Binding and leaching of trace elements in Portland cement pastes

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ABSTRACT

Portland cement contains trace elements originating from the raw materials and the fuels used for cement production. The trace elements are bound to some extent during cement hydration. A small fraction remains dissolved in the pore solution. The dissolved fractions of antimony, barium, chromium, lead, molybdenum and vanadium were quantified in the course of hydration of four different Portland cements. The development of heavy metal concentrations signifies the relevant hydration products for the binding of heavy metals. For chromate and molybdate a substitution for sulfate in ettringite was found. Vanadium and antimony are most likely not bound in ettringite. Barium precipitates as barium sulfate. For lead no clear trends could be observed. Leaching experiments were carried out and the concentrations of the leachates were compared to pore solution concentrations to check if the solubility of the heavy metals is relevant or if the leaching process is controlled by diffusion.

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1. Introduction

The main raw materials of cement, limestone and clay or marl, naturally contain variable amounts of trace elements and potentially hazardous heavy metals. Another source of contaminants are secondary and primary fuels. Table 1 gives an overview of median heavy metal and trace element contents of the raw materials and some exemplary fuels.

As a result Portland cement contains different heavy metals in variable amounts. The leaching of these heavy metals from cementitious building materials has been in the focus of German authorities for more than 20 years. Many leaching experiments were carried out using deionised water, but since leaching depends strongly on the composition and pH-value of the water these results cannot directly be transferred to real leaching conditions. In order to make a realistic prognosis on the leaching, the binding mechanisms and the relevant mineral phases have to be known. In this study the heavy metals antimony, barium, lead, chromium, molybdenum and vanadium were selected representing metals with very different chemical properties.

1.1. Barium

Barium is an alkaline earth metal and therefore bounds in oxidation stage $+2$. According to [3] in cement clinker barium is incorporated in C_2S replacing calcium. The ionic radius of Ba^{2+} is 18 to 30% larger than Ca^{2+} depending on the coordination number (see [4]). Therefore the replacement of Ca^{2+} is limited to compounds with high coordination

numbers. A replacement of Ca^{2+} in C_3S is hindered by the larger size of Ba^{2+}.

Investigations of the fate of barium during hydration are described in [5] and [6]. In both references barium carbonate was added to the system and the precipitation of barium sulfate was observed. Unlike the calcium salts barium sulfate is significantly less soluble than the carbonate.

1.2. Lead

Lead belongs to the carbon group and occurs in the oxidation states $+2$ and $+4$. It is an amphoteric element meaning that the solubility of PbO and $Pb(OH)_2$ is increasing at low and high pH (>10) [7]. For crushed mortars an increase of Pb solubility at high pH is not observed [8] or very low [9] indicating adsorption or structural retention in the presence of hydration products of cement. Some authors suggest a replacement of Ca^{2+} by Pb^{2+}. Since the ionic radius of Pb^{2+} is only about 13% larger than Ca^{2+} [4], this ion exchange is plausible. Relevant hydration products might be the C-S-H phases [10] or ettringite [11].

A very profound study on the binding of lead is described in [12]. In the first step sorption isotherms for pure C_3S, C_3A, C_4AF and pre-hydrated C_3S and pre-hydrated C_3A were determined by adding $Pb(NO_3)_2$. Ettringite and monosulfate were not considered. The highest affinity was found towards C_4AF. Pre-hydrated and unhydrated C_3S also showed a high sorption. For unhydrated C_3S saturation was observed at about $3 \cdot 10^{-5}$ mol lead per g C_3S. Due to the adsorption the hydration was stopped. For C_3A the sorption was low and precipitation of PbO was observed.

The second step was a ^{29}Si NMR study on C_3S and hydrated C_3S. The spectra of pre-hydrated C_3S showed a new peak which was assigned to the end group Si-O-Pb [12]. Further investigations with X-ray

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Table 1
Median contents of trace elements/heavy metals in raw materials and fuels used for cement production.

Trace element/heavy metal	Raw materials [1]			Fuels [2]		
	Limestone mg/kg	Clay mg/kg	Marl mg/kg	Hard coal mg/kg	Petroleum coke mg/kg	Used tires mg/kg
As	<5	15	5	9	0.5	1.6
Ba	52	321	154	–	–	–
Cr	7	105	53	14	4.3	137
Cu	13	29	24	18	2.4	68
Mo	<5	<5	<5	–	–	–
Ni	<7	43	28	23	263	90
Pb	<10	27	14	27	13	125
Sb	10	7	8	1	0.6	136
V	14	128	90	39	758	19
Zn	13	78	48	63	16	6100

Fig. 2. Experimental (leached) and predicted (modelled) equilibrium concentrations of Cr in the leachate of a crushed concrete (sample E2 [9]).

absorption spectrometry at a synchrotron beamline showed that lead is bound to three oxygen atoms in a trihedral pyramid with covalent bonding. That is, the oxidation stage of lead has changed to $+4$. Silicon and calcium were found in the further surroundings. In case of unhydrated C_3S $Pb(OH)_3^-$ is adsorbed at the surface, thereby blocking the hydration. For the binding in C-S-H phases Moulin confirmed the end group Si-O-Pb which was detected in the NMR study.

The sorption of lead to C_4AF is attributed to the ferric octahedron [12].

1.3. Antimony

Antimony is a semimetal which belongs to the Pnictogens (5th main group). It bounds in the oxidation stages -3, $+3$ and $+5$ [4]. According to Bhatty cement clinker contains antimony in the form of calcium antimonates [13]. The oxidation stage in these compounds is $+5$. In contact with water the pentavalent antimony forms $Sb(OH)_6^-$ oxyanions. Cornelis et al. investigated the interactions of $Sb(OH)_6^-$ with Portland cement and its most relevant hydration products [14]. Sorption experiments with ettringite, portlandite, C-S-H and monosulfate showed that C-S-H and monosulfate have the most pronounced interactions with $Sb(OH)_6^-$. For C-S-H Cornelis et al. found an adsorption to the surface close to calcium ions. Monosulfate and possibly other AFm phases may form solid solutions with a so-called antimonate-AFm $(Ca_4Al_2[Sb(OH)_6]_2(OH)_{12}\cdot3H_2O)$. The investigations include the synthesis of antimonate-AFm and the experimental investigation and thermodynamic modelling of antimonate leaching from powdered hardened cement pastes at different pH values. The modelling should confirm the relevant phases for the binding of antimonate. Although the fitting of the experimental results was not perfect, the modelling still leads to the conclusion that at a pH close to 13 a solid solution of AFm phases and antimonate-AFm possibly together with adsorption to C-S-H may be relevant [14]. In cement paste with a very high content of Sb (1000 mg/kg) the mineral Romeite $(Ca_{1.13}Sb_2O_6(OH)_{0.26}\cdot0.74H_2O)$ may precipitate.

1.4. Chromium, molybdenum and vanadium

Chromium and molybdenum belong to the same group of the periodic table (6th secondary group), whereas vanadium belongs to the adjacent group (5th secondary group). All three heavy metals bound in
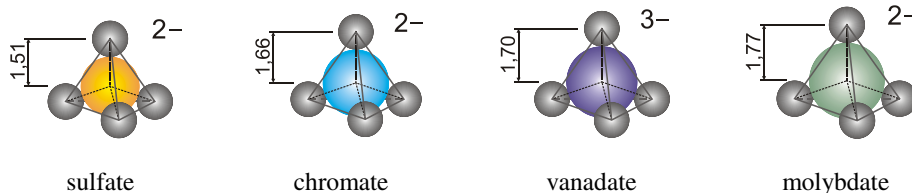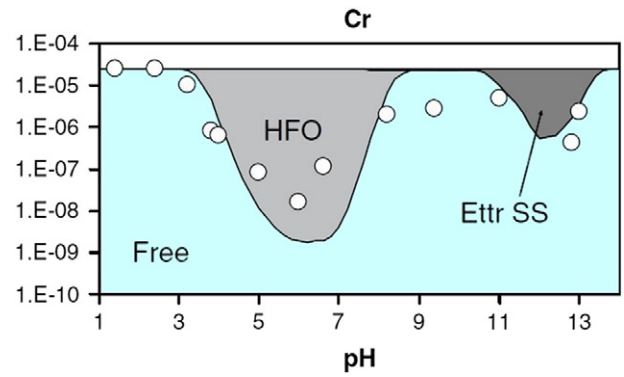
various oxidation stages. The highest are $+6$ for chromium and molybdenum and $+5$ for vanadium. In these oxidation stages chromium, molybdenum and vanadium can form oxyanions with a tetrahedral structure. These tetrahedral ions can possibly replace sulfate in its compounds. Fig. 1 compares the different oxyanions. It is apparent that the heavy metal ions are a bit larger. Vanadate is a trivalent ion. Therefore charge balancing would be necessary.

For chromium numerous investigations on the binding in cement clinker and cement hydration products are described in literature. According to [15] chromium is primarily incorporated in the silicate phases during the clinker burning process. In addition K_2CrO_4 or $K_2Cr_2O_7$ may be formed. The relevant oxidation stages of chromium in cement clinker are $+3$ and $+6$. Moulin found a proportion of 53% Cr^{VI} in doped clinker regardless of the oxidation state of the chromium added before clinker burning. After hydration chromium is still present in both oxidation stages [12].

Sorption experiments with $Cr(NO_3)_3\cdot9H_2O$ on C_3S, C_3A, C_4AF, prehydrated C_3S and pre-hydrated C_3A are described in [12] and [16]. The sorption isotherms show that Cr^{III} is well adsorbed by all of these phases [12]. The reaction products of C_3S + lime water with Cr^{III} (hydrated for 28 d), pre-hydrated C_3S + lime water with Cr^{III} (equilibrated for 72 h), C_3A + lime water with Cr^{III} (hydrated for 7 d), pre-hydrated C_3A + lime water with Cr^{III} (equilibrated for 72 h) and C_4AF + lime water with Cr^{III} (hydrated for 7 d) were analysed with X-ray absorption spectrometry. The concentration of Cr^{III} was 0.005 mol/l. In all samples the coordination of Cr^{III} was octahedral. For the C_3S samples Moulin states that the retention can be explained by the formation of a chromium containing hydrogarnet: $Ca_3[Cr(OH)_6 - (SiO_4)_{x/4}]_2$ [12]. In contrast Omosoto et al. state an exchange of Cr^{III} for Si^{4+} in C-S-H [16]. The experiments of both references confirm that no precipitation of $Cr(OH)_3$ occurs.

In case of C_3A aluminium in C_3AH_6 is substituted by Cr^{III}; additionally $CrOOH$ precipitates [12]. C_4AF has similar hydration products $(C_3(A,F)H_6)$ which also allow substitution of Cr^{III} for Al^{III} (or Fe^{III}). In addition Moulin found a chromium containing phase that could not be specified. It has to be questioned whether the chromium minerals precipitate in an undoped system (without an external chromium source).

Equivalent investigations were carried out with Cr^{VI} doping (with Na_2CrO_4). The sorption of Cr^{VI} on C_3S is rather low [12]. Experiments described in [16] and [17] confirm this finding. In this reference the

Fig. 1. Oxyanions, bond length in Å taken from [4].