Monatshefte für Chemie 134, 735–743 (2003)
DOI 10.1007/s00706-002-0581-9

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Invited Review

Stability of Lead(II) Arsenates

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Received October 11, 2002; accepted October 30, 2002

Summary. Predictions of lead arsenate solubility and thermodynamic stability have been based on the value of the solubility constant for a precipitate with the general composition $Pb_3(AsO_4)_2$. The solubility of this precipitate is high and lead arsenate is considered to be unsuitable for lead and arsenic control in the environment. Standard *Gibbs* energy of formation for bayldonite, duftite, mimetite, philipsbornite, and schultenite can be found in the literature from solubility studies. From these data, stability diagrams were established for the environmentally relevant lead containing solid phases – anglesite, cerussite, schultenite, and mimetite. The diagrams lead to the conclusion that mimetite is a lead arsenate that can be used for remediation techniques.

Keywords. Solubility; Lead arsenate; Mimetite; Environment.

Introduction

Synthetic lead arsenates became important when, in 1893, *Moulton* recommended their use as insecticides [1]. *Murphy* and *Aucott* [2] estimate that 22×10^6 kg of lead arsenate had been used in the state of New Jersey, USA, during the period from 1900 to 1980. Lead arsenate is the general designation for a precipitate with the attributed formula $Pb_3(AsO_4)_2$. In former times it could also designate the lead hydrogenarsenate ($PbHAsO_4$) or even lead pyroarsenate ($Pb_2As_2O_7$) [1].

Minerals containing lead and arsenate are relatively numerous but rare in nature. Mimetite is probably the most common secondary lead arsenate mineral [3]. Lead arsenate minerals incorporate other cations and anions in their crystal structure. Only schultenite, mimetite, sahlinite, and georgiadesite contain lead as a single cation. Table 1 shows names and formulae of lead arsenate minerals with the simplest stoichiometries.

Arsenic is widespread in nature, generally at low concentrations. The mean values of arsenic content in soils, the earth's crust, and sediments are quoted by

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Dedicated to Professor *Heinz Gamsjäger* on the occasion of his 70th birthday

Table 1. Simple lead(II)-containing arsenate minerals

Mineral	Stoichiometry
Schultenite	$PbHAsO_4$
Mimetite	$Pb_5(AsO_4)_3Cl$
Sahlinite	$Pb_{14}(AsO_4)_2O_9Cl_4$
Georgiadesite	$Pb_{16}(AsO_4)_4(OH)_6Cl_{14}$
Helmutwinklerite	$PbZn_2(AsO_4)_2 \cdot 2H_2O$
Duftite	$PbCu(AsO_4)(OH)$
Gabrielsonite	$PbFe(AsO_4)(OH)$
Arsendescloizite	$PbZn(AsO_4)(OH)$
Bayldonite	$PbCu_3(AsO_4)_2(OH)_2$
Hedyphane	$Pb_3Ca_2(AsO_4)_3Cl$
Philipsbornite	$PbAl_3(AsO_4)_2(OH)_5 \cdot H_2O$
Beudantite	$PbFe_3(AsO_4)(SO_4)(OH)_6$
Arsentsumebite	$Pb_2Cu(AsO_4)(SO_4)(OH)$
Jamesite	$Pb_2Zn_2Fe_5(AsO_4)_5O_4$

Sparks [4] as 6, 1.5, and 7.7 mg kg^{-1}. Higher concentrations of arsenic can be found in localized regions where arsenosulphide deposits exist, and in residues from mining and ore processing, metallurgy, industry, agriculture, and wood preservation.

The major environmental concern about arsenic is not related to its presence in soils, sediments, and solid wastes in anomalous amounts but the possibility of it being present in the percolating waters in anomalous concentrations. The total concentration of arsenic in the aqueous systems percolating in oxidized zones is determined predominantly by the solubility of solid metal arsenates and it was found that As(V) species are predominant under moderate to high oxidation conditions [5]. Changes in temperature, redox potential, *pH*, and ionic composition of percolating aquatic solutions promote the formation of different solid phases giving associations of minerals. Cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), and anglesite ($PbSO_4$) are the most commonly reported secondary lead minerals associated with lead arsenates and their presence can control the lead concentration in the aquatic environment.

In order to understand the relationship between the possible association of these solid phases and the composition in percolating waters it is necessary to have accurate values for the solubility of lead containing minerals. Cerussite, hydrocerussite, and anglesite have established values for their standard *Gibbs* energy of formation, but almost no experimental results are recorded in the literature for the solubility of lead arsenates. *Magalhães et al.* [6] have reported experimental results for schultenite, duftite, and bayldonite at 298 K, *Inegbenebor et al.* [3] reported experimental results for the mimetite–pyromorphite solid solution at the same temperature, *Schwab et al.* [7] determined the standard *Gibbs* energy of formation of philipsbornite at 333 K, and an approximate value for the solubility constant of $Pb_3(AsO_4)_2$ is used from *Chukhlantsev*'s [8] experimental data obtained at 294 K. *Roussel et al.* [9] estimated the value of 10^{-15} for the solubility constant of beudantite, at 298 K, using the standard *Gibbs* energy of formation of

Table 2. Standard *Gibbs* energies of formation, at 298 K, of lead minerals

Mineral	$\Delta_f G^\circ/\text{kJ mol}^{-1}$	Ref.
Anglesite	– 813.21	[10, 11]
Cerussite	– 625.3	[10]
Schultenite	– 809.62	[6, 10–12]
Mimetite	– 2675.5	[3, 10–12]
Duftite	– 961.6	[6, 10–12]
Bayldonite	– 1810.6	[6, 10–12]
Philipsbornite	– 4333.8[a]	[7]

[a] at 333 K

Table 3. Standard *Gibbs* energies of formation, at 298.15 K, of relevant species

Species	$\Delta_f G^\circ/\text{kJ mol}^{-1}$	Ref.
H_2O (l)	– 237.141	[10]
CO_2 (g)	– 394.37	[10]
Cu^{2+} (aq)	65.52	[10]
Pb^{2+} (aq)	– 24.40	[10]
OH^- (aq)	– 157.328	[10]
Cl^- (aq)	– 131.27	[10]
AsO_4^{3-} (aq)	– 648.41	[11]
$HAsO_4^{2-}$ (aq)	– 714.60	[11]
$H_2AsO_4^-$ (aq)	– 754.33	[11, 12]
$H_3AsO_4^o$ (aq)	– 767.11	[11, 12]
SO_4^{2-} (aq)	– 744.63	[10]

plumbojarosite ($Pb_{0.5}Fe_3(SO_4)_2(OH)_6$) and assuming an equilibrium state between both minerals. Table 2 presents the standard *Gibbs* energy of formation of the relevant lead minerals calculated from experimental solubility constants combined with the standard *Gibbs* energy of formation given in Table 3.

It is the aim of this work to establish stability diagrams for the environmentally relevant lead containing solid phases – anglesite, cerussite, schultenite, and mimetite – from the experimentally determined thermodynamic data. The derived stability diagrams will be used to explain some observed environmental processes, to analyse the accuracy of the value of the solubility constant determined by *Chukhlantsev* [8] for a precipitate with the general formula $Pb_3(AsO_4)_2$, and shed some light on the use of lead arsenates for disposal purposes.

Stability Diagrams

Stability field diagrams for the secondary lead(II) arsenate minerals schultenite, mimetite, duftite, and bayldonite together with lammerite ($Cu_3(AsO_4)_2$), olivenite ($Cu_2(AsO_4)(OH)$), cornubite ($Cu_5(AsO_4)_2(OH)_4$), and clinoclase ($Cu_3(AsO_4)(OH)_3$) have already been drawn and discussed by *Magalhães et al.* [6], and *Inegbenebor et al.* [3] for $a_{\text{lead}} = 10^{-7}$, and $a_{\text{chloride}} = 10^{-3}$, 10^{-2}, and 10^{-1}. A stability field diagram for the lead(II) arsenate minerals, schultenite and mimetite, is shown

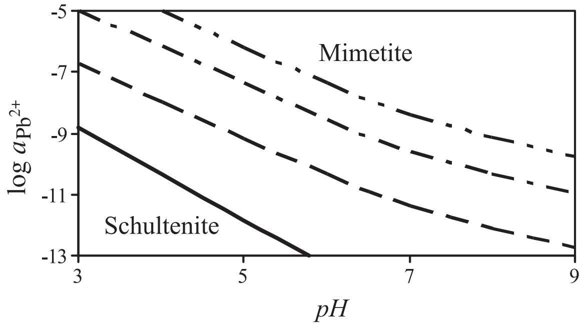

Fig. 1. Stability field diagram for schultenite and mimetite, $a_{\mathrm{chloride}} = 10^{-3}$. The solid line corresponds to a three phase equilibrium schultenite–mimetite–aqueous solution. Dashed curves correspond to equilibrium of mimetite and aqueous solutions of total arsenate activity 10^{-8} (– · · –), 10^{-6} (– · –), and 10^{-3} (–––), and $a_{\mathrm{chloride}} = 10^{-3}$

in Fig. 1. Using the thermodynamic data from Tables 2 and 3 the equilibrium boundary for the transformation

$$3\mathrm{PbHAsO_4(s)} + 2\mathrm{Pb^{2+}(aq)} + \mathrm{Cl^-(aq)} \rightleftharpoons \mathrm{Pb_5(AsO_4)_3Cl\,(s)} + 3\mathrm{H^+(aq)} \qquad (1)$$

was calculated, at 298 K, to be given by the expression

$$\log a_{\mathrm{Pb}^{2+}} = -4.33 - 1.5\,pH \qquad (2)$$

for $a_{\mathrm{chloride}} = 10^{-3}$, which corresponds to a weakly saline groundwater [3]. In Fig. 1 the curves corresponding to total arsenate activity of 10^{-8}, 10^{-6}, and 10^{-3}, and $a_{\mathrm{chloride}} = 10^{-3}$ calculated from the dissolution reaction

$$\mathrm{Pb_5(AsO_4)_3Cl\,(s)} + 6\mathrm{H^+(aq)} \rightleftharpoons 5\mathrm{Pb^{2+}(aq)} + 3\mathrm{H_2AsO_4^-(aq)} + \mathrm{Cl^-(aq)} \qquad (3)$$

are also plotted.

Associations of lead arsenate minerals with anglesite and especially with cerussite can be found in nature [3]. Anglesite is a secondary lead(II) mineral derived from oxidation of lead containing sulfides and sulfosalts that can change to cerussite and mimetite [13, 14]. The transformation of one mineral into another can be indicated by Eqs. (4)–(6), from which the equilibrium boundaries drawn in the stability field diagram of Fig. 2 were established.

$$\mathrm{PbSO_4(s)} + \mathrm{CO_2(g)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{PbCO_3(s)} + \mathrm{SO_4^{2-}(aq)} + 2\mathrm{H^+(aq)} \qquad (4)$$

$$\begin{aligned} &\mathrm{PbCO_3(s)} + 4\mathrm{Pb^{2+}(aq)} + \mathrm{Cl^-(aq)} + 3\mathrm{HAsO_4^{2-}(aq)} \rightleftharpoons \\ &\rightleftharpoons \mathrm{Pb_5(AsO_4)_3Cl\,(s)} + \mathrm{CO_2(g)} + \mathrm{H_2O\,(l)} + \mathrm{H^+(aq)} \end{aligned} \qquad (5)$$

$$\begin{aligned} &\mathrm{Pb_5(AsO_4)_3Cl\,(s)} + \mathrm{SO_4^{2-}(aq)} + 3\mathrm{H^+(aq)} \rightleftharpoons \\ &\rightleftharpoons \mathrm{PbSO_4(s)} + 4\mathrm{Pb^{2+}(aq)} + \mathrm{Cl^-(aq)} + 3\mathrm{HAsO_4^{2-}(aq)} \end{aligned} \qquad (6)$$

Using the thermodynamic data from Tables 2 and 3 the equilibrium boundaries for the Eqs. (4)–(6) were calculated, at 298 K, under the following conditions: $P\mathrm{CO_2}/p^\circ = 10^{-3.47}$, $a_{\mathrm{sulfate}} = 10^{-4}$, $a_{\mathrm{chloride}} = 10^{-3}$, and $a_{\mathrm{arsenate}} = 10^{-8}$ (full lines), and the change in the mimetite stability field with increasing arsenate

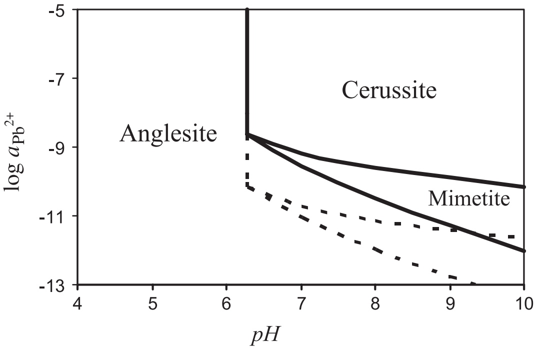

Fig. 2. Stability field diagram for anglesite, cerussite, and mimetite. The boundaries in full lines are drawn for $a_{\text{chloride}} = 10^{-3}$, $a_{\text{arsenate}} = 10^{-8}$, $a_{\text{sulfate}} = 10^{-4}$, and $PCO_2/p^\circ = 10^{-3.47}$. Each full line corresponds to a three phase equilibria – two adjacent solid phases and aqueous solution. Dotted lines indicate the change in the mimetite stability field with increasing total arsenate activity ($a_{\text{arsenate}} = 10^{-6}$)

activity ($a_{\text{arsenate}} = 10^{-6}$) is shown by the dotted lines. As can be seen from Eqs. (4)–(6) relations between mimetite and the other secondary lead minerals are complicated as they involve several variables. The diagram presented in Fig. 2 is an attempt to delineate a possible relation between mimetite and the two other environmentally important lead minerals. The values assigned to the necessary variables were based on literature data. For the relation between the carbon dioxide partial pressure (PCO_2) and the standard pressure (p°) of the normal atmosphere the value referred by *Robins* [15] was considered. *Williams* [16] presented the value of 1.2×10^{-4} mol dm^{-3} for the world average river water concentration of sulfates, and *Sparks* [4] refers that typical sulfate concentrations in groundwaters fall in the range 3×10^{-4} to 2×10^{-3} mol dm^{-3}. The value of 10^{-4} was considered for the total activity of sulfate in the calculations of the equilibrium boundaries of anglesite with the other solid phases. Typical chloride concentrations in groundwaters fall in the range 3×10^{-5} to 2×10^{-3} mol dm^{-3} [4]. The value of 10^{-3} used for the total activity of chlorides corresponds, as referred, to a weakly saline groundwater [3]. Natural waters in general contain low levels of total arsenic. *Williams* [17] suggested that the normal values for total arsenic in natural waters must be in the range 10^{-8} to 10^{-7} mol dm^{-3}, and *Sadiq* [18] assumed total arsenic concentrations in seawater to be 10^{-8} mol dm^{-3}. *Sadiq* [19] also mentioned that arsenic in contaminated groundwaters can reach values as high as 10^{-6} mol dm^{-3}. Higher values for sulfates and arsenates can be found in localized regions as is the case of generation of acid mine drainage.

Discussion and Conclusions

Lead arsenate solubility is generally considered to be high and the solid unsuitable for lead and arsenic control in the environment. In the absence of more accurate data, predictions of lead arsenate solubility and thermodynamic stability have been based on the value of the solubility constant determined by *Chukhlantsev* [8] for a precipitate with the general composition $Pb_3(AsO_4)_2$ ($\log K_{S0} = -35.39$). This value has been used in compilations and as reference to discuss the solubility and stability of lead arsenates in the environment. It is present in the *Sillen* and *Martell* [20] compilation of stability constants. *Hess* and *Blanchar* [21], to predict the relative stability of several arsenates in soils, compared their experimental results for the solubility constant of a precipitate with the formula $Pb_3(AsO_4)_2 \cdot 4H_2O$ with *Chukhlantsev*'s [8] value. The experimental data presented by *Hess* and *Blanchar* [21] show that solutions of *pH* 2.90, 3.64, and 4.23 were in equilibrium with $PbHAsO_4$, but other solid phases could be present since the formulae of the precipitates were determined by chemical analysis. *Chukhlantsev*'s [8] value was used by *Monhemius* [22] to delineate the solubility curve of $Pb_3(AsO_4)_2$ in order to modulate possible techniques of heavy metals removal from leach liquors in hydrometallurgical processes. Later *Robins* [15] also used this value to outline the stability diagram for the lead(II)–arsenic(V)–water system. The outlined diagram for equal activities of lead and arsenic, and $PCO_2/p^\circ = 10^{-3.47}$ showed that lead(II) arsenate ($Pb_3(AsO_4)_2$) would be a stable phase for lead(II) and arsenate activities higher than 10^{-5}, and *pH* in the range 2 to 8 with arsenic and lead activities of 10^{-1}. More recently *Sadiq* [19] suggests that most of the thermochemical data on As species published until 1981 were not reliable. For the reaction

$$Pb_3(AsO_4)_2(s) + 2H^+(aq) \rightleftharpoons 3Pb^{2+}(aq) + 2HAsO_4^{2-}(aq) \qquad (7)$$

Sadiq [18, 19] presented the value of the solubility constant extrapolated to zero ionic strength, at 298 K, as $\log {}^*K^\circ_{pS0} = -9.07$. This value is higher than that obtained from *Chukhlantsev*'s [8] experiments which indicates a more soluble solid phase than assumed previously. *Sadiq* [18, 19] arrived at the conclusion that $Pb_3(AsO_4)_2$ was a rather soluble solid.

The widespread use of *Chukhlantsev*'s [8] solubility data for prediction of lead arsenate behavior in the environment deserves an analysis of the solid phase composition that gave this value and a comparison with the known values of the solubility constant determined for the lead arsenates presented in Table 2. *Chukhlantsev* [8] prepared a precipitate of lead arsenate, with an atomic Pb/As ratio of 1.51, by pouring together, at 60°C, lead acetate and sodium arsenate in the stoichiometric proportion of 3:2. *Mellor* [1] referred in 1929 that there was no easy process to prepare $Pb_3(AsO_4)_2$ by wet methods and stated that this solid was relatively unstable and could only exist within very limited conditions. *Tartar* and *Robinson* [23] had concluded in 1914 that pure lead arsenate with the composition $Pb_3(AsO_4)_2$ could not be obtained from the mixture of aqueous solutions of lead acetate and sodium arsenate. These authors mentioned that reaction between lead acetate and sodium arsenate was affected by temperature, concentration, and rate of addition of reagents. Mixtures with different final compositions could be obtained. In fact *Chukhlantsev* [8] indicated that the chemical analysis of his precipitates only gave the mean chemical composition of the solid and no other information was presented in order to draw conclusions about the actual composition of the precipitate.

Chukhlantsev [8] calculated the solubility constant for lead arsenate from experimental values of *pH* and the total concentration of lead. The total concentration of arsenate was calculated assuming the solid dissolved congruently according to the established stoichiometry. As stated by *Tartar* and *Robinson* [23] the precipitate should be a mixture of phases and independent determinations of the total concentration of arsenate should be done.

The value of the solubility constant given by *Chukhlantsev* [8] for lead arsenate with the formula $Pb_3(AsO_4)_2$ may not be accurate, as the solid was not well characterised. The attempt to incorporate the solid phase with the formula $Pb_3(AsO_4)_2$ in the diagram of Fig. 1, using the solubility constant proposed by *Chukhlantsev* [8], showed that it is thermodynamically unstable in relation to schultenite and mimetite. No stability field was possible to define.

The diagram of Fig. 1 shows that schultenite will be a stable phase only for low *pH*, low activity of chloride ions, and relatively high concentrations of lead and arsenate. Mimetite is a much less soluble solid phase and is formed even from weakly saline groundwaters. *Symes et al.* [24] reported the presence of schultenite in a heavily oxidized outcrop of the Deer Hills Vein, Cumbria, England, partly filled with beudantite. These authors pointed out that schultenite appears to be a weathering product of arsenic- and lead-rich sulphide veins.

Figures 1 and 2 show that schultenite and anglesite occupy the same stability field and changes from one phase to another may occur. *Spencer* [25] described the first occurrence of schultenite. Pseudomorphs of anglesite after schultenite and mimetite crystallized on anglesite and mixed with bayldonite and schultenite were found in Tsumeb, Namibia. *Falls et al.* [13] reported the existence in King County, Washington, USA, of well isolated crystals of schultenite and schultenite associated with pale yellow mimetite crystals tufted with younger generation mimetite and cerussite. In the same place it was common to find cerussite pseudomorphs of mimetite and associations of mimetite, cerussite, and anglesite. The stability field diagrams (Figs. 1 and 2) illustrate the chemical conditions under which the various solid phases crystallize from aqueous solutions and can explain the described paragenetic sequences.

Schultenite is very rare as mineral but solids with the same composition and crystal structure have long been synthesised (*Berzelius* was the first to prepare it in 1819 [1]) and they have widespread use as pesticides in agriculture. Typical lead arsenate pesticides are usually mixtures that contain lead hydrogenarsenate [23, 26]. *McDonnell* and *Graham* [27] suggested that hydrolysis of lead hydrogenarsenate from the pesticides resulted in chemical burning of leaves as a result of its changing to mimetite and formation of acidic solutions. This process is shown by Eq. (1) and can be predicted from Fig. 1.

In contrast to the current statement that lead arsenate is a moderately soluble solid, Fig. 2 shows that mimetite must be the lead arsenate phase to be considered on discussing solubility and stability of lead and arsenate containing compounds. Mimetite is isostructural with pyromorphite ($Pb_5(PO_4)_3Cl$) and all members of the pyromorphite–mimetite solid solution have the same value for the solubility constant, at 298 K, within experimental error [3]. The composition of the solid solution members is congruent with the composition of the aqueous solution in relation to the relative total amounts of dissolved phosphates and arsenates. *Nriagu* [28] proposed in the early 1970s the precipitation of lead phosphates as a method to immobilize lead in contaminated soils and wastes due to low solubility of these solids. Diagrams of Figs. 1 and 2 show that mimetite is a very stable lead arsenate phase under very low total concentrations of lead and arsenate and it has a stability field that covers the *pH* range of natural waters, even when they contain dissolved carbonate and sulfate ions. The crystallization of mimetite is a method already used to remove dissolved arsenic from aqueous solutions [29]. The mobility of arsenate can be increased by the presence of phosphates and particular attention has to be given to this fact for disposal purposes. The very low solubility of mimetite will assure trace concentrations of lead and arsenate in the aquatic systems under oxidizing conditions. Mimetite must be considered when stability diagrams for lead(II) and arsenic(V) containing systems are constructed.

Acknowledgements

The authors thank *E. Königsberger* from Murdoch University, Perth, Australia, for all helpful comments and advice.

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