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► **To cite this version:**

N. Chen, E. Kim, Z. Arthur, R. Daenzer, J. Warner, et al.. XAFS Study of Arsenical Nickel Hydroxide. Journal of Physics: Conference Series, 2013, 430, pp.012092. 10.1088/1742-6596/430/1/012092 . hal-00843815

HAL Id: hal-00843815

<https://hal.science/hal-00843815>

Submitted on 12 Jul 2013

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XAFS Study of Arsenical Nickel Hydroxide

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Abstract To Investigate the role played by nickel co-ions in contributing to the stability of arsenic, fluorescence XAFS measurements at both arsenic K-edge and nickel K-edge, respectively, on amorphous arsenical nickel hydroxide, crystalline arsenical nickel hydroxide, and annabergite reference compounds have been carried out. The XAFS results indicate that the arsenic-bearing nickel hydroxides have a well-defined arsenic local structure with multiple coordination shells, suggesting a compound formation mechanism instead of surface adsorption. The degradation of the arsenic local structure in the crystalline arsenical nickel hydroxide is observed. The XAFS of annabergites are compared to that of the arsenical nickel hydroxide and possible structural models are discussed.

1. Introduction

Coprecipitation of arsenic(V) with ferric iron from hydrometallurgical solutions is widely used for the removal and immobilization of arsenic in uranium mine tailings. Other common co-ions in the industrial solutions such as nickel and aluminum have been found enhancing the arsenic retention under certain coprecipitation conditions [1]. In order to understand the process of arsenate coprecipitation with nickel hydrides under the industrially relevant geochemical conditions, we investigate several laboratory prepared reference compounds formed under the similar conditions of the uranium mine tailings neutralization process. The samples include two types: arsenical nickel hydrides and annabergites, and in each group samples of different long range ordering are studied. The analysis of the data are mainly based on the FEFF [2] modeling of EXAFS in the k-space and the FDMNES [3] modeling in the XANES of these samples.

2. Experimental

Five samples were prepared: amorphous arsenical nickel hydroxide (sample-1), crystalline arsenical nickel hydroxide (sample-2); amorphous annabergite, and two crystalline annabergite samples with different crystallinity: sample-4 and sample-5, respectively. Synthesis of the amorphous arsenical nickel hydroxide was performed by adding aqueous arsenate into a nickel sulfate solution, with a final Ni:As molar ratio of 4:1 [4]. Sodium hydroxide was used to maintain a pH of 8 during this process. Crystalline arsenical nickel hydroxide was synthesized using a nearly identical method: in place of nickel sulphate, a commercially-available crystalline nickel hydroxide (theophrastite) was used. Amorphous annabergite was synthesized by separately dissolving nickel sulphate and arsenate, then adding the two solutions together at pH 2 with a Ni:As ratio of 1.5:1 [5]. This combined solution was then fed through a pump into a vessel containing pH 7 de-ionized water; the pH was kept constant by the addition of sodium hydroxide. Crystalline annabergite was produced by first following the method

for synthesizing amorphous annabergite. After pumping the Ni-As solution into the pH 7 de-ionized water vessel, the mixture was then filtered, and the filtrate was dried and re-suspended in a reactor with pH 7 de-ionized water. The reactor was then heated to 95 °C for 120 hours.

The Ni and As K-edge XAFS data were collected at the HXMA beamline [6] at the Canadian Light Source. Mono crystals Si(220) and Si(111) were used, respectively, and the beamline Rh mirrors were used for both experiments. Data collection was performed in transmission mode for concentrated samples or in fluorescence mode by using a 32 element Ge detector. The energy calibration was made by using metal foils downstream to the sample.

3. Results and Discussion

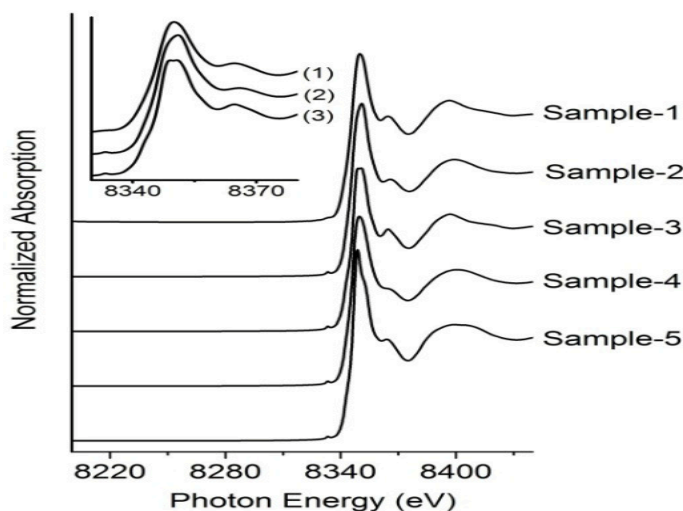


Figure 1. Ni K-edge XANES. (1) crystalline nickel hydroxide; (2) amorphous arsenical nickel hydroxide; (3) crystalline arsenical nickel hydroxide; (4) amorphous annabergite; (5) crystalline annabergite, respectively. The insert highlights the difference in the white line peak shape between sample nickel hydroxide samples with and without arsenic.

Figure 1 shows the Ni K-edge XANES for nickel hydroxide reference data [7] and for sample 2-5 measured in this study. A general similarity exists among these data presumably reflecting the presence of the common NiO₆ octahedron. Close examination reveals the differences between the arsenic-bearing samples (sample 2-5) and the crystalline nickel hydroxide (sample-1). First of all, compared to the pure nickel hydroxide (sample-1) the arsenic-bearing samples all have a significantly more prominent pre-edge feature at 8333.1eV due to the distortion of the NiO₆ octahedron; secondly, they have their whiteline peak either being asymmetric (Fig. 1 insert trace-2) or split into multiple peaks (Fig. 1 insert trace-3). These indicate that the Ni in the arsenical nickel hydroxides have multiple types of Ni local environments in contrast to the single type in the pure nickel hydroxide. Given that the molar ratio of Ni:As is 4:1 in these samples, these observations indicate the sensitivity of the Ni K-edge XANES to the presence of arsenic in the samples, as not all Ni are influenced by the As presence.

The EXAFS at Ni and As K-edges of the samples are shown in Fig. 2. The presence of the low level arsenic (126.22 μmol/g) in the crystalline arsenical nickel hydroxide appears to have a minimal structural impact to the nickel hydroxide matrix: the EXAFS of the crystalline arsenical nickel hydroxide (sample-3) is virtually identical to that of the pure nickel hydroxide in literature [7]. On the other hand, the EXAFS of the amorphous arsenical nickel hydroxide (sample-2) has clear deviations from that of pure nickel hydroxide, e.g. the shifting of feature B (Fig. 2a) and the smearing in the region D (Fig. 2a). These differences are attributed as due to the presence of relatively heavy arsenic loading in this sample (1612.29 μmol/g) and the size of the crystallites in the sample (see below).

Interestingly, these differences also make the amorphous arsenical nickel hydroxide (sample-2) resembling to a certain extent that of the amorphous annabergites (sample-4). FEFF modeling (not shown) based on the nickel hydroxide crystallographic data indicates that when the crystallite size is about 5.7 Å the calculated EXAFS would qualitatively reproduce all the features of the EXAFS of sample-2 (Fig. 2a), suggesting a morphological interpretation for the XRD “amorphous” nature of the sample-2.

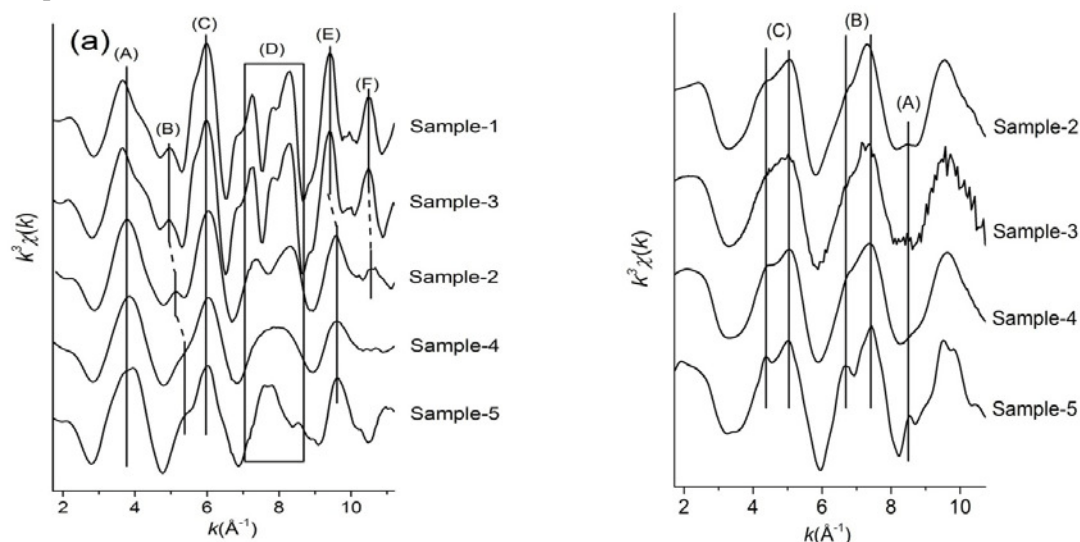


Figure 2. EXAFS $k^3\chi(k)$. (a) Ni K-edge data for sample 1-5; (b) As K-edge data or sample 2-5.

Figure 3b shows the As K-edge $k^3\chi(k)$ of the four arsenic-containing samples. The first noticeable observation is that the arsenical nickel hydroxides (Fig. 3b, sample 2-3) are strikingly similar to those of annabergites (Fig. 3b sample 4, 5), regardless of their long range order properties. Secondly, the multiple shell nature of the EXAFS of the arsenical nickel hydroxide (Fig. 3b sample-2, 3) indicates that the arsenate reacts with the nickel hydroxide leading to multiple coordination shells of arsenic local structure or a compound formation. Combined these observations we conclude that the nickel cation seems to lead to formation of an annabergites-like compound in the coprecipitation with arsenic(V) at around pH 8.

To further understand the nature of the arsenical nickel hydroxide we carried out FDMNES [3] simulations of the annabergites experimental XANES data. Figure 4 shows a comparison between the FDMNES results and the As K-edge experimental data. First, from the results in the left and the middle panel of Fig. 4 a clear correlation between the cluster sizes used in the calculation and the XANES features beyond the whiteline. When compared to the experimental data shown in Fig. 4 (right panel) it is apparent that the two crystalline annabergites samples possess both of the feature A and B (Fig. 4 middle), this is consistent with their expected large crystallite sizes. On the other hand, for the amorphous annabergite (Fig. 4 right panel: sample-4) the feature B is completely missing; it can be shown that simple broadening of the calculated data for model 4 (Fig. 4 middle, 6.1 Å cluster size) will not be able to account for the spectral difference near feature B. Therefore, these FDMNES calculations appear to be a rather sensitive method in predicting the size of the crystallite in a coprecipitated compound, if a structural model exists.

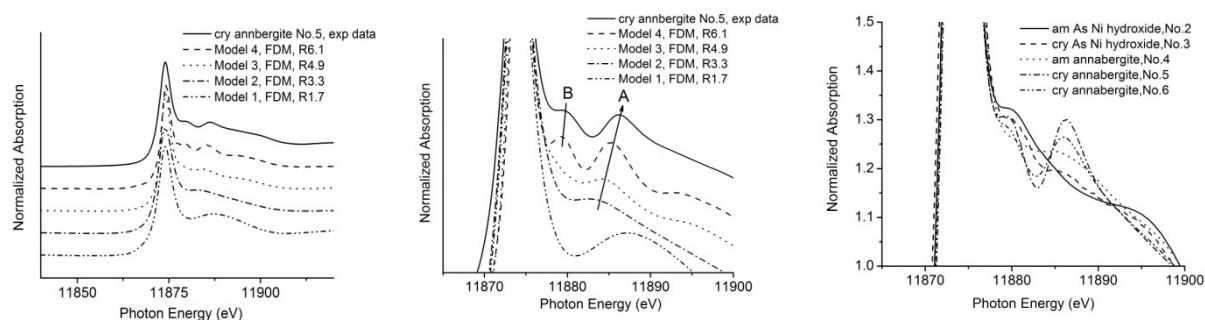


Figure 4. FDMNES calculation for annabergite XANES. *Left panel:* Experimental XANES of crystalline annabergites (solid) and a series of FDMNES calculations (Model 1 to 4) with increasing cluster sizes, 1.7 Å, 3.3 Å, 4.9 Å, and 6.1 Å. *Middle panel:* a close-up view of the same data in the left panel, in the region near the whiteline. Notice that the feature A of the calculated spectra appears first appears when the first As-Ni shell is included in the calculation, then gradually approaches the correct photo energy as the cluster size increases; while the feature B does not appear until the cluster includes the third group of As-Ni interatomic distance at 6.06 Å for the annabergite structure. *Right panel:* Experimental XANES for the samples 2-6 in the same region as that in the middle panel (see text for more discussion).

Finally, for the arsenical nickel hydroxides (Fig. 4 right: sample 2 and 3), two preliminary observations can be made: first, detail XANES comparison in the shown region indicates that the crystalline arsenical nickel hydroxide (Fig.4 right: sample 3) possesses both the A and B features of annabergite but at rather different branching ratio; second, the amorphous arsenical nickel hydroxide (Fig. 4 right: sample 2) does not have the feature A as that in annabergite. These observations reveal the subtle, presumably longer range structural differences exist between the two groups of the compound, even though the EXAFS (Fig. 3b) strongly suggest a similar local atomic structure.

4. Conclusions

Arsenical nickel hydroxide formed under the similar geochemical conditions as that in typical uranium mine tailings neutralization process possesses a well-ordered arsenic local structure which bears strong resemblance to that in the annabergite; FDMNES calculations successfully simulate the experimental XANES of annabergite; the FDMNES results identify XANES features that can be used as indicators for specific atomic cluster sizes at nanoscale.

Acknowledgements

The research described was supported by NSERC of Canada through a CRD grant to GPD and DTJ. The experiments were performed at the Canadian Light Source, which is supported by the NSERC of Canada, the NRC Canada, the CIHR, the Province of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan.

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