Chemical Speciation of Arsenic in Uranium Raffinates

N. Chen,[1] J. Cutler,[1,2] D.-T. Jiang,[1,3] T. Kotzer,[4]

[1]Canadian Light Source Inc. (CLSI), Saskatoon, Saskatchewan, Canada
[2]Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada
[3]Department of Physics, University of Saskatchewan, Saskatoon, Saskatchewan, Canada
[4]Department of Geological Sciences, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

Introduction

The high-grade uranium deposits in the Athabasca Basin in northern Saskatchewan, Canada, account for approximately one-third of the world's total uranium production [1]. Along with the uranium, many of these deposits contain significant amounts of arsenic (up to 10% of the ore) as Ni-Fe-Co-As-S minerals. A majority of the arsenic is leached from the ore during mill processes such as solvent extraction and uranium precipitation. The dissolved arsenic within these tailings is the primary contaminant of concern because of its potential to affect downstream biological receptors. Generally, the arsenic is removed from the acidic hydrometallurgical solution (raffinate) by precipitation with ferric iron and lime (lime chips), producing low-solubility ferric arsenates. As a result, knowledge of the arsenic speciation in these mine tailings and its stability in the environment is of paramount importance.

In order to study the speciation of arsenic within the mine tailings, neutralization of the natural raffinates was simulated via a series of laboratory experiments that used synthetic raffinate solutions at different pH's. As it would for the real mine tailings, the synthesis resulted in the formation of dilute, semi-amorphous arsenic-bearing precipitates that were difficult to characterize by means of traditional x-ray techniques. However, the sample phases were less complex than in real tailings, so the sample composition was better controlled. Arsenic K-edge x-ray absorption fine structure (XAFS) spectroscopy was used to probe the atomic local structure of ferric-, nickel- and aluminum-arsenate phases. This work indicates that in neutralized raffinate, an arsenic phase that is structurally similar to amorphous scorodite (i.e., $FeAs_{0.976}O_4\_2.39H_2O$) [2] dominates the arsenic speciation in the synthetic raffinate precipitates. The XAFS analysis for the As K-edge and Fe K-edge $k^2\chi(k)$ and $k^3\chi(k)$ spectra further indicates that amorphous scorodite has a microcrystalline scorodite As and Fe local coordination environment.

Methods and Materials

Several synthetic raffinate samples, precipitated at pH values of 2.18 (No. 1-1), 3.15 (No. 1-2), 4.04 (No. 1-3), and 6.09 (No. 1-4), respectively, were supplied by
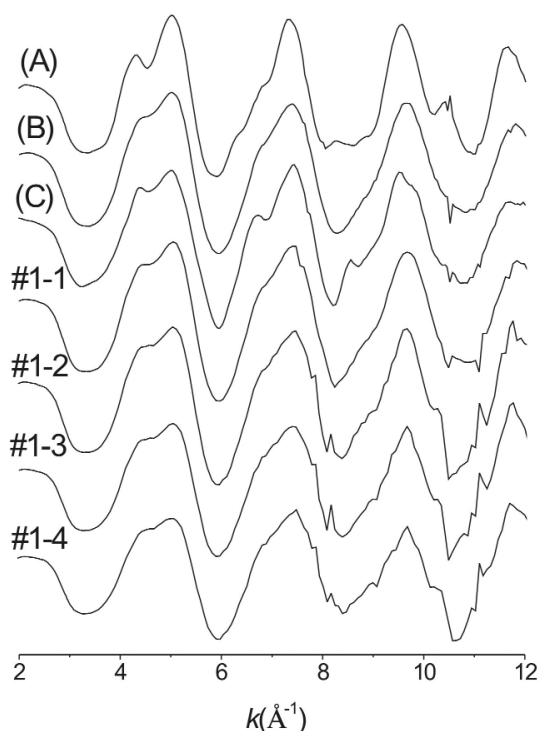

FIG. 1. A comparison of the k versus $k^3\chi(k)$ of crystalline (A) and amorphous (B) scorodite, crystalline annabergite (C), and the neutralized raffinate precipitate at 2.18 (No. 1-1), 3.15 (No. 1-2), 4.04 (No. 1-3), and 6.09 (No. 1-4).

COGEMA Resources Inc. Model reference compounds of crystalline and amorphous scorodite, crystalline annabergite [$Ni_3(AsO_4)_2.8H_2O$)], and arsenate-adsorbed crystalline goethite (α-FeOOH) having an Fe/As doping ratio of 10/1 and 4/1 were analyzed. The scorodite samples were prepared by G. Demopoulos at McGill University [2], whereas arsenate-adsorbed goethite samples were prepared by CLS.

XAFS spectra (Fig. 1) were collected by using the PNC-CAT bending magnet beamline (20-BM) over the energy range of 11,667-12,818 eV (ring conditions of 7 GeV and ~97-102 mA) with Si<111> monochromator crystals. The energy of the recorded XAFS data were calibrated at the Au K-edge energy (11,919.7 eV) by using a gold foil.

Results

XAFS spectra (Fig. 1) collected on the neutralized raffinate precipitates and related model reference compounds were evaluated using two data analysis tools. The first was principal component analysis (PCA), which was used to determine the number of major As-bearing components in the neutralized raffinate samples. Then As-Fe bond distances for the major As species in the samples were determined from R-space curve fitting.

Principal Component Analysis

PCA was carried out on the four neutralized raffinate precipitates. The relative importance of these components, as indicated by their eigenvalues (weights), is on the order of 1.977 (80%), 0.247 (10%), 0.135 (5%), and 0.104 (4%), respectively. The first component has well-resolved spectral oscillations. The second component may also be real, although its importance appears to be much less. The remaining two components are not likely to have any real spectral significance and are tentatively attributed to errors in post-edge background subtraction and random noise. This conclusion is supported by the fact that spectral reproductions that use only one component adequately reproduce the $k^3\chi(k)$ spectra, while spectral reproductions using two components yield a comparable spectrum with only a slight improvement in the residuals.

Target transformations, used to delineate among major and minor components in the raffinate precipitates, suggest that amorphous scorodite and crystalline annabergite are the major and minor components, respectively. Other model components, including crystalline scorodite and arsenate-adsorbed goethite samples, are less likely to be present. Overall, the results of the PCA indicate that there are, at most, two As-bearing phases within the precipitates, with amorphous scorodite dominating.

R-space Curve Fitting

Curve fitting was performed in R space on the Fourier transform of the $k^2\chi(k)$ and $k^3\chi(k)$ spectra collected for amorphous scorodite (Fig. 2) and the synthetic neutralized raffinate. The As-Fe interatomic distance for amorphous scorodite was determined to be close to that of crystalline scorodite (i.e., 3.35 Å) and was used to evaluate the local structural environment for As within the neutralized raffinate samples. Fitting residuals were used to evaluate the magnitude of the error on the estimated As-Fe interatomic distance. This was accomplished by progressively increasing the value for R, at fixed values different from the initial best fit value for R, until the residual became twice the starting value. The same approach was adopted with progressively decreasing fixed R values. On the basis of
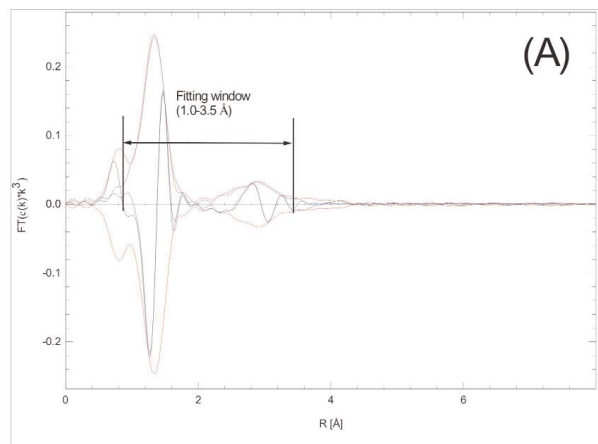

FIG 2. *A comparison of the experimental R-space data and the best fit to the amorphous scorodite data. The red and blue solid lines are the magnitude of the Fourier transform for the experimental and calculated data, respectively. The solid black and dashed blue lines are the imaginary parts of the Fourier transform for the experimental and the calculated data, respectively.*

the results from this process, the error for the As-Fe interatomic distance was estimated to be approximately ±0.02 to 0.03 Å.

Good consistency is found between the fitting results for $k^2\chi(k)$ and $k^3\chi(k)$ data. Fitting results shows that the As-Fe interatomic distance and the iron coordination number for amorphous scorodite exactly match those obtained for crystalline scorodite, indicating that the two have identical As local structures. More interesting is the fact that the iron coordination number and average As-Fe interatomic distance for the neutralized raffinate are very close to those of the amorphous scorodite. The As-Fe interatomic distance is slightly shorter than that of the amorphous scorodite, indicating the presence of a second, minor, As-bearing phase, which is either a nickel arsenate, Fe-As coprecipitate, arsenate adsorption on goethite, or amorphous ferrihydrite [3].

Discussion

R-space curve fitting indicates two things. First, amorphous scorodite has an As-Fe interatomic distance close to that of crystalline scorodite [4], determined by both As K-edge and Fe K-edge XAFS data. This conclusion is further supported by the coordination number for arsenic and iron. Second, As-Fe interatomic distances determined for the neutralized raffinate sample at different pH's are close to those for amorphous scorodite but significantly different from those for As-Fe in the arsenate adsorbed cases, where the distance would be around ~3.24 Å [3, 5], indicating that the major

precipitate has a scorodite-like local structure. This result is also supported by the Fe coordination number relative to the central adsorbing arsenic.

Overall, spectral similarities obtained from the two data processing approaches indicate that the amorphous scorodite model compound is chemically and structurally similar to crystalline scorodite. Furthermore, the scorodite-like nature of the local As structure within the major As-bearing phase in neutralized raffinate precipitate suggests that the dominant phase is amorphous scorodite. This finding has important environmental significance, since amorphous scorodite can sequester large amounts of arsenic (As/Fe = 1).

References
[1] D. Langmuir, J. Mahoney, A. Macdonald, and J. Rowson, Geochim. Cosmochim. Acta **63**, 3379–3394 (1999).
[2] Y.F. Jia, G.P. Demopoulos, N. Chen, J.N. Cutler, and D.T. Jiang, *Hydrometallurgy 2003 – Fifth International Conference in Honor of Professor Ian Ritchie – Volume 2: Electrometallurgy and Environmental Hydrometallurgy,* 1925-1935 (2003).
[3] G.A. Waychunas, B.A. Rea, C.C. Fuller, and J.A. Davis, Geochim. Cosmochim. Acta **57**, 2251-2269 (1993).
[4] D.T. Jiang, "X-ray absorption fine structure spectroscopy-synchrotron radiation," Chap. 4, Vol. 30 in *Synchrotron Radiation: Earth, Environmental and Materials Applications*, short course edited by G.S. Henderson and D.R. Baker (Mineralogical Association of Canada, 2002).
[5] B.J. Moldovan, D.T. Jiang, and M.J. Hendry, Environ. Sci. Technol. **37**, 873-879 (2003).