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Waste Materials in Construction: Putting Theory into Practice

HEAVY METAL BINDING MECHANISMS IN CEMENT-BASED WASTE MATERIALS

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ABSTRACT: Field and laboratory experiments were carried out to elucidate the geochemical and hydrological mechanisms that are important to understand the binding mechanisms of heavy metals in landfills with cement based waste materials. The focus of the work was on Zn(II), firstly in sorption experiments with calcium-silicate-hydrate, and secondly as a component in the leachate from a field lysimeter experiment. The leachate of the lysimeter containing cemented electrofilter ashes was sampled during rain events in order to determine the leaching processes.

It was found that most of the rainwater was in intimate contact with the waste material in this field system and that while hydrological factors caused changes in concentrations of up to 100% (8-16μM), the concentration range was controlled by geochemical factors. The residence time of the water was sufficiently long to be able to describe Zn concentrations by thermodynamic calculations. The pH values in the leachate ranged between 12.5 and 13.1 where $Zn_2SiO_4(s)$ appeared to be the most stable phase. Comparison with laboratory experiments suggested that alternative mechanisms could be important. In the laboratory experiments Zn appeared to be incorporated into the calcium-silicate-hydrate frame forming solid solutions that have varying solubilities depending on the Ca/Zn ratio in the Ca_{1-x}-Zn_x-silicate-hydrates. The field data agreed well with this alternative model. Thermodynamic and kinetic factors are discussed and compared with respect to the geochemical and hydrological contributions.

INTRODUCTION

Today, over 80% of Switzerland's municipal waste is incinerated. The heavy metal-rich flue gases produced during incineration are scrubbed with electrostatic precipitators followed by aqueous washing treatments to remove acidic gases and potentially harmful heavy metals including mercury. The resulting electroprecipitator ash and the solid residues of the aqueous treatment are mixed. This filter ash (FA) is predominantly inorganic and is rich in heavy metals[1], and therefore, has to be handled as hazardous waste[2]. Though alternative processes designed to quantitatively separate heavy metals waste residues are in development[3,4], landfilling is at present a common practice.

In Switzerland, FA is mixed with cement before it is disposed of in mono landfills. Laboratory tests have shown a reduction in the heavy metal concentration in the leachate of cement-stabilized FA by factors of 5 to 20[5]. The mechanisms which reduce the mobility are still a matter of debate. Thus, the long-term leachability of the cemented FA cannot be predicted. In order to make such predictions, it is necessary to understand the geochemistry and hydrology of these systems. The hydrology of a landfill determines whether and how long water can come into contact with the solid material. The geochemical processes determine the reactions between the solid phase and the leachate.

Depending on the composition of the landfill and the residence time of the water in contact with the solid phases, concentration of elements are kinetically or thermodynamically controlled. In recent work, Johnson et al.[6] and Kersten[7] have shown the usefulness of thermodynamic calculations for the interpretation of the heavy metal concentrations in the leachates of a landfill with municipal solid waste incinerator ash. However, kinetic factors play an important role for slow geochemical processes that cannot be estimated by thermodynamic calculations. For kinetically-controlled geochemical processes, the product concentrations may scale with the reactivity of the different reactants. Here, the known ligand exchange rates around hydrated metals can be used to estimate the reactivities, e.g. for dissolution[8,9] or adsorption[10] processes.

For our field studies, we have chosen a pilot landfill that was built for scientific research purposes[5,11]. The advantage of this site is that the landfill is completely filled and that CO_2 contamination of the leachate can be avoided. Of special interest was the investigation of the effect of preferential flow during rain events upon the concentrations of the dissolved cations and anions in the leachates.

Our field studies were accompanied by laboratory experiments and theoretical investigations about the geochemical reactions of importance. In this paper we have chosen Zn(II) as an example for a trace element. Cycling of Zn is of major interest due to its high concentration in the FA. Zn is also a suitable element for laboratory experiments because it is highly soluble and allows experiments above the detection limits of common methods of analysis.

EXPERIMENTAL

Materials. $CaCO_3$ (p.a.), $ZnCl_2$ (p.a.), KCl (p.a.), $CaCl_2$ (s.p.), NaCl (s.p.), NaOH and HCl titrisol at various concentrations, Si standard solution (1000ppm $SiCl_4$ in 5M NaOH) and concentrated HNO_3 (s.p.) were obtained from Merck. SiO_2 (Aerosil 300) was purchased from Degussa. All solutions were prepared from 17MΩ ultrapure water (Barnstead Nanopur) which was filtered through a 0.2 µm in-line filter. For the laboratory experiments the ultrapure water was boiled under Ar. HDPE-flasks for the field sampling and for the sorption experiments were leached with acid (~0.6M diluted from concentrated HNO_3).

The pilot landfill. The lysimeter is located next to the old landfill "Teuftal" in Mühleberg (Kanton Bern) and was constructed[5,11] for scientific research. The landfill contains cemented FA in form of cubic blocks that have an edge length of 0.5m. The plant is approximately 1.5m deep, has a surface area of 16m^2, and is covered with clay-silt (0.2m), gravel (0.8m), and humus (0.3m) layers. Additional installations at the existing sampling station were made to prevent the samples from CO_2 contamination and to prevent the drainage solutions from blocking the tubing.

Sampling and field measurements. Only under wet conditions did we find enough discharge for sampling. A measuring cell with a rotating stirrer and a cell volume of 0.04dm^3 was connected to the drainage outlet to measure temperature, conductivity and pH with a testo 252 field equipment. It was not possible to perform on-line pH measurements because pH-electrodes become unstable in basic solutions. The pH-electrodes were calibrated using Merck titrisol buffer solutions (7, 10, and 13). The conductivity cell was checked with KCl solutions. The conductivities and pH values were corrected for the temperature at 25°C. The temperature corrections for the conductivity measurements were based on leachate samples. Concentrated samples were diluted and the conductivities were measured at different temperatures between 6 and 27°C. The established framework was used to interpolate. HDPE-flasks (0.25dm^3) were filled with sample, sealed thightly, and stored for further investigations at about 10-12°C, which is close to the sampling temperature, to reduce the possibility of precipitation.

Sample analysis. Al, K, Na, Si, and Zn were measured with ICP-OES (Spectro, Spectroflame). The samples were diluted with acid by a factor of 5 to give a pH value of about 2. Diluted samples were analyzed for SO_4^{2-} and Cl using an IC (Sykam) equipment with a Sykam (A04) column. CO_3^{2-} was measured without pretreating the sample solutions using a TOC (Shimazu 5050) analyzer. The samples were sealed before the measurements to minimize CO_2 contamination.

Laboratory experiments. The experiments were carried out in a glove box under Ar. Calcium-silicate-hydrates (C-S-H) with a Ca/Si ratio of about 1 was synthesized after Atkins et. al[12] by mixing 12.11g of CaO (prepared by heating $CaCO_3$ at 900°C for 24 hours) with 12.89g SiO_2 and suspended in 0.5dm^3 water in a 1dm^3 HDPE bottle. This suspension was shaken for 7 days on a rotary shaker (Bühler, Swip SM 25) at 150rpm. The suspension was then centrifuged (10 minutes, 6000rpm). The separated solid was vacuum-dried. X-ray powder diffraction spectras of the product were in agreement with the spectra of C-S-H as obtained by Taylor[13].

Sorption experiments were performed in presaturated solutions (S1) with respect to C-S-H with a composition of [Si(IV)]=0.1mM, [Ca(II)]=3mM, [OH^-]=8.3mM, [Cl^-]=0.1M, [Na^+]=0.1M resulting in a pH value of 11.7. For the Zn experiments a stock suspension (S2) was prepared by adding 1g C-S-H to 0.5dm^3 of the presaturated solution and equilibrated for 7 days on the rotary shaker at 150rpm. Then, 1cm^3 of S2 was added to 50cm^3 S1 and was equilibrated, again for 7 days. Afterwards aliquots of a Zn stock solution was added to obtain final Zn concentrations of 0.96, 0.48, 0.19, 0.096, 0.048, 0.019, and 0.0048mM. The suspensions were equilibrated for 4, 28, 53 or 87 days. In a withdrawn sample the pH value was measured using a combined glass electrode (Metrohm 6.0202.100). The remaining sample was filtered (0.45µm nylon, Whatman) and acidified with 0.3cm^3 of concentrated HNO_3. Zn concentrations below 0.1ppm were measured by anodic stripping voltammetry (DP-ASV, Metrohm VA-Stand 694, VA-Processor 693) and above this value with AAS (Perkin-Elmer 5000).

THEORETICAL ASPECTS

Heavy metal solubility is controlled by a spectrum of very slow to fast geochemical processes. Most important are sorption, dissolution, and precipitation reactions at mineral surfaces and diffusion and transformation reactions in the solid phases. Reactions in solution are generally fast. The different processes can be classified in order of their rates as follows:

SOLID	<	SOLID SURFACE	<	SOLUTION
transformation ~ diffusion		desorption ~ dissolution < adsorption ~ precipitation < diffusion		reaction in solution

The importance of understanding whether a particular reaction is slow or fast is two-fold. For relatively slow reactions, hierarchy of importance is established depending upon the rates. For relatively fast reactions, equilibrium is attained. Thus, geochemical reactions are assigned to two different categories of processes: 1) thermodynamically and 2) kinetically controlled reactions.

Kinetic Control of Geochemical Processes. Investigations of kinetic processes have concentrated on the solid/water interface because of their importance in environmental systems. Mineral dissolution, sorption and complexation processes in solution have been systematically investigated. Although the many factors involved make predictions difficult, rates of adsorption[10] of cations onto mineral surfaces and the rates of dissolution[8,9] of these surfaces can be correlated with rates of ligand exchange in homogeneous solutions using linear free energy relationship (LFER). This has been discussed by Casey and Westrich[8], Ludwig and Casey[14], Ludwig et al.[9,15], and Casey and Ludwig[16] and is illustrated in Fig. 1. This illustration shows a cation (M) sorbed at the mineral/water interface which is dissolving. The surface is acting as a surface ligand that is replaced by water molecules. The rate-controlling reactions in desorption may be analogous to those of dissolution, and crystal growth to those of adsorption. The first order rate coefficients[17] for water exchange around a dissolved cation ranges from ~ 10^{-8} s^{-1} for $Rh^{3+}(aq)$ to ~ 10^{10} s^{-1} for $Cs^{+}(aq)$. The reactivity of a metal centre changes by the nature of the complexing ligands[9] (or by hydrolysis)[14] (Fig. 1B) or by the oxidation state[17]. The determined relationships can be used to rank the reactivities among different species. The reactivities for the different cations of the same oxidation state increase as

$$\mathrm{Pt} \ll \mathrm{Ru} \ll \mathrm{V} \ll \mathrm{Be} \ll \mathrm{Ni} \ll \mathrm{Mg} < \mathrm{Co} < \mathrm{Fe} \ll \mathrm{Mn} < \mathrm{Zn} < \mathrm{Cd} < \mathrm{Ca} < \mathrm{Ba} < \mathrm{Cu} < \mathrm{Pb} \qquad (2)$$

for the bivalent cations and as

$$\mathrm{Rh} \ll \mathrm{Ru} < \mathrm{Cr} \ll \mathrm{Al} \ll \mathrm{V} < \mathrm{Ga} < \mathrm{Fe} \ll \mathrm{In} \ll \mathrm{U} \ll \mathrm{La} \qquad (3)$$

for trivalent cations. The alkali metals are known to be highly reactive.

Thermodynamic Control of Geochemical Processes. At thermodynamic equilibrium, steady-state conditions are assumed; i.e., the rate of formation and decomposition of a particular species are equal. Model concepts, relationships between species, and the corresponding equilibrium constants are used to describe a system. In Fig. 5 the sorption isotherms for a metal ion at a mineral surface for some different cases after Stumm[18] are illustrated.

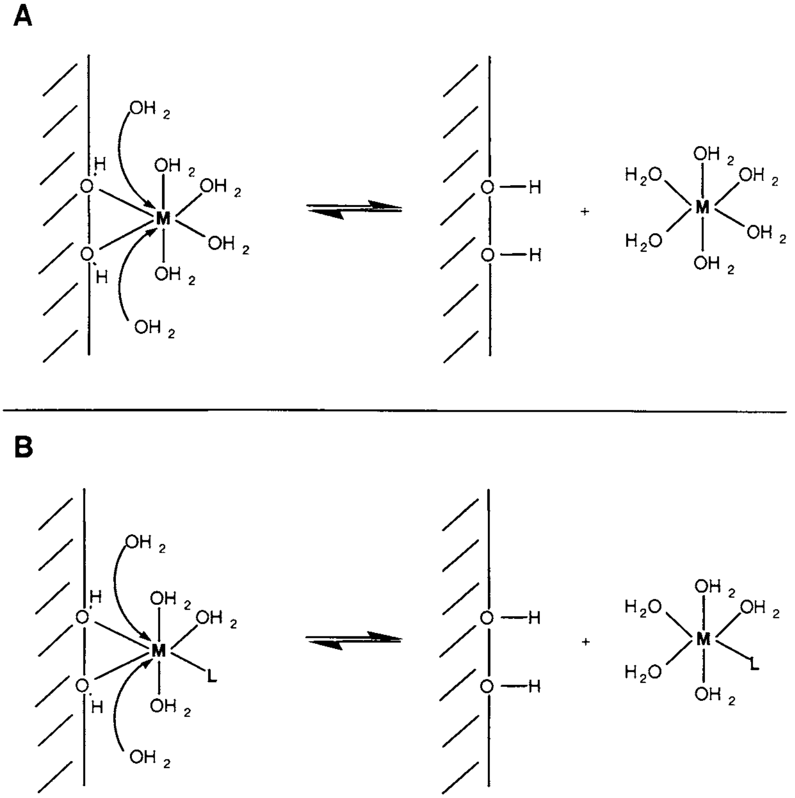

Fig. 1 A) Simplified reaction scheme for one possible rate controlling process during dissolution or adsorption. The process consists of more than one reaction step. M indicates a cation bound to surface hydroxyl-groups. Incoming waters replace the surface ligand at the metal center. B) Analogue scheme showing a complexing ligand that influences the reactivity of the metal center.

Heavy metals that are highly reactive according to the series shown in relationship (2) and (3) (e.g., Zn(II), Cd(II), Cu(II), Pb(II)) dissolve or desorb quickly into an undersaturated solution. These species can thus be potentially found in high concentrations in leachates. The amount present in the solid phase must be taken into account. Depending on the residence time of the water in the cement pores, the highly reactive elements reach solubility limits that are controlled by different mechanisms (Fig. 5).

In ideal cases, minerals such as simple mineral oxides, hydroxides and the orthosilicates dissolve congruently. For most silicates, this is not the case[19,20], as the reactive species leave the mineral structure only in the top layers. Further dissolution is then controlled by diffusion through the inert part of the mineral structure. If this process is very slow or not possible, the reaction is controlled by the reactivity of the silica frame work and not by the solubilities. Further restrictions to a simple model are posed by solid solution phases (e.g., $Ca_{1-x}Zn_xSiO_4$) that have different solubilities depending on the value x. The difficulty with solid solution interpretations in complex systems, is that it is not always known which species are involved, and also the behavior is very often not ideal. The predictions are therefore difficult.

Hydrological Control of Geochemical Processes. Leaching processes involving geochemical reactions depend on the solid/solution interactions. It is therefore of prime importance to understand the hydrological processes within a landfill. There are a number of indicators for preferential flow in landfill systems and because this water plays a minor role in leaching processes, it is important to assess the amount of water in intimate contact with the waste material, and the average residence time of water in the landfill.

In a simple model, we assume that there are preferential flow-paths. The water that has relatively short contact with the solid material is referred to as "fresh" rain water. In contrast the "old" landfill water preequilibrates in the cement pores. The partial discharge of "old" landfill water (Q_{old}) and of "fresh" rain water (Q_{fresh}) is then given by the equations[21]:

$$Q_{old} = Q_{total} \cdot c/c_{start} - Q_{start} \qquad (4)$$

and

$$Q_{fersh} = Q_{total} \cdot (c_{start} - c)/c_{start} \qquad (5)$$

where c, c_{start}, Q_{total}, and Q_{start} are respectively, the electric conductivity, the electric conductivity before the rain event, the total discharge, and the total discharge before the rain event. The sum of Q_{start}, Q_{old}, and Q_{fresh} gives the total discharge Q_{total}.

RESULTS AND DISCUSSIONS

The Zn concentrations in the leachate were found to be between 8 and 16μM after the rain event from June 21-23, 1996 (Fig. 2). The values are comparable to rain events sampled in the same season, irrespective of the discharge rates that range between 0.55 and 30.2dm^3/h. The dilution during a rain event appears to reduce concentrations by only 40 to 60% in all of the measured cases. In order to understand the effect of hydrology, it is necessary to study some additional parameters. The electric conductivity measured as a sum parameter shows reduction in salinity as the discharge increases. However, the change is not as large as one expects from the dilution. It becomes obvious when the conductivity starts to increase parallel to the discharge, before conductivity and discharge finally return to their starting values (Fig. 3B). Preferential flow calculations as defined by changes in conductivity (4, 5) indicate that only a small amount of water passes through the landfill without reacting with the cemented FA (Fig. 3C). It must be noted that the conductivities of the preferential flow water are assumed to be similar to the water from the reference field that is negligible in comparison to the landfill water. There is a direct correlation between Zn concentration and conductivity (Fig. 2). From this, we

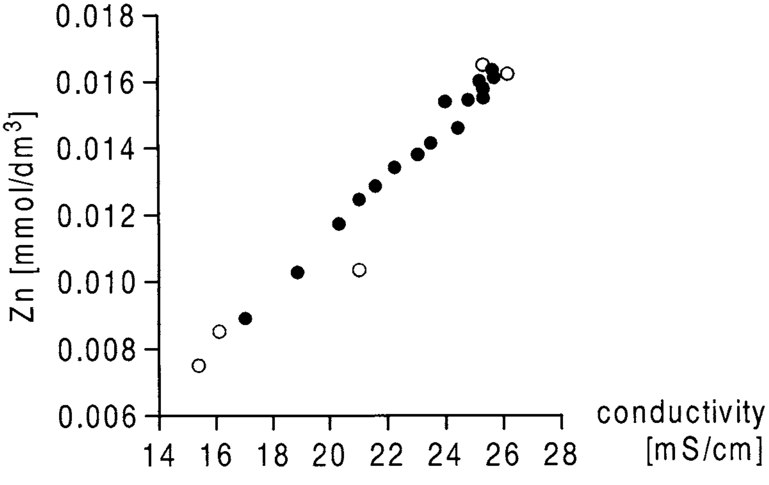

Fig. 2 The variation of Zn concentration in the leachate after a rain event. The symbols indicate the measurements before (○) and after (●) reaching the discharge maximum. The conductivity was used as a sum parameter that correlates well with the Zn, and most of the other cation and anion concentrations.

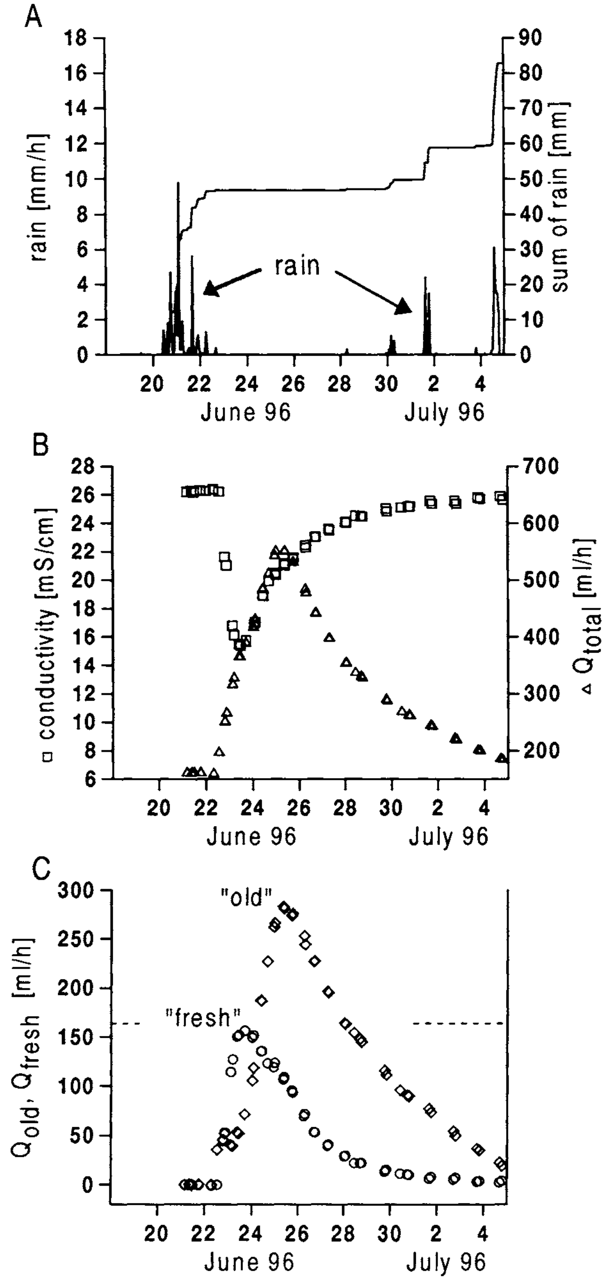

Fig. 3 A) rain and rain sum B) electric conductivity corrected for 25°C and C) discharge separated into "fresh" rain water and "old" landfill water using the conductivity as a tracer assuming equilibrium between the solution in the pores and the solid phases before the rain. The dashed line indicates the discharge (Q_{start}) before and after the rain event.

can obtain a value of concentration of Zn which is most probably in quasi equilibrium with our waste material. The processes that lead to this concentration must be related to the residence time of the water in the landfill. The residence time of the landfill water estimated from the total landfill volume ($24m^3$), the total pore volume (55%, $13.2m^3$)[5], the amount rainwater estimated to pass through the landfill (25%)[5] and an annual average precipitation of 1050mm is estimated to be on average 3 years. However, since there are large variations in flow, the residence time during strong rain events can be as low as a few weeks. According to the relationship (2), Zn(II) is very reactive. In agreement with the long residence time for pore water, we expect that Zn in the leachates is controlled by the solubility of solid Zn phases or by the adsorption/desorption equilibria at the surfaces.

The Zn content in FA ranges between 12 and 52g/kg[22]. From dissolution experiments[9] carried out at low pH-values, Ca_2SiO_4 was found to be more reactive than Zn_2SiO_4, but compared with other orthosilicates show high and similar reactivity. Westrich et al.[23] have studied the reactivities for $Ca_{1-x}Mg_xSiO_4$ solid solutions for x=0.5 and found that they were between those of the endmembers $Ca_2SiO_4(s)$ and $Mg_2SiO_4(s)$. From this point of view, we may expect that $Ca_{1-x}Zn_xSiO_4$ solid solutions may equilibrate comparably fast as their endmembers.

The Zn concentrations in the field leachate are presented in Fig. 4 as a function of pH. The lines represent the solubility limits for ZnO(s) and $Zn_2SiO_4(s)$. On the logarithmic scale, the secondary role of the hydrology become obvious. The changes of the Zn concentration during a rain event are much smaller than those expected from a change in the pH value. ZnO(s) and $Zn_2SiO_4(s)$ have been chosen because they are known to be the most insoluble phases for the systems under investigation.

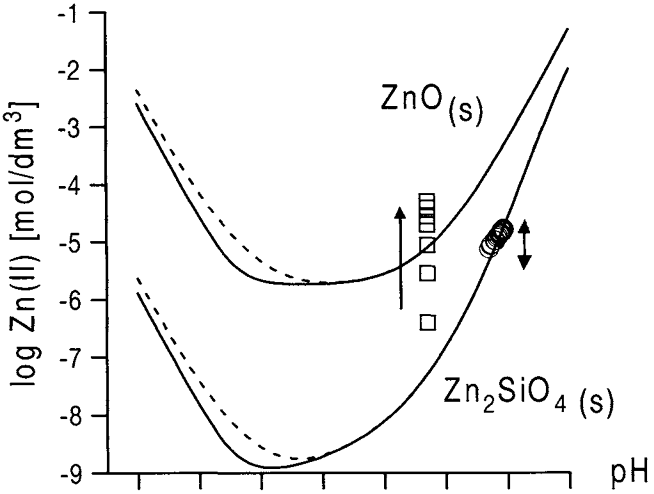

Fig. 4 The solubility curves of ZnO(s) and $Zn_2SiO_4(s)$ were calculated as a function of the pH values and compared with the field (O) and laboratory (□) experiments. The calculations considered all important species using Zn(II), Si(IV), OH^-, Cl^-, SO_4^{2-} and CO_3^{2-} as components. The deviations of the dashed from the solid lines indicate the influence of the present Cl^-, SO_4^{2-} and CO_3^{2-} ions in solution. The $Zn_2SiO_4(s)$ curve was calculated taking a solution in equilibrium with 2.8mM Si(IV) into account, which was the typical concentration before and after a rain event. The arrow on the right shows the variation of the Zn concentration during a rain event. The arrow on the left shows the direction towards higher Zn concentrations for the isotherm shown in Fig. 5.

The measured Zn concentrations in the field leachates are more than one order of magnitude below the solubilities of $Zn(OH)_2(s)$ or the even more stable ZnO(s), but are well represented by the calculated $Zn_2SiO_4(s)$ solubility curve. This indicates possible thermodynamic equilibrium with this solid phase, although other mechanisms may not be excluded. The laboratory data do not appear to be controlled by a single solid phase and are probably controlled by other mechanisms. The isotherm in Fig. 5 shows that relatively high Zn concentrations adsorb on C-S-H even after 4 days. A surface site density of $\sim 10^{-3.2}$mol/g was estimated from the first three adsorption measurements (•) which is in good agreement with the surface site densities measured for other silicates[24,25] and cement[26] minerals. The points shown as (■) are in the supersaturated region with respect to ZnO(s). Nevertheless, the concentrations in solution still increase with increasing total amount of Zn in the system. The fact implies control due to solid solution formation of Ca_{1-x}-Zn_x-S-H phases or surface precipitation at the C-S-H phase. Formation of $Zn(OH)_2$(s) as a precursor of the more stable ZnO(s) may not be excluded, but this seems unlikely because the solubility of the $Zn(OH)_2$(s) is higher than the Zn concentrations in solution. Additional experiments in the range below the saturation of ZnO(s) show that the Zn sorption increases with time (Table 1). We speculate that the effect is due to the slow diffusion of Zn into the C-S-H phase. These experiments are in good agreement with those of Kersten and Johnson[27] who conducted preliminary experiments with synthesized solid solutions that have solubilities well below that of ZnO(s) and depend on the Ca/Zn ratio in the solid phases. For comparison, the amount of Zn[11] in the cement phase of the landfill (0.23mmol/g, corrected for pore size) along with the corresponding Zn concentrations in the leachate are plotted in Fig. 5. Although, the laboratory experiments were carried out at a single pH value about one pH unit lower than the field values, a rough comparison shows that the concentrations in the leachate are in good agreement with the measured isotherm. The comparison of laboratory and field experiments shows that Zn concentrations in the leachate can be explained by the solubility of Zn_2SiO_4(s), or alternatively by surface nucleation or solid solution.

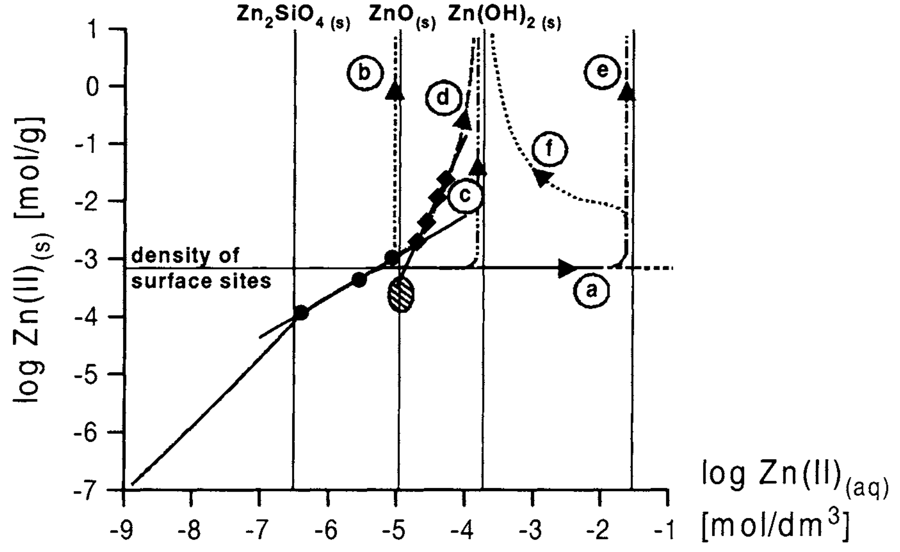

Fig. 5 Sorption isotherm of Zn(II) to C-S-H at a pH value of 11.7. The measurements indicated as (●) were undersaturated and those indicated as (■) were supersaturated with respect to ZnO(s). The different lines represent schematic isotherms that can be addressed to a) adsorption only, b) adsorption and heterogeneous nucleation for low activation energies, the line indicates the solubility for ZnO(s), c) the same as b) where the line indicates the solubility for $Zn(OH)_2$ (s), d) adsorption and surface precipitation via ideal solid solution, e) adsorption and heterogeneous nucleation of a metastable precursor, and f) the same as e) but with transformation of the precursor into the stable phase. The shown solubilities of the solid phases are only valid for the laboratory experiments. (The schematic isotherms were adapted from Stumm[18]) The hatched area represents the concentrations in the lysimeter.

Table 1: Decrease of aeqous Zn(II) with time in two laboratory experiments.

time [d]	$Zn(II)_{(aq)}$ [µM] (Zn_{tot}= 48µM)	$Zn(II)_{(aq)}$ [µM] (Zn_{tot}= 4.8µM)
4	8.7	0.39
28	6.1	0.24
53	4.1	0.19
87	3.5	0.17

CONCLUSIONS

The field data show that most of the rainwater is in intimate contact with the cemented FA leading to high salt concentrations in the leachate. The residence time of the water is sufficiently long to allow us to describe Zn concentrations by thermodynamic equilibrium calculations. The field Zn concentrations can be represented by solubility control with $Zn_2SiO_4(s)$. However, a comparison between field and laboratory data indicates that other mechanisms such as solid solution or surface nucleation could explain the field observations equally well. The Zn concentrations predicted by the sorption experiments at C-S-H are in good agreement with the concentrations measured in the field leachate and suggest that Zn mobility is indeed influenced by interactions with cement minerals.

It appears that the field system is sufficiently reactive that sorption and dissolution processes play an important role in the control of trace element concentrations. There is, however, no proof that solid diffusion and slow transformation processes do not play a role. It will be the task of future work to investigate binding and transformation mechanisms in the solid phase as well as to find methods of discerning thermodynamic and kinetic processes.

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