



MINERALOGIA, 45, No 1-2: 3-12 (2014)

DOI: 10.2478/mipo-2014-0001

www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND

POLSKIE TOWARZYSTWO MINERALOGICZNE



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Original paper

Dissolution of mimetite $Pb_5(AsO_4)_3Cl$ in malic acid solutions

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Received: July 24, 2013

Received in revised form: September 2, 2014

Accepted: September 24, 2014

Available online: October 30, 2014

Abstract. Mimetite $Pb_5(AsO_4)_3Cl$ is the most insoluble lead arsenate mineral and could be used in remediation techniques to reduce As(V) mobility in soils. However, low-molecular-weight organic acids such as malic acid increase its solubility. The effect of malic acid on the dissolution of mimetite strongly depends on the pH of the equilibrium solution. At low pH, mimetite is decomposed mostly by the mechanism of protonation. With increasing pH, the solubility of mimetite decreases and a greater influence in its dissolution is ascribed to complexation of Pb(II) by organic ligands. During dissolution experiments, the amount of arsenic released to solution was > 26% higher in organic solutions than in inorganic solutions, and the amount of lead was > 8% greater. The solubility product of mimetite (K_{sp}) was calculated in order to quantify the thermodynamic stability of the investigated mineral. The value obtained, i.e., -24.52 ± 0.49 fluctuates between the values of -21.69 ± 1.05 and -27.87 ± 0.42 reported in the literature.

Key-words: organic acid, lead, arsenic, solubility product

1. Introduction

Natural concentrations of lead and pentavalent arsenic in soils and waters are usually low and result from volcanism or leaching of rocks and minerals containing As(V) and Pb(II). However, concentration of these elements in the environment is locally greatly increased by anthropogenic processes such as combustion of fossil fuels, mining and smelting of metals, manufacturing of glass and the application of pesticides, etc. (Magalhaes, Silva 2003). Leaching of As(V) and Pb(II) from soils and residues containing

lead arsenates creates a risk to the biosphere and the quality of water (Bhumbla, Keefer 1994; Matschullat 2000).

Arsenic- and lead minerals are relatively numerous but in nature occur occasionally. Among secondary lead arsenates, the most common are schultenite [PbHAsO₄], mimetite [Pb₅(AsO₄)₃Cl], hydroxymimetite [Pb₅(AsO₄)₃OH] and sahlinite [Pb₁₄(AsO₄)₂O₉Cl₄]. However, mimetite as a final product of the transformation of lead arsenates in the environment is thought to be the most prevalent (Bajda 2011). Among all naturally occurring Pb-As minerals, mimetite is relatively insoluble and thermodynamically stable, particularly at pH > 5 which is characteristic to natural waters and soil solutions (Clara, Magalhaes 2002). As a result, it is considered to have great potential for remediation procedures (Bajda 2010). The mobility- and bioavailability of arsenic and lead can be controlled by mimetite crystallization (Twidwell et al. 1994). However, the stability of mimetite decreases at low pH and in the presence of organic acids. The dissolution of apatites through efficient ligand-promoted organic complexation of metals has been observed before (Welch et al. 2002; Manecki, Maurice 2008). Mimetite and apatite are isostructural (Pasero et al. 2010) which suggests that its dissolution may be analogously enhanced by low-molecular-weight organic acids (LMWOAs). The dissolution of mimetite in several LMWOAs and EDTA (ethylenediaminetetraacetic acid) has been investigated before (Bajda 2011), but malic acid was not included. Malic acid C₄H₆O₄ is naturally present in soils, especially in the rhizosphere where it is produced by the bacteria that live in the plant root environment (Jones 1998). Therefore, the experimental determination of the effect of malic acid on the solubility of mimetite in an acidic regime was the purpose of this study.

2. Materials and methods

2.1. Synthesis and characterization of Pb₅(AsO₄)₃Cl

To synthesise 10 g of Pb₅(AsO₄)₃Cl, 400 mL of solution containing 6.29 g of Na₂HAsO₄·7H₂O and 0.50 g of KCl were dissolved in redistilled water. An aliquot of 11.13 g of Pb(NO₃)₂ was dissolved in 400 mL of water in a separate beaker. The solutions were, drop-by-drop, mixed into a 5 L beaker filled initially with 2 L of continuously-stirred redistilled water using a peristaltic pump (2 mL min⁻¹). As the concentrations of substrates rose, a white precipitate formed. After the mixing of the solutions was complete, the suspension was allowed to settle and age for 24 h. The solution was decanted and the precipitate was washed with redistilled water and acetone. The synthetic mimetite powder was dried at 105°C for 24 h. The precipitate was characterized by X-ray diffraction using a Phillips PW 3020 X'Pert-APD Diffractometer system (with Cu anode and graphite monochromator) using a step scan mode at a step size of 0.05°2θ and a rate of 1 s per step.

2.2. Dissolution experiments

Batch dissolution experiments were carried out in two sets of 250 mL high-density polyethylene bottles containing 200 mL of malic acid solutions. The concentrations of malic acid selected for the experiments equated to 0.1, 0.5, 1, 5 and 10 mM. This range of

concentrations is characteristic of natural soil solutions (Jones 1998). Measured pH values for these solutions were 3.81, 3.40, 3.22, 2.88, and 2.74, respectively. Three inorganic solutions with pH adjusted using HNO₃ to 3.8, 3.2, and 2.8, values similar to those of the 0.1, 1.0 and 10.0 mM malic acid solutions, were used as controls, designated as c1, c2 and c3, respectively. In this way, the effect of malic acid could be evaluated regardless of pH. All experiments were unbuffered, allowing for the free drift of pH. Portions of 200 ± 0.1 mg of synthetic Pb₅(AsO₄)₃Cl were added to each bottle. The bottles with suspensions were manually shaken every day and after sampling. Aliquots of 8.5 mL were withdrawn 24, 48 and 120 h after starting experiments by syringe filtering without replenishing the solution after sampling. Concentrations of Pb and As(V) as well as pH were determined in each aliquot. All procedures and analyses were made at room temperature.

2.3. Analysis of solutions

The total Pb concentration was determined by atomic absorption spectroscopy using an AAS spectrometer Philips PU-9100x at 270 nm with calibration based on 7 standards: 1, 2.5, 5, 10, 15, 20, 25 mg Pb/L. Pentavalent As concentration was measured colorimetrically by the molybdenum blue method (Lenoble et al. 2003). Absorbance was measured at 870 nm using a Hitachi 1800 spectrophotometer calibrated with standards in the range of 0.01-5 mg As/L.

2.4. Solubility Product and thermodynamic stability

Speciation- and thermodynamic equilibrium calculations were performed by using computer program PHREEQC (Parkhurst 1995) and modified MINTEQ.v4 thermodynamic database. Thermodynamic data used for the calculations are listed in Table 1. The activities of ionic species were calculated from measured concentrations by converting the results from molarity to molality and applying of the Davies equation or extended Debye-Hueckel equations.

3. Results and discussion

3.1. The effect of pH on mimetite dissolution

Experiments on mimetite dissolution were performed using malic acid solutions of differing pH. A linear decrease of pH with increase in the concentration of malic acid C₄H₆O₄ (Fig. 1) indicates that the acidity results solely from the dissociation of malic acid H₂M according to the equations (Perrin 1965; Serjeant, Dempsey 1979):



The fluctuation of pH with time in unbuffered solutions is presented in Figure 2. The measured pH initially increased both in organic- and in inorganic solutions, than after 24 hours fell down (except for the 5 mM malic acid solution in which it decreased after 48 hours). This is probably a result of protonation of a mimetite surface, partly a result of

As(V) release and arsenate speciation in the form of HAsO_4^{2-} , H_2AsO_4^- , and H_3AsO_4^0 , which is strongly pH-dependent. The results presented in Figure 3 indicate that the solubility of mimetite increases with decreasing pH both in malic acidic solutions and in the inorganic controls. This is in accordance with previous reports (Magalhães, Silva 2003; Bajda, 2011).

TABLE 1

Thermodynamic data used for speciation calculations for $T = 298.15 \text{ K}$

Equilibrium reaction	log K298	Reference
$\text{H}_2\text{O} = \text{OH}^- + \text{H}^+$	-13.993	Alison et al. (1991)
$\text{H}_3\text{AsO}_4 = \text{H}_2\text{AsO}_4^- + \text{H}^+$	-2.24	Smith & Martell (1976)
$\text{H}_3\text{AsO}_4 = \text{H}_2\text{AsO}_4^{2-} + 2\text{H}^+$	-9.20	Smith & Martell (1976)
$\text{H}_3\text{AsO}_4 = \text{AsO}_4^{3-} + 3\text{H}^+$	-20.7	Smith & Martell (1976)
$\text{CO}_3^{2-} + 2\text{H}^+ = \text{CO}_2 + \text{H}_2\text{O}$	16.681	Ball & Nordstrom (1991)
$\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$	10.33	Ball & Nordstrom (1991)
$\text{HCO}_3^- + \text{H}^+ = \text{H}_2\text{CO}_3$	6.351	Ball & Nordstrom (1991)
$\text{Pb}^{2+} + \text{CO}_3^{2-} = \text{PbCO}_3$	6.478	Alison et al. (1991)
$\text{Pb}^{2+} + \text{CO}_3^{2-} + \text{H}^+ = \text{PbHCO}_3^+$	13.2	Alison et al. (1991)
$\text{Pb}^{2+} + 2\text{CO}_3^{2-} = \text{Pb}(\text{CO}_3)_2^{2-}$	9.938	Alison et al. (1991)
$\text{Pb}^{2+} + \text{Cl}^- = \text{PbCl}^+$	1.55	Alison et al. (1991)
$\text{Pb}^{2+} + 2\text{Cl}^- = \text{PbCl}_2$	2.2	Alison et al. (1991)
$\text{Pb}^{2+} + 3\text{Cl}^- = \text{PbCl}_3^-$	1.8	Alison et al. (1991)
$\text{Pb}^{2+} + 4\text{Cl}^- = \text{PbCl}_4^{2-}$	1.46	Alison et al. (1991)
$\text{PbAsO}_4^- + 2\text{H}^+ = \text{Pb}^{2+} + \text{H}_2\text{AsO}_4^-$	11.6746	Marini & Accornero (2007)
$\text{PbHAsO}_4 + \text{H}^+ = \text{Pb}^{2+} + \text{H}_2\text{AsO}_4^-$	4.1056	Marini & Accornero (2007)
$\text{PbH}_2\text{AsO}_4^+ = \text{Pb}^{2+} + \text{H}_2\text{AsO}_4^-$	-1.595	Marini & Accornero (2007)
$\text{Pb}^{2+} + \text{H}_2\text{O} = \text{PbOH}^+ + \text{H}^+$	-7.597	Alison et al. (1991)
$\text{Pb}^{2+} + 2\text{H}_2\text{O} = \text{Pb}(\text{OH})_2 + 2\text{H}^+$	-17.094	Alison et al. (1991)
$\text{Pb}^{2+} + 3\text{H}_2\text{O} = \text{Pb}(\text{OH})_3^- + 3\text{H}^+$	-28.091	Alison et al. (1991)
$\text{Pb}^{2+} + 4\text{H}_2\text{O} = \text{Pb}(\text{OH})_4^{2-} + 4\text{H}^+$	-39.699	Alison et al. (1991)
$2\text{Pb}^{2+} + \text{H}_2\text{O} = \text{Pb}_2\text{OH}^{3+} + \text{H}^+$	-6.397	Alison et al. (1991)
$3\text{Pb}^{2+} + 4\text{H}_2\text{O} = \text{Pb}_3(\text{OH})_4^{2+} + 4\text{H}^+$	-23.88	Alison et al. (1991)
$4\text{Pb}^{2+} + 4\text{H}_2\text{O} = \text{Pb}_4(\text{OH})_4^{4+} + 4\text{H}^+$	-19.988	Alison et al. (1991)
$\text{H}_2(\text{Malate}) = \text{H}^+ + \text{H}(\text{Malate})^-$	3.40	Perrin (1965)
$\text{H}(\text{Malate})^- = \text{H}^+ + \text{Malate}^{2-}$	5.11	Perrin (1965)
$\text{Pb}^{2+} + \text{Malate}^{2-} = \text{Pb}(\text{Malate})$	2.58	Khurana & Gupta (1972)
$\text{Pb}^{2+} + 2\text{Malate}^{2-} = \text{Pb}(\text{Malate})_2^{2-}$	3.27	Khurana & Gupta (1972)
$\text{PbOH}^+ + \text{Malate}^{2-} = \text{PbOH}(\text{Malate})^-$	2.6	Khurana & Gupta (1972)
$\text{PbOH}^+ + 2\text{Malate}^{2-} = \text{PbOH}(\text{Malate})_2^{3-}$	4.14	Khurana & Gupta (1972)

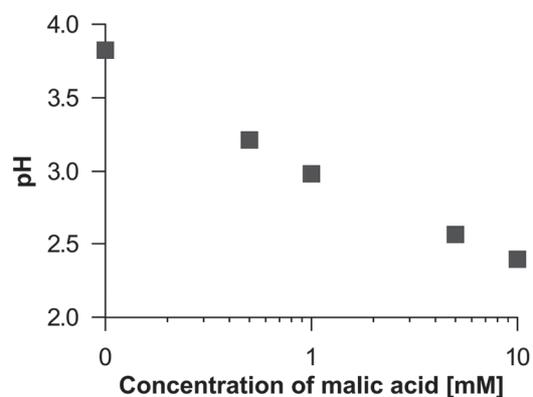


Fig. 1. Effect of malic acid concentration on the acidity of the solution (concentrations of malic acid: 0.1, 0.5, 1, 5, 10 mM)

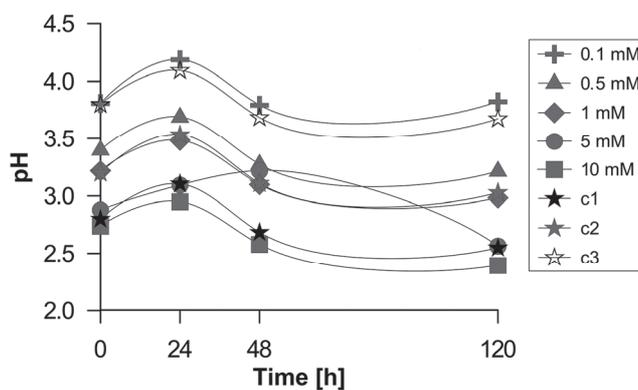


Fig. 2. Fluctuation of pH during 120 h of the dissolution experiment in organic acid (concentrations of malic acid: 0.1, 0.5, 1, 5, 10 mM) and inorganic controls (c1, c2, c3)

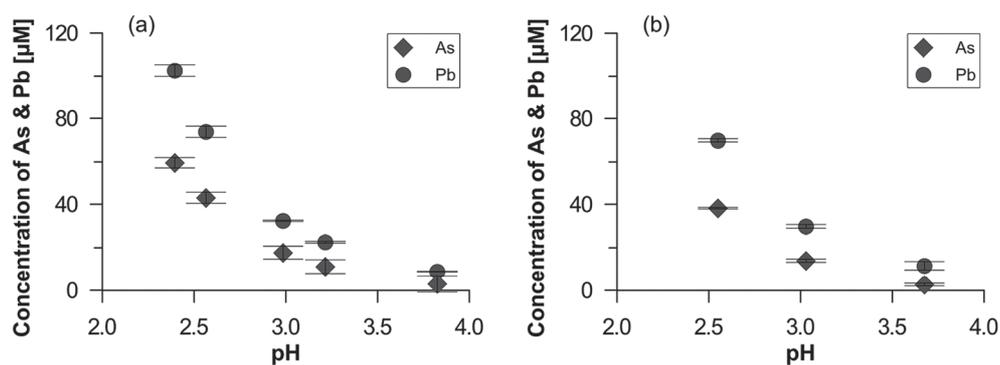


Fig. 3. Effect of pH on As(V) and Pb(II) release from mimetite in the presence of malic acid (a) and inorganic controls (b). Points represent averages of aliquots collected after 24, 48, and 120 h. Error bars: two standard deviations

3.2. The effect of malic acid on mimetite dissolution

The concentrations of Pb measured in solutions sampled after 24, 48 and 120 h of the experiment were similar to each other within two standard deviations (Fig. 4). The same was observed for As(V). This indicates that the system reached equilibrium at all pH values used in the experiments. The *t*-test was used to verify that there was no trend in the data from three consecutive analyses and that the slope was not significantly different from zero at the 95% significance level.

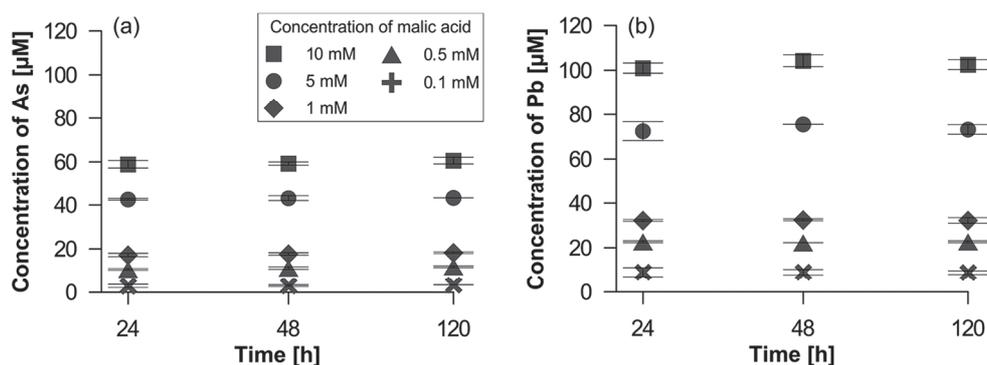


Fig. 4. Concentration of As(V) (a) and Pb(II) (b) during mimetite dissolution as induced by malic acid (average of duplicates). Error bars: two standard deviations.

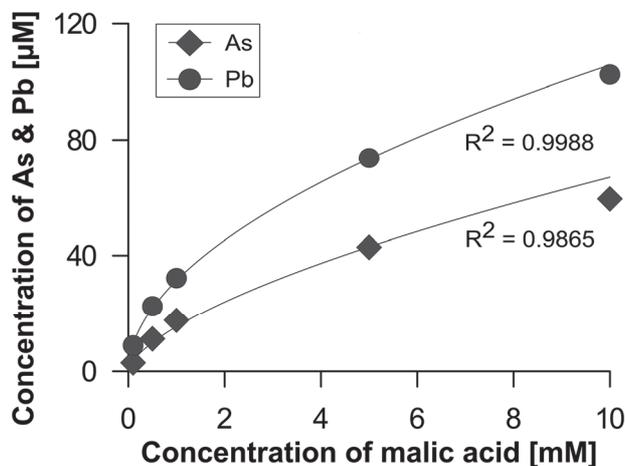


Fig. 5. Concentration of aqueous As(V) and Pb(II) in equilibrium with mimetite as a function of malic acid concentration

The concentrations of Pb and As released to the solution increase with the increase in the concentration of the malic acid (Fig. 5). A molar proportion Pb/As equal to 1.72 ± 0.07 for 5 mM and 10 mM malic acids compares with 1.67 in the solid. With the decrease of malic acid concentration, the ratio increases reaching 1.82 ± 0.11 , 2.01 ± 0.22 , and 2.98 ± 0.58

for 1, 0.5, and 0.1 mM acids, respectively. The errors were calculated from the standard deviation of the nine experiments, in which the results of three consecutive analyses were exactly two standard deviations of the triplicate results (experimental error).

The reason for the As-deficiency is unclear. This may result from selective adsorption of As-species on mimetite particulates present in the suspension or from the precipitation of small amounts of another As-bearing phases. The increase in incongruity of mimetite dissolution with the increase of pH has been observed previously (Bajda 2011).

Comparison of the patterns resulting from the dissolution experiments in the presence of malic acid with those of the control experiments (Fig. 3) indicates that malic acid enhances the solubility of mimetite. To eliminate the effect of pH, the experiment with 5 mM (pH = 2.57) is matched with control 1 (pH = 2.55) and the experiment with 1 mM (pH = 2.99) is matched with control 2 (pH = 3.03) in Figure 6. The increase of mimetite solubility measured by the difference between total As(V) released in the experimental samples and in the controls was 12.5% for 5 mM and 26.5% for 1 mM malic acid. For Pb(II), the difference was 5.6% and 8.6%, respectively. Mimetite dissolves in nitric acid (control experiments) by the mechanism of protonation, the efficiency of which is directly proportional to pH. With decreasing pH, mimetite solubility increases. In malic acid solutions, an additional dissolution mechanism takes place which involves the complexing of lead by organic ligand (Bajda 2011). Similar mechanisms have been described in the case of the dissolution of Pb-apatites in organic acids (Debela et al. 2010). Surface complexation by malate ligands enhances the dissolution processes on the mineral surface. Additionally, the presence of various Pb-malate complexes in solution shifts the dissolution reaction equilibrium, promoting the dissolution according to LeChatelier's principle.

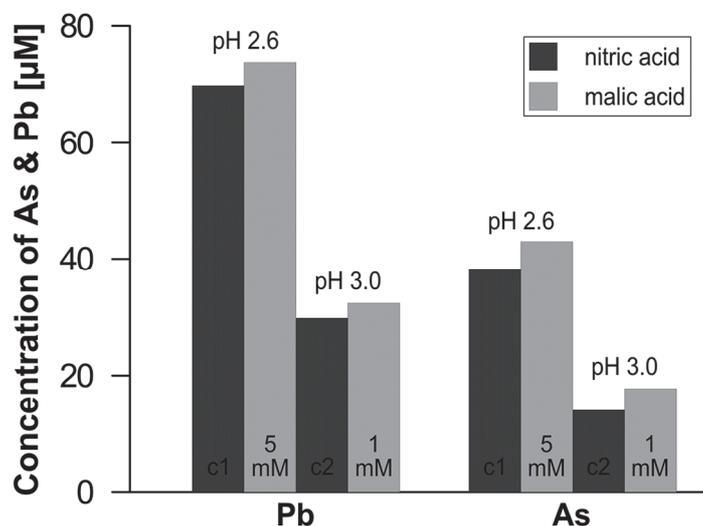


Fig. 6. Comparison of mimetite dissolution efficiencies in inorganic solutions (controls c1 and c2) and malic acid (samples 5 mM and 1 mM) at identical pH

The presence of low-molecular-weight organic acids enhances the solubility of mimetite (Bajda 2011). However, the effect of malic acid is less than that of other acids. Citric acid has the greatest influence on mimetite dissolution among organic acids investigated by Bajda (2011). A comparison of the concentrations of ions released into solution by malic acid in the present study and by citric acid in the study of Bajda (2011) at similar pH and under similar experimental conditions is presented in Figure 7. The experiments with 0.5 mM acids at equilibrium pH of 3.22 for malic acid and 3.48 for citric acid are matched. The observed concentrations equate to $22.6 \pm 0.5 \mu\text{M}$ As(V) and $11.3 \pm 1.2 \mu\text{M}$ Pb(II) in malic acid and $47.0 \pm 0.5 \mu\text{M}$ As(V) and $26.5 \pm 0.4 \mu\text{M}$ Pb(II) in citric acid. Two other LMWOAs investigated by Bajda (2011) also exhibited stronger effects. This indicates that, in terms of mimetite stability or mobilization of Pb and As in the environment, malic acid poses less of a threat than other organic acids.

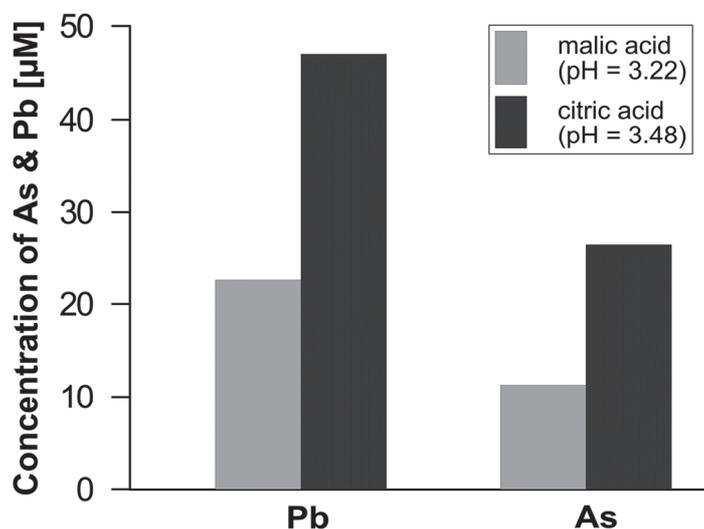
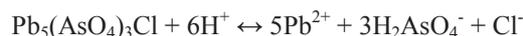


Fig. 7. Comparison of concentrations of As(V) and Pb(II) released to solution by 0.5 mM malic acid (this study) and citric acid (Bajda 2011) at similar pH and experimental conditions

4. Solubility product of mimetite

The solubility product of mimetite (K_{SP}) was calculated by using the results from the experiments with 5 mM and 10 mM malic acid, where congruent dissolution was observed. Based on measured pH and ion concentrations as well as the stoichiometry of Pb, As, and Cl in mimetite, equilibrium aqueous activities of Pb^{2+} , H_2AsO_4^- and Cl^- were calculated by applying the PHREEQC speciation model (Parkhurst 1995). Thermodynamic data used in the calculations are listed in Table 1. At equilibrium, K_{SP} is equal to the ion activity product (IAP) which for the dissolution reaction of $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ in acidic conditions:



can be written:

$$\log IAP = 5\log\{Pb^{2+}\} + 3\log\{H_2AsO_4^-\} + \log\{Cl^-\} + 6pH$$

where the brackets denote the activities. The average equilibrium logIAP values for 5 mM and 10 mM malic acid are similar and equal -24.53 ± 0.49 and -24.51 ± 0.49 , respectively. This value lies between the value of -21.69 ± 1.05 (at pH 2.1) reported by Bajda et al. (2007) and the results of Inegbenebor et al. (1989) who reported a K_{sp} equal to -27.87 ± 0.42 (at pH 2.36).

5. Environmental implication

The results of the experiments demonstrate that, as is the case with other LMWOAs, the presence of malic acid in solution enhances the solubility of mimetite. This can potentially result in decomposition of mimetite present in polluted soils and the release of Pb(II) and As(V) into natural waters. These elements may pose little threat to the environment when bound in the relatively stable form of mimetite $Pb_5(AsO_4)_3Cl$. Numerous remediation methods based on induced precipitation of lead apatites, including mimetite, have been proposed in the literature (Clara, Magalhaes 2002; Miretzky, Fernandez-Cirelli 2008; Bajda 2010). To ensure the long term efficiency of these methods, mineral stability should be maintained by minimizing exposure to solutions containing organic acids.

Acknowledgements. The research was financed by the AGH University of Science and Technology statutory grant no. 11.11.140.319.

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