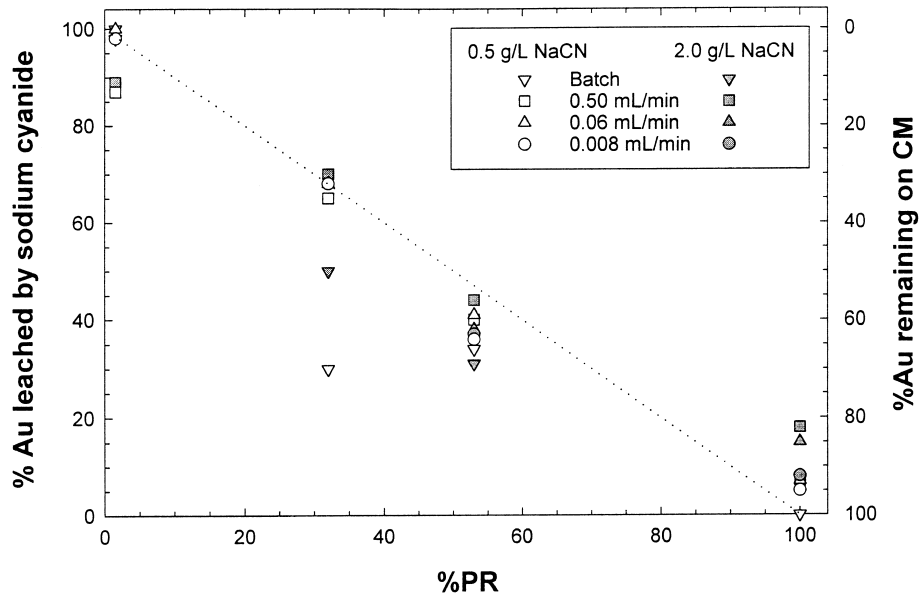
Fig. 6. Total percentage of gold leached by 0.5 and 2.0 g/l NaCN from CMs obtained from four autoclaved Goldstrike ores with varying values of %PR. Leaching was done in batch as well as in a column system at flow rates of 0.5, 0.06, and 0.008 ml/min.

that the mechanism controlling gold retention on the carbon during cyanide leaching may also control preg-robbing. The similarities between the naturally occurring carbon in Carlin ore and commercial activated carbon, combined with the well known uptake of aurocyanide complex by commercial activated carbon, suggest that the mechanism of gold retention by natural carbon is the same as that by commercial activated carbon, i.e. adsorption of aurocyanide complexes.

Sibrell and Miller [22,23] suggested that adsorption of the aurocyanide complex by activated carbon and graphite occurs preferentially at the edges of the aromatic sheets in the carbon structure. The edges of the aromatic sheets are expected to provide localized sites of mild polarity, resulting from defects in the aromatic structure, at which aurocyanide ion pairs undergo physical adsorption [14,22,24–26]. In this study, it was observed that the retention of gold by the CM was directly correlated to the %PR of the parent ore. Furthermore, a direct correlation was observed between the d-spacing of the carbon microcrystallite and %PR of the parent ore (Fig. 1), suggesting that aurocyanide complex adsorption by car-

bon is strongly related to d-spacing. Although carbon in Goldstrike ore has a consistent (~ 42 Å) microcrystallite dimension in the plane of the aromatic sheets (L_a dimension), the average d-spacing is greater for carbons from high preg-robbing ores (3.50 Å) than for carbons from low preg-robbing ores (3.36 Å) [8]. Since the L_a dimension in Goldstrike ore is relatively consistent, a given mass of carbon will have the same number of aromatic sheets regardless of preg-robbing behavior. Furthermore, the larger d-spacing of carbons from high preg-robbing ores will result in a greater exposed surface area in the L_c dimension relative to carbons from low preg-robbing ores. For example, 100 aromatic sheets from high preg-robbing ores would have a combined L_c length of 350 Å, whereas 100 aromatic sheets of carbon from low preg-robbing Goldstrike ore would have a combined L_c value of 336 Å. This increase in edge surface may not explain the different gold uptake behavior of these carbons, but it is consistent with the linearity of the correlation between d-spacing and %PR. Since d-spacing depends on the maturity of the carbon [13], additional considerations, such as the possibility of greater edge surface irregu-

larities in less mature carbons, may also be required to fully explain the correlation between d-spacing and %PR.

4.3. Kinetic effects

4.3.1. Ammoniacal thiosulfate

Fig. 7a–d shows leaching data from ammoniacal thiosulfate leaching of four CMs from autoclaved ores with varying %PR. For each CM, 50 ml of leachate was collected at flow rates of 0.5, 0.06, and 0.008 ml/min. The total %Au leached from all the CMs by ammoniacal thiosulfate was close to 100% as discussed earlier. The similarity in the leaching curves despite a flow rate variation of nearly two orders of magnitude suggests that the %Au leached depended primarily on the volume of lixiviant contacting the CM. For example, after 100 min of

leaching (50 ml lixiviant contacted at the fastest flow rate, and 5 ml at the medium flow rate), the fastest flow rate clearly reached equilibrium, while the medium flow rate did not, indicating a lixiviant volume limited process.

Although the above results suggest primarily volume-limited leaching, kinetic effects are also indicated by the observation that the slower flow rates achieved complete leaching at lower lixiviant volumes. Fig. 8 shows the direct relationship between the log flow rate and the average leachate volume required to achieve 90% of the total %Au leached. The volume limitation in ammoniacal thiosulfate leaching may be explained by the fact that gold dissolution by ammoniacal thiosulfate is enhanced by the mass of cupric ion contacting the CM [15,17,19], which would be dependent primarily on the volume of lixiviant passing the CM. In contrast,
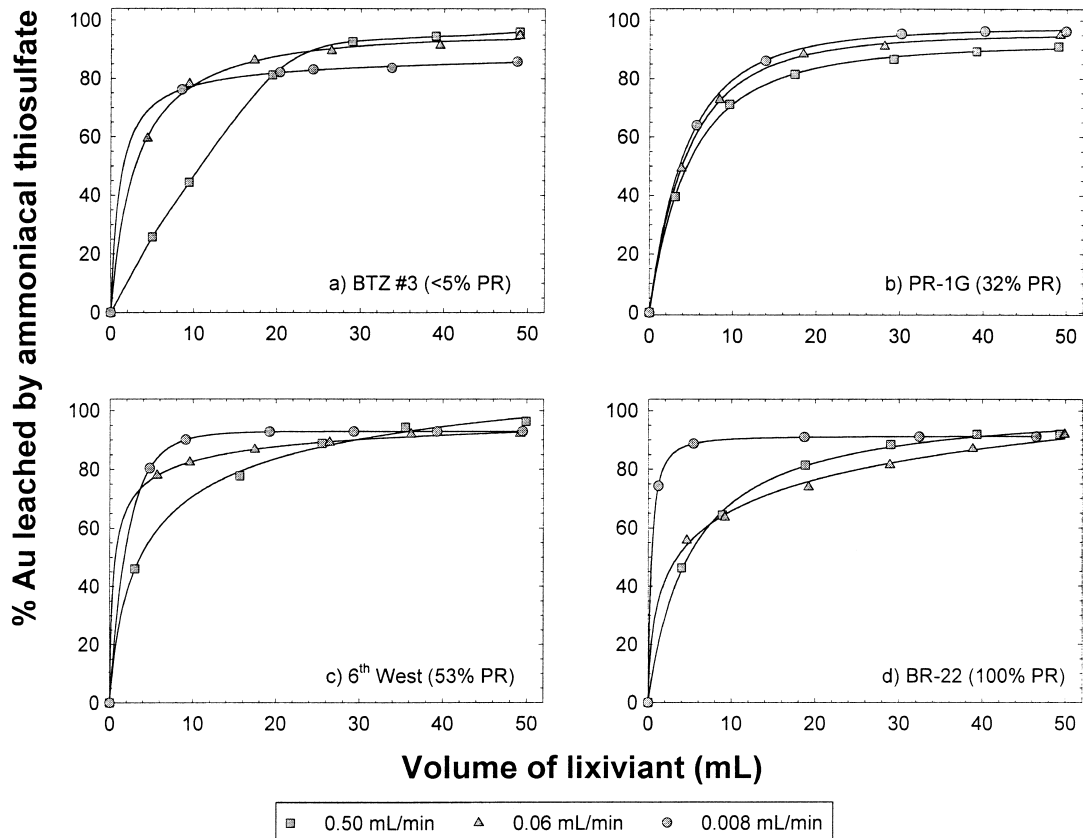

Fig. 7. The percentage of gold leached by ammoniacal thiosulfate per total volume of lixiviant used. Leaching was done at flow rates of 0.5, 0.06, and 0.008 ml/min on four CMs (a–d), which were demineralized from ores of increasing %PR.
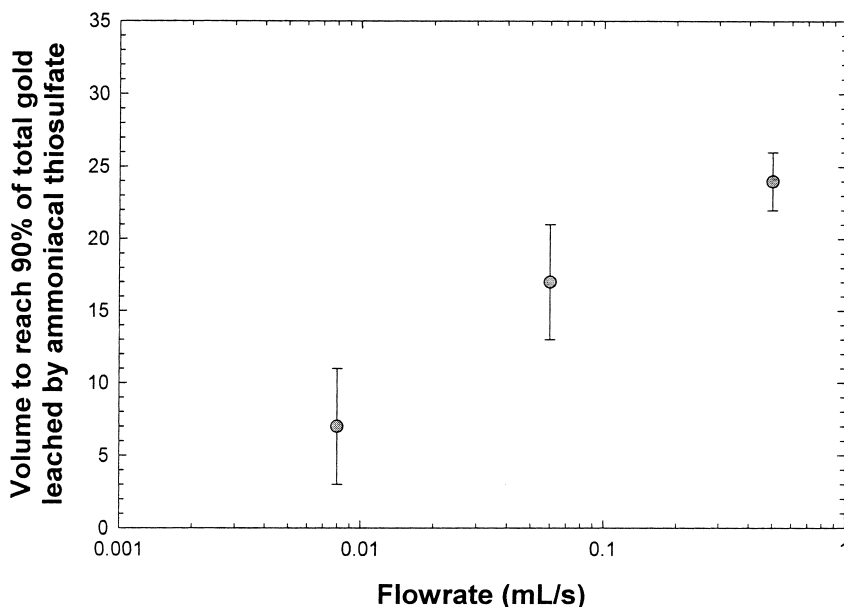
Fig. 8. The average volume of ammoniacal thiosulfate lixiviant needed to obtain 90% of the equilibrium value of gold leached from the four CMs studied.

the kinetic effect may be due to kinetic limitations of the re-oxidation of the cuprous ion, that might allow for improved regeneration of the cupric ion at slower flow rates, resulting in increased gold leaching.

4.3.2. Sodium cyanide

Fig. 9a–d shows the %Au leached by two concentrations of sodium cyanide (0.5 and 2.0 g/l) as a function of the volume of lixiviant passed through the CM. Leaching was performed at three flow rates (0.5, 0.06, and 0.008 ml/min) on four CMs from autoclaved ores with varying %PR values.

Sodium cyanide concentration in the lixiviant did not affect the total %Au leached from the CM, but it did affect the kinetics of gold dissolution. Less gold was solubilized in the first few aliquots at a given flow rate for the lower cyanide concentration (0.5 g/l NaCN) than for the higher concentration (2.0 g/l NaCN), presumably due to the lower driving force for solubilization or prevention of gold cyanide complex adsorption of the lower cyanide concentration. No gold was present in the first few aliquots of leachate after leaching CMs from the most preg-robbing ores with 0.5 g/l sodium cyanide (Fig. 9c–d), presumably because all of the gold initially solubi-

lized by sodium cyanide was adsorbed by the carbon present in the CM.

As was seen in the ammoniacal thiosulfate system, the relative similarity of the cyanide leaching curves at all flow rates suggest that leaching was limited primarily by the volume of lixiviant passing the CM. For CM from the non preg-robbing ore, sodium cyanide leaching at the slower two flow rates (0.07 and 0.008 ml/min) solubilized over 95% of the gold initially present, whereas sodium cyanide leaching at the fastest flow rate solubilized only 85% of the initial gold present. Since gold-cyanide complex was not taken up by the non preg-robbing CM, it is possible that the lower gold solubilization at the faster flow rate is due to a kinetic limitation on the dissolution of gold. The relatively high uptake of gold by CMs from preg-robbing ores obscured any kinetic limitation on the gold dissolution that may have been present in these CMs. In CMs from high preg robbing ores, less lixiviant volume was needed to achieve equilibrium gold dissolution at the fastest flow rate that at two slower flow rates. The kinetic advantage of leaching at the faster flow rate may due to a kinetic limitation on adsorption of aurocyanide complex by the carbon. Studies are currently being
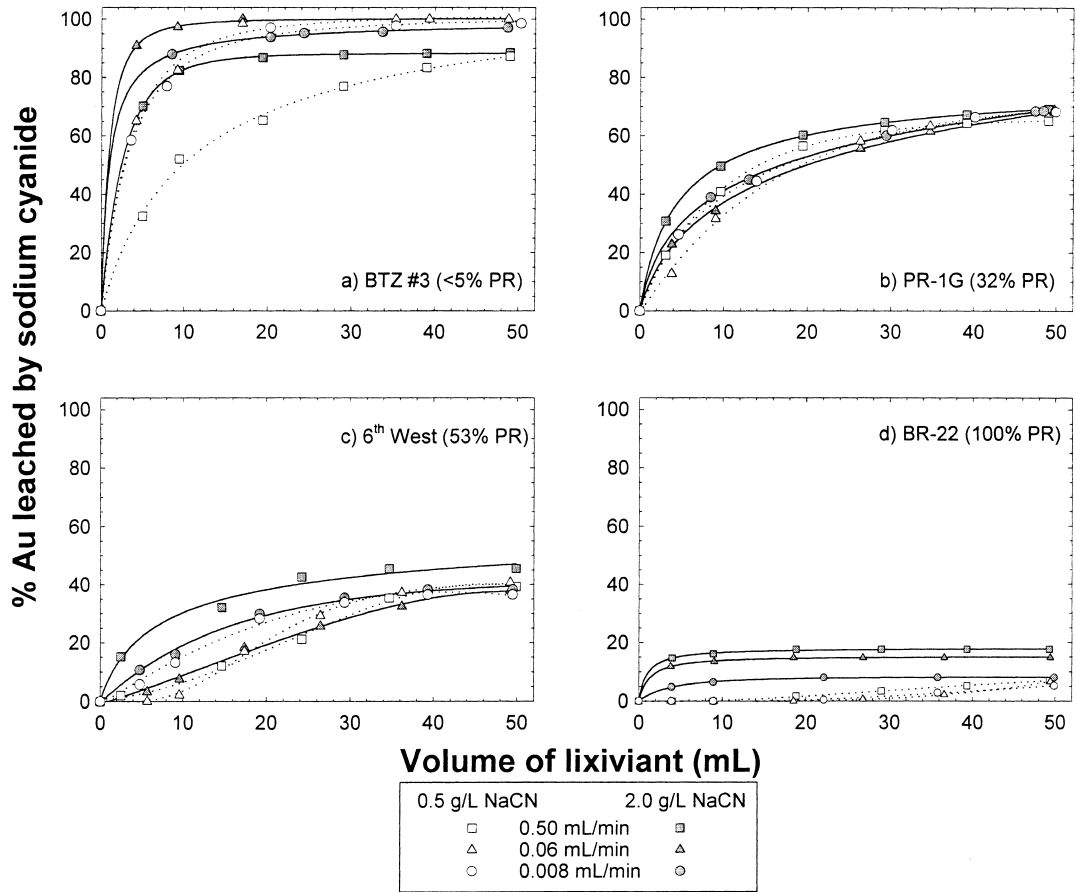
Fig. 9. The percentage of gold leached by 0.5 and 2.0 g/l NaCN per total volume of lixiviant used. Leaching was done at flow rates of 0.5, 0.06, and 0.008 ml/min on four CMs (a–d), which were demineralized from ores of increasing %PR.

performed to determine the effect of flow rate on aurocyanide adsorption by the CM.

Fig. 10 shows a direct relationship between %PR of the ore and the average volume needed to achieve 90% of the equilibrium leaching value. As the preg robbing behavior of the ore increased, not only did the equilibrium value of %Au leached decrease, but the time $(ml/ml\ min^{-1})$ required to reach equilibrium at any given flow rate also increased; hence, the preg-robbing behavior of the ore affects both the equilibrium leaching value and the leaching kinetics.

Fig. 6 shows nearly a 1:1 correlation between the preg-robbing behavior of the ore (%PR) and the retention of gold by the CM after leaching (100%–%Au leached). Both tests quantified the adsorption of aurocyanide complex by the naturally occurring

organic carbon, and it was expected that as %PR increased, the mass of gold retained by the CM would also increase However, since experimental conditions such as carbon to solution ratio, column vs. batch, addition of gold in solution, initial gold content, and autoclaving, differed between %PR tests performed by BGMI and the leaching experiments done in this study, a 1:1 correlation was not expected. The correlation can be explained as being due to the fact that regardless of the particular conditions of the experiment, nonpreg-robbing carbon does not take up aurocyanide complexes, whereas strongly preg-robbing carbons adsorb aurocyanide complex under most conditions. Only moderately preg-robbing carbons might be expected to show sensitivity to variations in experimental conditions,
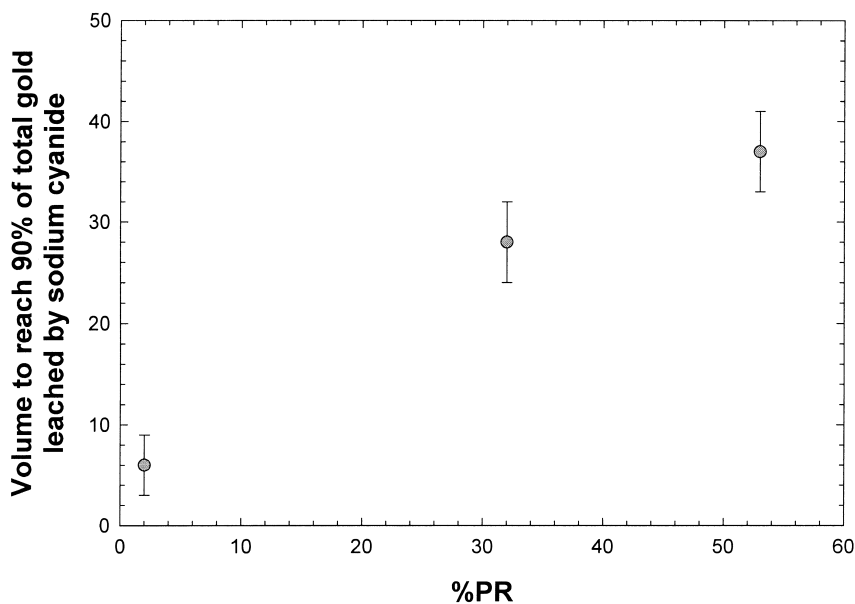
Fig. 10. The average volume of sodium cyanide lixiviant needed to obtain 90% of the equilibrium value of gold leached from the four CMs studied.

as shown by the variation in the correlation for sample PR-1G (32% PR).

Although the results from the %PR test correlate well to the gold retained during leaching by the CMs studied (Fig. 6), the fact that any gold was leached from the CM has implications for the %PR test. Depending on the kinetics of gold dissolution from the ore, the amenable gold originally in the ore may increase the mass of gold present in the solution by as much as 20 μg in the %PR test performed by BGMI. Since the value for %PR is determined by the change in solution gold concentration, ignoring the possible solubilization of the gold initially present in the ore may result in understanding the actual uptake of gold as much as 30%. Underestimation of %PR could be a partial explanation for the contradictory results of both low %PR and low %REC seen in some of the ores tested by BGMI.

5. Conclusions

Autoclaving low preg-robbing Goldstrike ore did not alter the XPS and FT-IR spectra of the associated CM, but CMs from autoclaved preg-robbing Gold-

strike ores showed increased oxidation of the carbon, most likely due to the formation of carboxylate functionality. Demineralization of Goldstrike ore concentrated the carbon and the gold without apparent chemical change to the carbon.

Ammoniacal thiosulfate leaching solubilized between 90% and 100% of the gold initially present in CMs from autoclaved Goldstrike ores. The concentration of gold remaining on the CMs following ammoniacal thiosulfate on leaching was relatively consistent despite variations in the preg-robbing behavior of the parent ore. Since gold retention by the CM during ammoniacal thiosulfate leaching did not depend on the preg-robbing behavior of the parent ore, the mechanism responsible for gold retention by the CM during ammoniacal thiosulfate leaching is not the same mechanism that controls the preg-robbing behavior of the parent ore. The kinetics of ammoniacal thiosulfate gold leaching depended primarily on the volume of lixiviant that had contacted the CM; however, a slight kinetic advantage was observed for leaching with slower flow rates.

The concentration of gold remaining with the CMs after sodium cyanide leaching was directly related to the %PR of the parent ore, suggesting that

the mechanism controlling gold retention on the carbon during cyanide leaching also controls preg-robbing. Although the concentration of sodium cyanide did not affect the total %Au leached from the CM, less gold was solubilized initially at the lower cyanide concentration relative to the higher sodium cyanide concentration. As was seen in the ammoniacal thiosulfate system, the kinetics of sodium cyanide leaching was also primarily limited by the volume of lixiviant passing the CM. However, kinetic limitations in gold dissolution and uptake by carbon were indicated at higher flow rates.

The limited uptake of gold by the naturally occurring organic carbon during ammoniacal thiosulfate leaching indicates similarity to commercial activated carbon. Additional physical similarities between the naturally occurring carbon in Goldstrike ore and commercial activated carbon suggest that gold retention by the carbon during cyanide leaching is controlled by the same mechanisms that control the adsorption of aurocyanide complex by commercial activated carbon.

Acknowledgements

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