Accepted Manuscript

A mechanism and thermodynamic model for the interaction of silicate minerals with lead-assisted gold electro-oxidation in a dilute cyanide medium

Rina Kim, Ahmad Ghahreman

PII: S0013-4686(19)31419-7

DOI: <https://doi.org/10.1016/j.electacta.2019.134574>

Article Number: 134574

Reference: EA 134574

To appear in: *Electrochimica Acta*

Received Date: 22 March 2019

Revised Date: 23 June 2019

Accepted Date: 21 July 2019

Please cite this article as: R. Kim, A. Ghahreman, A mechanism and thermodynamic model for the interaction of silicate minerals with lead-assisted gold electro-oxidation in a dilute cyanide medium, *Electrochimica Acta* (2019), doi: <https://doi.org/10.1016/j.electacta.2019.134574>.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A mechanism and thermodynamic model for the interaction of silicate minerals with lead-assisted gold electro-oxidation in a dilute cyanide medium

Rina Kim[†], Ahmad Ghahreman[‡]

Robert M. Buchan Department of Mining, Queen's University
25 Union Street West, Kingston, Ontario, Canada, K7L 3N6

Abstract

Gold (Au) oxidation kinetics in cyanide (CN) solutions can be increased by the addition of low concentrations of aqueous lead [Pb(II)]. However, the Pb(II) addition is not always effective in improving Au oxidation kinetics. The present study provides a mechanistic and thermodynamic view of the Pb-assisted Au oxidation process in the presence of silicate minerals and presents evidence that Pb adsorption onto the silicate minerals plays a substantial role in the oxidation kinetics. $\text{AuCN}_{(\text{ads})}$ film formation on the Au surface, in an Au-CN-H₂O system at a low overpotential range of linear sweep voltammetry (LSV), was confirmed through both electrochemical study and XPS analysis. Once Pb(II) was added into the system, $\text{AuCN}_{(\text{ads})}$ film formation was hindered, and the Au oxidation kinetics were significantly enhanced. However, the improving effect of Pb(II) on the Au oxidation process was reduced with the addition of quartz, due to Pb adsorption onto the quartz surface. As demonstrated through UV/Vis analysis and thermodynamic modeling, the cationic and neutral species, PbOH^+ , PbCN^+ and $\text{PbO}_{(\text{a})}$, were likely adsorbed onto the quartz surface. At lower CN concentration, the effect of quartz in reducing the Pb-assisted Au oxidation kinetics was more severe, and the Au oxidation was chemically controlled.

Keywords: Gold, Cyanide, Pb deposition, Adsorption, Quartz surface

[†] Corresponding author: Rina Kim (rk75@queensu.ca)

[‡] Corresponding author: Ahmad Ghahreman (ahmad.g@queensu.ca)

1. Introduction

Gold (Au) has a very high oxidation potential, as shown in Table 1, it can be oxidized to Au^+ or Au^{3+} ($E^\circ = +1.700$ and $+1.494$ V, respectively), and often occurs in nature as metallic Au or alloys of Au with silver (Ag) or other elements. Often gold is oxidized to a soluble form for gold extraction. Despite being a noble metal, Au can be oxidized rather easily when complexed with specific ligands such as cyanide (CN^-), chloride (Cl^-), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), and thiourea (NH_2CSNH_2). As shown in Table 1, the ligands considerably decrease the Au oxidation potential, and among them, CN is the most potent ligand, with a reduction potential of only -0.616 V $\text{Au}(\text{CN})_2^-/\text{Au}$.

Table 1. Various Au oxidation half reactions and the corresponding half-cell reduction potentials at 25°C (a: HSC Chemistry 5.1, 2002 [1], b: Marsden and House, 2006 [2])

Half reaction	Half-cell reduction potential, E° (V)
$\text{Au}^+ + \text{e}^- = \text{Au}$	$+1.700^{\text{a}}$
$\text{Au}^{3+} + 3\text{e}^- = \text{Au}$	$+1.494^{\text{a}}$
$\text{Au}(\text{CN})_2^- + \text{e}^- = \text{Au} + 2\text{CN}^-$	-0.616^{a}
$\text{AuCl}_2^- + \text{e}^- = \text{Au} + 2\text{Cl}^-$	$+1.127^{\text{a}}$
$\text{AuCl}_4^- + 3\text{e}^- = \text{Au} + 4\text{Cl}^-$	$+0.994^{\text{b}}$
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-} + \text{e}^- = \text{Au} + 2\text{S}_2\text{O}_3^{2-}$	$+0.153^{\text{b}}$
$\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+ + \text{e}^- = \text{Au} + 2\text{CS}(\text{NH}_2)_2$	-0.380^{b}

In previous electrochemical studies of Au oxidation in CN solutions, researchers have identified three significant oxidation peaks. The peaks follow a 3-step reaction scheme, represented as Eqs. 1-3, and each peak is believed to have a different rate-limiting step [3-8]. For the first and second peaks, at a lower overpotential region, the rate-limiting step is step 2 (i.e. Eq. 2), and for the rate-limiting step of the third peak at the most anodic potential is step 3 (Eq. 3). However, the reaction is more complicated in the third peak region because of Au

oxidation to Au^{3+} [5]. Although the first and second peaks have the same rate-limiting step, the current density, i.e. the reaction kinetics of the two peaks are quite different. Often the second peak has a higher current density, while the first peak has a very low current density [9-13]. The slow oxidation kinetics of the first peak is believed to be due to the formation of $\text{AuCN}_{(\text{ads})}$ passive film.

The passivating effect of the $\text{AuCN}_{(\text{ads})}$ film can be prohibited by the addition of some divalent ions, such as lead (Pb) or mercury (Hg) [9, 10, 14-16]. Soluble thallium (Tl) and bismuth (Bi) species have also shown similar improving effects on Au oxidation kinetics by prohibiting the $\text{AuCN}_{(\text{ads})}$ film formation [2, 17, 18]. The reaction is believed to be a cementation reaction, where the divalent metals are more noble than Au in the CN solutions. Therefore, Au is oxidized, and the divalent metal cations are reduced through cementation reactions. Pb, perhaps, is the most famous metal that has been used in the Au extraction industry to accelerate Au leaching kinetics via the cementation reaction, as shown in Eq. 4 [9]. The cementation reaction of Pb(II) with Au has been shown to enhance the Au oxidation peak. Jeffrey and Ritchie (2000a) [9] have shown that the first oxidation peak current density, at the most cathodic potential, is close to 0 mA/cm^2 during Au oxidation in CN solutions, with up to 20 mM CN, but the current density was increased to approximately 3.5 mA/cm^2 when only 1 ppm Pb(II) was added to the CN solution. Tshilombo and Sandenbergh (2001) [14] also presented a similar result, reporting a current density of about 7.0 mA/cm^2 for the first peak in a solution with 2500 mg/L NaCN ($\approx 50 \text{ mM}$ CN) and 1 ppm Pb(II) addition.

Recently, an Au-based sensor was developed for trace Pb detection, using the sensitivity of Au to Pb and their electrochemical interactions. Laschi et al. (2006) [19] studied the application of an Au-based screen-printed sensor to detect a trace amount of Pb (0.5 µg/L). Hung et al. (2010) and Xiahou et al. (2018) [20, 21] developed the colorimetric detection of Pb²⁺ (45 nM detection limit) by using Au nanoparticles (Au NPs) and alkanethiols; the deposited Pb on an Au NP surface activated the alkanethiol-induced aggregation of Au NPs. Xie et al. (2014) [22] also introduced a similar concept to detect Pb²⁺ (30 nM detection limit) as they used quartz crystal microbalance (QCM) coated with alkanethiols and Au NPs.

Nevertheless, Pb is not always practical for the improvement of Au oxidation kinetics. For example, the effect of Pb is lessened at low CN concentration, high pH, and high dissolved oxygen (DO) concentration [9, 13, 23]. Additionally, Pb adsorbs onto the surface of certain minerals, e.g. ferrihydrite, iron and aluminum oxyhydroxides, quartz, fly ash, and geopolymer [15, 24-28], tentatively making Pb ineffective for Pb-assisted oxidative dissolution of Au. To increase the effect of Pb on gold oxidation, often an excessive amount of Pb is used in real operations [29-34], which is not ideal from the environmental perspective. The addition of excess Pb is essential when the ore is mostly made up of silicate minerals because the silicate minerals highly contribute to the Pb adsorption.

Nonetheless, very few studies have been carried out on the interaction of Pb and silicate minerals, particularly because silicates have very low affinity to consume the gold extraction reagents such as cyanide, thus from the economic viewpoint making its study less critical for the gold extraction industry. However, the fact that silicate minerals increase Pb consumption in gold extraction adds to environmental concerns. A reasonable control over Pb and CN consumption is crucial in the gold industry because both Pb and CN are highly toxic and harm human health and ecosystem [35, 36].

Thus, in this study, the mechanism of the Pb effect on Au oxidation in CN solutions was

studied, concentrating on the interaction between silicate mineral, i.e. quartz, and Pb(II) ions. Under several different free CN and Pb(II) concentrations, the kinetics of the Au oxidation was observed, utilizing electrochemical test methods such as open circuit potential (OCP) measurement, linear sweep voltammetry (LSV), cyclic voltammetry (CV) and chronoamperometry. In the authors' knowledge, this is the first time that the effect of Pb(II) on Au oxidation in the presence of quartz has been studied. The study provides a mechanistic view of the Pb-assisted Au oxidation in the presence/absence of silicates, including electrochemistry, surface observation, adsorption studies, and thermodynamic modeling.

2. Materials and methods

2.1. Materials

The CN solution was prepared by dissolving sodium cyanide (NaCN, Fisher Scientific) in a sodium hydroxide (NaOH, Fisher Scientific) solution. All solutions were made from deionized (DI) water (resistivity 18.2 M Ω -cm). CN concentrations were adjusted at 300, 600, and 900 mg/L. Before testing, CN concentration was measured using a titrator (916 Ti-Touch, Metrhom), and a silver nitrate solution (0.0192 M AgNO₃, Ricca Chemical Company) was used as a titrant. Then, the lead nitrate salt [Pb(NO₃)₂, Fisher Scientific] was added into the CN solutions. As a silicate mineral, quartz powder (100% quartz, VWR), the particle size of less than 75 μ m, at a predetermined dosage was added to the CN solution to prepare a solid-liquid slurry with 50 g solids/L. The slurry pH was then regulated at 10.50 ($\pm$ 1%) using a NaOH solution. Compressed air was injected into the slurry at a flow rate of 1.38 L_{gas}/min/L_{slurry}, to maintain the DO concentration of the test solutions at 8.3 mg/L.

2.2. Test procedure

The electrochemical tests were conducted in a three-electrode cell. A 99.9986% pure Au

rod (VWR) with 3 mm diameter (surface area 0.07 cm^2) was used as a working electrode. The Au electrode was attached to copper wire and covered by epoxy resin (LECO). One side of the Au rod was polished and exposed to the test solution or the test slurry. The working electrode was immersed in the solution or slurry as a stationary electrode. The solution or slurry was magnetically stirred at 150 rpm, minimizing the vortex occurrence and ore particle settlement. After each test, the surface of the Au rod was polished using alumina and silicon carbide paper with a grit size of 1200 to 2400 to regenerate a fresh surface for the next test. A graphite rod was used as a counter electrode, and a glass-body Ag/AgCl/KCl electrode saturated with AgCl (0.199 V vs. SHE at 25°C) was used as a reference electrode. All potentials reported in this study were measured with respect to the reference electrode. A series of electrochemical tests were conducted using a Gamry Reference 600+ potentiostat at $21 \pm 1^\circ\text{C}$ under air injection. OCP was measured for an hour before the kinetics or polarization tests.

To investigate the kinetics of the Au electrodisolution in the CN solution or slurry, LSV and CV methods were mainly utilized. The tests were conducted in the potential range of -0.8 to $+1.0 \text{ V}$, and the sweep rate was 10 mV/s (which was found to be the most stable scan rate). Each CV test was run in three cycles to establish the changes in the working electrode surface. The chronoamperometry tests were conducted at several selected potentials, and $i-t$ curves were developed. While running the chronoamperometry tests, the solution samples were taken to measure Au and Pb concentrations. The elemental concentrations were measured by the atomic absorption spectrometer (iCE 3300 AAS, Thermo Fisher Scientific).

In the tests to study Pb adsorption onto the quartz surface, 5 mg/L Pb(II) was added to the solutions with different concentrations of CN or 50 g/L of quartz slurry, and Pb concentration was measured at 1, 3, 5, 10, 20, 30, 40, 50 and 60 min. The qualitative analysis of the different Pb species in the presence/absence of quartz and CN were done by UV/Vis

measurements (Thermo Scientific Genesys 10S UV/Vis), and the results were interpreted, combined with thermodynamic modeling of Pb speciation.

2.3. X-ray photoelectron spectroscopy analysis

To observe the surface species of the Au electrode, X-ray photoelectron spectroscopy (XPS) analysis was conducted. After a 3 h long chronoamperometry test, the Au electrode was rinsed with DI water, and sealed in a vacuum plastic sample bag until the XPS analysis was carried out. The XPS spectra were measured on a Kratos Nova AXIS spectrometer equipped with an Al X-ray source. The samples were mounted onto the coated aluminum platen using double-sided adhesive Cu tape. The samples were kept under high vacuum (10^{-9} Torr) overnight inside the preparation chamber before they were transferred into the analysis chamber (ultrahigh vacuum, 10^{-10} Torr) of the spectrometer. The XPS data were collected using Al K α radiation at 1486.69 eV (150 W, 15 kV), a charge neutralizer, and a delay-line detector (DLD) consisting of three multi-channel plates. Binding energies were referred to the C 1s peak at 285 eV. Survey spectra were recorded from -5 to 1200 eV at a pass energy of 160 eV (number of sweeps: 2), using an energy step size of 1 eV and a dwell time of 200 ms. High-resolution spectra were recorded in the appropriate regions at a pass energy of 20 eV, using a dwell time of 300 ms and an energy step size of 0.1 eV. The analyzed area on the specimens was about $300 \times 700 \mu\text{m}^2$ (lens mode: FOV 1) at this position. The incident angle (X-ray source/sample) was the magic angle of 54.74° , and the take-off angle (sample/detector) was 90° .

3. Results and discussion

3.1. Effect of lead salt without solid addition

Electrochemical tests were carried out at various CN concentrations to study the effect of

Pb(II) addition on Au oxidation kinetics. As illustrated in Figure 1(a), in the absence of Pb(II), a weak peak was identified between -0.3 and -0.1 V with a current density of less than 0.1 mA/cm^2 at 300, 600 and 900 mg/L CN. It is worth noting that the second peak was not observed, or weakly developed, at the lower CN concentrations of 300 and 600 mg/L CN. At 900 mg/L CN, the second and third peaks formed at approximately 0.23 and 0.55 V, respectively, and were more evident and pronounced than those at the lower CN concentrations.

The addition of 5 mg/L Pb(II), as shown in Figure 1(b), changed the trend of the LSV scans and noticeably improved the Au oxidation rate. As shown in Figure 1(b), the first current peak was much sharper with a higher current density at -0.35 V compared to that in the absence of Pb(II), and it became more pronounced with increasing the CN concentration from 300 to 900 mg/L. The increase in Au oxidation kinetics is connected to the cementation reaction between the aqueous Pb(II) species and the metallic Au, as shown in Eq. 4.

In Figure 1(b), a high first peak was observed regardless of the CN concentration level, but the shape of the first peak was different depending on the CN concentration. The current density was almost constant between -0.8 and -0.7 V when CN was 900 mg/L, but it sharply increased starting from -0.8 V when CN concentration was 300 and 600 mg/L CN. The reason for this difference can be explained via the OCP measurement results shown in Figure 2. The OCP measurement demonstrated a general trend at 300 and 600 mg/L CN, where it had slightly increased at the early stages of the measurement and then reached a plateau within an hour, at around -0.27 and -0.30 V, respectively. In contrast, at 900 mg/L CN, a sudden potential drop at 200 seconds was registered from -0.34 V to -0.77 V, and the potential eventually reached a plateau at -0.65 V, a significantly lower OCP value than the OCP readings of the tests with 300 and 600 mg/L CN. It should be noted that during the cementation reaction between Au and Pb(II), not only the Au oxidation but also the metallic

Pb precipitation occurred on the surface of the Au electrode, resulting in the potential drop. Thus, during the OCP measurement in a solution with 900 mg/L CN, the cementation reaction took place spontaneously, forming a layer of Pb on the working electrode surface and causing the significant potential drop.

Then, during the following LSV scan, when the potential was lower than the OCP, the Au oxidation reaction did not occur because the Pb layer on the Au, which had formed during the OCP measurement, is a very stable layer in this potential region. Once the anodic overpotential was applied to the electrode, the Au oxidation could occur, i.e. potential higher than OCP is needed to activate the Au oxidation process. In contrast, at 300 and 600 mg/L CN, the spontaneous cementation reaction could not proceed, thus no or insignificant Pb deposition had formed on the Au surface ahead of the LSV scan. Therefore, the Au oxidation by Eq. 4 could take place only if the potential had decreased to a region at which the Au oxidation and Pb deposition reactions were spontaneous. It was noted that when the potential was adjusted to a lower value, between -0.8 V and -0.3 V, Pb could play a significant role in accelerating the Au oxidation kinetics regardless of CN concentrations.

Several chronoamperometry tests were conducted to study the effect of Pb on Au oxidation kinetics in CN solutions. After measuring OCP, the Au electrode was polarized for 3 h at two different potentials of -0.35 or -0.4 V, in the presence and absence of Pb(II) in 900 mg/L CN solutions. In the absence of Pb(II), at -0.35 V, the current density linearly increased from 0 to 4000 s and then reached a maximum value of 0.60 mA/cm^2 , meaning that the Au oxidation kinetics had gradually increased in this period [Figure 3(a)]. After 4000 s, the current density reached a plateau, and then slightly decreased, perhaps suggesting that the Au surface had become slightly passivated at this point. Figure 4(a) shows the light-brown tarnished Au surface after the test. Through the analysis of the surface via the XPS method for C 1s and N 1s it was confirmed that the layer was AuCN, as shown in Figures 5(a) and 6(a) [37, 38]. The

exact binding energy values are shown in Table 2. At -0.40 V, on the other hand, without the Pb(II) addition, Au oxidation did not occur, as shown in Figure 3(a).

The introduction of 5 mg/L Pb(II) to the CN solution made a considerable difference, as shown in Figure 3(b); no significant current density was observed at -0.35 V. This result is consistent with the results of the LSV scan that the current density was dropped to 0 as soon as the potential had passed -0.35 V. It can be noted that -0.35 V is a 'boundary potential' that divides Au oxidation and passivation region in the presence of Pb. Figure 7 shows the evidence that the dissolved Au concentration, during the corresponding 3 h chronoamperometry test in Figure 3(b), was not significant only in the range of 6 - 11 mg/L at -0.35 V. Additionally, in Figure 8, the Eh-pH diagram of a Pb-H₂O system shows the possibility of Pb oxidation to Pb hydroxide or Pb oxide at this potential. Only the oxidation of the deposited Pb can occur at this condition, and the oxidized Pb cannot act as an activator for the Au oxidation process. In the author's previous study [13], XPS results showed that oxidized Pb passivated the Au surface and interfered with the oxidative dissolution of Au. The schematic picture in Figure 7 describes the retardation of Au dissolution caused by oxidized Pb film on the Au surface.

At -0.40 V, however, the current density was significantly improved to 4 - 6 mA/cm². The continuous reaction between the Pb and Au caused fluctuations in the current density. Figure 4(b) shows the etched Au surface after the corresponding chronoamperometry test in the presence of 5 mg/L Pb(II) and reflects significant Au oxidation kinetics. No AuCN passive film could be detected in the XPS analysis of the sample, as shown in Figures 5(b) and 6(b); the N 1s curve was too broad to correspond to a specific chemical species. The Au dissolution continuously occurred during the chronoamperometry test, and the Au concentration increased from 5.4 to 148.8 mg/L in 3 h (Figure 7).

Table 2. C 1s and N 1s binding energies from XPS peaks in Figures 5 and 6

Compound		Binding energy (eV)	
		0 mg/L Pb(II) at -0.35 V	5 mg/L Pb(II) at -0.40 V
C 1s	CO ₃ ²⁻	288.88	288.7
	C=O	287.78	287.19
	C-O	286.76	285.99
	C-N	285.72	N/A
	C-C	285	285
N 1s	CN	400.53	N/A

The Au concentration in the test solutions was measured after the chronoamperometry experiments (presented in Figure 9) to study the oxidative Au dissolution kinetics. The dissolved Au concentration in the 5 mg/L Pb(II)-containing solution, after the Au electrode oxidation at -0.40 V, was 148.8 mg/L (measured by AAS). Applying Faraday's equation, as shown in Eq. 5, and assuming 100% current efficiency, the dissolved Au concentration in the solution should be equal to 139.3 mg/L Au, which is consistent with the actual AAS measurement. On the other hand, only 7.7 mg/L of Au was detected in the solution without the Pb(II) addition at -0.40 V (Figure 9).

$$m = \frac{iAt}{nF} M \quad (5)$$

At -0.35 V, the dissolved Au concentration was dropped to 10.7 mg/L in the Pb(II)-containing solution, confirming that the potential of -0.35 V is, in fact, a boundary potential and Au was passivated by the oxidized Pb. Without Pb(II), at -0.35 V, 20.3 mg/L of Au was dissolved, but it was still far less than the concentration in the presence of Pb salt at -0.40 V.

3.2. Effect of lead addition in the presence of quartz mineral

3.2.1. Electrochemical test results

The effect of Pb(II) on Au oxidation kinetics is substantially different in the presence of silicate minerals. Quartz was used as a representative silicate mineral in this study. Generally, silicate minerals are not reactive in CN solutions, though the minerals can indirectly influence the Au oxidation process. Figure 10 shows the LSV scans of Au electrode oxidation at three different CN concentrations, in the presence of 5 mg/L Pb(II) with 50 g/L quartz, which is considerably different from the results of Figure 1(b), i.e. similar tests but without quartz. In the graphs of Figure 10, the Au oxidation peaks at -0.35 V are significantly depressed at 300 and 600 mg/L CN, despite the presence of Pb(II); this was because of the Pb adsorption onto the quartz surface, and consequently the lack of availability of Pb(II) ions in the solution to form an appreciable first peak by Eq. 4. Several tests to confirm the Pb adsorption onto the quartz surface were done, and the results will be discussed in section 3.2.2.

In the experiments of Figure 10, only 0.2 mg/L or less aqueous Pb(II), out of the 5 mg/L Pb(II) added, was left in the test solutions in the presence of quartz, and the balance of the Pb was adsorbed onto the quartz particles (section 3.2.2). To quantify the effect of only 0.2 mg/L Pb(II) on the Au oxidation kinetics, a set of LSV tests were conducted adding 0.2 mg/L Pb(II), but without quartz addition, at 300, 600 and 900 mg/L CN. The purpose of these tests was to clarify, if i) low concentrations of aqueous Pb(II) affect Au oxidation kinetics, or ii) quartz particles physically hinder Au oxidation, i.e. block the Au surface. With the former, one would expect an insignificant Au oxidation peak. As shown in Figure 11, with 0.2 mg/L Pb(II) the first peak was only clearly observed when the CN concentration was 900 mg/L CN, but the peak was not clear or only slightly developed at low CN concentrations of 300 and 600 mg/L CN. This confirms that the main reason for the depressed first peak is, in fact, the low

aqueous Pb species concentration, caused by its adsorption onto the quartz.

Additionally, from this result, it can be concluded that the rate-limiting factor of Eq. 4 is dependent on the reaction conditions, specifically CN concentration. When the CN concentration was low, i.e. 300 and 600 mg/L CN in this study, the concentration of aqueous Pb species was an essential factor to determine the Au oxidation reaction rate. The Au oxidation peak at -0.35 V was observed with 5 mg/L Pb(II) addition, but it was not observed when the Pb(II) concentration was 0.2 mg/L at 300 and 600 mg/L CN. On the other hand, at low Pb(II) concentration, the CN concentration was the rate-limiting factor, and at high enough CN concentration, 900 mg/L CN in this study, the Au oxidation kinetics were high, as shown in Figure 11.

To further clarify the Au oxidation behavior at lower CN concentrations, 300 and 600 mg/L, an LSV scan was conducted at different scan rates of 1, 5 and 10 mV/s in the presence of 5 mg/L Pb(II) and 50 g/L quartz. Generally, the peak current density is proportional to the square root of the scan rate ($i \propto \sqrt{v}$), but this was not the case in this study. As shown in Figure 12, the oxidation peak at -0.35 V decreased when the scan rate was increased from 1 to 10 mV/s, which implies that the Au oxidation process at low CN and Pb(II) concentrations obeyed CE mechanism, which represents chemical reaction (C) and electron transfer at the electrode surface (E), respectively.

From the schematic picture shown in Figure 13, the reaction between the solid Au surface and the liquid interface can be divided into three different steps i) the diffusion of reactants (CN and Pb(II) species in this study) from the bulk of the solution to the Au surface via the diffusion layer, ii) the chemical reaction between the reactants and the solid Au surface, and iii) the diffusion of the soluble reactions product (Au(CN)_2^- in this study) towards the bulk of the solution through the diffusion layer. The three steps of the reaction are in series; thus, one of the three steps, i.e. the slowest step, determines the overall reaction rate. From the LSV

test results shown in Figure 12, it appears that the chemical reaction between the Au surface and the reactants is the rate-limiting step of the Pb(II)-Au reaction system at low CN concentration. Generally, it is expected that the faster the scan rate, the thinner the diffusion layer, sometimes about several nanometers [39, 40]. In other words, if the reaction is diffusion controlled, the current density, consistent with reaction kinetics, should be improved with increasing the scan rate. However, in the present study, the current density was higher at lower scan rates, which means the chemical reaction of Eq. 4 takes a longer time to occur at low concentrations of reactants. The reaction kinetics were readily improved when more aqueous Pb(II) or CN was available in the system. Thus, it is fair to conclude that the reaction is chemically controlled at low CN concentration.

For comparison, a set of tests were carried out in a solution of 900 mg/L CN with 0.2 mg/L Pb(II) addition at 3 different scan rates of 1, 5 and 10 mV/s. As shown in Figure 14, the oxidation peak was improved with a higher scan rate. Thus, at high CN concentrations, the chemical reaction rate between Pb(II) and Au is fast, and the overall reaction rate is controlled by the diffusion of chemicals.

Figure 15 elucidates the effect of silicate minerals on Au oxidation kinetics in the presence of 5 mg/L Pb(II) at 900 mg/L CN. In the anodic direction of the CV scan in cycle 1, the trends of CV plots were approximately identical, regardless of the presence of quartz. However, the CV curves were different in the cathodic direction scan. In the absence of quartz, the high Au oxidation peak at -0.35 V was observed, and the current density was more pronounced than in the anodic scan. Even during the subsequent cycles 2 and 3, the high first peak was continuously evolved. In the presence of quartz, on the other hand, the first peak was not observed during the cathodic scan, and it was significantly lessened in cycles 2 and 3, compared to that in cycle 1. Without quartz, aqueous Pb(II) concentration was high enough for the reaction to proceed, however in the presence of quartz the Pb adsorption

onto the quartz limited the concentration of the Pb(II) available in the solution. Thus, it can be noted that the current density of the first peak, i.e. the Au oxidation kinetics, is limited by the Pb(II) concentration.

In the second and third cycles of the CV test in Figure 15(b), the second oxidation peak at around 0.25 V was observed, which had higher peak current density in the succeeding cycles. This is also mainly caused by the difference of aqueous Pb(II) concentration; the deposited Pb on the gold surface could be oxidized according to the Eh-pH diagram of Figure 8. The oxidized Pb would not be available as a reactant for the cementation reaction during the next cathodic scan, thus in the next cycle, less Pb would be available in the system, and less Pb can deposit on the gold surface with the cementation reaction. As a result, eventually, the oxidation kinetics at 0.25 V would resemble the case where no Pb(II) was added to the solution, as shown in Figure 1(a). Similar behavior was also reported in the author's previous study [13].

3.2.2. Adsorption tests

To further understand the Pb adsorption process onto the quartz surface, the Pb(II) concentration was measured in a 5 mg/L Pb(II) solution for an hour in the presence and absence of 50 g/L quartz of slurry. In Figure 16, the Pb(II) concentration change by time shows two different trends depending on the presence or absence of quartz. In the absence of quartz, Figure 16(a), Pb(II) concentration was in the range of 3.5-4.5 mg/L. At higher CN concentration, Pb(II) concentration during the first 10 min was slightly higher than that at lower CN concentration, but with time the Pb(II) concentration ranged between 3.60 and 3.90 mg/L in different CN concentration solutions. Likely the decrease in the Pb(II) concentration is related to its adsorption to the walls of the glass reactor. Salim and Cooksey [41] have studied Pb adsorption onto the surfaces of several different types of containers, and have

reported that 85-94% of 10^{-6} M Pb(II) was adsorbed on glass, polyethylene and stainless steel surfaces in an hour.

In the current study, about 1.10 to 1.40 mg/L Pb(II) was adsorbed onto the glass container [Figure 14(a)], which corresponds to 5.31×10^{-6} to 6.76×10^{-6} M, and this was consistent with the previous studies. In the presence of quartz, however, the Pb(II) concentration significantly decreased from 5 to less than 0.3 mg/L, as shown in Figure 16(b). After the initial 10 min of the tests, the Pb(II) concentration was rather stable above 0.1 mg/L at 300 mg/L CN. On the other hand, at higher CN concentration, 600-900 mg/L CN, the steady state Pb(II) concentration was 0.15-0.20 mg/L between 10 to 50 min, and the final concentration was 0.10-0.13 mg/L. Because no precipitation was observed in the absence of quartz, it can be noted that the drop in Pb(II) concentration in the presence of quartz is caused by Pb adsorption onto the quartz surface. This is in agreement with the findings of previous studies [24, 25], which had reported the possibility of Pb adsorption onto quartz surfaces.

The different surface group of quartz likely causes the Pb adsorption onto its surface. The surface groups of quartz can be changed depending on the solution pH (Eq. 6); in neutral pH range the main surface group is SiOH, and it converts to SiOH_2^+ or SiO^- when SiOH reacts with H^+ or OH^- , respectively [24, 42]. In the solution of this study, at pH around 10.5, likely the main surface group was SiO^- , which can adsorb cations due to its negative charge. The dominant Pb species in the test solution, pH 10.5, is PbOH^+ , as shown in thermodynamic modeling results (Figure 17 and Table 3), and this charge difference between a quartz surface and an aqueous ion makes the physisorption possible (Eq. 7) [24]. If SiOH_2^+ is present on a quartz surface, the anion species, HPbO_2^- , can be physisorbed onto the surface as well. The reaction between SiOH and the Pb species is chemisorption, shown by Eq. 8 [42-44]. Based on the thermodynamic modeling, the proportion of PbOH^+ at pH 10.5 is approximately 57 mol%. Thus, it implies that not only had the physisorption of the cationic species happened in

the conditions of the current study experiments, but possible other forms of adsorption had also occurred, because 96-98% of Pb had adsorbed onto the quartz surface, according to test results shown in Figure 16(b).

Table 3. Reactions and the corresponding equilibrium constants for thermodynamic modeling shown in Figure 17

Reaction	K	Reference
$\text{Pb}^{2+} + \text{CN}^- = \text{PbCN}^+$	5.01×10^2	Senanayake, 2008 [45]
$\text{Pb}^{2+} + \text{OH}^- = \text{PbOH}^+$	6.67×10^7	HSC Chemistry [1]
$\text{Pb}^{2+} + 2\text{OH}^- = \text{PbO}_{(a)} + \text{H}_2\text{O}$	1.17×10^{11}	HSC Chemistry [1]
$\text{Pb}^{2+} + 3\text{OH}^- = \text{HPbO}_2^- + \text{H}_2\text{O}$	1.18×10^{14}	HSC Chemistry [1]

Nevertheless, the Pb adsorption onto the quartz was not completed and some Pb(II), 0.10-0.13 mg/L, was still left behind in the solution in the test of Figure 16(b). From the thermodynamic modeling and the UV/Vis measurements, the negatively charged Pb species seemed to contribute to this amount. As shown in the UV/Vis results of Figure 18, when no quartz was added to the solution, a peak at 253-254 nm and a broad shoulder between 260 and 300 nm were observed at the 10 min mark, regardless of the presence of CN. These peaks are related to Pb-OH species. The evidence for this claim is presented in the supplementary document. The baseline UV measurements (Figure S1) of Pb(II) in 0.0005 M NaOH solution showed a peak at 253 nm, where the peak absorbance was proportional to the Pb(II) concentration. No significant peak was observed when Pb(II) was dissolved in DI water. Thus, it can be confirmed that the peak at 253 nm is related to Pb-OH species. In the presence of

CN, two peaks related to Pb-CN species (probably PbCN^+) at 265 and 285 nm were also observed, starting from 30 min into the experiment (the full-time UV/Vis results are presented in the supplementary material), and the peak absorbance was lower in NaCN solution than in NaOH solution. Those peak locations were in agreement with those of a previous study [46].

When Pb(II) was added to a quartz slurry in CN solution with 50 g quartz/L, no clear UV/Vis peak was present, except the broad peak from 250 to 300 nm, which was identical to the shoulder peak observed in the Pb-only solutions. Additionally, the overall peak of absorbance was decreased considerably. These observations confirm that i) Pb indeed adsorbs onto the quartz mineral, and ii) specific Pb species do not adsorb onto the quartz surface. In brief, the UV/Vis peaks at 265 and 285 nm in the presence of CN are related to PbCN^+ , which can adsorb onto the quartz surface via a physisorption mechanism owing to its positive charge. Similarly, the peak at 253 nm shown in Figure 18(a) is related to cationic Pb species, PbOH^+ . Besides, it appeared that the neutral species, $\text{PbO}_{(a)}$, increased the overall peak absorbance. In the baseline results of 0.2 mg/L Pb(II) solution (Figure S1), only a weak peak at 253 nm was observed, and the overall absorbance was not that significant, a considerably different result than with 5 mg/L Pb(II) with 50 g quartz/L. The 0.2 mg/L Pb(II) solution corresponds to the “left-over Pb(II) concentration” after the adsorption of Pb progressed in the experiments. Thus, the peak at 253 nm represents PbOH^+ , and $\text{PbO}_{(a)}$ and HPbO_2^- is attributed to the overall absorbance improvement and broad peak between 250 and 300 nm, respectively. It is fair to conclude that PbOH^+ , PbCN^+ , and $\text{PbO}_{(a)}$ species were more likely adsorbed onto the quartz surface, and HPbO_2^- was dominant in the slurry, with limited or no adsorption onto the quartz.

4. Conclusions

In this work, a series of electrochemical tests were carried out to determine the effect of Pb and/or silicate mineral on Au oxidation kinetics. The experiments demonstrated that oxidative Au dissolution kinetics in CN solutions could be enhanced with the addition of Pb(II) in the low overpotential region of around -0.35 V vs. Ag/AgCl. The mechanism for the process is the cementation reaction between metallic Au and aqueous Pb species. It was shown that a 5 mg/L Pb(II) addition could markedly enhance the Au oxidation rate at the higher CN loading (900 mg/L), while it was dependent on the solution conditions at 300 and 600 mg/L CN. The presence of silicate minerals such as quartz deactivated the role of Pb(II) in the Au oxidation, which was due to the adsorption of Pb onto the quartz surface. The Pb adsorption readily occurred regardless of the CN concentration. From the UV/Vis analysis and thermodynamic modeling, PbOH^+ , PbCN^+ , and $\text{PbO}_{(\text{a})}$ species were likely adsorbed onto the quartz surface, and HPbO_2^- was dominant in the slurry, with limited or no adsorption onto the quartz. The lower aqueous Pb(II) concentration resulting from the adsorption process depressed the effect of the added Pb(II) on the Au oxidation kinetics, specifically at 300 and 600 mg/L CN. The cementation reaction between Au and Pb(II) was shown to be a chemically controlled process at lower CN concentration, but it was under diffusion control at higher CN concentrations.

Acknowledgments

The authors would like to thank MITACS (Ref. IT07117) and Air Liquide for their financial support of this study.

Supplementary Material

Baseline UV/Vis measurements of Pb-OH species at different Pb(II) concentrations and fulltime UV/Vis measurements of Pb(II) in 0.0005 M NaOH or 900 mg/L NaCN solution.

References

1. HSC Chemistry 5.1 (2002). Chemical reaction and equilibrium software with extensive thermochemical database. Outokumpu Research Oy, Pori, Finland.
2. Marsden, J.O. and House, C.I. (2006). *The Chemistry of Gold Extraction* (2nd ed.). Englewood, CO, USA: SME.
3. Cathro, K.J. and Koch, D.F.A. (1964). The anodic dissolution of gold in cyanide solutions. *Journal of the Electrochemical Society*, 111(12), 1416–1420.
4. Mac Arthur, D.M. (1972). A study of gold reduction and oxidation in aqueous solutions, *Journal of the Electrochemical Society*, 119(6), 672-677.
5. Kirk, D.W., Foulkes, F.R., Graydon, W.F. (1978). A study of anodic dissolution of gold in aqueous alkaline cyanide. *Journal of the Electrochemical Society*, 125(9), 1436-1443.
6. Kirk, D.W., Foulkes, F.R., Graydon, W.F. (1979). Electron stoichiometry of anodic dissolution of gold in aqueous alkaline cyanide. *Journal of the Electrochemical Society*, 126(12), 2287-2288.
7. Kirk, D.W., Foulkes, F.R., Graydon, W.F. (1980). Gold passivation in aqueous alkaline cyanide. *Journal of the Electrochemical Society*, 127(9), 1962-1969.
8. Kirk, D.W. and Foulkes, F.R. (1980). Anodic dissolution of gold in aqueous alkaline cyanide solutions at low overpotentials. *Journal of the Electrochemical Society*, 127(9), 1993-1997.
9. Jeffrey, M.I. and Ritchie I.M. (2000a). The leaching of gold in cyanide solutions in the presence of impurities: I. The effect of lead. *Journal of the Electrochemical Society*, 147(9), 3257-3262.
10. Jeffrey, M.I. and Ritchie I.M. (2000b). The leaching of gold in cyanide solutions in the presence of impurities: II. The effect of silver. *Journal of the Electrochemical Society*, 147(9), 3272-3276.

11. Jeffrey, M.I. and Ritchie I.M. (2001). The leaching and electrochemistry of gold in high purity cyanide solutions. *Journal of the Electrochemical Society*, 148(4), D29-D36.
12. Bas, A.D., Safizadeh, F., Zhang, W., Ghali, E., Choi, Y. (2015). Active and passive behaviors of gold in cyanide solutions. *Transactions of Nonferrous Metals Society of China*, 25, 3442-3453.
13. Kim, R. and Ghahreman, A. (2019). The effect of ore mineralogy on the electrochemical gold dissolution behavior in various cyanide and oxygen concentrations; Effect of sulfidic ores containing heavy metals. *Hydrometallurgy*, 184, 75-87.
14. Tshilombo, A.F. and Sandenbergh, R.F. (2001). An electrochemical study of the effect of lead and sulphide ions on the dissolution rate of gold in alkaline cyanide solutions. *Hydrometallurgy*, 60, 55-67.
15. Kyle, J.H., Breuer, P.L., Bunney, K.G., Pleysier, R. (2012). Review of trace toxic elements (Pb, Cd, Hg, As, Sb, Bi, Se, Te) and their deportment in gold processing Part II: Deportment in gold ore processing by cyanidation. *Hydrometallurgy* 111-112, 10-21.
16. Nicol, M.J. (1980). The anodic behavior of gold: Part II – Oxidation in alkaline solutions. *Gold Bulletin*, 13(3), 105-111.
17. Guzman, L., Segarra, M., Chimenos, J.M., Cabot, P.L., Espiell, F. (1999). Electrochemistry of conventional gold cyanidation. *Electrochimica Acta*, 44, 2625–2632.
18. Sandenbergh, R.F. and Miller, J.D. (2001). Catalysis of the leaching of gold in cyanide solutions by lead, bismuth and thallium. *Minerals Engineering*, 14(11), 1379-1386.
19. Laschi, S., Palchetti, I., Mascini, M. (2006). Gold-based screen-printed sensor for detection of trace lead, *Sensors and Actuators B*, 114, 460-465.
20. Hung, Y., Hsiung, T., Chen, Y., Huang, Y., Huang, C. (2010). Colorimetric detection of heavy metal ions using labe-free gold nanoparticles and alkanethiols. *Journal of Physical Chemistry C*, 114(39), 16329-16334.

21. Xiahou, Y., Zhang, P., Wang, J., Huang, L., Xia, H. (2018). Simple synthesis of uniformly small gold nanoparticles for sensitivity enhancement in colorimetric detection of Pb^{2+} by improving nanoparticle reactivity and stability. *Journal of Materials Chemistry C*, 6, 637-645.
22. Xie, Y., Jin, Y., Huang, Y., Liu, G., Zhao, R. (2014). Highly selective piezoelectric sensor for lead(II) based on the lead-catalyzed release of gold nanoparticles from a self-assembled nanosurface. *Microchimica Acta*, 181, 1521-1527.
23. Dai, X. and Breuer, P.L. (2013). Leaching and electrochemistry of gold, silver and gold-silver alloys in cyanide solutions: Effect of oxidant and lead(II) ions. *Hydrometallurgy*, 133, 139-148.
24. Huang, P. and Fuerstenau, D.W. (2001). The effect of the adsorption of lead and cadmium ions on the interfacial behavior of quartz and talc. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 177, 147-156.
25. Reich, T.J., Das, S., Koretsky, C.M., Lund, T.J., Landry, C.J. (2010). Surface complexation modelling of Pb(II) adsorption on mixtures of hydrous ferric oxide, quartz and kaolinite. *Chemical Geology*, 275, 262-271.
26. Liu, Y. Yan, C., Zhang, Z., Wang, H., Zhou, S., Zhou, W. (2016). A comparative study on fly ash, geopolymers and faujasite block for Pb removal from aqueous solution. *Fuel*, 185, 181-189.
27. Novais, R., Buruberrri, L.H., Seabra, M.P., Labrincha, J.A. (2016). Novel porous fly-ash containing geopolymers monoliths for lead adsorption from wastewaters. *Journal of Hazardous Materials*, 318, 631-640.
28. Bao, S., Li, K., Ning, P., Peng, J., Jing, X., Tang, L. (2017). Highly effective removal of mercury and lead ions from wastewater by mercaptoamine-functionalised silica-coated magnetic nano-adsorbents: Behaviours and mechanisms. *Applied Surface Science*, 393,

457-466.

29. Kondos, P.D., Deschenes, G., Morrison, R.M. (1995). Process optimization studies in gold cyanidation. *Hydrometallurgy*, 39, 235-250.
30. Deschenes, G., Lacasse, S., Fulton, M. (2003b). Improvement of cyanidation practice at Goldcorp Red Lake Mine. *Minerals Engineering*, 16, 503-509.
31. Deschenes, G., Xia, C., Fulton, M., Cabri, L.J., Price, J. (2009a). Evaluation of leaching parameters for a refractory gold ore containing aurostibite and antimony minerals: Part I – Central zone. *Minerals Engineering*, 22, 799-808.
32. Deschenes, G., Xia, C., Fulton, M. (2009b). Determination of the leaching parameters for a refractory gold ore containing aurostibite and antimony minerals: Part II – AD Zone. *Minerals and Metallurgical Processing*, 26(2), 114-120.
33. Deschenes, G. and Fulton, M. (2013) Design of a leaching strategy to extract gold from Eleonore Mine ultra-fine sulfide concentrate. *Proceedings of World Gold Conference 2013*, Sep 26-29, Brisbane, QLD, Australia, 71-77.
34. Deschenes, G. (2015). Using synergy between cyanide, oxygen, and lead nitrate to improve extraction and reduce OPEX/CAPEX in the processing of sulphide-bearing gold ores. *Proceedings of World Gold Conference 2015*, Sep 29-Oct 1, Gauteng, South Africa, 263-272.
35. Lo, Y.C., Dooyema, C.A., Neri, A., Durant, J., Jefferies, T., Medina-Marino, A., de Ravello, L., Thoroughman, D., Davis, L., Dankoli, R.S., Samson, M.Y., Ibrahim, L.M., Okechukwu, O., Umar-Tsafe, N.T., Dama, A.H., Brown, M.J. (2012). Childhood lead poisoning associated with gold ore processing: a village level investigation – Zamfara state, Nigeria, October-November 2010. *Environmental Health Perspectives*, 120(10), 1450-1455.
36. Jaszczak, E., Polkowska, Ż., Narkowicz, S., Namieśnik, J. (2017). Cyanides in the

- environment – analysis – problems and challenges. *Environmental Science and Pollution Research International*, 24(19), 15929-15948.
37. Beamson, G. and Briggs, D. (1992). *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, New York, NY, USA: Wiley.
38. Moulder, J.F., Stickle, W.F., Sobol, P.E., Bomben, K.D. (1992). *Handbook of X-ray Photoelectron Spectroscopy (Ed. J. Chastain)*. Perkin-Elmer Corporation, USA.
39. Scholz, F. (Ed.) (2010). *Electroanalytical Methods: Guide to Experiments and Applications (2nd Ed.)*, Berlin, Heidelberg, German: Springer-Verlag.
40. Wang, J. (2006). *Analytical Electrochemistry (3rd ed.)*, Hoboken, NJ, USA: John Wiley & Sons, Inc.
41. Salim, R. and Cooksey, B.G. (1980). Adsorption of lead on container surfaces. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 106, 251-262.
42. Papirer, E. (Ed.) (2000). *Adsorption on Silica Surfaces*, New York, NY, USA: Marcel Dekker, Inc.
43. Gun'ko, V.M. and Turov, V.V. (2013). *Nuclear Magnetic Resonance Studies of Interfacial Phenomena*, CRC Press.
44. Liu, B., Wang, X., Du, H., Liu, J., Zhen, S., Zhang, Y., Miller, J.D. (2016). The surface features of lead activation in amyl xanthate flotation of quartz. *International Journal of Mineral Processing*, 151, 33-39.
45. Senanayake, G. (2008). A review of silver, lead, sulfide and carbonaceous matter on gold cyanidation and mechanistic interpretation. *Hydrometallurgy*, 90, 46-73.
46. Scoggins, M.W. (1972). Ultraviolet spectrophotometric determination of cyanide ion. *Analytical Chemistry*, 44(7), 1294-1296.

Figure 1. LSV scans of Au oxidation depending on CN concentration (a) in the absence of Pb, and (b) in the presence of 5 mg/L Pb

Figure 2. OCP distribution at different CN concentrations in the presence of 5 mg/L Pb.

Figure 3. Chronoamperometry test results at different potentials of -0.35 and -0.40 V in 900 mg/L CN solution: (a) 0 mg/L Pb ; (b) 5 mg/L Pb

Figure 4. Surfaces of Au electrode after 3 h long chronoamperometry test: (a) 0 mg/L Pb at – 0.35 V; (b) 5 mg/L Pb at –0.40 V

Figure 5. XP-spectra of C 1s on the Au surface after 3 h long chronoamperometry test: (a) 0 mg/L Pb at -0.35 V; (b) 5 mg/L Pb at -0.40 V

Figure 6. XP-spectra of N 1s on the Au surface after 3 h long chronoamperometry test: (a) 0 mg/L Pb at -0.35 V; (b) 5 mg/L Pb at -0.40 V

Figure 7. Change of Au concentration at different potentials during chronoamperometry tests in the presence of 5 mg/L Pb, and schematic pictures of the Au and solution interface

Figure 8. Eh-pH diagram of Pb-H₂O system: [Pb_{Tot}] = 10⁻⁶ (dash dot line), 10⁻⁵ (solid line) and 10⁻⁴ (dotted line) M

Figure 9. Final Au concentration after 3hr-chronoamperometry tests depending on the electrode potential and presence of lead salt at 900 mg/L CN

Figure 10. LSV scans of Au oxidation depending on CN concentration in the presence of 5 mg/L Pb and 50 g/L quartz

Figure 11. LSV scans of Au oxidation depending on CN concentrations in the presence of 0.2 mg/L Pb without quartz addition

Figure 12. LSV scans at different scan rates in the presence of 5 mg/L Pb and 50 g/L quartz at 8.30 mg/L DO (a) 300 mg/L CN, (b) 600 mg/L CN

Figure 13. Schematic of solid/liquid surface of Au oxidation in the presence of CN and Pb^{2+}

Figure 14. LSV scans at different scan rates in the presence of 0.2 mg/L Pb at 8.30 mg/L DO and 900 mg/L CN

Figure 15. Three cycles of CV scan (a) in the absence of quartz, (b) in the presence of 50 g/L quartz (900 mg/L CN and 5 mg/L Pb)

Figure 16. Change of Pb concentration with time at different CN concentration (a) in the absence of quartz; (b) in the presence of 50 g/L quartz (initial Pb concentration: 5 mg/L)

Figure 17. Thermodynamic modelling of Pb-OH-CN system (a) Pb-OH species; (b) PbCN^+

depending on different CN concentrations ($[\text{Pb}]_{\text{Tot}} = 2.41 \times 10^{-5} \text{ M}$)

Figure 18. UV/Vis measurements of Pb-containing solution in the presence/absence of quartz

(a) 5 mg/L Pb + 0.0005 M NaOH; (b) 5 mg/L Pb + 0.0005 M NaOH + 900 mg/L CN