EFFECTS OF THE IRON OXIDATION AND PRECIPITATION PROCESSES ON THE ARSENATE SORPTION AND COPRECIPITATION

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ABSTRACT. The main aim of this study was to assess the effects of ferrous iron oxidation, hydrolysis and precipitation of the ferric iron on the mechanisms of arsenate removal from acid mine drainage. The study was realized at the pH range 2.0 – 6.5. H2O2 was the oxidant used in the chemical test. A mixed culture of mesophilic iron-oxidizing chemolithotrophic bacteria (Acidithiobacillus ferrooxidans, Leptospirillum ferroxidans) carried out the ferrous oxidation in the biological test. NaOH was used as an alkalinizing agent which triggered the ferric iron hydrolysis and precipitation. The results showed that the total content of retained arsenic by ferric iron hydrous oxides and its speciation as geochemical fractions depended on the iron and phosphate concentrations in acid solution. The results showed that phosphate concentration lower than 6 mg/L limited the ferrous iron oxidation rate. At the tested experimental conditions, arsenic sorption by formed ferric iron hydrous oxides was the main mechanism for its removal from acid mine drainage, as the ratio between iron and phosphate determined the proportions between the geochemical fractions of scavenged arsenic.

Keywords: arsenate, ferric iron, ferrous iron oxidation, sorption, fractions

Introduction

Arsenic is a metalloid and it ranks 20th position among the most abundant chemical elements in the earth crust. The toxic element is a part of about 200 minerals that occur naturally usually as sulfides, arsenides, and oxides, closely related to igneous and sedimentary rocks (Bowell et al., 2014). Apart from pyrite/ sulfide oxidation, processes of reductive dissolution of iron minerals, arsenic desorption at pH higher than 7.0, and geochemical process lead to the natural release of the element to water (Ali et al., 2018). Arsenic occurs in natural waters both in organic and inorganic forms, as the arsenite, As(III), and arsenate, As(V). Arsenic is similar to its predecessor in group, phosphorous, but processes of oxidation, reduction, methylation play a significant role in its biogeochemical cycle. Based on close similarity between arsenate and phosphate, strong competitiveness exists between ions in the processes of adsorption-desorption processes, ion-exchange, solid-phase precipitation and biological uptake. However, the regular exposure to arsenic compounds causes adverse health effects like diabetes, neurological abnormalities, arteriosclerosis, renal effects, cardiovascular dysfunction, and carcinogenic risks in human beings (Abdul et al., 2015). For that reason, arsenic and arsenic compounds are included in group 1, carcinogens to humans, according to the International Agency for Research on Cancer (IARC). That was the reason the water standard of arsenic set by the Environmental Protection Agency (EPA) and recommended by the World Health Organization (WHO) to be reduced from 50 μg/L to 10 μg/L (WHO, 2001).

The previous studies have shown that goethite (α-FeOOH) possesses higher adsorption capacity and it removed arsenate more efficiently from spring waters both in batch and continuous way of operation in comparison to hematite (α-Fe2O3) (Zheleva et al., 2016; Zheleva and Georgiev, 2019). The leaching tests revealed that arsenate adsorbed mostly specifically with inner-sphere complexes formation between adsorbate and the mineral surface.

To study the role of processes of ferrous iron oxidation, hydrolysis and precipitation of generated ferric iron on the arsenic removal mechanisms at acidic pH was the main aim of this article.

Materials and methods

The effects of ferrous iron oxidation and ferric iron hydrolysis at acidic pH on the arsenic sorption/ precipitation were studied by batch tests. The study was carried out in polypropylene flasks with screw caps. A thermo-shaker provided a constant temperature (35°C for the bacterial oxidation, 55°C for the chemical oxidation) and agitation (200 rpm) during the tests. Hydrogen peroxide was used as a chemical oxidant in the abiotic test, while the process of the biological oxidation of ferrous iron was studied by a mixed culture of acidophilic iron-oxidizing chemolithotrophic bacteria consisted of Acidithiobacillus ferrooxidans and Leptospirillum ferroxidans, (~6x10^9 cells/ mL). The mixed culture was isolated from a copper slag deposit. The nutrient solutions for their growth contained the following salts (in g/L): (NH4)2SO4 – 0.4; MgSO4.7H2O – 0.4; KH2PO4.3H2O – 0.056; and FeSO4.7H2O – 14.9 (Tuovinen and Kelly,1973). Sulfuric acid solution (30%) buffered pH in the range of 1.8-1.9. The prepared acidic solution was spiked with arsenate (as K2HAsO4), so the concentration of toxic element was 250 μg/L. The ferric iron hydrolysis was triggered by manual addition of sodium hydroxide (1,0 N solution) periodically. The rate of oxidation, ferric iron precipitation, and arsenic sorption/ coprecipitation was studied by in situ measurements of pH, Eh, and sampling.

The ferrous iron concentration was calculated from the difference between the total iron and ferric iron concentration during the tests. The ferrous iron oxidation rate, g Fe^{2+}/(L.h) was calculated according to that equation:

$$\text{Fe}^{2+}_{\text{oxidized}} = \frac{(\text{Fe}^{2+}_{\text{iv}} - \text{Fe}^{2+}_{\text{v}})}{(t+n - t)}$$

where Fe^{2+}_{iv} and Fe^{2+}_{v} denote the ferrous concentration at the respective hour from the beginning of the test.

The samples were stored in a refrigerator at 8°C till analyses. The test duration was 75 hours. All experiments were performed in triplicate. The concentration of ferric iron and total iron in the samples was determined by a spectrophotometric method in the presence of sulfosalicylic acid at acidic and

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alkaline pH, respectively. The arsenic and phosphate concentrations were measured using a spectrophotometer MERCK SQ22 at 820 nm and a 20 mm cuvette (Johnson and Pilson, 1971).

Effect of the initial iron concentration on arsenate sorption/ co-precipitation at acidic pH
This effect was studied using a solution with content similar to that of the above-mentioned solution. The only difference between the variants was the initial iron concentration: 2.2, 1.7, 1.2, and 0.9 g/L, respectively.

Effect of the initial phosphate concentration on arsenate sorption/ co-precipitation at acidic pH
This effect was studied through tests with a solution similar to that of the above-mentioned solution. The only difference between the variants was the initial phosphate concentration: 18.3, 11.0, 6.6, and 3.3 mg/L, respectively.

A four-stage sequential extraction, based on that reported by Wenzel et al. (2001), was applied to the iron-contained residues deposited at the end of oxidation tests. The following arsenic factions were determined: 1) exchangeable (extracted with 0.05 M (NH₄)₂SO₄ for 4 h); 2) specifically surface-bound (extracted with 0.05 M NH₄H₂PO₄ for 16 h); 3) capulated in amorphous iron hydrous oxides (leached with 0.2 M ammonium oxalate buffer (pH 3.0), in dark for 4 h), and 4) capulated in crystalline iron hydrous oxides (extracted with 0.2 M ammonium oxalate buffer (pH 3.0) and 0.1 M ascorbic acid for 30 min at 90°C). The extracts from third and fourth fractions were treated before the arsenic analysis with UV light and H₂O₂ in a 705 UV Digestor, Metrohm for organic degradation and iron hydrolysis. The dropwise addition of 4N HCl dissolved the iron precipitates that had deposited on the bottoms' tubes. The total content of arsenic in the iron hydrous oxides residues was determined in the nitric acid's extract.

Results and discussion
The main characteristics of acid mine drainage generated as a result of oxidation of sulfides, both biological and chemical, are acidic pH, higher concentrations of iron, aluminium, sulfates as well as substantial concentrations of non-ferrous metals (copper, zinc, nickel, etc.,) and toxic elements (arsenic, uranium, etc.). Treatment of acid mine waters, both by active or passive methods, is based on the selective removal of each pollutant etc.,). Treatment of acid mine waters, both by active or passive methods, is based on the selective removal of each pollutant through a suitable alternation of oxidation, neutralization, reduction processes in some cases, and precipitation. The process of oxidation plays a crucial role in iron removal because a higher portion of the chemical element in acid mine drainage is in a ferrous state. The bacterial oxidation of ferrous iron plays the main role at acidic pH because the chemical oxidation by dissolved oxygen carries out with negligible rate at pH lower than 3.5. That process was studied by a mixed mesophilic iron-oxidizing chemolithotrophic bacteria which use ferrous iron as a donor of electrons in their metabolism while the final acceptor of electrons is the molecular oxygen:

\[
\text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}
\]

However, the iron-oxidizing bacteria yield a low amount of energy from that reaction which bacteria compensate by a higher rate of the substrate utilization (Silverman and Lundgren, 1959). For that reason, the rate of ferrous iron oxidation during the first 20 hours of the test was in the range of 0.03 – 0.04 g Fe²⁺/(L·h) despite the still low number of bacterial cells (Table 1). The ferrous iron oxidation is an acid-consuming process also and pH increased from 1.9 to above 2.15 during that period. Due to the gradual increase the bacterial cells, the rate of ferrous iron oxidation increased further up to 0.11 g Fe²⁺/(L·h) between 50 - 62 hours (Table 1). After that period of the test, ferrous iron concentration was too low which determined the sharp decrease in its rate of oxidation. Almost the same highest rate of bacterial ferrous iron oxidation was measured when the initial ferrous iron concentration varied in the range of 0.9 – 3.0 g/L (Table 2). The only difference was the total duration of the test needed to oxidize ferrous iron to the ferric state. In that case, the test's duration decreased from 75 to 30 hours.

Abiotic ferrous iron oxidation was carried out in the presence of hydrogen peroxide as the needed amount was calculated according to this reaction:

\[
2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}
\]

Trends in changes of pH, concentrations of ferric and total iron were similar to those already noticed in tests with the bacterial oxidation (Figure 1). However, chemical oxidation has an advantage because it could be realized with a rate significantly higher than the rate measured in the presence of bacterial cells. After all, the process could take place in a reactor at higher temperatures and the needed amount of oxidant could be added in a very short period.

The gradual addition of an alkalinizing agent (sodium hydroxide in that case) during the ferrous iron oxidation triggered the processes of ferric iron hydrolysis and precipitation. That was an acid-generating process that equilibrated with the acid-consuming character of the ferrous iron oxidation. That was the reason for buffering pH in the range of 2.2 – 2.4 between 22 and 58 hours of the test (Table 1).

Table 1. Bacterial oxidation of ferrous iron by acidophilic iron-oxidizing bacteria and the effect of sodium hydroxide addition on the ferric iron precipitation

<table>
<thead>
<tr>
<th>Time, h</th>
<th>pH</th>
<th>Fe²⁺, mg/L</th>
<th>Fe³⁺, mg/L</th>
<th>Consumption of NaOH, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.92</td>
<td>18</td>
<td>3050</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>2.15</td>
<td>880</td>
<td>2955</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>2.27</td>
<td>920</td>
<td>2945</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>2.31</td>
<td>865</td>
<td>2760</td>
<td>0</td>
</tr>
<tr>
<td>34</td>
<td>2.30</td>
<td>825</td>
<td>2540</td>
<td>9.7</td>
</tr>
<tr>
<td>42</td>
<td>2.28</td>
<td>710</td>
<td>2200</td>
<td>53.2</td>
</tr>
<tr>
<td>50</td>
<td>2.23</td>
<td>615</td>
<td>1955</td>
<td>184.8</td>
</tr>
<tr>
<td>54</td>
<td>2.46</td>
<td>425</td>
<td>1320</td>
<td>763</td>
</tr>
<tr>
<td>58</td>
<td>1.55</td>
<td>220</td>
<td>656</td>
<td>774</td>
</tr>
<tr>
<td>62</td>
<td>3.33</td>
<td>16</td>
<td>20</td>
<td>786</td>
</tr>
<tr>
<td>64</td>
<td>3.95</td>
<td>5.5</td>
<td>11</td>
<td>79.2</td>
</tr>
<tr>
<td>70</td>
<td>6.14</td>
<td>0.0</td>
<td>4.2</td>
<td>109.6</td>
</tr>
<tr>
<td>75</td>
<td>6.52</td>
<td>0.0</td>
<td>1.5</td>
<td>28.2</td>
</tr>
</tbody>
</table>

It is well-known that ferric iron precipitate at acidic pH mainly as poorly crystalline hydrous ferric oxides minerals as sulfate-containing schwertmannite [Fe₂O₃(OH)₂SO₄], jarosite [M₂Fe₃(SO₄)₂(OH)₆], where M is usually H₂O⁺, K⁺, Na⁺ or NH₄⁺, as well as goethite (Wang et al., 2006). The key factors controlling the mechanism of iron precipitation are pH,
concentrations of ferric iron, sulfates, and monovalent cations (H\(^+\), K\(^+\), Na\(^+\)):

\[
8\text{Fe}^{3+} + 14\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_4\text{O}_6\text{(OH)}_8\text{SO}_4 + 24\text{H}^+
\]

\[
\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+
\]

Fig. 1. Chemical oxidation of ferrous iron through multiple additions of hydrogen peroxide at 55°C

In the beginning, mostly in the case of bacterial oxidation, the colour of the solution turned into deep red which was an indication for the building up of ferric iron in the solution and its partial precipitation as jarosite mainly. However, the alkalinizing agent was added at regular intervals during the test so that the ferric iron concentration never exceeded 1000 mg/L and redox potential (Eh) of the solution measured was always lower than + 600 mV. Those experimental conditions provoked goethite formation mainly as a result of ferric iron hydrolysis. For that reason, the ferric iron concentration decreased significantly between 26 and 62 hours and the colour of precipitate deposited at the flask bottom turned in yellow-orange. The main advantages of goethite in comparison to jarosite and schwertmannite are a lower value of sludge volume index and higher settling velocity (Georgiev et al., 2017), while the values of properties as surface area and sorption capacity are comparable (Cornell and Schwertmann, 2003). For that reason, goethite is still one of the final products preferred during the iron removal processes at an industrial scale.

Table 2. Effect of the bacterial oxidation of ferrous iron and the ferric iron precipitation on the final arsenic concentration at the test’s end

<table>
<thead>
<tr>
<th>Initial content of ferrous iron, g/L</th>
<th>The maximum rate of bacterial oxidation of ferrous iron, g/L.h</th>
<th>Total consumption of NaOH, g/L</th>
<th>Final As concentration, µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.15 – 0.16</td>
<td>2.78</td>
<td>4.7</td>
</tr>
<tr>
<td>2.2</td>
<td></td>
<td>2.06</td>
<td>4.8</td>
</tr>
<tr>
<td>1.7</td>
<td></td>
<td>1.65</td>
<td>5.6</td>
</tr>
<tr>
<td>1.2</td>
<td></td>
<td>1.24</td>
<td>8.2</td>
</tr>
<tr>
<td>0.9</td>
<td></td>
<td>0.91</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Fig. 2. Consumption of sodium hydroxide (with accumulation) during the bacterial oxidation of ferrous iron

The higher amount of sodium hydroxide was added between 40 to 60 hour since the test’s start when more than of 2.0 g/L ferric iron had precipitated and the average iron removal rate was in the range of 0.08 – 0.1 g Fe\(_{\text{tot}}\)/L.h (Table 1). The highest rate of bacterial ferrous iron oxidation was measured in the same stage of the test which revealed the positive effect of ferric removal (the end product of bacterial metabolism) on ferrous iron utilization.

The precipitation of ferric iron consumed 2.79 g/L sodium hydroxide totally which led to increasing pH almost to neutral point (Figure 2). Almost 90% of that amount has consumed for buffering pH in the range of 2.2-3.3. The same trend of an alkalinizing consumption was noticed in the tests where the initial concentration of ferrous iron decreased gradually from 3.0 to 0.9 g/L. In those cases, the consumed amount gradually decreased to 0.91 g NaOH/L for the variant with the initial ferrous iron content of 0.9 g/L (Table 2). The amount of sodium hydroxide (2.62 g/L) consumed in the abiotic test was in the same range as the biotic test with an initial ferrous iron content of 3.0 g/L. The only difference was the rather shorter duration of the abiotic test (Figure 1).

The ferric iron precipitation was an efficient process for arsenic removal contained in the acidic solution. Two main processes have a role for arsenate removal at such conditions (acidic pH, a higher concentration of iron, ferric iron hydrolysis). Arsenate coprecipitation with ferric iron is one of the processes that could take place and it carried out in acidic effluents with higher arsenate concentration where the molar ratio between iron and arsenic is in the range lower than 10:1. The distinguishing feature of that process is linearity between iron and arsenic removal. Arsenate sorption on the surface of already precipitated poorly crystalline hydrous ferric oxide is the second process which is typical for acidic effluents with a substantial lower molar ratio of Fe/As. The distinguishing feature of that process is that arsenate removal carried out with a delay in comparison to iron removal. The results about arsenate removal revealed that the process carried out at an almost constant rate and with some delay in comparison to the periods with the highest iron removal rate (Figure 3). For example, the rate of ferric iron precipitation during the first 15 hours of bacterial oxidation of ferrous iron was too low which determined the very low rate of arsenate removal too. The rate of arsenate removal increased significantly to 10 µg/(L.h) at 30 hours when already approximately 8.5% of the initial iron content had precipitated. It is interesting to note that during the next 20 hours of the test, pH buffered in a very narrow range (2.23 - 2.31) with
an almost constant rate of iron precipitation. At such a condition, the rate of arsenate removal decreased twice despite the precipitation of another 25% of the iron in solution. The higher rate of arsenate removal (15.2 μg/(L·h)) was measured after 58 hours, when the rate of iron precipitation reached over 0.1 g/(L·h), despite the substantial acidification of the solution to 1.6 (Figure 3).

For that reason, the desorption process, in that case, carry out only after significant changes in environmental conditions (as pH, Eh, etc.) which enhances the bond’s breaking.

The tests with different initial ferrous iron content revealed that it hadn’t an effect on the final arsenate concentration (Table 2). In all tested variants, where the molar ratio Fe/As ranged from 18000:1 (with 3.0 g/L initial Fe content) to 5333:1, the final arsenate concentration was lower than 5 μg/L. This revealed that the poorly crystalline hydrous ferric oxides possessed surface area and sorption capacity sufficient to adsorb arsenic at acidic pH.

Table 4. Arsenic fractions in iron oxyhydroxides precipitated due to the bacterial oxidation of ferrous iron and hydrolysis

<table>
<thead>
<tr>
<th>Index</th>
<th>Fe(II)-</th>
<th>Fe(II)-</th>
<th>Fe(II)-</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO₄³⁻</td>
<td>3.0 g/L</td>
<td>0.9 g/L</td>
<td>3.0 g/L</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>30.5 mg/L</td>
<td>30.5 mg/L</td>
<td>11.0 mg/L</td>
</tr>
<tr>
<td>As(III)</td>
<td>30.0 g/L</td>
<td>3.0 L</td>
<td>11.0 g/L</td>
</tr>
</tbody>
</table>

Scorodite formation (FeAsO₄·2H₂O) is an example of arsenate coprecipitation with iron as the final concentration of toxic element is lower than 10 μg/L (Singhania et al., 2005). That process is used in the treatment of industrial effluents with very high arsenic concentration and the maintenance of appropriate conditions (a higher temperature and seeding rate) provokes the scorodite formation. At lower temperatures, for example in the weathering zone of mineral deposits, arsenic precipitate as its amorphous counter-parts (FeAsO₄·xH₂O). Scorodite is stable at acidic pH while at higher values it transforms to goethite with concomitant release of arsenate (Dove and Rimstidt, 1985). Such evidence of the redissolution of arsenate wasn’t observed in the study even though the process of neutralization was carried out almost to neutral point (Figure 3).

Besides the arsenate adsorption, the ferric iron oxyhydroxides removed very efficiently phosphates also (Figure 3). It is well-known that arsenic and phosphorus belong to the same group which determined their chemical similarities as well
as strengthens competitiveness between both elements for the adsorption positions, especially at neutral and slightly alkaline pH (Frau et al., 2008). However, the curves of arsenate and phosphate removal didn’t reveal an effect of competition between both anions. It could be explained with the different processes which took place for their removal - arsenate adsorption on the surface of poorly crystalline hydrous ferric oxides and phosphorus coprecipitation with iron (probably as FePO₄·2H₂O), respectively. Regarding the phosphorus removal, the molar ratio of Fe:PO₄ during the tests ranged from 16 (at 30.5 mg/L initial phosphate content) to 1600 (at 3.0 mg/L initial phosphate content) as the phosphate coprecipitation with iron was quite possible at higher initial phosphate concentration. It is well-known that ferric phosphate is virtually insoluble and at strongly alkaline pH converses to ferric hydroxide (Robins et al., 1991).

The bacterial activity at mine deposits depends on several important environmental factors as the concentrations of available forms of phosphorus and nitrogen are among the most frequently limiting (Tuovinen et al., 1971). Phosphorus is an element, essential for life which plays a crucial role in the storage of energy, the structure of cell membranes, and the encoding of genetic information. For that reason, the effect of phosphate concentration on the rates of ferrous iron oxidation and arsenate removal was studied by a set of tests. The results showed that a phosphate concentration higher than 11.0 mg/L, the rate of bacterial ferrous iron oxidation was almost the same as that measured when phosphate concentration was 30.5 mg/L (Table 3). When the initial phosphate concentration dropped further to 3.0 mg/L, the ferrous iron oxidation rate decreased almost twice. It revealed the strong limiting effect on the bacteria which phosphat had when the environment was deficit toward that nutrient. Regardless of the lower rate of bacterial ferrous iron oxidation, the total consumption of sodium hydroxide for ferric iron precipitation was in a narrow range. Most likely in the tests where the phosphate was in deficit, some part of the ferrous iron was oxidized chemically with molecular oxygen due to the regular addition of the alkalinizing agent and the existence of microzones with alkaline pH for a very short period. However, the arsenate removal at all tested phosphate concentration was a very efficient process as about 98.2% of the initial amount was sorbed by the ferric iron oxyhydroxides and the residual arsenate concentration was always lower than permissible concentration.

The applied arsenic fractionation by sequential leaching revealed the strong effect of studied factors on the toxic element speciation. First of all, the arsenic’s total content retained by the ferric iron hydrous oxides varied in a narrow range in all variants where the initial ferrous iron content was the same (Table 4). When the initial ferrous iron concentration decreased from 3.0 to 0.9 g/L, the retained arsenic's total content increased considerably and reached 126.5 μg/g. At such conditions, more than 50% of that amount was an exchangeable fraction, i.e. a fraction formed due to non-specific adsorption of hydrous ferric oxides and mobilizing easily in an environment with a higher concentration of competitive anions, such as sulfate. The insignificant content of specifically adsorbed arsenic (6.5 %) revealed that its retention during ferric iron precipitation had carried with intense competition with available phosphate. When the arsenic retention was carried out in an environment with a lower concentration of phosphate (which is a case type for the mine sites), the content of specifically adsorbed arsenic increased on account of the lower content of arsenic presented as an exchangeable fraction. The arsenate encapsulation in the hydrous iron oxides lattice was the next step in the toxic element removal at acidic pH. The poorly crystalline hydrous ferric oxides, which had precipitated at the very beginning of the process, acted as seeds during the ferric iron hydrolysis and following crystal’s growth. In this way, the initially adsorbed arsenate on the surface of hydrous ferric oxides had covered by the new layers of precipitates, and the process ended with encapsulation of the toxic element within the crystal lattice of deposited iron oxide. In that way, the reducible fraction of heavy metals and toxic elements in the solid samples formed (Tessier et al., 1979). In that case, the reducible fraction of arsenic in freshly deposited ferric iron oxides was specified in two subfractions - arsenic capsulated in amorphous and arsenic capsulated in crystalline iron oxides, respectively (Table 4). The distinction between those subfractions was determined by the redox conditions at which redoxolysis of the toxic element contained minerals took place. Both processes lead to arsenic release and re-dissolution. The arsenic capsulated in the amorphous iron oxides were significantly higher than the arsenic capsulated in the crystalline counterpart. The reason was the lower temperature and atmospheric pressure at which ferric iron precipitation took place. The concentration of iron and phosphate in mine waters had a strong effect on arsenic encapsulation in the deposited hydrous iron oxides as the lower iron content (0.9 g/L) and higher phosphate content (30 mg/L) determined the lowest percent of that fraction (20%, Table 4).

**Conclusions**

1. The results showed that the rate of bacterial ferrous iron oxidation was constant for the tested ferrous iron concentration range, while the rate decreased significantly when the phosphate concentration was lower than 6 mg/L.
2. Arsenate adsorption processes on the surface of poorly crystalline hydrous ferric oxides and their further growth due to ferric iron precipitation were the primary mechanism for arsenic removal from acid mine waters. As a result of that process, the residual arsenic concentration was lower than maximum permissible water levels (10 μg/L), regardless of the ratio between iron to arsenic.
3. The iron content, phosphate content, and iron to phosphate ratio in acid mine drainage substantially affected the total amount of arsenic retained by ferric iron hydrous oxides and the proportions between the geochemical fractions of the toxic element.

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