The Effect of Potential Aqueous Pollutants on the Solubility of Pb^{+2} in Cerussite—Calcite Phases

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The results of this work show:

1. Pb^{+2} is rapidly immobilized from aqueous solutions using calcite or aragonite, $CaCO_3$, and the Pb^{+2} is precipitated as $PbCO_3$ (cerussite) on the surface of the $CaCO_3$ (the Pb^{+2}—$CaCO_3$ phases),

2. using $CaCO_3$, the concentration of Pb^{+2} in certain solutions can be reduced below environmentally tolerated concentrations, and

3. organics present in solutions and natural waters can mobilize Pb^{+2} from Pb^{+2}—calcite phases; with effluent waters from a paper factory, and $1:1$ Ca^{+2}—$EDTA$ being more effective than lignin sulfonates, $1:1$ Ca^{+2}-tartrate, soap, detergent, water from a sewage treatment plant, and ordinary river water.

(Keywords: Pb^{+2}—calcite phases; Pb^{+2}-immobilization; Pb^{+2}-mobilization)

Der Einfluß von Verunreinigungen wäßriger Lösungen auf die Löslichkeit von Pb^{+2} in Cerussit—Calcit Phasen

Die Ergebnisse dieser Arbeit zeigen, daß:

1. Pb^{+2} aus wäßrigen Lösungen mit Calcit oder Aragonit, $CaCO_3$, rasch entfernt werden kann, wobei Pb^{+2} als $PbCO_3$ (Cerussit) an der Oberfläche von $CaCO_3$ (den Pb^{+2}—$CaCO_3$-Phasen) niedergeschlagen wird,

2. sich die Pb^{+2}-Konzentration in bestimmten Lösungen mit $CaCO_3$ unter die nach Ö-Norm erlaubte Grenze senken läßt,

3. organische Substanzen in wäßrigen Lösungen und natürlichen Wässern zunächst in Pb^{+2}-Calcit-Phasen fixiertes Pb^{+2} wieder mobilisieren können, wobei die Abwässer einer Papierfabrik und $1:1$ Ca^{+2}—$EDTA$ stärker wirken als Ligninsulfonate, $1:1$ Ca^{+2}-Tartrat, Seife, Waschmittel, Wasser einer Kläranlage und gewöhnliches Flußwasser.

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Introduction

The immobilization of pollutant heavy metals by sediments and the mobilization of heavy metals by aqueous organics are subjects of ecological interest[1]. As long as metal pollutants are bound in solid compounds they present less of a biological danger than when they are solubilized. Lead is a common pollutant which is accumulated by biological systems[2]. Lead in the plus two oxidation state, Pb^{+2}, forms a slightly soluble carbonate[3]. Thus Pb^{+2} can be precipitated from natural waters[4] in the presence of the naturally-occurring minerals calcite and aragonite, $CaCO_3$.
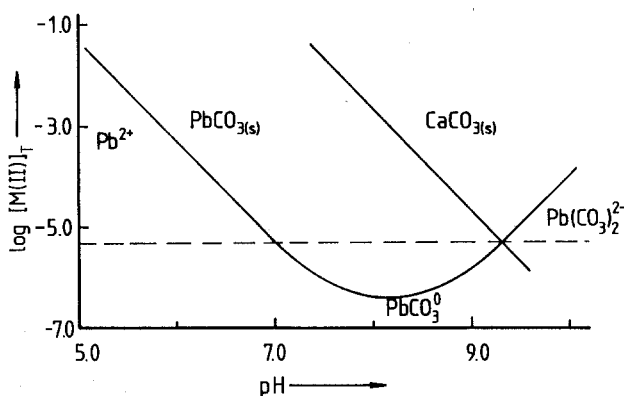

Fig. 1. Solubility of cerussite ($PbCO_3$) and calcite ($CaCO_3$) as a function of pH ($25\,°C$, $I = 0.3\,M$ $NaClO_4$, $\log\,p_{CO_2} = -3.5$); the dashed line denotes the environmetally tolerated Pb^{+2} concentration (1 ppm)

Fig. 1 shows a solubility diagram of the cerussite—calcite system based on the data of *Bilinski* and *Schindler*[5]. The use of carbonate to precipitate pollutant metals has been a subject of discussion. In fact it is common knowledge among prospectors who use metal analyses of waters to detect the presence of lead—zinc deposits that when such waters pass over calcite and/or dolomite the content of dissolved lead and zinc drops below the detectable limit[6].

The aims of this work are:

1. to characterize the Pb^{+2}—calcite and Pb^{+2}—aragonite phases in terms of the rates of Pb^{+2} precipitation, the Pb^{+2} compound produced, and the distribution of the compound on calcite and aragonite, and

2. to determine how rapidly soluble organics mobilize Pb^{+2} using the Pb^{+2}—calcite phase as a model for precipitated heavy metal pollutants.

Experimental

Pb^{+2}—Calcite and Pb^{+2}—Aragonite Phases

Aqueous solutions $10^{-2}\,M$ or $10^{-3}\,M$ in Pb^{+2}, as the NO$_3^-$, were placed in dynamic contact with calcite (E. Merck, Darmstadt) or aragonite (Institute for Mineralogy, Montanuniversität Leoben, Austria) for a period of several days. The calcite and aragonite samples were powders. The Pb^{+2} and Ca^{+2} contents of the solutions were determined by atomic absorption spectroscopy (Perkin-Elmer Model 400) as a function of time. Samples of Pb^{+2}—calcite in which 13.5 mole% and 7.4 mole% of the Ca^{+2} was replaced by Pb^{+2} were prepared for the study of the solubilization for Pb^{+2} by dissolved organics.

X-ray powder patterns of the Pb^{+2}—calcite and Pb^{+2}—aragonite phases were examined using a Philips X-ray diffractometer with a copper source. Additionally the surfaces of the Pb^{+2}—calcite and—aragonite phases were examined microscopically. Samples of natural calcite and aragonite were embedded in a resin, and the surface was polished and exposed to $10^{-2}\,M$ Pb^{+2} (as NO$_3^-$) solutions. The resulting samples were examined at various depths with an electron microprobe (Applied Research Laboratory, Sunnyvale, Calif., Model ARL-SEMQ).

Solutions

Solutions were prepared from water which was twice distilled from an all quartz apparatus, reagent grade chemicals and commercially available products. The commercial products were: Dash detergent; Holländerin hand soap; and the lignin sulfonates, Hansa-Am S (NH$_4^+$), Zewa-SL (Na$^+$), Collex-XB (Ca^{+2}) and Collex-SL (Ca^{+2}) from Lignin-Chemie Waldhof-Holmen GmbH, Düsseldorf.

Natural waters were used in several experiments. These waters were collected in Austria from the Mur River at Leoben-Göss, below the Leykam Paper Factory at Niklasdorf, the sewage treatment facility at Trofaiach, and both in Mur River and the Pöls Creek below the Pöls Paper Factory near Judenburg.

Mobilization of Pb^{+2} from Pb^{+2}—Calcite Phases by Soluble Organics

A known weight of the Pb^{+2}—calcite was placed in a beaker or the frit of a circulation apparatus previously described[7]. A known volume of the solution containing the soluble organic was introduced, and stirred over or circulated through the Pb^{+2}—calcite. At various times samples of the solution were removed, centrifuged or filtered, and analyzed for Pb by atomic absorption spectroscopy. Standards showed that Pb^{+2} was not absorbed on the glass of the beakers or sample tubes.

Results

Pb^{+2}—Calcite and —Aragonite Phases

Fig. 2 shows the uptake of Pb^{+2} by calcite and aragonite exposed to a solution $10^{-3}\,M$ in Pb^{+2}. The uptake of Pb^{+2} is accompanied by an equivalent release of Ca^{+2}. The particle size of the calcite was less than

that of the aragonite. Thus it appears that Pb^{+2} uptake on aragonite is faster than on calcite.

Samples of the Pb^{+2}—calcite and Pb^{+2}—aragonite phases were examined microscopically. Both showed crystal formation on the surface of the original mineral. The X-ray powder pattern of samples of the Pb^{+2}—calcite phases yielded the data which are summarized in Fig. 3. The X-ray pattern for the sample is a simple combination of those of calcite and cerussite, and no shifts in peak position are observed. Thus cerussite ($PbCO_3$) and calcite ($CaCO_3$) are the only compounds present and no mixed carbonate formation is suggested. Electron microprobe examinations of samples of calcite and aragonite exposed to $10^{-2}\,M$ Pb^{+2} solutions for one week were performed. The X-ray emission data for the surface and 0.1 mm below the surface are summarized in Table 1.

Table 1. *Electron microprobe analyses of* $CaCO_3$ *crystals exposed to* $10^{-2}\,M\,Pb^{+2}$ *for one week.* x_{PbCO_3} *and* x_{CaCO_3} *are mole fractions* $PbCO_3$ *and* $CaCO_3$

Mineral	Position	x_{PbCO_3}	x_{CaCO_3}
Calcite	surface	0.80	0.20
	bulk	0.00	1.00
Aragonite	surface	0.86	0.14
	bulk	0.00	1.00

The surface contains Pb and little Ca, and 0.1 mm below the surface Ca and no Pb.

All data suggest that the exposure of calcite or aragonite to Pb^{+2} solutions results in the formation of $PbCO_3$ (cerussite) on the $CaCO_3$, and that little Ca is present in the $PbCO_3$.

Mobilization of Pb^{+2} from Pb^{+2}—Calcite Phases

The Pb^{+2}—calcite phase prepared by the method described in Exp. and characterized in the previous section was exposed to a variety of complexing agents and potentially polluted waters to determine their effectivenesses in mobilizing Pb^{+2}.

The mobilization of Pb^{+2} by a $1:1$ Ca^{+2}—ethylenediaminetetra-acetate (*EDTA*) solution is shown in Fig. 4. The complex formation constant[3] between Pb^{+2} and *EDTA* is about $10^{17.5}$ and *EDTA* represents an example of a soluble organic having a high affinity for Pb^{+2}. The data in Fig. 4 show that the available Pb^{+2} is solubilized in approximately five hours.
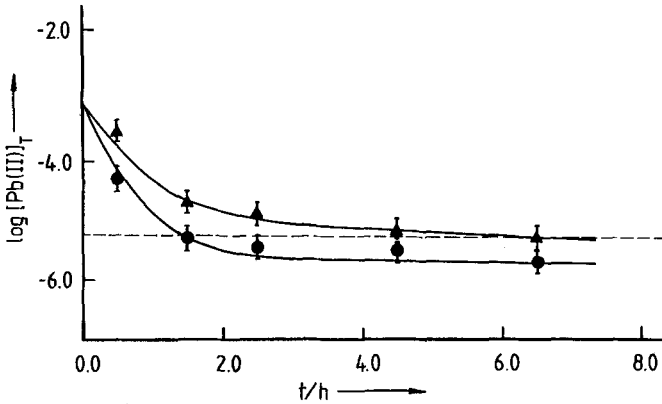
Fig. 2. Pb^{+2} uptake as a function of time by CaCO$_3$ (1.0 g calcite/1.0 g aragonite was placed in dynamic contact with 80 cm^3 of a 10^{-3} M Pb^{+2} solution, initial $pH = 6.3$); the dashed line denotes the environmetally tolerated Pb^{+2} concentration (1 ppm), calcite (▲), aragonite (●)
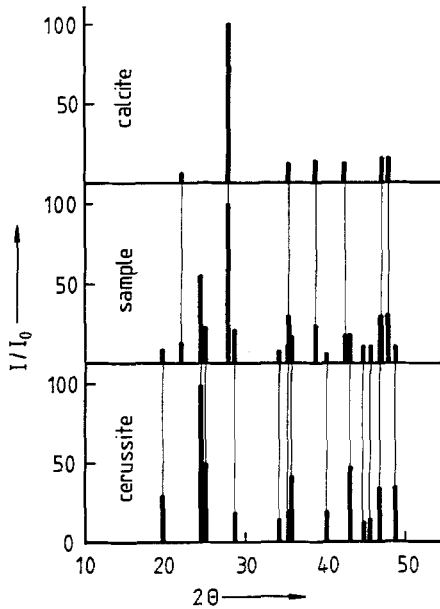

Fig. 3. X-ray analysis, I/I_0 versus 2θ, of calcite exposed to Pb^{+2} (1.0 g calcite was exposed to a 10^{-2} M Pb^{+2}, initial $pH = 5.8$, or to a 10^{-3} M Pb^{+2} solution for about 8 h)

Fig. 4 also shows the solubilization of Pb^{+2} by samples of water containing effluent from the Pöls Paper Factory near Judenburg. Data are shown for samples taken 0.5 and 8 km downstream from the outflow of the paper factory which were collected during January 1983. Samples taken at distances greater than 25 km after water from the Pöls Creek enters the Mur River did not solubilize Pb^{+2}. The data show the time required for maximum solubilization by the 0.5 km sample to be the same as that of Ca^{+2}—$EDTA$. When this water sample was exposed to a Pb^{+2}—calcite phase for times greater than about five hours, the pH increased markedly and Pb^{+2} was reprecipitated.

Fig. 5 shows the mobilization of Pb^{+2} from a Pb^{+2}—calcite phase by a 0.1% soap solution (Holländerin hand soap), 0.1% detergent solution (Dash detergent), and lignin sulfonate solutions of 0.1% and 0.4% by weight. Lignin sulfonates of the NH_4^+, Na^+ and Ca^{+2} types were used and no differences in rate were noted. The points plotted are averages for the four lignin sulfonates listed in Exp. The time for mobilization of Pb^{+2} by lignin sulfonates is the same order of magnitude as Ca^{+2}—$EDTA$ and effluent waters from the Pöls Paper Factory.

Waters taken from the Mur River at Leoben-Göss and below the Leykam Factory at Niklasdorf during December 1982 did not mobilize Pb^{+2} from the Pb^{+2}—calcite phase. Additionally, sewage water, which had undergone secondary treatment at the Trofaiach facility, and $1:1$ Ca^{+2} tartrate at 10^{-3} M did not mobilize Pb^{+2} from the Pb^{+2}—calcite phase.

Discussion

The data shown in this study suggest that Pb^{+2} can be removed quickly and efficiently from waters polluted with heavy metals by the addition of calcite or aragonite. The removal of Pb^{+2} by aragonite occurs more rapidly than by calcite. This observation is consistent with the fact that cerussite ($PbCO_3$) has an aragonite structure. It is clear that the removal of Pb^{+2} by calcite or aragonite can be inhibited by the presence in solution of complexing agents having a large affinity for the metal ion. Figs. 1 and 2 show that within natural pH conditions soluble Pb can be reduced to below 1 ppm, a level tolerated by environmental agencies (Ö-Norm). The $PbCO_3$ (cerussite) formed is deposited on the surface of the calcite or aragonite as shown by the data in Table 1 and Fig. 3. Because of its abundance, calcite is the mineral of choice in practical applications. The advantage of this method over others, such as hydroxide precipitation, is that the pH is in part controllable by the carbonate coming from the calcite and atmospheric carbon dioxide.

The mobilization of Pb^{+2} is rapid when the Pb^{+2}—calcite phase is exposed to a solution containing $1:1$ Ca^{+2}—$EDTA$ (Fig. 4). $EDTA$ has
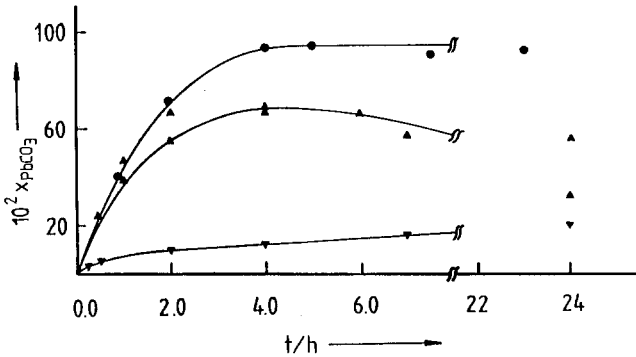
Fig. 4. Mobilization of Pb^{+2} from Pb^{+2}—calcite phase, mole fraction of available Pb^{+2} mobilized versus time (20 mg of calcite with 7.4 or 13.5 mole % PbCO$_3$ was exposed to 50 cm^3 of the following solutions: (●) $10^{-3}M$ 1:1 Ca^{+2}—$EDTA$, $pH_{initial} = 5.6$; (▲) Pöls water, 0.5 km, $pH_{initial} = 4.5$; (▼) Pöls water, 8 km, $pH_{initial} = 6.8$. The final pH's in all cases were 6.8
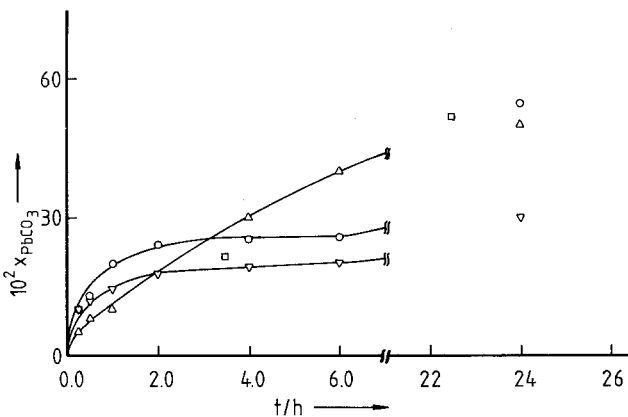

Fig. 5. Mobilization of Pb^{+2} from Pb^{+2}—calcite phase, percent of available Pb^{+2} mobilized versus time. (10 mg of calcite with 7.4 or 13.5 mole % PbCO$_3$ was exposed to 50 cm^3 of the following solutions: (□) 0.1% soap, $pH_{initial} = 8.7$; (△) 0.1% detergent, $pH_{initial} = 8.5$; (○) 0.1 and (▽) 0.4% lignin sulfonate, $pH_{initial} = 5.8$, $pH_{final} = 6.5$

a strong affinity for Pb^{+2} with the Pb^{+2}—$EDTA$ complex formation constant being $10^{17.5}$. However, the data in Fig. 4 show that effluent waters from paper mills such as the Pöls Paper Factory are as potent as the strongest complexing agents (e.g. $EDTA$) in solubilizing a heavy metal such as Pb^{+2} from the Pb^{+2}—calcite phase. Such waters will likely solubilize Pb^{+2} from sediments. Waters coming from paper

factories using the sulfite pulping process contain lignin sulfonates as well as a large variety of other organic compounds like sugars, and organic acids[8]. Such compounds contain functionalities such as sulfonate, phenol, hydroxyl and carboxylic acid groups which can potentially complex metals.

The reasons for the reprecipitation of Pb^{+2} by Pöls water 0.5 km (Fig. 4) may involve the oxidation of the organics in the effluent waters converting hydroxyl groups to aldehydes and ketones. In general aldehydes and ketones are poorer complexing agents than hydroxyl groups.

Lignin sulfonates, a soap and a detergent mobilize Pb^{+2} from the Pb^{+2}—calcite phase (Fig. 5). Lignin sulfonates at 0.1 and 0.4% are not as effective in mobilizing Pb^{+2} as Pöls water, 0.5 km, and increasing concentrations do not cause an increase in mobilized Pb^{+2}. As discussed earlier effluent water of the Pöls-type contain many organic complexing agents in addition to lignin sulfonates. The lack of increased mobilization of Pb^{+2} with increasing lignin sulfonate concentration may be due to an aggregation phenomenon.

The waters from the Leykam Paper Factory at Niklasdorf do not mobilize Pb^{+2} from the Pb^{+2}—calcite phase. This facility does not produce cellulose but uses waste paper and therefore, does not have such a variety of organic compounds in its effluent waters.

The effects of the waters and complexing agents used in this study on biological systems should be a point of ecological concern. The divalent cations Ca^{+2} and Mg^{+2} are known to stabilize biological membranes[9]. It is clear that when these metals are complexed and removed or displaced by other metals from the membrane a destabilization occurs which can have dramatic effects on influx and efflux processes[10,11]. These processes are essential to the viability of the membrane.

Another question of interest which evolves from this work is the bioavailability of the remobilized lead. Biological membranes will take up lead, and complexation by organics can alter this process. It is known that complexation of heavy metals can enhance the uptake process. An example is the effect of *NTA* (nitrilotriaceticacid) on metal uptake, which has resulted in its removal from detergents in some countries[2]. With this background it would be of interest to ascertain the effects of compounds such as lignin sulfonates in the uptake of heavy metals by biological systems.

Acknowledgements

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