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Prediction of chemical speciation in stabilized/solidified wastes using a general chemical equilibrium model II: Doped waste contaminants in cement porewaters

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Abstract

In the previous paper, SOLTEQ demonstrated its ability to represent chemical speciation in the pure s/s binder systems. The objective of this paper is to provide a method for representing doped waste contaminants in SOLTEQ so that their speciation can be determined. To evaluate this method, model predictions were compared with measured concentrations in the porewaters expressed from cement pastes doped with various metal salts. Among doped metals, only mercury showed concentrations that indicated primary control by precipitation. The other metals, such as Cr(VI), Cd, Pb, and Na, showed behaviors that imply sorption as a major immobilization mechanism. The Langmuir isotherm was found to be well suited to describe the sorption of Na^+ ions onto the effective surface of CSH. To support the sorption of metal anions onto presumably negatively charged silica surface in cement porewater, a hypothesis of "super-equivalent adsorption" is proposed.

Keywords: Waste management; Adsorption; Modeling; Pore solution

The solidification/stabilization (s/s) technologies have been widely applied to inorganic contaminants such as metals and radionuclides, because typical s/s technologies are effective in chemically immobilizing them. Glasser [1] summarized important immobilization mechanisms in the cement-based binder system being 1) precipitation with hydroxide due to high pH, with silicates, or as Ca-containing salts; 2) sorption onto high surface area CSH, and 3) lattice incorporation into crystalline phases. Investigating the controlling mechanism for immobilization of a specific contaminant (e.g., Pb, Cd) has been an objective in many efforts.

In the previous paper, SOLTEQ [2] demonstrated its ability to represent the chemical speciation in the pure s/s binder systems when used with a proper input preparation method. For a complete prediction of the s/s waste's behavior using a chemical equilibrium model, the doped waste contaminants should be suitably represented so that the controlling mechanisms immobilizing them can be well reflected in the prediction.

The objective of this paper is to provide a method for representing doped waste contaminants so that chemical speciation in the s/s waste can be predicted using a chemical equilibrium model, SOLTEQ. Comparison of model prediction with measured concentrations in the porewaters expressed from cement pastes doped with various metal salts was used to verify this method.

1. Methodology

Trussell and Batchelor [3] investigated the porewater concentrations of heavy metals (Cd, Cr(VI), Pb, and Hg) in 28-day-old Portland cement pastes over a range of doped metals concentrations (100, 1,000, and 10,000 ppm) and water-to-cement (w/c) ratios (0.4, 0.7, and 1.0). Heavy metal ions were added into the water for cement hydration in the forms of $Cd(NO_3)_2$, Na_2CrO_4, $Pb(NO_3)_2$, and $Hg(NO_3)_2$. Accordingly, considerable amounts of Na ions were doped in the cement pastes.

To predict these metal concentrations in the porewater, precipitation was assumed as a dominant immobilization mechanism. SOLTEQ [2] was used to find controlling solids from SOLTEQ database for each heavy metal ion as well as alkali metal ion. Measured concentrations of all components were input to SOLTEQ to determine possible solid phases such as hydroxides, silicates, and so on. A list

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of oversaturated or nearly saturated solids with respect to measured concentrations of these metal ions was obtained.

The compositions of cement hydrates from Portland cement binder were determined using the input preparation methods for SOLTEQ as illustrated in the previous paper. To obtain the equilibrium concentration of a specific heavy metal, each listed solid for precipitation of that metal was equilibrated in SOLTEQ with the obtained compositions of cement hydrates with the improved combination of K_{sp} values (−5.19 for portlandite, −44.91 for ettringite, −27.49 for C_4AH_{13}, and Reardon's CSH model [4]). The equilibrium concentrations calculated by SOLTEQ were compared with the measured concentrations to decide whether precipitation controls the chemical speciation and, if precipitation controls, which is the controlling solid for a specific metal ion.

Alkali metal ions are known to sorb onto cement hydrates [5,6]. The previous paper illustrated the effectiveness of Taylor's model in predicting the alkali partitioning. This model was modified to describe the effect of sodium ion added with contaminants. The doped alkali ion was assumed to be readily soluble [6] and not to be associated with clinker phases. The result from this modification was compared with experimental data. The contribution of alkali ions from cement was calculated using the input preparation method for SOLTEQ described in the previous paper.

2. Results and discussion

A list of possible solid phases from the SOLTEQ database for precipitation of each metal is given in Table 1. Table 1 also shows the dominant aqueous species of each metal in cement porewater as predicted by SOLTEQ for pH values about 13.2.

The equilibrium concentrations of each metal with respect to the listed solids were compared with measured concentrations [2]. The results are shown in Fig. 1. Measured concentrations of all components lie below precipitation lines for the selected solids.

The measured hexavalent chromium (Cr(VI)) concentrations are far from the equilibrium concentrations with respect to two possible solids (K_2CrO_4 and $PbCrO_4$). SOLTEQ predicted little change in Cr speciation, with nearly all of the component remaining as CrO_4^{-2}. However, as Trussell and Batchelor [3] indicated, considerable amounts were removed from solution in the experiment. Considering differences in measured concentrations among differently dosed pastes and SOLTEQ prediction results with possible solid phases, precipitation cannot be the controlling mechanism for hexavalent chromium. Possible explanations for this disappearance from solution could come from sorption of anion CrO_4^{-2} onto a certain solid phases in cement pastes or from lattice incorporation of CrO_4^{-2} in place of SO_4^{-2} in ettringite as indicated by Glasser [1].

Lead and cadmium show similar tendency in this comparison. Their hydroxides were the most stable phases in the SOLTEQ database. However, as shown in the Fig. 1, the predictions approach the measured points for the 10,000 ppm doses, but cannot account for the differences in measured concentrations among differently dosed cement pastes. If sorption of their anionic species ($Pb(OH)_4^{-2}$ and $Cd(OH)_4^{-2}$) onto some solids occurs, it could be a plausible mechanism to account for this immobilization behavior. Lead can be reduced in solution phase by replacing calcium in Ca-containing crystalline solid phases [1].

Mercury shows the behavior expected for precipitation control. Although there are slight differences in measured concentrations among differently dosed pastes, the trend line, along with pH, is very close to the precipitation lines, especially that of montroydite (HgO). If we consider some uncertainty involved in values of the solubility product (K_{sp}) of these solids or some errors in measurements, precipitation could be a controlling mechanism for immobilization of mercury in the cement porewaters.

Alkali metals (Na, K) are widely understood to sorb onto cement hydrates [5–8]. According to Fig. 1, the precipitation lines are about an order of magnitude away from measured points. Sodium shows a slightly sorption-like behavior, because there are some differences in measured concentrations among differently doped samples. However, this tendency is not apparent in measured potassium concentrations. The points of measured log concentrations form a line with a slope of about 1.2 with respect to pH. This implies possible formation of another solid containing potassium that depends on pH and controls potassium concentrations in cement porewaters.

To investigate the sorption behavior of alkali metals in the cement porewaters, as shown in Table 2, the amounts of sorbed alkali metal concentrations were calculated by subtracting the measured concentrations from the available concentrations as calculated according to Taylor [6] at the given hydration time plus the contributions from doped alkali metal (only for Na). The sorbed amount was normalized on the basis of CSH concentrations (Table 2), because CSH can represent not only the amount of total cement hydrates at a given w/c ratio but can provide most of surface area for sorption in a cement paste as indicated by Glasser

Table 1
Possible solid phases and dominant aqueous species for each metal by SOLTEQ

Metal	Possible solid phases	Dominant aqueous species[†]
Cr(VI)	K_2CrO_4, $PbCrO_4$	CrO_4^{-2}
Pb	$Pb(OH)_2$, $PbCrO_4$	$Pb(OH)_4^{-2}$
Cd	$Cd(OH)_2$, $CdSiO_3$	$Cd(OH)_4^{-2}$
Hg	$Hg(OH)_2$, Montroydite (HgO)	$Hg(OH)_3^{-}$
Na	Na_2CrO_4, Glaserite* ($K_3Na(SO_4)_2$)	Na^+
K	K_2CrO_4, Syngenite* ($K_2Ca(SO_4)_2H_2O$), Arcanite (K_2SO_4)	K^+

Note: K_{sp} values of SOLTEQ (or MINTEQA2) database used for the listed solid phases except *glaserite and syngenite [4].

[†] Dominant at pH values of 13.2 and higher.

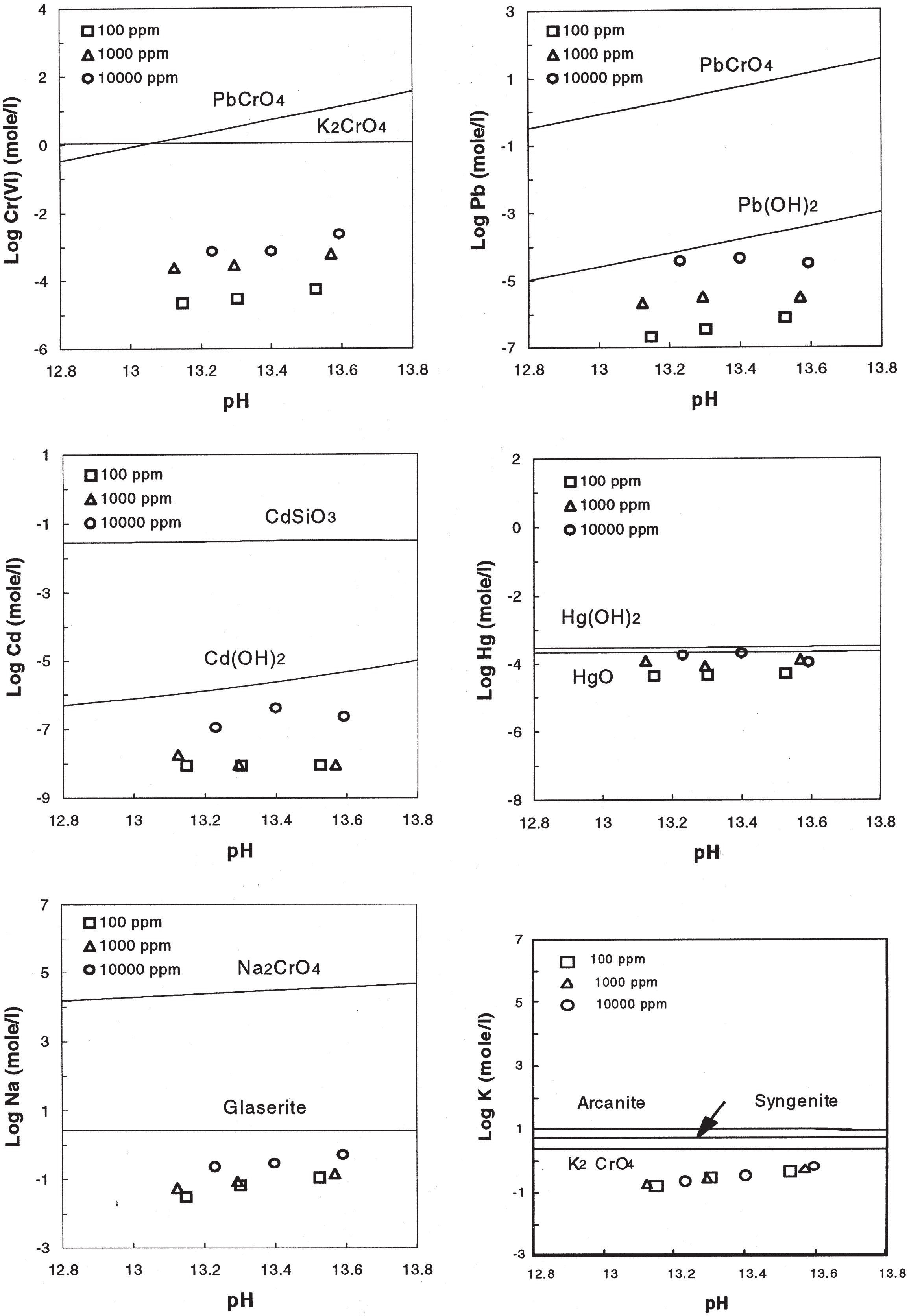

Fig. 1. Comparison between the SOLTEQ predicted equilibrium concentrations with respect to possible solid phases and measured concentrations in the pore-waters of cement pastes doped with 100, 1000, and 10000 ppm metal in Trussell's experiment [2].

Table 2
Sorbed amounts of alkali metals and concentrations of CSH

Metal dosage	100 ppm			1000 ppm			10000 ppm		
(W/C ratio)	0.4	0.7	1.0	0.4	0.7	1.0	0.4	0.7	1.0
Na (M)									
a. Released from cement	0.381	0.191	0.124	0.368	0.187	0.123	0.396	0.194	0.127
b. Doped	0.006	0.005	0.005	0.055	0.049	0.046	0.592	0.508	0.475
c. Total (∓a + b)	0.387	0.196	0.129	0.423	0.236	0.168	0.988	0.702	0.602
d. Measured	0.114	0.067	0.031	0.145	0.091	0.056	0.521	0.292	0.237
e. Modified Taylor model	0.212	0.138	0.101	0.235	0.168	0.133	0.532	0.494	0.472
f. Sorbed (∓c − d)	0.273	0.128	0.098	0.278	0.145	0.112	0.467	0.410	0.365
K (M)									
g. Released from cement	0.551	0.275	0.179	0.531	0.270	0.177	0.572	0.281	0.184
h. Measured	0.460	0.321	0.171	0.558	0.286	0.183	0.698	0.352	0.233
i. Modified Taylor model	0.359	0.217	0.153	0.351	0.214	0.151	0.368	0.221	0.156
j. Sorbed (∓g − h)	0.091	−0.046	0.008	−0.027	−0.016	−0.006	−0.126	−0.071	−0.049
CSH (M) from SOLTEQ input preparation method	8.92	4.46	2.90	8.61	4.38	2.87	9.27	4.55	2.97

[1] and Jennings and Tennis [9]. The amount sorbed per amount CSH was related with the alkali concentrations in solution. This relationship is shown in Fig. 2. Taylor's model [6], modified to consider the doped Na amount, was applied to predict the alkali sorption behavior.

As shown in Fig. 2, the Taylor model [6] is a linear sorption model. Although the Taylor model was a good estimator for alkali ions in pure binder systems [10], it does not show a corresponding ability to predict Trussell's experimental data [2]. Measured sodium (Na) shows sorption-related behavior to some extent in that the sorbed amount increases with increase of solution concentrations. However, there is considerable difference between the model prediction and calculation based on measured data. The difference becomes more pronounced as w/c ratio increases. Moreover, the data points do not appear to be well fitted by a linear sorption relation.

For potassium (K), the measured data do not show any indication that sorption is important. The calculated amounts of potassium sorbed are near zero and show no trend with potassium concentration in solution. Potassium might be controlled by precipitation of a new type of K-containing solid as indicated earlier. Some points are below zero, which indicates possibility of K^+ desorption or inaccuracy of assumptions in calculating the contributions of potassium from cement.

Water-to-cement ratio has an effect on hydration of cement and availability of CSH sorption area. Increasing w/c ratio increases the hydration rate of cement pastes [11]. Experimental data of Jennings and Tennis [9] on various w/c

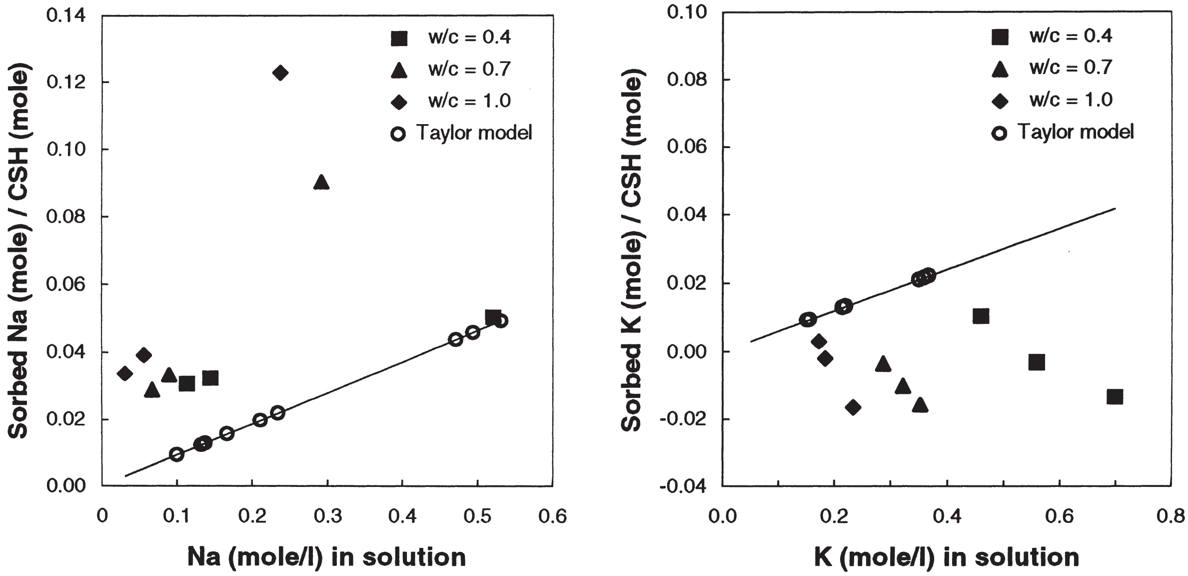

Fig. 2. Relationship between the sorbed amount per amount of CSH and the concentrations in solution for sodium (Na) and potassium (K). The Taylor model modified considering the doped Na amount was applied to predict the alkali sorption behavior.

Table 3
Revised amounts of sorbed Na and amounts of available CSH

Metal dosage	100 ppm			1000 ppm			10000 ppm		
(W/C ratio)	0.4	0.7	1.0	0.4	0.7	1.0	0.4	0.7	1.0
α (Equation 1)	0.757	0.839	0.867	0.757	0.839	0.867	0.757	0.839	0.867
Na (M)									
a. Released from cement	0.349	0.198	0.131	0.337	0.194	0.130	0.363	0.201	0.134
b. Doped	0.006	0.005	0.005	0.055	0.049	0.046	0.592	0.508	0.475
c. Total (∓a + b)	0.355	0.203	0.136	0.392	0.243	0.175	0.954	0.709	0.609
d. Measured	0.114	0.067	0.031	0.145	0.091	0.056	0.521	0.292	0.237
e. Sorbed (∓c − d)	0.241	0.135	0.105	0.247	0.152	0.119	0.433	0.417	0.372
f. CSH (M) from SOLTEQ input preparation method	7.63	4.74	3.18	7.35	4.65	3.15	7.92	4.83	3.26
g. β (Equation 2)	0.388	0.722	0.852	0.388	0.722	0.852	0.388	0.722	0.852
h. Available CSH (M) (∓f × g)	2.96	3.42	2.71	2.85	3.36	2.68	3.07	3.49	2.78

ratios also show this trend. This means that more hydration products (CSH, etc.) become available and that more clinker-associated alkalies become dissolved at the same hydration time in higher w/c ratio paste than in the lower w/c ratio paste. Increasing w/c ratio increases the measured N_2 sorption area of cement paste and most of this area is provided by CSH. Jennings and Tennis [9] suggested this increase in measured surface area is related to formation of CSH that is more open and has more surface area available for sorption.

The input preparation method for SOLTEQ and Taylor's empirical approach [6], on which the method was based, do not consider the effects of w/c ratios on hydration and available surface area of CSH. To incorporate these effects into the SOLTEQ input preparation method, a set of regression equations [Eqs. (1) and (2)] was developed using experimental data presented in Jennings and Tennis [9] and using a set of Avrami-type nonlinear equations:

$$\alpha = 1 - \exp(-2.15(w/c - 0.314)^{0.172}) \qquad (1)$$

$$\beta = 1 - \exp(-2.46(w/c - 0.289)^{0.732}) \qquad (2)$$

where α is the relative hydration rate with respect to w/c ratio, w/c is the w/c ratio of a cement paste, and β is the ratio of N_2 accessible area to total surface area or fraction of available CSH sorption area to total CSH sorption area.

The alkali released from cement and the amount of CSH at the given hydration time was revised to allow the effects of w/c ratio on hydration rate by applying Eq. (1) to the SOLTEQ input preparation method. Available CSH fraction at the given w/c ratio was obtained from Eq. (2). The amount of available CSH was calculated by multiplying the total amount of CSH at a given hydration time by the available CSH fraction at a given w/c ratio. Table 3 shows the calculation of the revised amounts of sorbed Na and the amounts of the available CSH. Accordingly, the sorption plot of Na in Fig. 2 was revised by evaluating the revised amount of sorbed Na per unit mass of available CSH. The revised plot is given in Fig. 3.

The normalized data points in Fig. 3 were found to be best fitted by Langmuir sorption isotherm [$q = 0.208 \times 4.89c/(1 + 4.89c)$, $r^2 = 0.9125$] rather than a linear isotherm. Sodium is widely used as a background electrolyte for various sorption experiments and it is proposed to form ion-pair complexes or outer-sphere complexes with negatively charged surface hydroxyl groups on the hydrous oxide surfaces such as SiO_2 [12]:

$$\equiv SOH + Na^+ + H_2O \leftrightarrow \equiv SO^-(H_2O)(Na^+ + H^+) \qquad (3)$$

If these ion-pair complexes exist and if the Na follows the surface complexation reaction depicted in Eq. (3), the equilibrium relationship will reproduce the Langmuir isotherm at fixed pH as indicated by Morel and Hering [13]. Therefore, good curve fitting of data points to Langmuir isotherm supports the assumption [5] of the sorption of Na on nega-

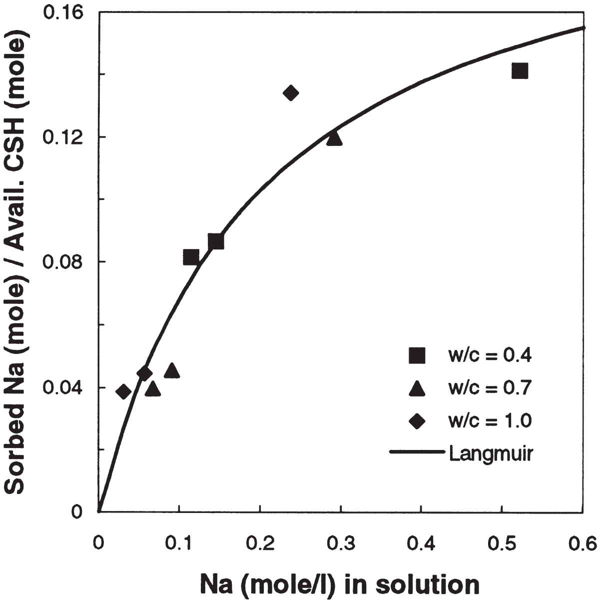

Fig. 3. Revised Na^+ sorption plot for Trussell's experimental data [2] considering the effects of w/c ratio on hydration rate and available CSH sorption area.

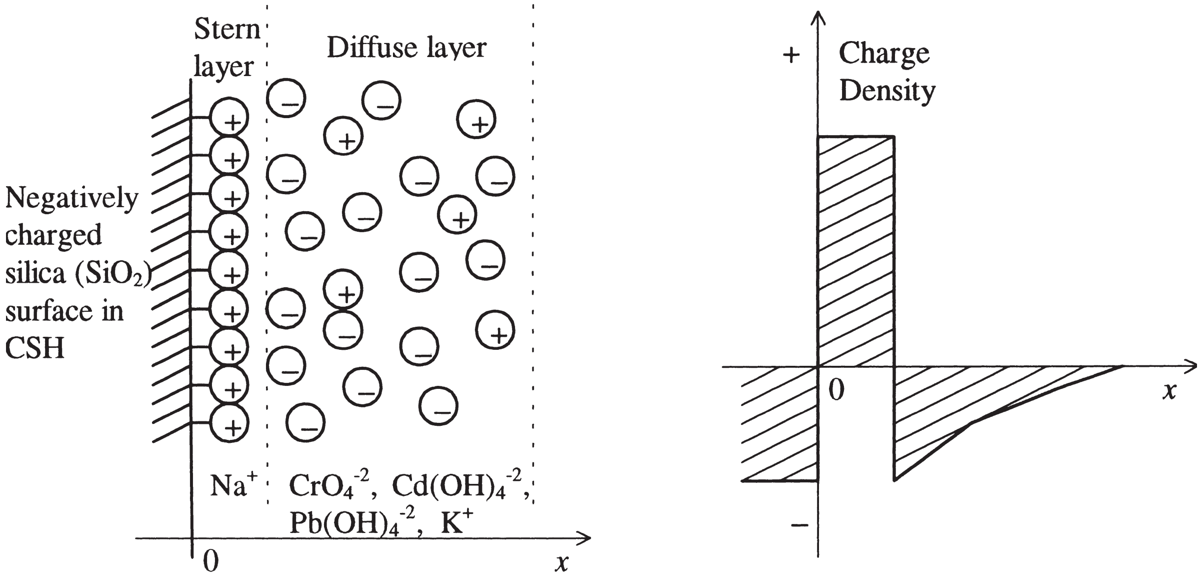

Fig. 4. "Super-equivalent adsorption" hypothesis for sorption of metal anions facilitated by strong Na sorption on negatively charged silica surface of CSH in cement porewaters. (Adapted from Stumm and Morgan [15].)

tively charged silica surface of CSH in high pH cement porewaters.

If the hypothesis [5] of alkali sorption onto negatively charged surface on CSH is true, sorption is not likely to be important factor for heavy metals, which are all anions at high pH values of cement porewater. However, these metals are found at concentrations much lower than predicted by precipitation in Trussell's experiments [2], which supports the assumption of sorption. Cheng and Bishop [14] believed that sorption was an important mechanism controlling concentrations of Pb and Cd. Specific sorption of these species (e.g., inner sphere surface complex of Pb) could be possible, but evidence of this is rarely available at the high pH regions of cement porewaters. Lattice incorporations of these metals (e.g., CrO_4^{-2} substitution for SO_4^{-2} in ettringite; Pb can substitute Ca in the cement hydrates) are also possible, but Hg and Cd were not known to participate the lattice incorporation [1].

To support the mechanism of sorption of the metal anions onto the presumably negative surface at high pH, a hypothesis of "super-equivalent adsorption" [15] is proposed. This hypothesis is illustrated in Fig. 4. According to Stumm and Morgan [15], ions are adsorbed in the Stern layer by electrostatic and specific interactions. "Super-equivalent adsorption" occurs when the specific interaction surpasses the electrostatic one and thus the positive charge of the Stern layer becomes greater than the negative charge of the surface.

There is little information about specific interaction between sodium and negatively charged surface. However, the Na ion-pair surface complexes, if they exist, should have much stronger interaction with the surface in high ionic strength and high pH solutions like cement porewaters. As illustrated in Fig. 4, sodium ions build a strong Stern layer around negatively charged silica surface of CSH so that the positive charge at the Stern layer due to Na sorption can exceed the negative charge of the surface. Net positive charge at the outside boundary of the Stern layer facilitates the nonspecific sorption (mainly by electrostatic interaction) of metal anions such as CrO_4^{-2}, $Cd(OH)_4^{-2}$, and $Pb(OH)_4^{-2}$.

To support this hypothesis, the calculated amount of each of these metals removed from solution was compared with that of sodium in Fig. 5. As shown in Fig. 5, the

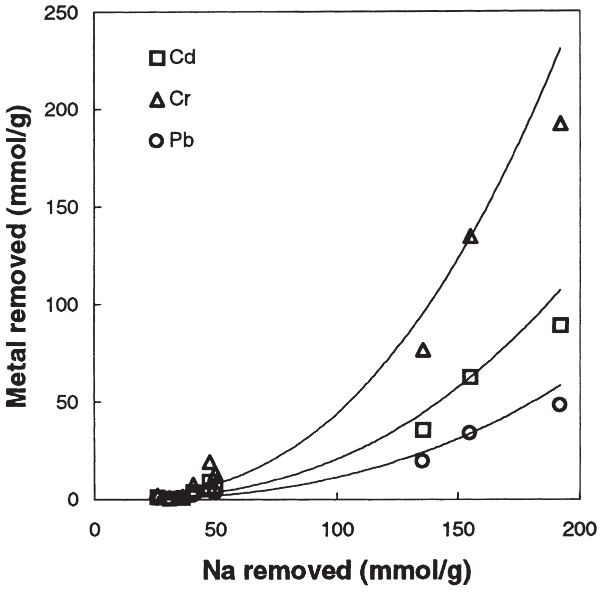

Fig. 5. Relationship between the removed Na^+ and removed metals species (CrO_4^{-2}, $Cd(OH)_4^{-2}$, and $Pb(OH)_4^{-2}$) based on Trussell's experiment.

amount of removed metal dramatically increases with increase of sorbed sodium. This indicates the removal of these metal anions is directly related with that of Na. This relation agrees with that predicted by the hypothesis of super-equivalent adsorption.

3. Conclusions

SOLTEQ simulations that assume only precipitation as a immobilization mechanism did not represent well the chemical speciation of doped metals in the cement porewaters. When compared with simulation results, only mercury showed concentrations controlled by precipitation of a solid (montroydite, HgO). The other metals, such as Cr(VI), Cd, Pb, and Na, showed behaviors that imply sorption as a major immobilization mechanism. The behavior of potassium revealed possible formation of unknown K-containing solid that is dependent on pH.

Uncorrected isotherms for sodium sorption on CSH showed a sorption-like relationship but a very high level of variability; potassium did not show sorption-like behavior. The isotherm for Na was modified considering the effect of w/c ratio on hydration rate and available fraction of CSH surface area. The modified plot was well fitted by Langmuir isotherm. This supports the assumption that the Na^+ ions are sorbed onto the surface of CSH in the cement porewaters.

Removal of some metals that exist as anions at high pH found in cement porewaters ($CrO_4{}^{-2}$, $Cd(OH)_4{}^{-2}$, and $Pb(OH)_4{}^{-2}$) appears to be the result of sorption. The ability of anions to sorb onto an originally negative surface is described by the hypothesis of super-equivalent adsorption. It assumes that the sorption of anions is facilitated by net positive charge at the outside boundary of Stern layer due to strong Na sorption onto negatively charged silica surface of CSH. This hypothesis is partially supported by a comparison between the sorbed metals and the sorbed Na.

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