Arsenic speciation and sorption in acid mine drainage and the polluted water of the Kosva river basin, Russia

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Abstract. Acid mine drainage (AMD) of the abandoned coal mines of the Kizelovsky coal basin (the Urals, Russia) is one of the worst natural disasters in the region. Acidic sulphate waters with a high content of metals freely flow into the surface water bodies. Arsenic, found in elevated concentrations in AMD, is an element of concern due to its potential toxicity to humans and animals. The aim of this work is determination of chemical speciation of inorganic arsenic in AMD as well as the surface water and groundwater affected by mine drainage, and assessment the natural removal of As from mine drainage due to adsorption on precipitated hydrous ferric oxide (HFO). Geochemical speciation (PHREEQC) revealed that arsenic occurs in all water samples as As(V). Surface complexation model shows that, HFO induced by the natural attenuation process may remove 46–85% of total arsenic in AMD and only 28% in polluted groundwater (on average).

1. Introduction
Arsenic (As) is a ubiquitous element in the environment and an extremely toxic one to humans and animals. This element may be released into the environment from both natural and anthropogenic sources. High concentrations of arsenic are usually found in sulfide minerals, among of which pyrite is the most abundant. The crystal structure of pyrite can contain appreciable amount of As (up to 0.5%) [1]. The presence of pyrite as a minor component in coals is ultimately responsible for the formation of acid mine drainage (AMD) with elevated concentrations of arsenic and other metals.

Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5) but in natural waters it is mostly found in its inorganic form as oxyanions of As(III) (arsenite, AsO\(_3^\text{3-}\)) or As(V) (arsenate, AsO\(_4^{\text{3-}}\)) [2]. The most important factors controlling As speciation are the redox potential (Eh) and pH. Arsenate generally predominates under oxidizing conditions, while arsenite predominates when conditions become sufficiently reducing [1]. Under oxidising conditions, H\(_2\)AsO\(_4\) is dominant at low pH (less than about pH 6.9), whilst at higher pH, HAsO\(_4^{\text{2-}}\) becomes dominant. Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H\(_3\)AsO\(_3\) will predominate [2–4].

The guideline value for As in drinking water recommended by the World Health Organization (WHO) is 0.01 mg/L. In the Russian Federation, the maximum admissible concentration (MAC) for As in drinking water is also 0.01 mg/L. The current water standards for arsenic make no differentiation between arsenite and arsenate considering only the total As content in the water [1]. Generally, trivalent arsenic compounds are more toxic than their pentavalent counterparts, and the
inorganic arsenic compounds are more toxic than the organoarsenicals. Elemental arsenic is one of the least toxic forms of the element [5].

Arsenite adsorbs less strongly than arsenate in the typical pH range of natural water and is more mobile [1]. Arsenate is strongly adsorbed to the surface of several common minerals, such as ferrihydrite and alumina, a property that constrains its hydrologic mobility. Arsenite adsorbs less strongly and to fewer minerals, which makes it the more mobile oxyanion [6]. Acid mine drainage often contains arsenic in the form of arsenite or arsenate along with much higher concentrations of dissolved iron. After exposure to air, AMD turns brown due to precipitation of hydrous ferric oxide (HFO) as visible floc. The precipitated HFO may effectively remove most of the arsenate from water through adsorption.

Knowledge of the mechanisms controlling arsenic mobility and its natural attenuation processes is important for assessing the risk of arsenic contamination, and for developing effective measures for treatment of mine drainage and remediation of the polluted natural water. The purpose of this work is to ascertain the main inorganic forms of arsenic in acid mine drainage as well as in the surface and groundwater affected by AMD, and to assess arsenic removal by adsorption on precipitated HFO in the process of natural attenuation. All calculations based on thermodynamic principles were performed using hydrochemical modeling.

2. Materials and methods
The study area is located within the territory of the closed Kisel Coal basin in the Urals, Russia. Acid mine drainage outflows onto the surfaces and enters into the Kosva River, one of tributaries of the Kama river. As the original information for model calculations, the data of hydrochemical monitoring of the territory (for 2017) carried out by LLC "Permenergoaudit" were used [7, 8]. The samples of AMD, as well as groundwater and the surface waters both impacted and not impacted by mine drainage, are considered in the paper. The location of the sampling points is shown in figure 1.

Figure 1. Location of the sampling points (adopted from [7]).
Contents of total As and Fe in AMD, in both the groundwater and river water are shown in the table 1. In the AMD, As concentration ranges from 0.017 to 0.082 mg / L. The highest As concentrations are found in samples taken from mine named after Nadezhda Krupskaya (further “Krupskaya” mine). However, the greatest contributor to the Kosva river pollution is the outflow from the mine named after Mikhail Kalinin (further “Kalinin” mine) due to the large volume of the drainage [9]. In the Kosva river, just downstream of the fall of the AMD from the “Kalinin” mine (point 2R), the concentration of arsenic, except of one sample, does not exceed 0.005 mg / L.

Table 1. Content of total As and Fe in AMD, groundwater and river water, mg / L.

| Sample                  | As Min | As Max | As Mean | Fe Min | Fe Max | Fe Mean | pH | N of samples |
|-------------------------|--------|--------|---------|--------|--------|---------|----|--------------|
| Acid mine drainage      |        |        |         |        |        |         |    |              |
| “Kalinin” mine          | 0.028  | 0.039  | 0.034   | 1105.0 | 1355.79| 1195.37 | 2.97| 3            |
| “The 1th of May” mine   | 0.017  | 0.021  | 0.019   | 97.0   | 164.03 | 122.54  | 2.7 | 3            |
| “Krupskaya” mine        | 0.051  | 0.082  | 0.068   | 1461.8 | 1675.0 | 1558.03 | 3.1 | 3            |
| Groundwater impacted by AMD |        |        |         |        |        |         |    |              |
| Well 634                | 0.005  | 0.010  | 0.007   | 145.43 | 1144.0 | 796.14  | 5.3 | 3            |
| Spring 407              | 0.005  | 0.005  | 0.005   | 2.53   | 8.90   | 5.64    | 6.5 | 3            |
| Spring 417a             | 0.014  | 0.035  | 0.021   | 7.64   | 12.8   | 9.82    | 4.9 | 3            |
| Natural groundwater     |        |        |         |        |        |         |    |              |
| Spring 643              | 0.005  | 0.005  | 0.005   | 0.44   | 0.44   | 0.44    | 7.5 | 1            |
| River water             |        |        |         |        |        |         |    |              |
| 1R                      | 0.006  | 0.013  | 0.010   | 0.23   | 0.40   | 0.33    | 7.1 | 4            |
| 2R                      | 0.005  | 0.019  | 0.009   | 3.86   | 9.98   | 7.10    | 5.7 | 4            |
| 3R                      | 0.005  | 0.014  | 0.009   | 1.80   | 2.52   | 2.09    | 7.5 | 4            |
| 4R                      | 0.005  | 0.022  | 0.010   | 1.75   | 2.29   | 2.01    | 7.4 | 4            |

The distribution of arsenic species in water under natural conditions and surface complexation model to predict the sorption behavior of As were performed using the PHREEQC program code (version 3) [10] with the WATEQ4f database [11]. In addition to chemical composition, the input parameters included data of pH, Eh, and temperature of water. No redox (Eh) measurements were made during sampling. In the modeling, parameter pe was previously calculated by PHREEQC based on the available data for NH_4^+/NO_3^- redox couple. The modeling of surface complexation reactions was performed for acid mine water and for the most polluted groundwater discharged as a spring. Adsorption of As on HFO was simulated using the diffuse double layer model described in [12]. The double layer model defines strong and weak sites of adsorption. Strong sites defined in the WATEQ4f database as Hfo_s correspond to a smaller subset of surface sites with a high affinity for cation sorption. Weak sites defined as Hfo_w represent common reaction sites available for the sorption of protons, cations and anions [12, 13]. In the model, HFO was defined as Fe(OH)_3. The surface areas of HFO were considered as 600 m^2 / g [12]. The HFO surface included sites of strong and weak adsorption with densities of 0.005 mol sites/mol HFO and 0.2 mol sites / mol HFO, respectively [12]. The amount of precipitated Fe(OH)_3 was accepted taking into account the ferric ions content calculated when modeling the equilibrium concentrations of components and species in solutions.

3. Results
The simulation results are shown in the figure 2. The bar charts represent the percent distribution of the inorganic arsenic species in water samples as well as mean values of pH (figure 2a) and the total As (figure 2b) in them. In all samples, the main inorganic forms of arsenic are arsenates. The arsenites have negligible concentrations in the model, on the order of 10^{-17}–10^{-20} M / L. After equilibration,
major arsenic species in the acidic mine water with pH 2.6–3.2 are H₂AsO₄⁻ (78–90%) and H₃AsO₄ (10–22%). In contaminated groundwater (springs 407 and 417a, well 634) and surface water (2R) with pH 4.2–6.6, the predominant As(V) species is also H₂AsO₄⁻ (79–97%) and the second major form is HAsO₄²⁻ (2.6–20.7%), the content of H₃AsO₄ does not exceed 0.4%. In the water samples with neutral pH (spring 643, 1R, 3R, 4R), the distribution of arsenic forms is dominated by HAsO₄²⁻ (48–71%) and H₂AsO₄ (30%–52%). The distribution of arsenate species in all samples as function of pH are shown in figure 3. This result is in compliance with dependences reported in [1–4]. In regards to relation of arsenate species distribution with As concentration, no correlations were found (figure 4).

Figure 2. Distribution of arsenic species, pH and total As content in the samples (mean values).

Figure 3. Arsenate speciation as a function of solution pH.
Figure 4. Distribution of arsenic species as a function of total As concentration.

The modeling of surface complexation on the HFO was carried out for the outflows of the mines "Krupskaya", "Kalinin", "The 1th of May", and the spring 417a. According to the equilibrium calculations, content of ferric ions changes from 34% to 72% of the total dissolved iron in acid mine waters (table 2).

Table 2. Distribution of ferrions.

| Sample       | $\text{Fe}_{\text{tot}}$, mg/L | $\text{Fe}^{3+}$, mg/L | $\text{Fe}^{3+}$, % |
|--------------|-------------------------------|------------------------|---------------------|
| “Kalinina” mine | 1195.37                       | 426.3                  | 34                  |
| “1th of May” mine | 122.54                        | 70.1                   | 61                  |
| “Krupskoy” mine | 1558.03                       | 619.9                  | 49                  |
| Spring 417a   | 5.64                          | 1.7                    | 44                  |

The calculations have shown that, in the AMD from the “Kalinin” and “Krupskaya” mines, 84–85% of arsenic can be removed from the solution during hydrous ferric oxide precipitation despite the competition of arsenate with other anions and cations (such as $\text{SO}_{4}^{2-}$, $\text{PO}_{4}^{3-}$, $\text{Mn}^{2+}$, $\text{Cu}^{2+}$, $\text{Zn}^{2+}$, $\text{Cd}^{2+}$, $\text{Pb}^{2+}$) (table 3). The average concentrations of the remained arsenic in the solutions are decreased to the values closed to MAC or even lower (on average to 0.005 and 0.011 mg / L, respectively for these two mine drainages). The percentage of ferric ions in the AMD sampled from the “1th of May” mine is higher compared to other mine drainage samples, but the HFO formed by these ions can adsorb only 46% of arsenic dissolved in the same solution since the total concentration of iron here is much lower. However, in the last case, the concentration of dissolved arsenic also reduces to MAClevel (to 0.01 mg / L in average).

Table 3. Removal of As by adsorption on HFO formed from ferric ions (mean values).

| Sample       | $\text{Adsorbed As}$, mg L | $\text{Adsorbent}$, HFO, mg L | % As Removed |
|--------------|-----------------------------|-----------------------------|--------------|
| “Kalinin” mine | 0.0285                      | 5.96×10^{-9}                | 995.0        | 85           |
| “1th of May” mine | 0.0087                      | 4.86×10^{-10}               | 147.2        | 46           |
| “Krupskaya” mine | 0.0563                      | 8.85×10^{-9}                | 1369.3       | 84           |
| Spring 417a   | 0.0007                      | 0.003                       | 6.3          | 28           |

In the AMD samples, adsorption occurs on weak areas represented as Hfo_wOH. The formed complexes of arsenate and adsorbent are identified as Hfo_wH$_2$AsO$_4$, Hfo_wHAsO$_4$, and Hfo_wOHAsO$_4$. The form of Hfo_wH$_2$AsO$_4$ accounts for about 98-99% of the all sorbed arsenic.
The surface complexation reactions of arsenate adsorption to Hfo defined in the WATEQ4f database and used in the model are follows [12]:

\[
\text{Hfo}_w\text{OH} + \text{AsO}_4^{3-} + 3\text{H}^+ = \text{Hfo}_w\text{H}_2\text{AsO}_4 + \text{H}_2\text{O} \tag{1}
\]

\[
\text{Hfo}_w\text{OH} + \text{AsO}_4^{3-} + 2\text{H}^+ = \text{Hfo}_w\text{HAsO}_4 + \text{H}_2\text{O} \tag{2}
\]

\[
\text{Hfo}_w\text{OH} + \text{AsO}_4^{3-} = \text{Hfo}_w\text{OHAsO}_4^{3-} \tag{3}
\]

In the contaminated water from the spring 417a, total As concentration reaches the values typical for AMD located in this coalfield area (0.014–0.035 mg / L), but the total iron content is relatively low (7.6–12.8 mg / L). In this case, the results of surface complexation modeling are not so satisfactory. In the two samples (with pH 4.2 and 4.7), the modeling suggests that only 5–6% of arsenic may be removed from the solution by adsorption. In these two samples, the arsenic remained in the soluble form (0.033 and 0.013 mg / L) exceeds the guideline value (0.01 mg / L). Formation of arsenate and adsorbent complexes proceeds mainly by the reactions (1–2). Only in one of three samples (with pH 5.9) the model result shows adsorption of 76% of total dissolved arsenic. In this sample, concentration of arsenic remained in the solution decreases to 0.004 mg / L. In this latter case, 80% of sorbed As forms complexes as Hfo_wOHAsO_4^{3-} (reaction (3)).

4. Conclusions
Arsenic in the mine drainages and contaminated natural water of the area under study occurs in the oxidized state (As^{5+}), the species of which are known to be less soluble and less toxic for living organisms [1, 5]. Arsenates are more easily removed from solution by adsorption than arsenites.

Surface complexation modeling was performed to estimate the quantity of arsenic removed by adsorption on ferrihydrite formed from the iron dissolved in the same water. Modeling of adsorption was carried out according to the most conservative scenario when the only estimated concentration of ferric ion was taken into account to calculate the amount of precipitated ferrihydrite. The results showed that concentration of ferric ions in AMD is enough to remove arsenic below the MAC level. The opposite is the case in the contaminated groundwater. The ferric ions concentration in it may not be enough to remove arsenic below the MAC level. However, when AMD or contaminated water with high concentration of soluble iron, arsenic, and other toxic inorganic impurities mixed with oxygenated surface waters, the dissolved Fe^{2+} will continue to oxidize to Fe^{3+} and precipitate as HFO contributing to removal of residual As and the trace metals by adsorption.

Based on the simulation results, it can be said that low concentrations of arsenic in the Kosva river just downstream of the AMD inflow (sample 2R) are caused not only by dilution but also by adsorption of arsenates on HFO. However, since the adsorption/desorption processes are dynamic in nature, there is the risk of recontamination of the Kosva river by arsenic. Elevated concentrations of total As in the samples taken close to the river mouth (3R and 4R) may indicate its re-mobilization.

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