

ORIGINAL RESEARCH PAPER

Neutralization of arsenic pollutants, contained in natural waters: The theoretical analysis of solubility of some arsenates and optimization of the processes

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ABSTRACT

Arsenic belongs to chemical elements, which are often found in natural waters and make it unsuitable for consumption without special treatment. Neutralization of arsenic pollutants of natural waters by converting them into insoluble form is one of the perspective methods of dearsenication. Precipitation (by iron or aluminium coagulants, lime) and adsorption (by oxides and hydroxides of iron, aluminium or manganese) are among the most popular dearsenication methods. The use of these chemicals entails the formation of poorly soluble arsenates. Since the possibility of the release of arsenic compounds into the water due to the dissolution of formed arsenates depends on its solubility under appropriate conditions, it is necessary to have information about the dependence of arsenates solubility on pH. According to the calculations the solubilities of arsenates of iron(III), aluminium, manganese(II) and calcium are highly dependent on pH. At pH<4, the solubilities of these arsenates increase in the sequence $\text{FeAsO}_4 - \text{Mn}_3(\text{AsO}_4)_2 - \text{AlAsO}_4 - \text{Ca}_3(\text{AsO}_4)_2$. Above pH 4 dependence changes and solubilities of these arsenates increase in the sequence $\text{FeAsO}_4 - \text{AlAsO}_4 - \text{Mn}_3(\text{AsO}_4)_2 - \text{Ca}_3(\text{AsO}_4)_2$.

Keywords: Solubility; Equilibrium Concentration; Iron(III) Arsenate; Aluminium Arsenate; Manganese(II) Arsenate; Calcium Arsenate.

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INTRODUCTION

Water is one of the most important resources of our planet, because for their vital functions all organisms require water without harmful impurities. But anthropogenic and natural factors often make the surface and ground water sources unfit for drinking purpose therefore it is necessary to clean it [1].

Arsenic belongs to chemical elements, which are often found in natural waters and make it unsuitable for consumption without special treatment [1, 2].

At present the maximum acceptable concentration of arsenic in drinking water is 10 µg/l (for the the

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European Union and Ukraine) [3, 4]. Whereas in many countries the content of arsenic in natural water can be up to 1000 µg/l or higher, what is significantly higher than the permissible concentration. For example, in Kurdistan, Iran's western province, the level of arsenic in some water sources reaches 1480 µg/l [5]; in Antafahasta (Chile) the content of arsenic in natural waters reaches 860 µg/l [6]; in Xinjiang Province (China), the concentration of arsenic in the groundwater is 1200 µg/l; in Rehe and Ruihai region of Yunnan alkaline thermal water of hot springs contains arsenic in the range from 83 µg/l to 687000 µg/l [7]. Also, natural waters with

a high content of arsenic are typical for countries such as India, Bangladesh, Taiwan, Vietnam, USA, Mexico, Argentina, Hungary, Ghana, etc. [8].

Long-term consumption of arsenic compounds, contained in drinking water, can cause serious health problems. Cancer (blood, lungs, skin, sinuses, liver, etc.), endocrine, neurological and immunological disorders and genotoxic effect are among the most common consequences of consumption of water, which is polluted by arsenic compounds [1, 2, 9].

It makes dearsenication the necessary stage of the drinking water treatment.

Arsenic removal can be performed by various methods which include precipitation (coagulation/filtration, lime softening, etc), adsorption, ion exchange, membrane processes (microfiltration, ultrafiltration, nanofiltration, reverse osmosis) and others [2]. The precipitation methods are generally based on the usage of iron or aluminium coagulants (coagulation) or lime (lime softening). Adsorption removal of arsenic compounds is often adsorption on oxides and hydroxides of iron, aluminium or manganese.

The use of these chemicals entails the formation of poorly soluble arsenates. Since the possibility of the release of arsenic compounds into the water due to the dissolution of formed arsenates depends on its solubility under appropriate conditions, it is necessary to have information about the dependence of arsenates solubility on pH. Current studies, dealing with arsenates' solubility, are related to geochemistry, geology and metallurgy, while there are no articles on the comparison of the solubility of arsenates, yielded via the application of the most common WT-reagents.

According to the reference data, ferric(III) arsenate is significantly less soluble than calcium or aluminium arsenates ($pK_{S_{Ca_3(AsO_4)_2}} = 18.71$; $pK_{S_{Al_2(AsO_4)_3}} = 15.80$; $pK_{S_{FeAsO_4}} = 20.24$), which makes the application of iron coagulants and adsorbents more perspective than the usage of lime softening and aluminium coagulants and adsorbents. According to the literature, the additional significant advantage is that iron hydroxide absorbs arsenic compounds almost twice better than aluminium hydroxide and binds it tightly [1, 10].

Compounds of manganese are among the popular components of the adsorbents for arsenic compounds removal from aqueous phase. Although the equilibrium constant of manganese(II) arsenate is much smaller than ferric(III) arsenate

($pK_{S_{Mn_3(AsO_4)_2}} = 32.66$), the maximum allowable concentration of manganese in tap water is 0.05 mg/l, while for iron it is much higher 0.2 mg/l [3, 4]. This factor considerably limits the usage of manganese adsorbents due to the threat of severe secondary pollution of water by manganese compounds.

THEORETICAL BACKGROUND. ARSENIC COMPOUNDS IN NATURAL WATERS

In water arsenic can be encountered in the form of various substances, either organic or inorganic. Its type and concentration depend on many factors. The most important factors among these are: the type of water basin; pH of water; redox conditions; composition of rocks near water sources; biological and chemical processes occurring in the water body, etc.

One of the main ways of arsenic release into natural waters is the leaching of arsenic substances from rocks. Mechanisms of arsenic migration are governed by lots of physical and chemical processes. Acid-base and redox balance in water, adsorption, formation of organic compounds (methylation and other processes) hold the main place among these processes. Arsenate acid (H_3AsO_4), arsenite acid (H_3AsO_3) and products of its dissociation are the main forms of arsenic migration in natural waters. For sulfide ground waters the main migration forms of arsenic are anions of thioarsenite acid ($HAsS_2$). According to [11], in neutral natural waters the main forms are: in oxidizing conditions - $H_2AsO_4^-$ and $HAsO_4^{2-}$, less H_3AsO_4 (only in very acidic waters) and AsO_4^{3-} (in very alkaline waters); under reductive conditions - H_3AsO_3 , less $H_2AsO_3^-$ (only in alkaline waters). $HAsO_3^{2-}$ and AsO_3^{3-} almost never occur in the natural pH range (exist only in very alkaline waters). Fig. 1 shows the Eh-pH diagram for As- H_2O system. This diagram shows the prevailing forms of inorganic arsenic compounds at different redox and acid-base conditions.

In sulfide waters with low Eh the anion AsS_2^- is the dominant form, but in very acidic waters $HAsS_2$ is the predominant form [11]. Fig. 2 shows the Eh-pH diagram for As-S- H_2O system.

As seen in Fig. 2, under oxidative conditions, As-S compounds are transformed first into arsenites and then into arsenates.

As a result of biochemical processes Arsenic inorganic compounds are converted to organic ones. Methylation reactions play very important

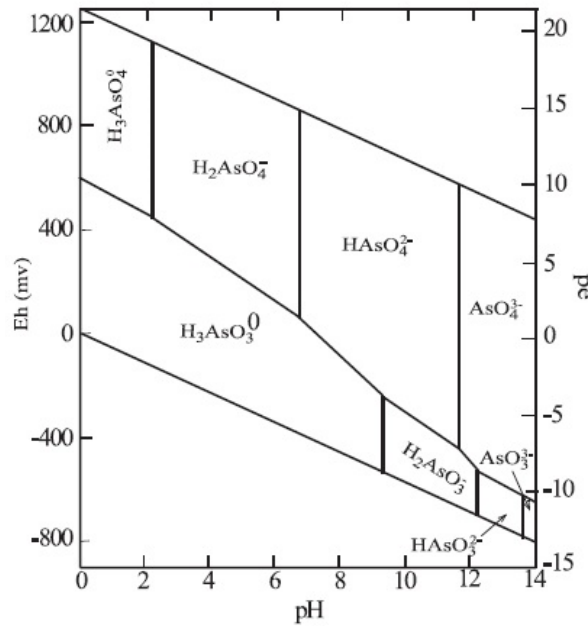


Fig. 1. Eh-pH diagram for As-H₂O system at temperature 25°C and 1 bar pressure [11, 12].

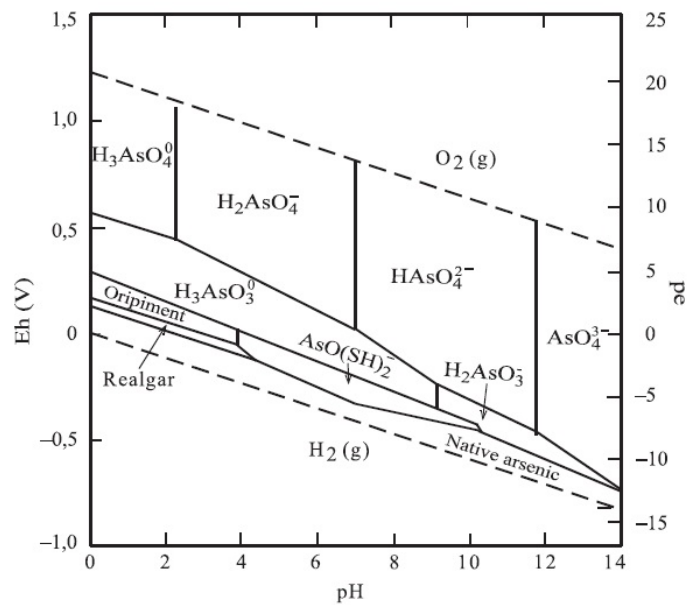
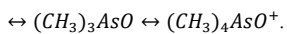
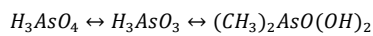
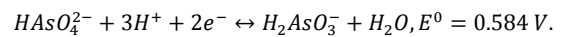
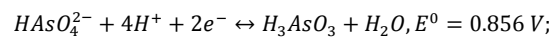
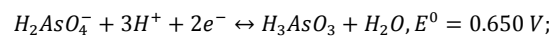
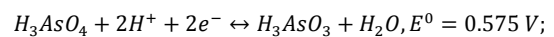


Fig. 2. Eh-pH diagram for As-S-H₂O system at temperature 25°C and 1 bar pressure [11, 13].

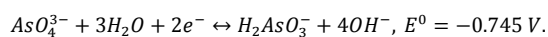
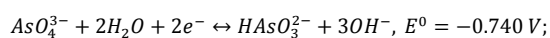
role in this transformation. Monomethylarsonic acid ($\text{CH}_3\text{AsO}(\text{OH})_2$, MMAA) and dimethylarsonic acid ($(\text{CH}_3)_2\text{AsO}(\text{OH})$, DMAA) and their anions are the main arsenic organic components of natural waters. According to [11], the formation of organic arsenic compounds may be as follows:



In the acidic solutions transformation of As(V) to As(III) takes place according to these redox reactions [11, 14, 15]:



In alkaline conditions the following reactions take place [11, 15]:



Biomethylation is the main process that leads to the formation of monomethylarsonic acid ($\text{CH}_3\text{AsO}(\text{OH})_2$, MMAA) and dimethylarsonic acid ($(\text{CH}_3)_2\text{AsO}(\text{OH})$, DMAA). This process occurs involving methylation biological agent. During biomethylation inorganic arsenic compounds are converted to organic arsenic substances by using living organisms (algae, bacteria, fungi, etc.). In other words, the more intense activity the microorganisms possess, the higher concentration of organic arsenic compounds is observed. That's why in the warm season DMAA and MMAA concentration in the water is higher than in the cold period.

According to [11, 16] arsenic can form stable compounds with humic substances, especially with fulvic acids. This process is more characteristic for As(V), than for As(III). This type of arsenic organic substances is typical for areas where there are peat bogs, and also for the water bodies with high content of humic substances (Netherlands, Denmark).

In different types of waters various types of arsenic compounds can be dominant. Thus, for fresh surface water H_2AsO_4^- and HAsO_4^{2-} are the most typical, but in the case of high biological activity in the water body reduction of As(V) to As(III) may take place, then H_3AsO_3 is the most characteristic form. Also under the influence of microorganisms biomethylation with MMAA and DMAA formation can occur. The last two processes (bioreduction of As(V) to As(III) and biomethylation) are particularly characteristic for lakes in the summer period.

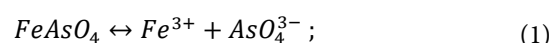
For ground waters there is no typical form of arsenic. The form of arsenic compounds present in groundwater primarily depends on the redox conditions and pH. These indicators vary greatly for different ground waters, so generalizations are not possible. But under oxidative conditions compounds of As(V) prevail, and under reductive conditions compounds of As(III) are more typical. Since in general compounds of As(V) are more typical for natural waters, further calculations are performed in relation to the arsenates.

MATERIALS AND METHODS

Some of these derivations (dependences of FeAsO_4 and AlAsO_4 solubilities on pH) were presented at IWA Specialist Conference in 2016 [1]. But optimization of neutralization of arsenic pollutants, contained in natural waters, is not possible without these dependencies.

Derivation of the dependence of iron(III) and aluminium arsenates solubility on pH

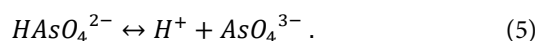
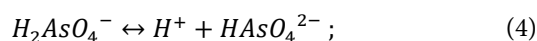
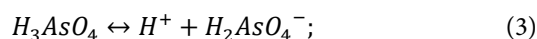
Let's calculate the solubility of iron(III) arsenate. The process of FeAsO_4 solid phase dissolving is accompanied by electrolytic dissociation:



for which the equilibrium state at specified temperature is described by the equilibrium constant:

$$K_{S_{\text{FeAsO}_4}} = [\text{Fe}^{3+}] \cdot [\text{AsO}_4^{3-}] \quad (2)$$

Arsenic acid dissociation occurs in three stages:



Dissociation constants for each stage are derived from the previous reactions:

$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{AsO}_4^-]}{[\text{H}_3\text{AsO}_4]}; \quad (6)$$

$$K_2 = \frac{[\text{H}^+][\text{HAsO}_4^{2-}]}{[\text{H}_2\text{AsO}_4^-]}; \quad (7)$$

$$K_3 = \frac{[\text{H}^+][\text{AsO}_4^{3-}]}{[\text{HAsO}_4^{2-}]}. \quad (8)$$

According to material balance of iron(III) arsenate solubility:

$$S_{\text{FeAsO}_4} = [\text{Fe}^{3+}]; \quad (9)$$

$$S_{\text{FeAsO}_4} = [\text{AsO}_4^{3-}] + [\text{HAsO}_4^{2-}] + [\text{H}_2\text{AsO}_4^-] + [\text{H}_3\text{AsO}_4], \quad (10)$$

where S_{FeAsO_4} is the solubility of FeAsO_4 , mol/L. The value of equilibrium concentrations of arsenate particles, which form the part of the FeAsO_4 solubility equation, can be expressed through the FeAsO_4 equilibrium constant using previous equations:

$$[\text{AsO}_4^{3-}] = \frac{K_{S_{\text{FeAsO}_4}}}{[\text{Fe}^{3+}]}; \quad (11)$$

because $S_{\text{FeAsO}_4} = [\text{Fe}^{3+}]$, then:

$$[AsO_4^{3-}] = \frac{K_{S_{FeAsO_4}}}{S_{FeAsO_4}} \quad (12)$$

In accordance with prior equations:

$$[HAsO_4^{2-}] = \frac{[H^+][AsO_4^{3-}]}{K_3} \quad (13)$$

as $[AsO_4^{3-}] = \frac{K_{S_{FeAsO_4}}}{S_{FeAsO_4}}$, then:

$$[HAsO_4^{2-}] = \frac{[H^+] \cdot K_{S_{FeAsO_4}}}{S_{FeAsO_4} \cdot K_3} \quad (14)$$

After that:

$$[H_2AsO_4^-] = \frac{[H^+][HAsO_4^{2-}]}{K_2} = \frac{[H^+] \cdot [H^+] \cdot K_{S_{FeAsO_4}}}{K_2 \cdot S_{FeAsO_4} \cdot K_3} = \frac{[H^+]^2 \cdot K_{S_{FeAsO_4}}}{S_{FeAsO_4} \cdot K_2 \cdot K_3} \quad (15)$$

$$[H_3AsO_4] = \frac{[H^+][H_2AsO_4^-]}{K_1} = (16)$$

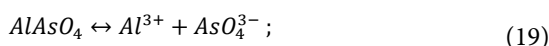
$$\frac{[H^+]}{K_1} \cdot \frac{[H^+]^2 \cdot K_{S_{FeAsO_4}}}{S_{FeAsO_4} \cdot K_2 \cdot K_3} = \frac{[H^+]^3 \cdot K_{S_{FeAsO_4}}}{S_{FeAsO_4} \cdot K_1 \cdot K_2 \cdot K_3}$$

As a result, the material balance equation of iron(III) arsenate solubility takes the following form:

$$S_{FeAsO_4} = \frac{K_{S_{FeAsO_4}}}{S_{FeAsO_4}} + \frac{[H^+] \cdot K_{S_{FeAsO_4}}}{S_{FeAsO_4} \cdot K_3} + \frac{[H^+]^2 \cdot K_{S_{FeAsO_4}}}{S_{FeAsO_4} \cdot K_2 \cdot K_3} + \frac{[H^+]^3 \cdot K_{S_{FeAsO_4}}}{S_{FeAsO_4} \cdot K_1 \cdot K_2 \cdot K_3} \quad (17)$$

$$S_{FeAsO_4} = \sqrt{K_{S_{FeAsO_4}} \cdot \left(\frac{[H^+]^3 + [H^+]^2 \cdot K_1 + [H^+] \cdot K_1 \cdot K_2 + K_1 \cdot K_2 \cdot K_3}{K_1 \cdot K_2 \cdot K_3} \right)} \quad (18)$$

Calculation of aluminium arsenate solubility is performed similarly. As aluminium has the same valence as iron(III), the derivation of the dependence of $AlAsO_4$ solubility on pH doesn't have significant differences. The process of $AlAsO_4$ solid phase dissolving is accompanied by electrolytic dissociation:



for which the equilibrium state at specified temperature is described by the equilibrium constant:

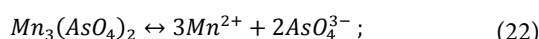
$$K_{S_{AlAsO_4}} = [Al^{3+}] \cdot [AsO_4^{3-}] \quad (20)$$

As a result of the series of formula transformation (similar to formulas (3-17)), the following formula can be obtained:

$$S_{AlAsO_4} = \sqrt{K_{S_{AlAsO_4}} \cdot \left(\frac{[H^+]^3 + [H^+]^2 \cdot K_1 + [H^+] \cdot K_1 \cdot K_2 + K_1 \cdot K_2 \cdot K_3}{K_1 \cdot K_2 \cdot K_3} \right)} \quad (21)$$

Derivation of the dependence of manganese(II) and calcium arsenates solubility on pH

As manganese(II) and calcium have different valence than iron(III) and aluminium, the derivations of the dependences of $Mn_3(AsO_4)_2$ and $Ca_3(AsO_4)_2$ solubilities on pH have some differences. Let's calculate the solubility of manganese(II) arsenate. The process of $Mn_3(AsO_4)_2$ solid phase dissolving is accompanied by electrolytic dissociation:



for which the equilibrium state at specified temperature is described by the following equilibrium constant:

$$K_{S_{Mn_3(AsO_4)_2}} = [Mn^{2+}]^3 \cdot [AsO_4^{3-}]^2 \quad (23)$$

According to material balance of $Mn_3(AsO_4)_2$ solubility the following formulas can be obtained:

$$[Mn^{2+}] = 3 \cdot S_{Mn_3(AsO_4)_2} \quad (24)$$

$$2 \cdot S_{Mn_3(AsO_4)_2} = [AsO_4^{3-}] + [HAsO_4^{2-}] + [H_2AsO_4^-] + [H_3AsO_4] \quad (25)$$

where $S_{Mn_3(AsO_4)_2}$ is the solubility of $Mn_3(AsO_4)_2$, mol/L.

The value of equilibrium concentrations of arsenate particles, which form the part of the $Mn_3(AsO_4)_2$ solubility equation, can be expressed through the $Mn_3(AsO_4)_2$ equilibrium constant using previous equations (6-8, 22-25):

$$[AsO_4^{3-}] = \sqrt{\frac{K_{S_{Mn_3(AsO_4)_2}}}{[Mn^{2+}]^3}} \quad (26)$$

because $[Mn^{2+}] = 3 \cdot S_{Mn_3(AsO_4)_2}$, then:

$$[AsO_4^{3-}] = \sqrt{\frac{K_{S_{Mn_3(AsO_4)_2}}}{27 \cdot S_{Mn_3(AsO_4)_2}^3}} \quad (27)$$

In accordance with equations (6-8, 27):

$$[HAsO_4^{2-}] = \frac{[H^+][AsO_4^{3-}]}{K_3} = \frac{[H^+]}{K_3} \cdot \sqrt{\frac{K_{S_{Mn_3(AsO_4)_2}}}{27 \cdot S_{Mn_3(AsO_4)_2}^3}} \quad (28)$$

Then:

$$[H_2AsO_4^-] = \frac{[H^+] \cdot [HAsO_4^{2-}]}{K_2} = \frac{[H^+]}{K_2} \cdot \frac{[H^+]}{K_3} \quad (29)$$

$$\sqrt{\frac{K_{S_{Mn_3(AsO_4)_2}}}{27 \cdot S_{Mn_3(AsO_4)_2}^3}} = \frac{[H^+]^2}{K_2 \cdot K_3} \cdot \sqrt{\frac{K_{S_{Mn_3(AsO_4)_2}}}{27 \cdot S_{Mn_3(AsO_4)_2}^3}}$$

$$[H_3AsO_4] = \frac{[H^+] \cdot [H_2AsO_4^-]}{K_1} = \frac{[H^+]}{K_1} \cdot \frac{[H^+]^2}{K_2 \cdot K_3} \cdot \frac{K_{SMn_3(AsO_4)_2}}{27 \cdot S_{Mn_3(AsO_4)_2}^3} = \frac{[H^+]^3}{K_1 \cdot K_2 \cdot K_3} \cdot \frac{K_{SMn_3(AsO_4)_2}}{27 \cdot S_{Mn_3(AsO_4)_2}^3} \quad (30)$$

As a result, the material balance equation of the solubility of manganese(II) arsenate takes the following form:

$$2 \cdot S_{Mn_3(AsO_4)_2} = \sqrt{\frac{K_{SMn_3(AsO_4)_2}}{27 \cdot S_{Mn_3(AsO_4)_2}^3}} \quad (31)$$

$$\left(1 + \frac{[H^+]}{K_3} + \frac{[H^+]^2}{K_2 \cdot K_3} + \frac{[H^+]^3}{K_1 \cdot K_2 \cdot K_3}\right);$$

$$S_{Mn_3(AsO_4)_2}^{2,5} = \sqrt{\frac{K_{SMn_3(AsO_4)_2}}{108} \cdot \left(1 + \frac{[H^+]}{K_3} + \frac{[H^+]^2}{K_2 \cdot K_3} + \frac{[H^+]^3}{K_1 \cdot K_2 \cdot K_3}\right)}$$

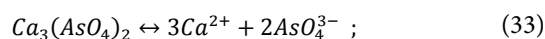
$$S_{Mn_3(AsO_4)_2}^{2,5} = \sqrt{\frac{K_{SMn_3(AsO_4)_2}}{108} \cdot \left(\frac{[H^+]^3 + [H^+]^2 \cdot K_1 + [H^+] \cdot K_1 \cdot K_2 + K_1 \cdot K_2 \cdot K_3}{K_1 \cdot K_2 \cdot K_3}\right)}$$

$$S_{Mn_3(AsO_4)_2} = \left(\frac{K_{SMn_3(AsO_4)_2}}{108}\right)^{0,2} \quad (32)$$

$$\left(\frac{[H^+]^3 + [H^+]^2 \cdot K_1 + [H^+] \cdot K_1 \cdot K_2 + K_1 \cdot K_2 \cdot K_3}{K_1 \cdot K_2 \cdot K_3}\right)^{0,4}$$

Calculation of the solubility of calcium arsenate is performed similarly. As calcium has the same valence as manganese(II), the derivation of the dependence of $Ca_3(AsO_4)_2$ solubility on pH doesn't have significant differences. The process of $Ca_3(AsO_4)_2$ solid phase dissolving is accompanied

by electrolytic dissociation:



for which the equilibrium state at specified temperature is described by the following equilibrium constant:

$$K_{SCa_3(AsO_4)_2} = [Ca^{2+}]^3 \cdot [AsO_4^{3-}]^2 \quad (34)$$

As a result of the series of formula transformation (similar to formulas (24-31)), the following formula can be obtained:

$$S_{Ca_3(AsO_4)_2} = \left(\frac{K_{SCa_3(AsO_4)_2}}{108}\right)^{0,2} \quad (35)$$

$$\left(\frac{[H^+]^3 + [H^+]^2 \cdot K_1 + [H^+] \cdot K_1 \cdot K_2 + K_1 \cdot K_2 \cdot K_3}{K_1 \cdot K_2 \cdot K_3}\right)^{0,4}$$

RESULTS AND DISCUSSION

Using the values of equilibrium constants of $FeAsO_4$, $AlAsO_4$, $Mn_3(AsO_4)_2$ and $Ca_3(AsO_4)_2$ along with dissociation constants of arsenate(V) acid ($K_1=6,46 \cdot 10^{-3}$, $K_2=1,15 \cdot 10^{-7}$, $K_3=3,16 \cdot 10^{-12}$) in obtained formulas (18, 21, 32, 35), the solubility of arsenates of iron(III), aluminium, manganese(II) and calcium at different pH can be calculated. Calculations are performed by using of Microsoft Excel. Table 1 demonstrates theoretical solubility of some arsenates.

Results of the calculations are interpreted via the dependency $lgS = f(pH)$. As the logarithmic scale is useful for large ranges displaying. Fig. 3 shows the appropriate dependences.

The graph and table indicate that the solubilities

Table 1. Theoretical solubility of some arsenates.

pH	S_{FeAsO_4} , mol/L	S_{AlAsO_4} , mol/L	$S_{Mn_3(AsO_4)_2}$, mol/L	$S_{Ca_3(AsO_4)_2}$, mol/L
0	1,57	$2,61 \cdot 10^2$	$2,06 \cdot 10^1$	$1,27 \cdot 10^4$
1	$5,11 \cdot 10^{-2}$	8,48	1,33	$8,21 \cdot 10^2$
2	$2,01 \cdot 10^{-3}$	$3,34 \cdot 10^{-1}$	$1,00 \cdot 10^{-1}$	$6,16 \cdot 10^1$
3	$1,35 \cdot 10^{-4}$	$2,25 \cdot 10^{-2}$	$1,15 \cdot 10^{-2}$	7,11
4	$1,27 \cdot 10^{-5}$	$2,11 \cdot 10^{-3}$	$1,74 \cdot 10^{-3}$	1,07
5	$1,27 \cdot 10^{-6}$	$2,10 \cdot 10^{-4}$	$2,75 \cdot 10^{-4}$	$1,70 \cdot 10^{-1}$
6	$1,33 \cdot 10^{-7}$	$2,21 \cdot 10^{-5}$	$4,53 \cdot 10^{-5}$	$2,79 \cdot 10^{-2}$
7	$1,85 \cdot 10^{-8}$	$3,06 \cdot 10^{-6}$	$9,34 \cdot 10^{-6}$	$5,76 \cdot 10^{-3}$
8	$4,45 \cdot 10^{-9}$	$7,38 \cdot 10^{-7}$	$2,99 \cdot 10^{-6}$	$1,84 \cdot 10^{-3}$
9	$1,36 \cdot 10^{-9}$	$2,25 \cdot 10^{-7}$	$1,16 \cdot 10^{-6}$	$7,13 \cdot 10^{-4}$
10	$4,33 \cdot 10^{-10}$	$7,19 \cdot 10^{-8}$	$4,64 \cdot 10^{-7}$	$2,86 \cdot 10^{-4}$
11	$1,55 \cdot 10^{-10}$	$2,57 \cdot 10^{-8}$	$2,04 \cdot 10^{-7}$	$1,26 \cdot 10^{-4}$
12	$8,70 \cdot 10^{-11}$	$1,44 \cdot 10^{-8}$	$1,29 \cdot 10^{-7}$	$7,93 \cdot 10^{-5}$
13	$7,70 \cdot 10^{-11}$	$1,28 \cdot 10^{-8}$	$1,17 \cdot 10^{-7}$	$7,19 \cdot 10^{-5}$
14	$7,60 \cdot 10^{-11}$	$1,26 \cdot 10^{-8}$	$1,15 \cdot 10^{-7}$	$7,11 \cdot 10^{-5}$

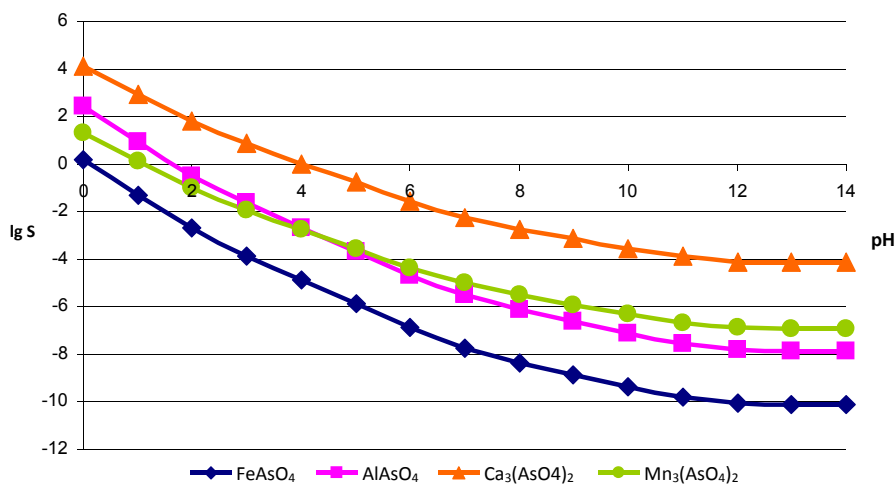


Fig. 3. Effect of pH on the solubility of some arsenates.

of these arsenates are highly dependent on pH. At low pH they are soluble, and at high pH – insoluble. Below pH 4, the solubilities of these arsenates increase in the sequence FeAsO_4 – $\text{Mn}_3(\text{AsO}_4)_2$ – AlAsO_4 – $\text{Ca}_3(\text{AsO}_4)_2$. At $\text{pH} > 4$ dependence changes and solubilities of these arsenates increase in the sequence FeAsO_4 – AlAsO_4 – $\text{Mn}_3(\text{AsO}_4)_2$ – $\text{Ca}_3(\text{AsO}_4)_2$. Thus FeAsO_4 is the least soluble in the whole pH range. Consequently, it is advisable to remove arsenic compounds from waters at high pH by using iron reagents.

The model, shown above, is approximate, since among many processes, taking place in reality, just one process was considered.

The formation of complexes between iron(III), aluminium, manganese(II), calcium and OH^- ions, redox reactions, sorption processes and interaction with different substances, that are present in the water, were not taken into account in order to avoid excessive complication of the system.

It can be assumed that in the pH range, characterized by the minimum solubility of hydroxides (according to reference data it is 6,5-7,5 for Al(III) and 6,5 for Fe(III)), arsenates are removed by adsorption on the surface of hydroxides and oxide-hydroxides, and in the case of other pH values the main process is the formation of insoluble arsenates.

CONCLUSIONS

In water arsenic can be encountered in the form of various substances, either organic or inorganic. Its type and concentration depend on many factors. The most important factors among these are: the

type of water basin; pH of water; redox conditions; composition of rocks near water sources; biological and chemical processes occurring in the water body, etc. But in general compounds of As(V) are more typical for natural waters.

Dearsenication is the necessary stage of the drinking water treatment due to bad consequences of long-term consumption of arsenic compounds, contained in drinking water.

Arsenic removal can be performed by various methods which include precipitation (coagulation/filtration, lime softening, etc), adsorption, ion exchange, membrane processes (microfiltration, ultrafiltration, nanofiltration, reverse osmosis) and others. The precipitation methods are generally based on the usage of iron or aluminium coagulants (coagulation) or lime (lime softening). Adsorption removal of arsenic compounds is often adsorption on oxides, oxide-hydroxides and hydroxides of iron, aluminium or manganese. The use of these chemicals entails the formation of poorly soluble arsenates.

According to the calculations the solubilities of arsenates of iron(III), aluminium, manganese(II) and calcium are highly dependent on pH. At low pH they are soluble, and at high pH – insoluble. At $\text{pH} < 4$, the solubilities of these arsenates increase in the sequence FeAsO_4 – $\text{Mn}_3(\text{AsO}_4)_2$ – AlAsO_4 – $\text{Ca}_3(\text{AsO}_4)_2$. Above pH 4 dependence changes and solubilities of these arsenates increase in the sequence FeAsO_4 – AlAsO_4 – $\text{Mn}_3(\text{AsO}_4)_2$ – $\text{Ca}_3(\text{AsO}_4)_2$. Thus FeAsO_4 is the least soluble in the whole pH range.

Consequently, it is advisable to remove arsenic

compounds from waters at high pH by using iron(III) reagents.

The model, shown above, is approximate, since among many processes, taking place in reality, just one process was considered. The formation of complexes between iron(III), aluminium, manganese(II), calcium and OH⁻ ions, redox reactions, sorption processes and interaction with different substances, that are present in the water, were not taken into account in order to avoid excessive complication of the system.

It can be assumed that in the pH range, characterized by the minimum solubility of hydroxides (according to reference data it is 6,5-7,5 for Al(III) and 6,5 for Fe(III)), arsenates are removed by adsorption on the surface of hydroxides and oxide-hydroxides, and in the case of other pH values the main process is the formation of insoluble arsenates.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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